SUPPORTING INFORMATION

Modeling Competitive Adsorption of Mixtures of Volatile Organic Compounds in a Fixed-Bed of Beaded Activated Carbon

Dereje Tamiru Tefera,[1] Zaher Hashisho,[1*] John H. Philips,[2] James E. Anderson,[3] Mark Nichols[3]

[1] University of Alberta, Department of Civil and Environmental Engineering, Edmonton, AB T6G 2W2, Canada
[2] Ford Motor Company, Environmental Quality Office, Dearborn, MI 48126 USA
[3] Ford Motor Company, Research and Advanced Engineering, Dearborn, MI 48121 USA
* Corresponding author, Department of Civil and Environmental Engineering, Edmonton, AB T6G 2W2, Canada Tel.: +1-780-492-0247; fax: +1-780-492-0249. E-mail: hashisho@ualberta.ca

Derivation of isotherm equation for competitive adsorption

The single component Langmuir isotherm model was extended by Butler and Ockrent [1] to predict competitive adsorption of mixture of binary components. Later, Jain and Snoeyink [2] revealed the limitation of that extension of and proposed a new form of the competitive isotherm for binary mixtures of organic compounds from wastewater (equation S1 and S2) wherein $(q_{m1}>q_{m2})$. [3]

$$q_1=\frac{(q_{m1}-q_{m2})b_1C_1}{1+b_1C_1}+\frac{q_{m2}b_1C_1}{1+b_1C_1+b_2C_2} \quad \text{S1}$$

$$q_2=\frac{q_{m2}b_2C_2}{1+b_1C_1+b_2C_2} \quad \text{S2}$$

The model for adsorption of competing binary mixtures was then modified for the prediction of ternary $(q_{m1} > q_{m2} > q_{m3})$ mixtures from an aqueous system [4].

$$q_1=\frac{(q_{m1}-q_{m2})b_1C_1}{1+b_1C_1}+\frac{(q_{m2}-q_{m3})b_1C_1}{1+b_1C_1+b_2C_2}+\frac{q_{m3}b_1C_1}{1+b_1C_1+b_2C_2+b_3C_3} \quad \text{S3}$$

$$q_2 = \frac{(q_{m2}-q_{m3})b_2C_2}{1+b_1C_1+b_2C_2} + \frac{q_{m3}b_2C_2}{1+b_1C_1+b_2C_2+b_3C_3} \quad \text{S4}$$

$$q_3 = \frac{q_{m3}b_3C_3}{1+b_1C_1+b_2C_2+b_3C_3} \quad \text{S5}$$

In the current study, the model for competitive adsorption in a ternary system was extended for n-component mixtures of VOCs to describe adsorption from a gas stream and tested with an eight-component VOCs mixture in which ($q_{m1} > q_{m2} > q_{m3} > q_{m4} > \cdots\cdots\cdots\cdots\cdots > q_{m7} > q_{m8}$).

$$q_1 = \frac{(q_{m1}-q_{m2})b_1C_1}{1+b_1C_1} + \frac{(q_{m2}-q_{m3})b_1C_1}{1+b_1C_1+b_2C_2} + \frac{(q_{m3}-q_{m4})b_1C_1}{1+b_1C_1+b_2C_2+b_3C_3} + \frac{(q_{m4}-q_{m5})b_1C_1}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4} + \frac{(q_{m5}-q_{m6})b_1C_1}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+\ b_5C_5} + \frac{(q_{m6}-q_{m7})b_1C_1}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+b_5C_5+b_6C_6} + \frac{(q_{m7}-\ q_{m8})b_1C_1}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+b_5C_5+b_6C_6+b_7C_7} + \frac{q_{m8}b_1C_1}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+b_5C_5+b_6C_6+b_7C_7+b_8C_8} \quad \text{S6}$$

$$q_2 = \frac{(q_{m2}-q_{m3})b_2C_2}{1+b_1C_1+b_2C_2} + \frac{(q_{m3}-q_{m4})b_2C_2}{1+b_1C_1+b_2C_2+b_3C_3} + \frac{(q_{m4}-q_{m5})b_2C_2}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4} + \frac{(q_{m5}-q_{m6})b_1C_1}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+\ b_5C_5} + \frac{(q_{m6}-q_{m7})b_2C_2}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+b_5C_5+b_6C_6} + \frac{(q_{m7}-\ q_{m8})b_2C_2}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+b_5C_5+b_6C_6+b_7C_7} + \frac{q_{m8}b_2C_2}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+b_5C_5+b_6C_6+b_7C_7+b_8C_8} \quad \text{S7}$$

