Supplementary Information

This appendix gives supplementary information to the isothermal measurements and the MBDoE algorithm. Section A gives more detailed information on the preliminary isotherm measurements, the measurement uncertainty of the gravimetric suspension balance, and isotherm parameter bounds during parameter estimation. The measurement uncertainty is critical for the χ^2- and t-test. Section B gives a plot of the progression of the MBDoE experiments for the Type III isotherm, and Section C gives the same plot for the Type V isotherm.

A General experimental information

A.1 Preliminary isotherm measurements

Three measurements are needed for an adsorption isotherm with a magnetic suspension balance: The first measurement is a blank measurement without sample where the basket is exposed to a high-density gas, usually Nitrogen (N_2), at varying pressures. According to

$$m_{\text{signal}} = m_{\text{basket}} - \rho_{\text{N}_2} \cdot V_{\text{basket}} \,, \tag{22}$$

a linear function between the mass signal m_{signal} and the density ρ_{N_2} is expected. When calibrating Eq. (22) to the results of the blank measurement, m_{basket} is the y-axis intercept while V_{basket} is the slope.

Once these two parameters are known, the second measurement is performed as was the first, but including the sorbent sample. This buoyancy measurement is performed with Helium (He) as Nitrogen would adsorb and distort the results. According to

$$m_{\text{signal}} = (m_{\text{basket}} + m_{\text{sor}}) - \rho_{\text{He}} \left(V_{\text{basket}} + V_{\text{sor}}\right) \,, \tag{23}$$

mass and volume of the adsorbent sample m_{sor} and V_{sor} can be determined by calibrating a linear function to the results of the buoyancy measurement. An example of blank and buoyancy measurement is shown in Figure 12, resulting to $m_{\text{basket}} = 7.8269\,\text{g}$, $V_{\text{basket}} = 0.9863\,\text{cm}^3$, $m_{\text{sample}} = 8.6378\,\text{g} - 7.8269\,\text{g} = 0.8109\,\text{g}$, and $V_{\text{sample}} = 1.3598\,\text{cm}^3 - 0.9863\,\text{cm}^3 = 0.3735\,\text{cm}^3$.

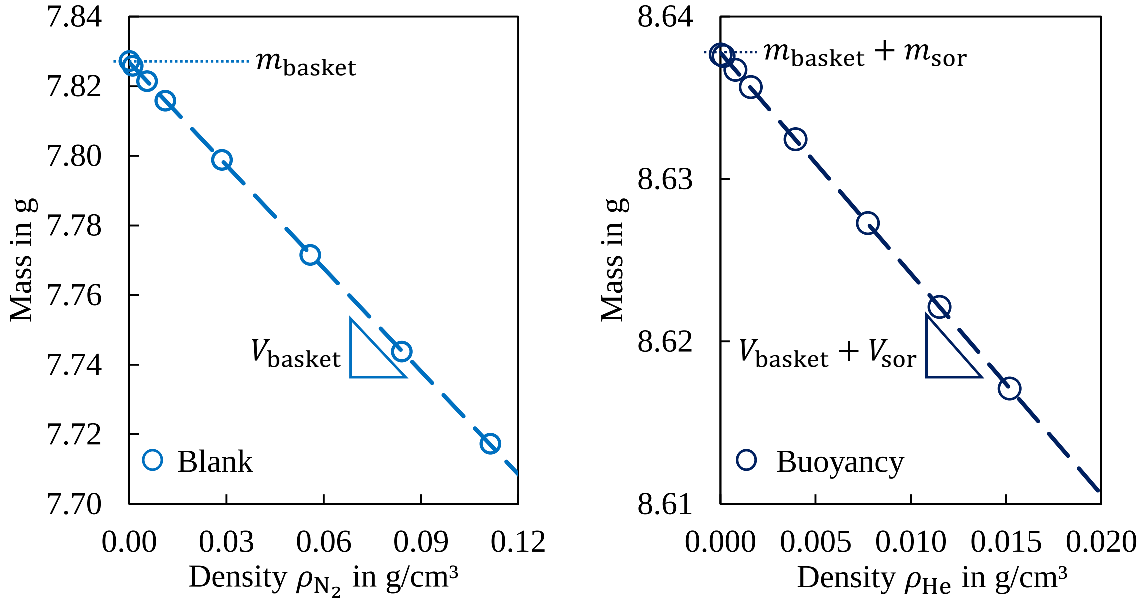

Figure 12: Blank measurement (left) and buoyancy measurement (right). The measurements are aimed to determine mass and volume of the basket as well as mass and volume of the adsorbent sample.

