Liquid Phase Adsorption by Microporous Coordination Polymers: Removal of Organosulfur Compounds

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SUPPORTING INFORMATION

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I. MCP Activation Procedures

MOF-5, MOF-177: Millward, A.R.; Yaghi, O.M. *J. Am. Chem. Soc.* **2005**, *127*, 17998-17999.

HKUST-1: Rowsell, J.L.C.; Yaghi, O.M. *J. Am. Chem. Soc.* **2006**, *128*, 1304-1315.

MOF-505: Chen, B.; Ockwig, N.W.; Millward, A.R.; Contreras, D.S.; Yaghi, O.M. *Angew. Chem. Int. Ed.* **2005**, *44*, 4745-4749.

UMCM-150: Wong-Foy, A.G.; Lebel, O.; Matzger, A.J. *J. Am. Chem. Soc.* **2007**, *129*, 15740-15741.

II. Materials and Methods

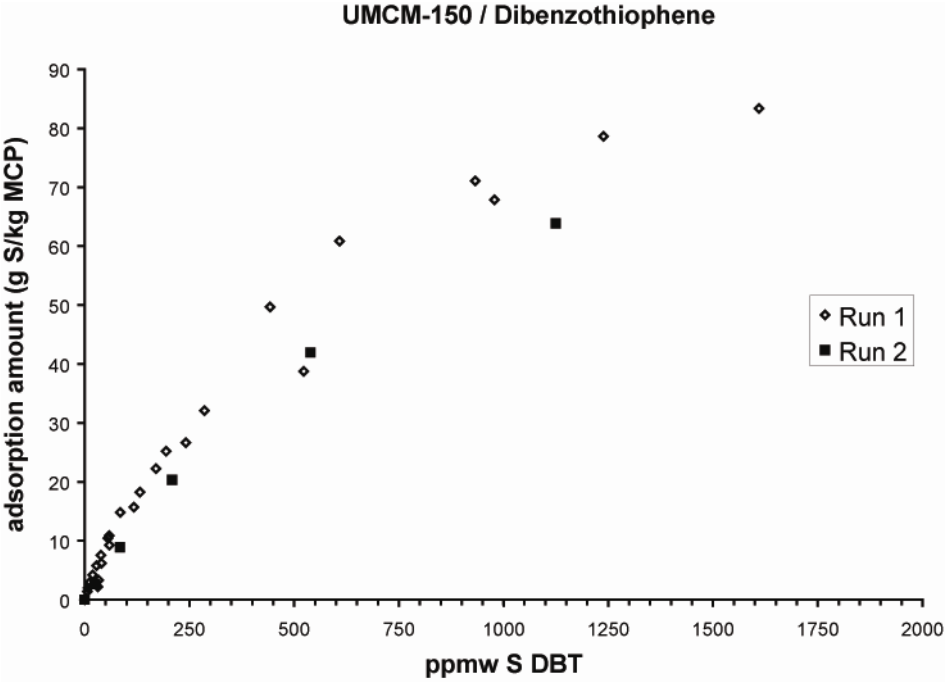
Benzothiophene, (97 %, Acros), dibenzothiophene (99%, Acros), 4-6-dimethyldibenzothiophene (97%, Aldrich), and isooctane (HPLC grade, Fisher) were used as received. Na(Y) zeolite (powder) was obtained from Strem Chemicals and used as received. Sulfur concentrations were determined using a Shimadzu GC-2010 equipped with a capillary column (L = 15 m, ID = 0.25 mm) and outfitted with both a flame ionization detector (FID) and flame photometric detector (FPD). Isotherm capacities were determined using the FID detector and were calibrated using control solutions of known sulfur concentration.

III. Batch Adsorption Procedure

In a typical experiment, ~10, 15, and 20 mg (precisely weighed) of MCP were added to three GC vials. Isooctane (500 μL) was added to each vial. Aliquots (20.0, 50.0, 100, 250, and 500 μL) of 3000 ppmw S benzothiophene or dibenzothiophene in isooctane, or 1000 ppmw S 4,6-dimethyldibenzothiophene in isooctane were added sequentially. Between aliquots, the vials were agitated on a shaker for 2 hours (benzothiophene), 3.5 hours (dibenzothiophene), or 12 hours (4,6-dimethyldibenzothiophene) and then analyzed by GC. Equilibration times were determined for each organosulfur compound by monitoring (GC) the concentration change until no further changes in the adsorption capacity were observed.

IV. Regeneration Experiment

UMCM-150 was added to a GC vial. DBT (1 mL, 3000 ppmw S) in isooctane was added to the solid. The vial was agitated on a shaker overnight. The DBT solution was removed and the UMCM-150 was rinsed with isooctane (6 × 20 mL) over a 24 hour period to remove adsorbed DBT. The isooctane solution was removed and the regenerated UMCM-150 was used to plot an isotherm using the batch adsorption procedure given in Section III. The results are shown below.



