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Supplementary file for ''Probing adsorbent heterogeneity using Toth isotherms'

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Table 1: Toth adsorption isotherm parameters obtained using a non-linear regression analysis. Also given is the optimized error function, the sum of the errors squared (ERRSQ = $(q_{experimental} - q_{predicted})^2$).

Note: The units of binding affinity depend on the units of the equilibrium pressure or concentration in the experimental isotherm. If the pressure is expressed in terms of bar, then the unit of the binding affinity will be equal to 1/bar. Similarly, the units of the number of adsorption sites, N(K) depends on the unit of the amount adsorbed. If the amount adsorbed is expressed in terms of μmol/g, the N(K) will be expressed in terms of μM/g. The Toth isotherm parameters were obtained in this work based on the experimental data adapted from the cited references.

Adsorbent	Template used for synthesis or adsorbate used to obtain isotherms	q_m	*b*	*t*	ERRSQ	Sample name as reported in the original works	Units of binding affinity, *K*	Units of *N*(*K*)	Reference
Polymer 1	Ethyl adenine-9-acetate	6686.956	1.081	0.126	17.505	---	mM^{-1}	μmol/g	[1]
Polymer 2	9-Ethyl adenine	399.970	0.566	0.158	8.079	---	mM^{-1}	μmol/g	[2]
Polymer 3	Cholosterol	119.137	0.590	1	1899.098	---	mM^{-1}	μmol/g	[3]
Polymer 4	Diclofenac	23.59077	0.179	1	1.224	MIP 0	mM^{-1}	μmol/g	[4]
Polymer 5	Diclofenac	26.2276	0.061	1	2.334	MIP 10	mM^{-1}	μmol/g	[4]
Polymer 6	Diclofenac	19.056	0.231	1	2.152	MIP 20	mM^{-1}	μmol/g	[4]
Polymer 7	Diclofenac	17.448	0.289	1	1.670	MIP 30	mM^{-1}	μmol/g	[4]
Polymer 8	Mefanamic acid	18.921	0.227	0.943	0.393	MIP 0	mM^{-1}	μmol/g	[4]
Polymer 9	Mefanamic acid	22.371	0.081	1	12.318	MIP 10	mM^{-1}	μmol/g	[4]
Polymer 10	Mefanamic acid	19.739	0.290	0.836	1.097	MIP 20	mM^{-1}	μmol/g	[4]
Polymer 11	Mefanamic acid	15.751	0.325	1	0.556	MIP 30	mM^{-1}	μmol/g	[4]
Polymer 12	Sinapic acid	161.586	0.075	1	3383.223	MIP1	L/mmol	μmol/g	[5]
Polymer 13	Sinapic acid	44.370	0.068	1	152.405	MIP3	L/mmol	μmol/g	[5]
Polymer 14	Ibuprofen	315.178	7.988	0.585	327.468	MIP	L/mg	mg/g	[6]
Polymer 14	Naproxen	248.674	47.534	1	74.706	MIP	L/mg	mg/g	[6]
Polymer 14	Clofibric acid	294.781	24.935	0.911	223.132	MIP	L/mg	mg/g	[6]
Polymer 14	Diclofenac	358.369	7.634	0.687	100.417	MIP	L/mg	mg/g	[6]
Polymer 14	Ketoprofen	307.448	21.051	0.810	302.721	MIP	L/mg	mg/g	[6]
Al-soc-MOF1	Methane	556.601	126.298	1	194.648	Al-soc-MOF1	bar^{-1}	v/v*	[7]
MOF-905	Methane	432.172	71.296	1	228.517	MOF-905	bar^{-1}	v/v*	[8]
LMA-738	Methane	11408.666	3.906	0.295	724.077	LMA-738	bar^{-1}	v/v*	[9]

MAXSORB	Methane	3235.945	1.965	0.274	565.934	MAXSORB	bar^{-1}	v/v*	[9]
VR93	CO_2	6962.065	3.265	0.416	1.127	VR93	bar^{-1}	mg/g	[10]
MAXSORB	CO_2	9847.422	2.408	0.264	0.854	MAXSORB	bar^{-1}	mg/g	[10]
Merck	Caffeine	1.330	0.408	0.660	$1.5x10^{-5}$	Merck	L/mol	mol/L	[11]
Phenomenex	Caffeine	1.146	0.430	0.670	$1.66x10^{-5}$	Phenomenex	L/mol	mol/L	[11]
Vydac	Caffeine	0.353	0.406	0.446	$1.89x10^{-5}$	Vydac	L/mol	mol/L	[11]
Merck	Phenol	3.359	0.433	0.572	$7x10^{-4}$	Merck	L/mol	mol/L	[11]
Phenomenex	Phenol	2.455	0.380	2.455	$6x10^{-4}$	Phenomenex	L/mol	mol/L	[11]
Vydac	Phenol	0.891	0.412	0.742	$2x10^{-5}$	Vydac	L/mol	mol/L	[11]

*v/v = volume of adsorbent/volume of methane adsorbed

Table 2: Multi-site Langmuir isotherm parameters and the corresponding error function calculated using non-linear regression analysis technique. The experimental data were adapted from the cited references.