The third measurement is the actual adsorption isotherm with adsorptive and the sample. Because all parameters except the adsorbate mass are known, Eq. (24) yields the adsorbed mass m_{ad}. The volume of the adsorbate within the adsorbent pores is usually set to 0 leading to a negligible error for the buoyancy correction.

$$m_{\text{signal}} = (m_{\text{basket}} + m_{\text{sor}} + m_{\text{ad}}) - \rho_{\text{ad}} \left(V_{\text{basket}} + V_{\text{sor}} + \cancelto{\approx 0}{V_{\text{ad}}} \right) . \tag{24}$$

Based on the mass signal m_{signal}, the mass-specific loading X can be calculated according to Eq. (25).

An analysis of the measurement uncertainty of the loading u_X with the gravimetric suspension balance is given in Appendix A.2 and results to approximately $u_X = 0.02\,\text{g}\,\text{g}^{-1}$.

$$X = \frac{m_{\text{ad}}}{m_{\text{sample}}} = \frac{m_{\text{signal}} - m_{\text{sor}} - m_{\text{basket}}}{m_{\text{sor}}} . \tag{25}$$

A.2 Measurement uncertainty of the gravimetric suspension balance

Here, we estimate the maximal measurement uncertainty of the magnetic suspension balance, which occurred at high relative pressure with water. The measurement uncertainty of the loading X (Eq. (25)) for an adsorption isotherm has two components: One component is the uncertainty in x-direction (i.e., relative pressure p_{rel}) and one is the uncertainty in y-direction (i.e., loading X) according to:

$$u^2_{X,\,\text{Isotherm}} = u^2_X + \left(\frac{\partial X\,(p_{\text{rel}})}{\partial p_{\text{rel}}} u_{p_{\text{rel}}}\right)^2 . \tag{26}$$

Based on the definition of the loading X from Eq. (25), the uncertainty of the loading u_X can be determined through Gaussian error progression [34]:

$$u^2_X = \left(\frac{u_{\text{signal}}}{m_{\text{sor}}}\right)^2 + \left(\frac{m_{\text{basket}} - m_{\text{signal}}}{m^2_{\text{sor}}} u_{m_{\text{sor}}}\right)^2 + \left(\frac{m_{\text{signal}} - m_{\text{sor}}}{m^2_{\text{sor}}} u_{m_{\text{basket}}}\right)^2 . \tag{27}$$

The uncertainty of the relative loading $u_{p_{\text{rel}}}$ can be calculated according to:

$$u^2_{p_{\text{rel}}} = \left(\frac{u_p}{p_{\text{sat}}}\right)^2 + \left(\frac{-p}{p^2_{\text{sat}}} u_{p_{\text{sat}}}\right)^2 . \tag{28}$$

All unknown uncertainties u_p, $u_{p_{\text{sat}}}$, u_{signal}, $u_{m_{\text{sor}}}$, and $u_{m_{\text{basket}}}$ are determined next. The uncertainties for pressure p and saturation pressure p_{sat} are quite simple as they are given by the measurement uncertainty of the pressure and temperature sensors. The pressure sensor has an uncertainty of 5 % of the measurement range. Since this is a measurement uncertainty of Type B [34] the value is divided by $\sqrt{3}$, so $u_p = 0.05\,\%\cdot 1\,\text{bar}/\sqrt{3} = 28.9\,\text{Pa}$. The uncertainty of $u_{p_{\text{sat}}}$ can be calculated according to

$$u^2_{p_{\text{sat}}} = \left(\frac{\partial p_{\text{sat}}}{\partial T} u_T\right)^2 , \tag{29}$$

with $u_T = 0.1\,\text{K}/\sqrt{3} = 0.06\,\text{K}$. The partial derivative of the saturation pressure with respect to the temperature is calculated numerically with the equation of state for the saturation pressure from TILMedia [36] for the respective adsorptive.