$$q_3 = \frac{(q_{m3}-q_{m4})b_3C_3}{1+b_1C_1+b_2C_2+b_3C_3} + \frac{(q_{m4}-q_{m5})b_3C_3}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4} + \frac{(q_{m5}-q_{m6})b_3C_3}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+\ b_5C_5} + \frac{(q_{m6}-q_{m7})b_3C_3}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+b_5C_5+b_6C_6} + \frac{(q_{m7}-\ q_{m8})b_3C_3}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+b_5C_5+b_6C_6+b_7C_7} + \frac{q_{m8}b_3C_3}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+b_5C_5+b_6C_6+b_7C_7+b_8C_8} \quad \text{S8}$$

$$q_4 = \frac{(q_{m4}-q_{m5})b_4C_4}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4} + \frac{(q_{m5}-q_{m6})b_4C_4}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+\ b_5C_5} + \frac{(q_{m6}-q_{m7})b_4C_4}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+b_5C_5+b_6C_6} + \frac{(q_{m7}-\ q_{m8})b_4C_4}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+b_5C_5+b_6C_6+b_7C_7} + \frac{q_{m8}b_4C_4}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+b_5C_5+b_6C_6+b_7C_7+b_8C_8} \quad \text{S9}$$

$$q_5 = \frac{(q_{m5}-q_{m6})b_5C_5}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+\ b_5C_5} + \frac{(q_{m6}-q_{m7})b_5C_5}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+b_5C_5+b_6C_6} + \frac{(q_{m7-}\ q_{m8})b_5C_5}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+b_5C_5+b_6C_6+b_7C_7} + \frac{q_{m8}b_5C_5}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+b_5C_5+b_6C_6+b_7C_7+b_8C_8} \quad \text{S10}$$

$$q_6 = \frac{(q_{m6}-q_{m7})b_6C_6}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+b_5C_5+b_6C_6} + \frac{(q_{m7-}\ q_{m8})b_6C_6}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+b_5C_5+b_6C_6+b_7C_7} + \frac{q_{m8}b_6C_6}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+b_5C_5+b_6C_6+b_7C_7+b_8C_8} \quad \text{S11}$$

$$q_7 = \frac{(q_{m7-}\ q_{m8})b_7C_7}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+b_5C_5+b_6C_6+b_7C_7} + \frac{q_{m8}b_7C_7}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+b_5C_5+b_6C_6+b_7C_7+b_8C_8} \quad \text{S12}$$

$$q_8 = \frac{q_{m8}b_8C_8}{1+b_1C_1+b_2C_2+b_3C_3+b_4C_4+b_5C_5+b_6C_6+b_7C_7+b_8C_8} \quad \text{S13}$$

General isotherm equation for the ith component

The general form for the competitive adsorption isotherm equation for the ith adsorbate in a mixture of n VOCs could then be written as:

$$q_{e,i} = \sum_{k=i}^{n} \frac{b_i c_i a_k}{1+\sum_{j=1}^{k} b_j c_j} \quad \text{S14}$$

where:

a_k=$(q_{m,k} - q_{m,k+1})$ for k= i to n-1

and $a_k = q_{m,n}$, for k = n

Calculation of isotherm parameters

The pure component Langmuir isotherm parameters were determined by linearizing the corresponding isotherm equation (equation S15) and fitting the resulting equation to measured isotherm data (Figure S1), obtained by completing a mass balance on a reactor loaded with 4 to 5g of BAC and adsorbing at 25^{o}C where air is used as carrier gas. In equation S15 the slope of the line is $\left(\frac{1}{b_i q_{m,i}}\right)$, the y-intercept is $\left(\frac{1}{q_{m,i}}\right)$. Hence, b_i and $q_{m,i}$ can be readily calculated at 25^{o}C.