V. MCP Surface Areas and Pore Volumes

Table S1.

MCP	Langmuir Surface Area (m^2/g)	Pore Volume (cm^3/g)[a]
UMCM-150	3100[b]	1.11
MOF-505	1830[c]	0.71
HKUST-1	2260[d]	0.79
MOF-5	4170[d]	1.31
MOF-177	5640[d]	1.86

a) Pore volumes were calculated using the SOLV routine in PLATON (v. 1.10, University of Glasgow, 2006). The default probe radius of 1.2 Å was used with a grid spacing of 0.2 Å. All solvent molecules (bound and free) were removed from the structure generated from the published CIF files prior to use of the SOLV routine. For UMCM-150 and MOF-177, disorder in the structures was not removed as it did not appreciably affect the pore volume.

b) Wong-Foy, A.G.; Lebel, O.; Matzger, A.J. *J. Am. Chem. Soc.* **2007**, *129*, 15740-15741.

c) Chen, B.; Ockwig, N.W.; Millward, A.R.; Contreras, D.S.; Yaghi, O.M. *Angew. Chem. Int. Ed.* **2005**, *44*, 4745-4749.

d) Wong-Foy, A.G.; Matzger, A.J.; Yaghi, O.M. *J. Am. Chem. Soc.* **2006**, *128*, 3494-3495.

VI. Kinetic Diameters

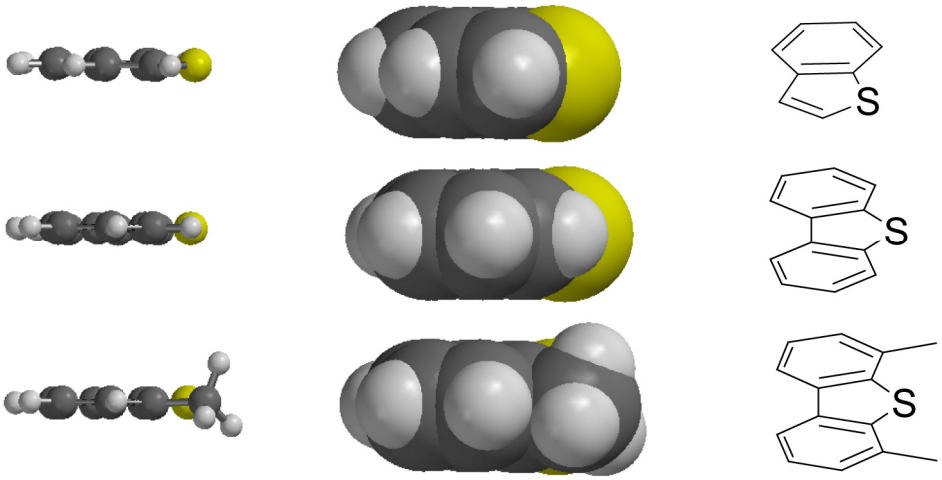


Figure S1. Kinetic diameters were approximated using the minimum cross-sectional area and were found to be 5.45 Å for benzothiophene (top), 5.54 Å for dibenzothiophene (middle), and 5.97 Å for 4,6-dimethyldibenzothiophene (bottom).

VII. Adsorption Isotherm Data Tables

(a) MOF-177

	concentration	adsorption amount
	(ppmw S)	*(g S/kg sorbent)*
BT	0.00	0.00
	103.62	0.41
	107.04	0.42
	108.64	0.77
	332.19	1.38
	341.44	1.50
	354.86	1.69
	675.86	3.82
	700.76	3.94
	729.12	4.70
	1259.09	6.79
	1305.45	5.73
	1326.62	8.65
	1851.00	8.79
	1880.07	8.78
	1917.17	8.23
DBT	0.00	0.00
	89.28	0.86
	90.42	0.91
	101.44	0.86
	288.36	2.89
	289.53	3.15
	333.72	2.36
	614.70	6.22
	620.69	6.60
	680.59	6.43
	1172.94	11.45
	1176.13	12.48
	1266.18	11.33
	1739.66	18.34
	1755.58	18.73
	1851.52	15.58
DMDBT	0.00	0.00
	27.64	0.28
	30.77	0.31
	34.65	0.39
	89.51	0.94
	98.68	1.06
	110.66	1.36
	192.69	2.03
	210.40	2.24
	235.32	2.43
	369.32	3.99
	392.31	4.55
	427.85	5.20
	559.17	6.26
	591.85	6.13
	616.78	8.70