The uncertainty of the mass signal u_{signal} is not only determined by the micro scale, but rather from the accuracy of the control of the suspension balance [37]. This control uncertainty is in practice calculated as half of the oscillation amplitude of the mass signal during equilibrium. For our suspension balance, the amplitude of the oscillation in equilibrium is around 45 µg, which leads to an uncertainty of the mass signal of $u_{\text{signal}} = 0.45\,\text{mg}/2/\sqrt{3} = 0.13\,\text{mg}$.

The uncertainty of the masses of the basket ($u_{m_{\text{basket}}}$) and the basket plus the adsorbent ($u_{m_{\text{sor}}}$) are more challenging to determine as they are calculated from linear regression of the buoyancy measurements. According to Bevington et al. [38], the uncertainty of the y-intercept with uncertain x- and y-values is calculated as:

$$u_{\text{y-intercept}} = \frac{1}{\Delta} \sum_{i=1}^{n_{\text{exp}}} \frac{x_i^2}{u_{y_i}^2} \,. \tag{30}$$

In Eq. (30), the uncertainty $u_{\text{y-intercept}}$ corresponds to $u_{m_{\text{basket}}}$ or $u_{m_{\text{sor}}}$, n_{exp} is the number of experiments, x_i are the density values ρ_i on the x-axis, u_{y_i} are the uncertainties of the measurements in the mass signal $u_{\text{signal}} = 0.13\,\text{mg}$, and Δ [38] is calculated according to:

$$\Delta = \sum_{i=1}^{n_{\text{exp}}} \frac{1}{u_{y_i}^2} \sum_{i=1}^{n_{\text{exp}}} \frac{x_i^2}{u_{y_i}^2} - \left(\sum_{i=1}^{n_{\text{exp}}} \frac{x_i}{u_{y_i}^2} \right)^2 \,. \tag{31}$$

When inserting the Helium density for the blank measurements and the Nitrogen density for the buoyancy measurements as x_i and the uncertainty of the mass signal u_{signal} as u_{y_i}, the uncertainties result to $u_{m_{\text{basket}}} = 0.0733\,\text{mg}$ and $u_{m_{\text{sor}}} = 0.0732\,\text{mg}$. Inserting all values into Eq. (26) and (27) leads to a maximal uncertainty of the loading of $u_{X,\,\text{Isotherm}} = 0.0202\,\text{g}\,\text{g}^{-1}$.

A.3 Parameter bounds of isotherm models

Table 8: Overview of the isotherm model parameter bounds during MBDoE. The bounds were never reached during fitting.

Model	Parameter	Lower bound	Upper bound	Unit
Sips Eq. (1)	X_{eq}	0	2	$\mathrm{g\,g^{-1}}$
	$X_{\mathrm{eq},T}$	-20	20	$\mathrm{g\,g^{-1}}$
	b	0	50	$\mathrm{Pa\,Pa^{-1}}$
	b_T	-20	20	$\mathrm{Pa\,Pa^{-1}}$
	n	0	20	-
	n_T	-20	20	-
DA Eq. (3)	X_{eq}	0	2	$\mathrm{g\,g^{-1}}$
	$X_{\mathrm{eq},T}$	-20	20	$\mathrm{g\,g^{-1}}$
	E	0	1000	$\mathrm{J\,kg^{-1}}$
	E_T	-200	200	$\mathrm{J\,kg^{-1}}$
	n	0	20	-
	n_T	-20	20	-
BET Eq. (2)	X_{eq}	0	2	$\mathrm{g\,g^{-1}}$
	$X_{\mathrm{eq},T}$	-20	20	$\mathrm{g\,g^{-1}}$
	g	0	10 e5	-
	g_T	-200	200	-
	C	0	50	-
	C_T	-20	20	-
	n	0	20	-