$$\frac{1}{q_{e,i}} = \frac{1}{b_i q_{m,i} c_i} + \frac{1}{q_{m,i}} \quad \text{S15}$$

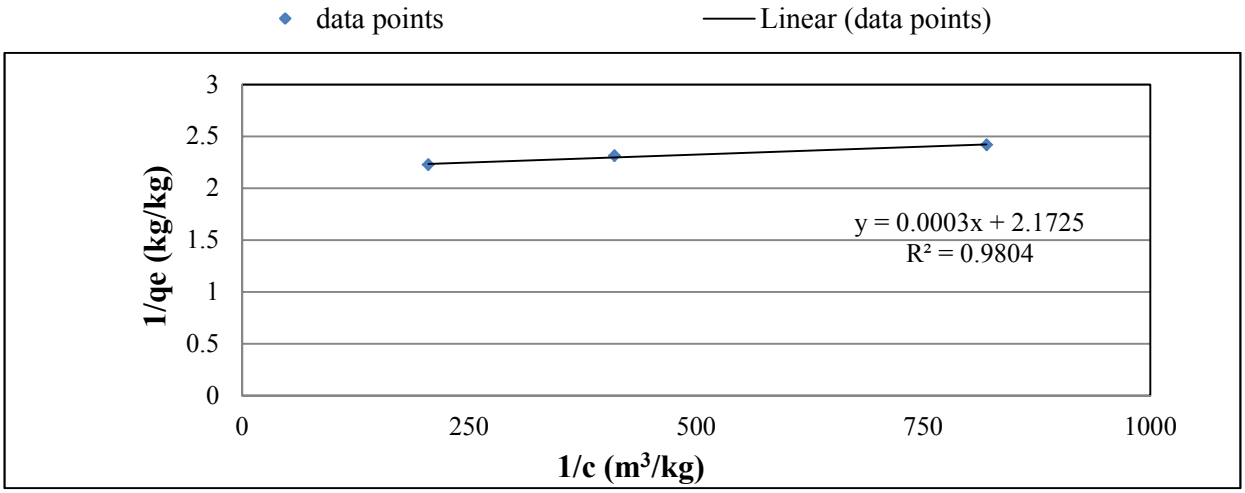
The temperature-dependent Langmuir affinity coefficient, b_i, can be calculated as a function of temperature using equation S16

$$b_i = b_{o,i}\exp\left(\frac{-\Delta H_{ad,i}}{R_g T}\right) \quad \text{S16}$$

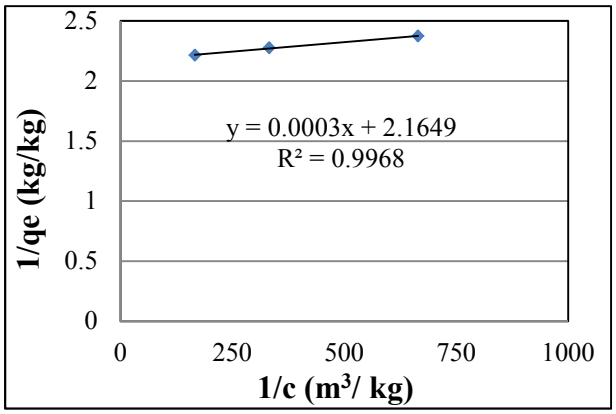
Knowing the value of b_i at 25 ^{o}C (using Figure S1 and equation S15), $b_{o,i}$ can be calculated using equation S17:

$$b_{o,i} = \frac{b_i \text{ at } 25℃}{\exp\left(\frac{-\Delta H_{ad,i}}{R_g T}\right)} \quad \text{S17}$$

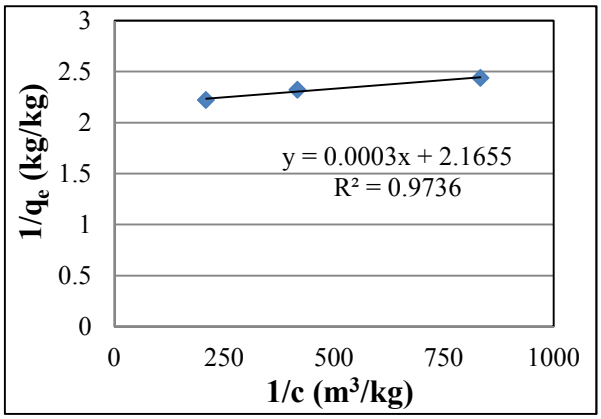
Where T=298K in equation S17.