(b) MOF-5

	concentration	adsorption amount
	(ppmw S)	*(g S/kg sorbent)*
BT	0.00	0.00
	76.10	0.55
	79.13	0.72
	94.72	0.76
	249.77	1.81
	260.16	2.36
	305.15	2.56
	533.49	4.07
	552.49	5.34
	642.40	5.65
	1051.06	7.82
	1093.03	9.72
	1187.12	11.90
	1621.40	12.21
	1656.69	15.56
	1780.94	16.39
DBT	0.00	0.00
	28.54	0.97
	41.05	1.32
	60.66	1.94
	102.02	3.25
	142.22	4.40
	209.12	6.20
	242.88	7.44
	335.27	9.74
	474.98	13.10
	603.97	15.09
	782.19	18.45
	1003.53	23.01
	1158.32	23.89
	1360.76	28.25
	1589.36	34.37
DMDBT	0.00	0.00
	5.15	0.27
	9.15	0.51
	14.29	0.90
	19.40	0.92
	31.65	1.74
	38.15	2.26
	49.92	2.97
	72.55	4.06
	93.38	5.24
	117.44	6.53
	174.31	8.69
	200.30	9.97
	262.36	12.77
	334.77	14.88

(c) HKUST-1

	concentration	adsorption amount
	(ppmw S)	*(g S/kg sorbent)*
BT	0.00	0.00
	37.81	1.02
	42.38	1.21
	52.06	1.57
	133.97	3.38
	151.32	3.95
	192.90	4.76
	319.63	7.48
	356.92	8.65
	463.22	9.49
	775.53	13.83
	842.00	15.50
	972.59	17.36
	1363.25	20.85
	1461.21	21.87
	1489.98	30.63
DBT	0.00	0.00
	10.01	1.46
	13.47	2.02
	18.01	3.59
	42.07	4.97
	49.19	6.95
	81.13	11.61
	100.77	11.81
	138.74	15.93
	252.97	24.15
	323.72	25.68
	491.52	30.85
	784.86	38.15
	892.09	39.86
	1131.23	44.06
	1515.05	43.17
DMDBT	0.00	0.00
	2.34	0.43
	2.61	0.61
	2.76	0.96
	5.54	3.81
	7.38	1.51
	9.02	2.12
	9.25	5.34
	14.31	3.18
	21.76	8.00
	27.08	9.04
	79.73	11.31
	146.37	14.69
	229.45	13.60
	371.66	12.80
	400.70	18.07

(d) UMCM-150

	concentration	adsorption amount
	(ppmw S)	*(g S/kg sorbent)*
BT	0.00	0.00
	22.72	1.81
	27.07	2.25
	43.41	3.18
	99.94	5.74
	121.35	6.91
	165.84	9.80
	275.47	12.20
	317.29	14.58
	415.68	19.65
	709.82	22.75
	811.81	25.16
	954.01	32.45
	1240.08	37.45
	1406.26	37.42
	1591.26	42.48
DBT	0.00	0.00
	6.26	1.41
	8.47	1.99
	11.44	2.85
	19.49	4.20
	28.54	5.81
	31.69	2.18
	33.43	3.31
	39.13	7.56
	39.74	6.20
	55.54	10.41
	58.65	10.86
	59.10	9.24
	84.85	14.81
	117.58	15.71
	132.02	18.25
	170.18	22.26
	194.76	25.19
	241.16	26.64
	285.69	32.10
	442.99	49.68
	523.23	38.77
	608.47	60.84
	932.53	71.09
	978.33	67.84
	1238.44	78.62
	1609.47	83.35
DMDBT	0.00	0.00
	1.44	0.87
	1.95	1.29
	2.73	2.31
	8.03	2.97
	9.39	4.39
	10.95	7.92
	11.86	7.36
	15.73	10.82
	31.23	17.78
	38.00	17.95
	67.68	24.27
	145.01	32.45
	175.26	32.14
	265.39	36.86
	423.79	39.53

(e) MOF-505

	concentration	adsorption amount
	(ppmw S)	*(g S/kg sorbent)*
BT	0.00	0.00
	6.78	1.35
	6.83	3.20
	7.53	1.71
	25.88	5.95
	28.27	4.65
	43.29	10.49
	93.36	10.73
	94.54	13.62
	164.39	22.63
	324.56	23.06
	360.64	28.30
	614.13	39.34
	719.51	41.69
	942.58	43.34
	1284.94	52.95
DBT	0.00	0.00
	0.00	1.22
	0.00	0.84
	0.00	1.67
	1.10	2.42
	1.12	3.74
	1.25	5.83
	1.61	5.45
	1.63	8.50
	2.23	5.43
	2.71	2.64
	4.84	19.11
	7.40	14.06
	7.42	12.08
	28.21	19.96
	160.29	37.13
	258.15	28.47
	535.75	31.18
	885.40	41.85
	915.02	38.57
	1181.06	44.01
	1582.46	47.30
DMDBT	0.00	0.00
	0.62	0.65
	0.83	1.75
	0.85	0.75
	3.85	5.54
	4.41	2.23
	4.60	6.39
	5.40	2.56
	6.51	5.92
	11.58	13.54
	13.57	14.37
	14.34	15.58
	113.90	25.08
	150.20	25.17
	188.46	24.99
	447.52	25.41