Supplementary Material

Activated biocarbons derived from molasses as a new tailored CO2 adsorbents

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# Supplementary Data

**Langmuir Isotherm**

The Langmuir isotherm, which is the simplest model, was designed to characterize the adsorption of the gas-solid phase. It is also used to quantify and compare the maximum adsorption capacity of different sorbents. The Langmuir theory postulates monolayer coverage of adsorbate; adsorption occurs at specific homogeneous sites (all sites are equal, resulting in equal adsorption energies). Once an adsorbate molecule occupies a site, no more adsorption can take place at that site. The sorbent has a limited capacity for the adsorbate (Elmorsi, 2011; Günay et al., 2007):

$q=\frac{q\_{mL}b\_{L}p}{1+b\_{L}p}$ **(S1)**

where qmL is the maximum adsorption capacity [mmol/g], bL is the Langmuir constant [bar-1], p is pressure [bar], q is the adsorbed quantity under p pressure [mmol/g].

**Freundlich Isotherm**

The Freundlich model describing an adsorption on heterogeneous surfaces with different adsorption energies (Ayawei et al., 2015a; Ayawei et al., 2015b) according to equation (S2):

$q=k\_{F}p ^{n\_{F}}$ **(S2)**

where kF is the Freundlich constant [mmol/g], nF is the heterogeneity factor.

**Sips Isotherm**

The Sips model is frequently utilized for the description of the heterogeneous adsorbents such as for example, activated carbons (Delavar et al, 2010, Ning et al., 2006). It is reduced to the Freundlich model at low adsorbate concentrations, and at high adsorbate concentrations, it is similar to the Langmuir model (Travis and Etnier, 1981) and can be expressed by an equation (S3):

$q=\frac{q\_{mS}b\_{S}p^{n\_{S}}}{1+b\_{S}p^{n\_{S}}}$ **(S3)**

where qmS is the maximum adsorption capacity [mmol/g], bS is the Sips constant [bar-1], nS is the heterogeneity factor.

Analyzing the Sips model it should be noticed that the parameters presented in the Sips equation (S3) are dependent on the temperature:

$b\_{S}=b\_{0}exp(\frac{Q}{RT\_{0}})(\frac{T\_{0}}{T}-1)$ **(S4)**

$n\_{S}=n\_{0}+α(1-\frac{T\_{0}}{T})$ **(S5)**

$qm\_{S}=qm\_{0}exp\left\{x(1-\frac{T\_{0}}{T})\right\}$ **(S6)**

**Toth Isotherm**

The Toth isotherm model is next empirical equation developed to enhance isotherm fitting between experimental and calculated data. The Toth isotherm model is useful in describing heterogeneous adsorption systems, which settles with both low and high-end boundaries of the concentration (Jafari Behbahani and Jafari Behbahani, 2014; Padder and Majunder, 2012) according to equation (S7):

$q=\frac{q\_{mT}b\_{T}p}{(1+(b\_{T}p)^{nT})^{\frac{1}{nT}}}$**(S7)**

where qmT is the maximum adsorption capacity [mmol/g], bT is the Toth constant [bar-1], nT is the heterogeneity factor.

**Fritz-Schlunder Isotherm**

Fritz and Schlunder elaborated an empirical equation (S8) that can fit a wide range of experimental results because of many coefficients in the isotherm (Yaneva et al, 2013):

$q=\frac{q\_{mFS }b\_{FS}p}{1+q\_{mFS}pn\_{FS}}$**(S8)**

where qmFS is the maximum adsorption capacity [mmol/g], bFS – the Fritz-Schlunder constant [bar-1], nFS is the Fritz-Schlunder model exponent.

**Radke-Prausnitz Isotherm**

The Radke-Prausnitz model has several significant properties that make it the preferred choice for most adsorption systems with low adsorbate concentrations. At a low adsorbate concentration, the isotherm model reduces to a linear isotherm. At a high adsorbate concentration, it approaches the Freundlich isotherm, and when nRP = 0, it becomes a Langmuir isotherm. Another essential property of this isotherm is that it gives a good fit over a wide range of adsorbate concentrations. Radke – Prausnitz equation can be expressed as (S9) (Radke and Prausnitz, 1972):

$q=\frac{q\_{mRP}b\_{RP}p}{(1+b\_{RP}p)^{n\_{RP}}},$**(S9)**

where qmRP is the maximum adsorption capacity [mmol/g], bRP is the Radke-Prausnitz constant [bar-1], nRP is Radke-Prausnitz model exponent.

**The sum of the squares of the errors**

The sum of the squares of the errors (SSE) can be expressed as follows (S10) (Ho, 2004):

$SSE=\sum\_{i=1}^{n}(q\_{e,calc}-q\_{e,exp})\_{i}^{2}$**(S10)**

# Supplementary Figures and Tables

## Supplementary Figures



**Supplementary Figure S1.** The plots: ln(qm) versus T (a), ln(b) versus 1/T (b), and n versus 1/T (c) applied to the calculation of the Sips parameters in equations (S4-S6) for MB\_1:1



**Supplementary Figure S2.** The plots: ln(qm) versus T (a), ln(b) versus 1/T (b), and n versus 1/T (c) applied to the calculation of the Sips parameters in equations (S4-S6) for MB\_1:2



**Supplementary Figure S3.** The plots: ln(qm) versus T (a), ln(b) versus 1/T (b), and n versus 1/T (c) applied to the calculation of the Sips parameters in equations (S4-S6) for MB\_1:4



**Supplementary Figure S4.** N2 adsorption at a temperature of 20 °C

## Supplementary Tables

Supplementary Table S1. Parameters of the Sips model for CO2 adsorption at different temperatures

|  |  |  |  |
| --- | --- | --- | --- |
|  | **MB\_1:1** | **MB\_1:2** | **MB\_1:4** |
| Temperature | qmS | bS | nS | qmS | bS | nS | qmS | bS | nS |
| [oC] | [mmol/g] | [bar-1] |  | [mmol/g] | [bar-1] |  | [mmol/g] | [bar-1] |  |
| 0 | 9.447 | 1.132 | 0.712 | 17.279 | 0.546 | 0.747 | 26.231 | 0.365 | 0.801 |
| 10 | 8.993 | 0.926 | 0.739 | 17.032 | 0.429 | 0.757 | 27.577 | 0.285 | 0.847 |
| 20 | 8.648 | 0.730 | 0.760 | 16.646 | 0.339 | 0.786 | 27.495 | 0.208 | 0.853 |

**Supplementary Table S2.** Parameters determined from Sips equation

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Activated Biocarbon | b0[bar-1] | Q [kJ/mol] | n0 | α | χ | qmo [mmol/g] |
| **MB\_1:1** | 0.66 | 15 | 0.76 | 0.59 | 1.27 | 9.42 |
| **MB\_1:2** | 0.30 | 16 | 0.78 | 0.55 | 0.56 | 17.31 |
| **MB\_1:4** | 0.18 | 19 | 0.86 | 0.65 | -0.59 | 26.49 |

**Supplementary Table S3.** CO2/N2 selectivity calculated on the basis of Ideal Adsorbed Solution Theory (IAST)

|  |  |
| --- | --- |
| Activated Biocarbon | SIAST |
| **MB\_1:1** | 16.5 |
| **MB\_1:2** | 14.2 |
| **MB\_1:4** | 13.2 |

**Supplementary References**

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