Adsorbent	Isotherm parameters						Reference
Polymer 1	N_1, μmol/g	16.548	N_2, μmol/g	259.280	N_3, μmol/g	0	[1]
	K_1, mM^{-1}	3.975	K_2, mM^{-1}	0.026	K_3, mM^{-1}	0	
	ERRSQ						
Polymer 2	N_1, μmol/g	23.132	N_2, μmol/g	95.121	N_3, μmol/g	0	[2]
	K_1, mM^{-1}	5.810	K_2	0.044	K_3, mM^{-1}	0	
	ERRSQ						
Polymer 3	N_1, μmol/g	119.137	N_2, μmol/g	0	N_3, μmol/g	0	[3]
	K_1, mM^{-1}	1.695	K_2, mM^{-1}	0	K_3, mM^{-1}	0	
	ERRSQ	1899.098					
Polymer 12	N_1, μmol/g	176.940	N_2, μmol/g	0	N_3, μmol/g	0	[5]
	K_1,L/mmol	5.915	K_1,L/mmol	0	K_3,L/mmol	0	
	ERRSQ	1275.963					
Polymer 13	N_1, μmol/g	45.756	N_2, μmol/g	0	N_3, μmol/g	0	[5]
	K_1,L/mmol	9.395	K_1,L/mmol	0	K_3, L/mmol	0	
	ERRSQ	216.061					

Table 3: Freundlich, Langmuir-Freundlich isotherms and their binding affinity distribution model.

Note: K_F and n are the Freundlich isotherm constants. The parameter, q_m is the maximum adsorption capacity usually expressed in terms of mmol/g, a and m are Langmuir-Freundlich isotherm constants. The parameter is m is related to the heterogeneity of the adsorbent and ranges from 0 to 1, where 1 signifies a homogeneous adsorbent and $m < 1$ means the material is heterogeneous.

Theoretical isotherm	Affinity spectra of the theoretical isotherm	Reference
$q = K_F C_e^n$	$N(K) = 2.303 K_F n(1 - n^2) K^{-n}$	[12]
$q = \frac{q_m a p^m}{1 + a p^m}$	$N(K) = q_m a m (1/K)^m \frac{\left[\left(1 + 2a(1/K)^m + a^2(1/K)^{2m} + 4a(1/K)^m m^2 - a^2\left(\frac{1}{K}\right)^{2m} m^2 - m^2\right)\right]}{\left(1 + a(1/K)^m\right)^4}$	[13]

Table 4: Toth, Langmuir-Freundlich and Freundlich isotherm parameters and the corresponding error function calculated using a non-linear regression analysis technique.

Note: The experimental data were adapted from the cited references.*

Adsorbent		Toth		Freundlich		Langmuir-Freundlich		Reference
VR93	CO_2	q_m, mg/g	6962.065	k	26.044	q_m, mg/g	552.898	[10]
		b, bar^{-1}	3.265	n	0.419	a, bar^{-1}	0.205	
		t	0.416	ERRSQ	112501.544	m	0.827	
		ERRSQ	1.127			ERRSQ	0.475	
MAXSORB	CO_2	q_m, mg/g	9847.422	k	34.004	q_m, mg/g	1337.919	[10]
		b, bar^{-1}	2.408	n	0.385	a, bar^{-1}	0.189	
		t	0.264	ERRSQ	9503.187	m	0.899	
		ERRSQ	0.854			ERRSQ	1.370	
Polymer 14	Ibuprofen	q_m, mg/g	315.178	k	21.564	q_m, mg/g	276.543	[6]
		b, L/mg	7.988	n	0.416	a, bar^{-1}	0.034	
		t	0.585	ERRSQ	632.017	m	0.774	
		ERRSQ	327.468			ERRSQ	295.861	
Polymer 14	Naproxen	q_m, mg/g	248.674	k	22.098	q_m, mg/g	248.675	[6]
		b, bar^{-1}	47.534	n	0.431	a, bar^{-1}	0.021	
		t	1	ERRSQ	1140.810	m	1	
		ERRSQ	74.706			ERRSQ	74.70617	

* It is worth to mention here Toth isotherm can produce better fit than Langmuir-Freundlich isotherm at higher pressures and for few cases, especially at lower pressures, Langmuir-Freundlich isotherm can provide a better fit than the Toth isotherm. It is essential to test the best-fit isotherm using a suitable regression analysis. If the experimental equilibrium data follows the Langmuir-Freundlich or a Freundlich isotherm, then we can use the affinity distribution functions given in Table 3 of the supplementary information).