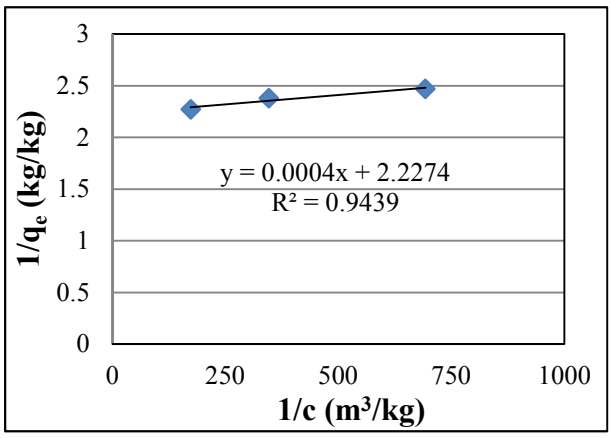
a



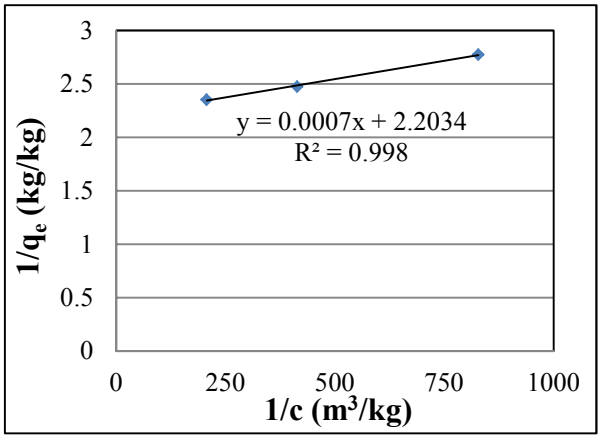
b



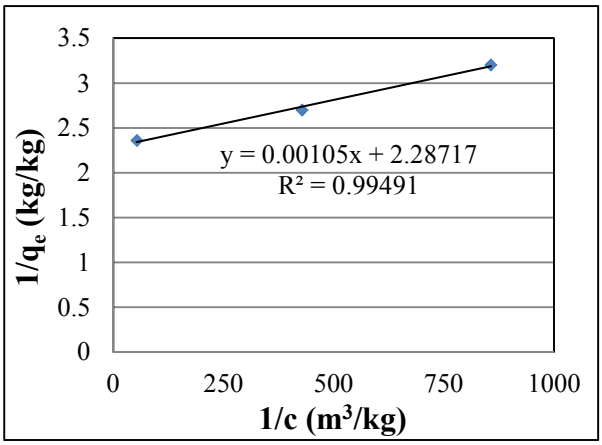
c



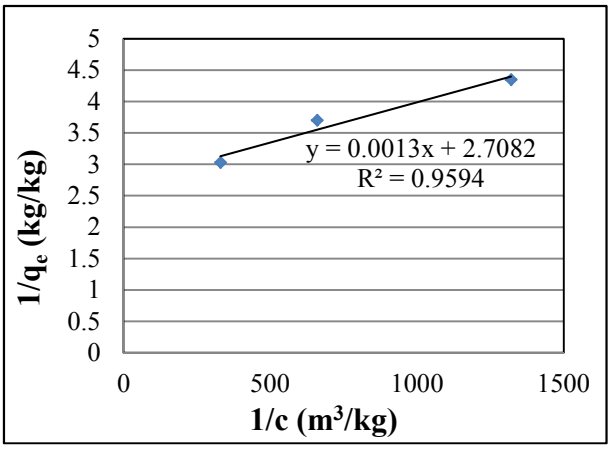
d



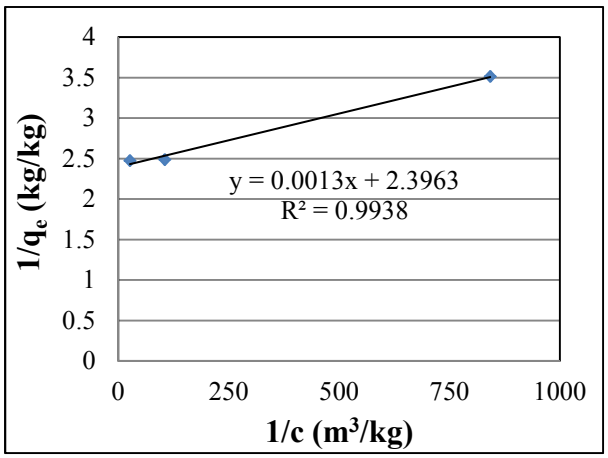
e



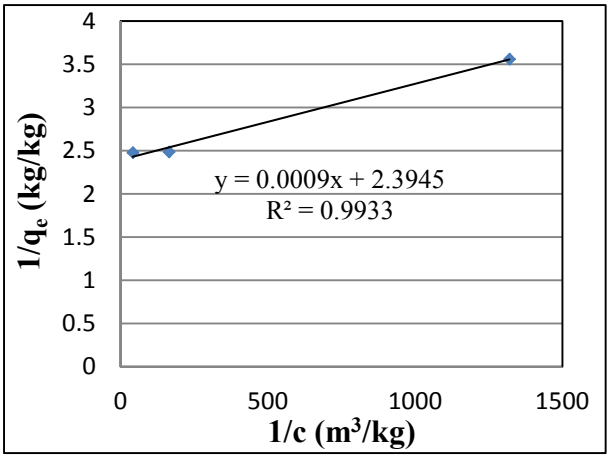
f



g



h



i

Figure S1. Calculation of Langmuir isotherm parameters for individual compounds (a) 1,2,4-trimethylbenzene, (b) 2,2-dimethylpropylbenzene, (c) indane, (d) n-decane, (e) 2-butoxy ethanol, (f) 2-heptanone, (g) n-heptane, (h) n-butyl acetate, and (i) n-butanol.

Table S1 shows Langmuir isotherm parameters for each compound: the maximum adsorption capacity ($q_{m,i}$), the Langmuir affinity coefficient at 25°C (b_i at25°C) and the pre-exponential constant in the temperature dependent Langmuir affinity coefficient ($b_{o,i}$).

Table S1. Langmuir isotherm parameters at 25°C

Compound	$q_{m,i}$ (kg/kg)	b_i at 25°C (m^3/kg)	$b_{o,i}$ (m^3/kg)
1,2,4-trimethylbenzene	0.46	7242	9.73E-12
2,2-dimethylpropylbenzene	0.46	7216	9.38E-12
indane	0.46	5338	8.64E-13