B Application of MBDoE to a Type III isotherm

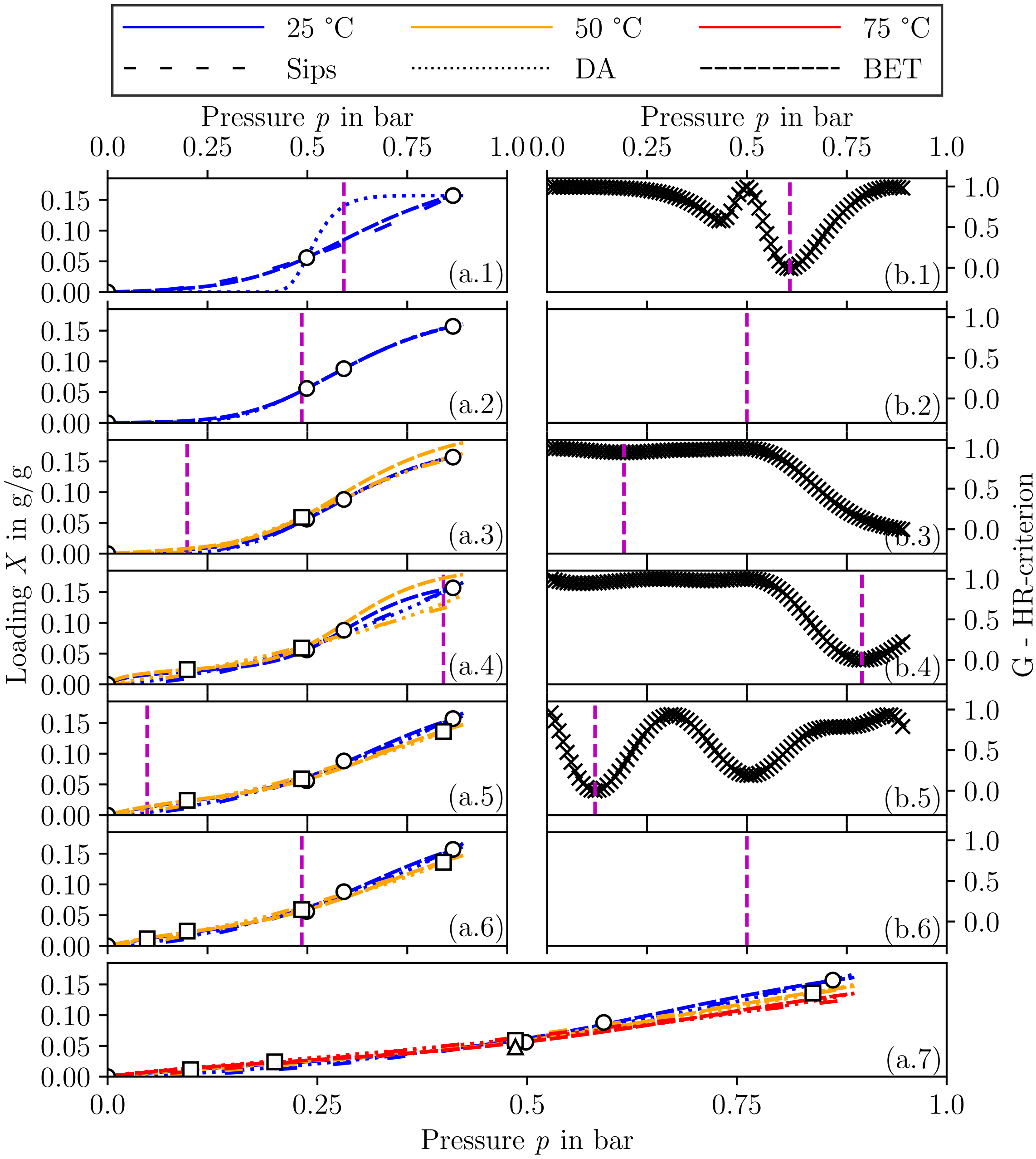

Figure 13: Experimental design for the Type III isotherm with Lewatit VP OC 1065/H_2O. The left column (a.1)-(a.7) shows the measurement points for 25 °C (circles), 50 °C (squares), and 75 °C (triangles) and the fitted models. The right column (b.1)-(b.6) shows the objective function and the minimia found by the solver (purple dashed lines).