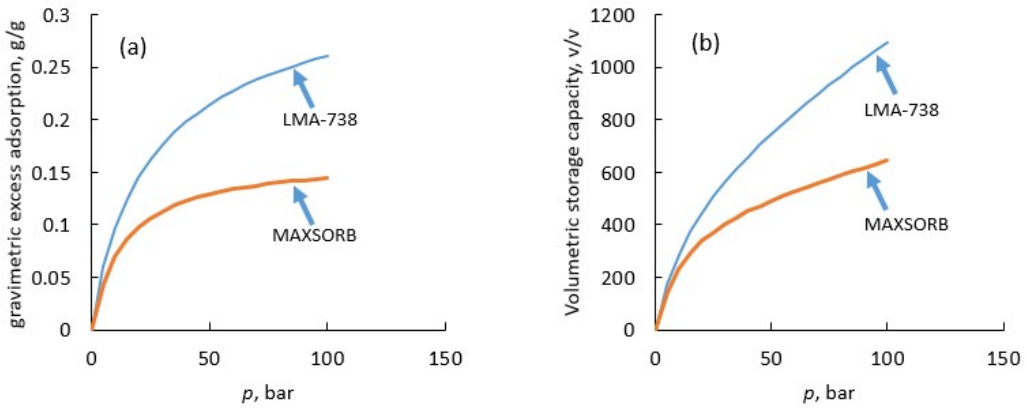

Figure 1: Methane storage capacity: (a) gravimetric capacity and (b) volumetric storage capacity. Figure 1a was adapted from the works of Casco et al.[9] The volumetric storage capacity was calculated using the procedure below.

Step 1: Let the amount adsorbed at 10 bar and 298 K be equal to 0.0972 g of CH_4/g of adsorbent. This is experimentally measured value and thus corresponds to excess adsorption.

Step 2: At STP conditions, 1 g of CH_4 occupies 1.4115 L. Thus g of CH_4/g of adsorbent will be equal to 0.0972 x 1.4115 = 0.1372 L/g or 137.298 cm^3 of CH_4/g of adsorbent.

Step 3: According to the NIST fluid page, at 10 bar and 298 K, the bulk density of methane is 0.006588 g/cm3.

Step 4: If the pore volume of an adsorbent is 2.25 cm^3/g (This is the pore volume of LMA-738. Then each gram should contain 2.25 cm^3 of pore space. This means the amount of methane that can be filled in unit mass of adsorbent that contains pores of volume 2.25 cm^3 will be equal to 0.006588*2.225 = 0.014824 g of CH_4/g of adsorbent.

Step 5: At STP conditions, 0.014824 g of CH_4/g of adsorbent should be equal to 0.014824 x 1.4115 = 0.020924 L of CH_4/g of adsorbent. This is the approximate amount of methane that will be stored in the adsorbent pores as bulk gas at 10 bar and 298 K.

Step 6: Thus the total adsorption will be equal to 0.1372 L/g (from **step 2**) + 0.020924 L of CH_4/g of adsorbent (from **step 5**) = 0.158221625 L of CH_4/g of adsorbent.

Step 7: If the skeletal or He density of the adsorbent is equal to 1.8 g/cm3 or 1800 g/L. Then the volumetric storage capacity is equal to 0.158221625 L of CH_4/g of adsorbent x 1800 g of adsorbent/L of adsorbent = 284 L/L.

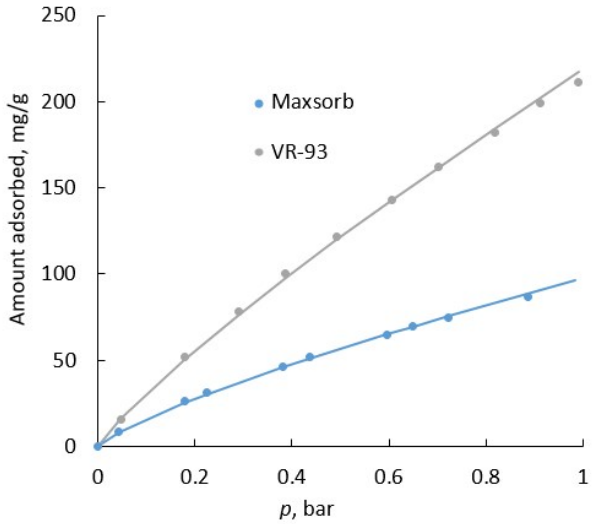

Figure 2: CO_2 adsorption isotherm at 298 K for Maxsorb and VR-93. The experimental data was adapted from the works of Silvestre-Albero et al.[10]

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