n-decane	0.45	4455	6.08E-13
2-butoxyethanol	0.45	3148	2.34E-13
2-heptanone	0.44	2287	1.78E-13
n-heptane	0.37	2083	5.01E-12
n-butyl acetate	0.42	1843	9.87E-15
n-butanol	0.42	1710	1.52E-15

Table S2 shows the physical properties of the adsorbates studied.

Table S2. Physical properties of the adsorbates

Compound	Formula	$M_{A,i}$ [5] (g/mol)	$\left(\sum v\right)_{A,i}$	ΔH_{vap} [6, 7] (kJ/mol)	α [8, 9] (10^{-24}cm^3)	γ [6, 8-10] (mN/m)	IP [8, 9,10] (eV)
1,2,4-trimethybenze	C_9H_{12}	120.20	152.06	39.2	15.87	28.70	8.27
2,2-dimethylpropylbenzene	$C_{11}H_{16}$	148.20	192.98	46.74	19.59	28.80	7.71
indane	C_9H_{10}	118.20	127.90	49.05	15.48	27.50	8.40
n-decane	$C_{10}H_{22}$	142.30	168.3	38.75	19.10	23.90	10.20
2-butoxyethanol	$C_6H_{14}O_2$	118.20	137.68	47.06	13.00	27.40	10.00
2-heptanone	$C_7H_{14}O$	114.20	148.70	39.5	13.51	24.80	9.37
n-heptane	C_7H_{16}	100.21	147.18	36.66	13.60	20.14	9.90
n-butyl acetate	$C_6H_{12}O_2$	116.20	133.72	36.14	12.61	24.35	10.10
n-butanol	$C_4H_{10}O$	74.10	91.28	43.29	8.71	25.57	10.14