C Application of MBDoE to a Type V isotherm

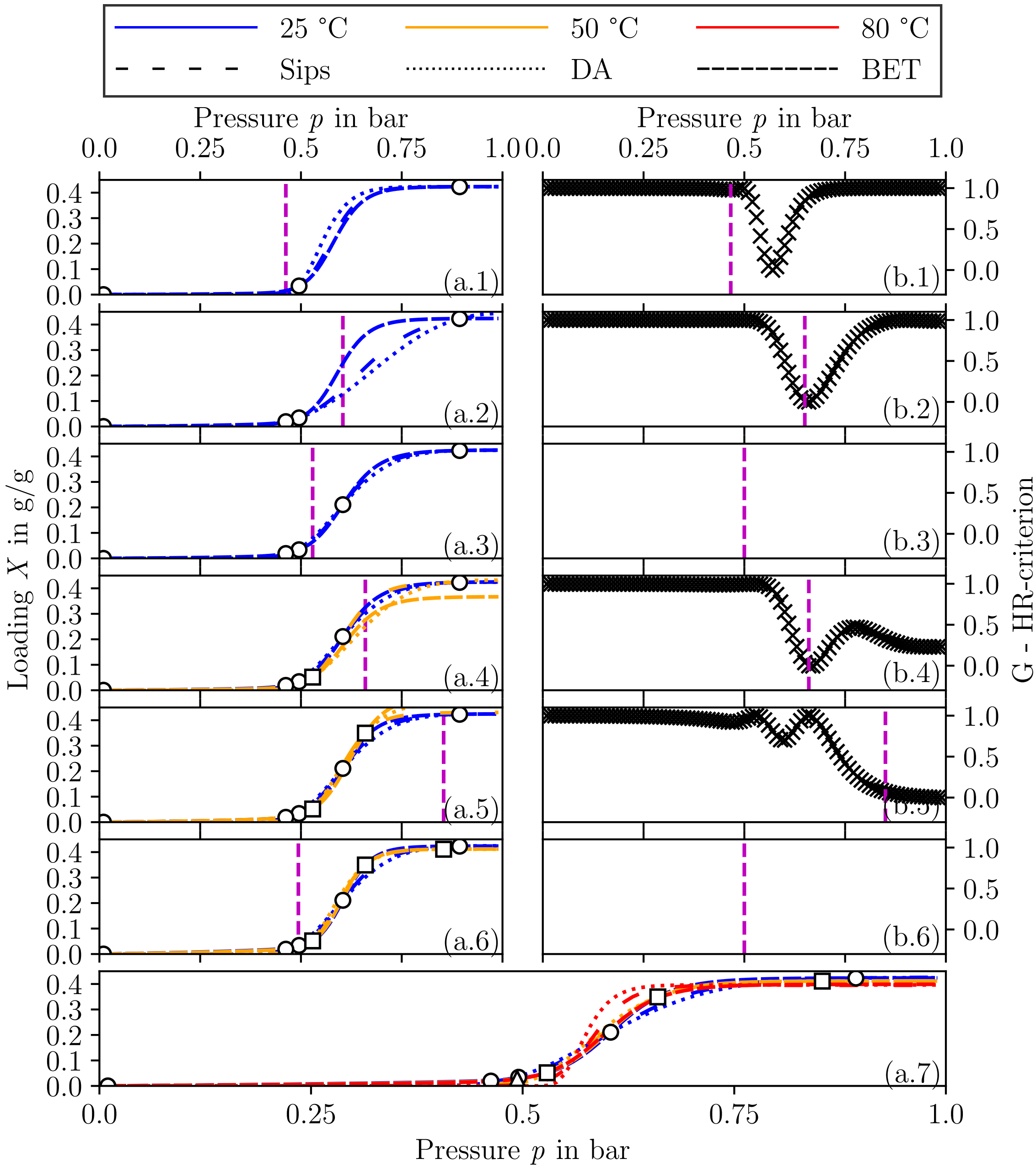

Figure 14: Experimental design for the Type V isotherm with BAM-P109/H_2O. The left column (a.1)-(a.7) shows the measurement points for 25 °C (circles), 50 °C (squares), and 80 °C (triangles) and the fitted models. The right column (b.1)-(b.6) shows the objective function and the minimia found by the solver (purple dashed lines).