Characterization of the adsorbent porosity

Characterization of the adsorbent porosity is described in detail in our previous work [11]. The porosity of BAC samples was analyzed using a micropore surface analysis system (IQ2MP, Quantachrome) using N_2 as probe molecule. The micropore volume and pore size distribution were determined using the V-t and density function theory (DFT) models, respectively. The values for w_{mic} , volume averaged micropore width (for heat of adsorption calculation) and r_p, the volume averaged pore radius (based on the micropore, mesopore and macropore half-widths) are calculated from the instrument output data as $\sum(w_{mic,m}\, f_m)$ and $\sum(r_{p,m}\, f_m)$, respectively, where f_m is pore volume fraction of the m^{th} pore size range. The value for w_{mic} is 1.02nm, and the value of r_p is 1.1nm.

Computation of the Biot number and surface to pore diffusion flux

Biot number [12], surface to pore diffusion flux ratio, φ_i, [13],the external mass transfer resistance coefficient, $k_{film,i}$, [12, 14] and the surface diffusion coefficient, D_s [15] were calculated using the following equations:

$$Bi_{p,i} = \frac{k_{film,i} d_p}{2D_{eff,i}} \quad \text{S18}$$

$$\varphi_i = \frac{\rho_b D_{s,i} q_{e,i}}{D_{eff,i} C_{o,i}} \quad \text{S19}$$

$$k_{film,i} = \frac{[1+1.5(1-\varepsilon_b)] D_{AB,i}}{d_p} \left(2 + 0.644\left(\mathrm{Re_p}^{1/2} \mathrm{Sc_i}^{1/3}\right)\right) \quad \text{S20}$$

$$D_s = D_{so} exp\left(\frac{-E_{a,i}}{R_g T}\right) \quad \text{S21}$$

where D_{so} is the pre-exponential factor ($10^{-4} cm^2/s$) and the activation energy of adsorption, E_a is given as $E_{a,i} = 5.38 R_g T_{bi}$ [15] wherein T_{bi}, is the boiling point of the adsorbates. **Table S3** provides definition of the other parameters used in equations S18-S21.

Table S3.Values of pore diffusion, surface diffusion and external mass transfer coefficient at 25°c

Compound	$D_{eff,i}$ (cm^2/s)	$D_{s,i}$ (cm^2/s)	$k_{film,i}$ (cm/s)	$Bi_{p,i}\left(\frac{k_{film,i} d_p}{2D_{eff,i}}\right)$	$\varphi_i\left(\frac{\rho_b D_{s,i} q_{e,i}}{D_{eff,i} C_{o,i}}\right)$
1,2,4-trimethylbenzene	1.69E-05	5.75E-22	21.85	4.70E+04	5.04E-12
2,2-dimethylpropylbenzene	1.52E-05	3.26E-23	27.77	5.03E+04	8.17E-13
Indan	1.70E-05	1.96E-22	22.42	4.61E+04	1.93E-12
n-decane	1.55E-05	2.81E-18	21.45	4.82E+04	2.43E-08
2-butoxyethanol	1.70E-05	4.81E-18	22.10	4.88E+04	1.35E-08
2-heptanone	1.73E-05	7.72E-19	19.91	4.65E+04	1.76E-09
n-heptane	1.85E-05	5.59E-14	21.13	4.44E+04	2.45E-06
n-butyl acetate	1.71E-05	1.68E-16	22.81	4.90E+04	1.70E-07
n-butanol	2.15E-05	9.37E-16	18.67	4.85E+04	4.96E-07

Comparison of modelled and measured amount adsorbed

Table S4 and Table S5 compare the modelled and experimentally measured [5] amount adsorbed for each component in the binary and eight component mixtures, respectively.

Table S4. Comparison of modelled and experimentally measured amount adsorbed for the binary mixture

Name	**Modelled amount adsorbed (g/g)**	**Measured amount adsorbed (g/g)**	**MRAE (%)**
n-heptane	0.012	0.004	200
n-decane	0.403	0.406	0.74
total amount adsorbed	0.414	0.41	1

Table S5. Comparison of modelled and experimentally measured amount adsorbed for the eight components mixture

Name	**Modelled amount adsorbed (g/g)**	**Measured amount adsorbed (g/g)**	MRAE (%)
n-butanol	0.006	0.001	600
n-butyl acetate	0.011	0.004	202
2-heptanone	0.020	0.018	9
2-butoxyethanol	0.031	0.028	12
n-decane	0.067	0.069	4
indane	0.073	0.075	3
1,2,4-trimethylbenzene	0.083	0.084	1
2,2-dimethylpropylbenzene	0.125	0.129	2
total amount adsorbed	0.416	0.407	2

References:

1. Butler, J. A. V.; Ockrent, C., Studies in electrocapillarity. Part III: The surface tensions of solutions containing two surface-active solutes. *J. Phys. Chem.* **1930,** *34*, (12), 2841-2859.
2. Jain, J. S.; Snoeyink, V. L., Adsorption from bisolute systems on active carbon. *Journal of the Water Pollution Control Federation* **1973,** *45*, (12), 2463-2479.
3. Jain, J. S.; Vernon, L. S., Adsorption from Bisolute Systems on Active Carbon. *Journal (Water Pollution Control Federation)* **1973,** *45*, (12), 2463-2479.
4. Alkhamis, K. A.; Wurster, D. E., Prediction of adsorption from multicomponent solutions by activated carbon using single-solute parameters. Part II--Proposed equation. *AAPS PharmSciTech* **2002,** *3*, (3), E23.
5. Wang, H.; Jahandar Lashaki, M.; Fayaz, M.; Hashisho, Z.; Philips, J. H.; Anderson, J. E.; Nichols, M., Adsorption and desorption of mixtures of organic vapors on beaded activated carbon. *Environmental Science and Technology* **2012,** *46*, (15), 8341-8350.
6. Bowen, D. H. M., HIST 15-Perry's heavyweight handbook for chemical engineers. *Abstracts of Papers of the American Chemical Society* **2008,** *236*.

7. Smith, J. M.; Van Ness, H. C.; Abbott, M. M., *Introduction to chemical engineering thermodynamics*. 7th ed.; McGraw-Hill: Boston, 2005; p xviii, 817 p.
8. Lide, D. R., *CRC Handbook of Chemistry and Physics*. 89th ed ed.; Lide, D.R., Ed; CRC Press: Boca Raton, FL, 2008.
9. Ullmann, F., Ullmann's Encyclopedia of Industrial Chemistry. In VCH: Weinheim: Germany, 1985; Vol. 40 Volume Set.
10. Giraudet, S.; Pré, P.; Tezel, H.; Le Cloirec, P., Estimation of adsorption energies using the physical characteristics of activated carbons and the molecular properties of volatile organic compounds. *Carbon* **2006,** *44*, (12), 2413-2421.
11. Lashaki, M. J.; Fayaz, M.; Wang, H.; Hashisho, Z.; Philips, J. H.; Anderson, J. E.; Nichols, M., Effect of adsorption and regeneration temperature on irreversible adsorption of organic vapors on beaded activated carbon. *Environmental Science and Technology* **2012,** *46*, (7), 4083-4090.
12. Sontheimer, H., Crittenden, J. C., and Summers, S., *Activated carbon for water treatment*. 2nd Ed ed.; DVGWForschungsstelle,: Engler-Bunte Institut, Universitat Karlsruhe,Karlsruhe, Germany., 1988.
13. Do, D. D.; Rice, R. G., On the relative importance of pore and surface diffusion in non-equilibrium adsorption rate processes. *Chemical Engineering Science* **1987,** *42*, (10), 2269-2284.
14. Jarvie, M. E.; Hand, D. W.; Bhuvendralingam, S.; Crittenden, J. C.; Hokanson, D. R., Simulating the performance of fixed-bed granular activated carbon adsorbers: Removal of synthetic organic chemicals in the presence of background organic matter. *Water Research* **2005,** *39*, (11), 2407-2421.
15. Suzuki, M., *Adsorption engineering*. Tokyo : Kodansha ; Amsterdam ; New York : Elsevier: 1990.