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Mathematical Formulation of Sigmoidal Water Adsorption: Klotz vs Weighted Dual-Site Langmuir in mmen-Mg2(dobpdc)

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Summary

Amine-functionalised metal-organic frameworks (MOFs), specifically mmen-Mg2(dobpdc), are premier candidates for Direct Air Capture (DAC) due to their exceptional CO2 capacity and fast kinetics. While it is well-established that humidity does not significantly inhibit CO2 capacity in these materials, the co-adsorption of water is frequently neglected in process modelling. This omission leads to significant errors in mass and energy balances, as the thermal energy required to recover co-adsorbed water during regeneration poses a substantial techno-economic penalty. This study addresses this gap by identifying the optimal isotherm parameters for two advanced mathematical frameworks: the Weighted Dual-Site Langmuir (W-DSL) model and the Klotz method.

Parameters were determined using non-linear regression to minimise the Sum of Squared Residuals (SSR). Results indicate that the W-DSL model provides a superior fit (R2 = 0.9988; SSR = 0.4017) compared to the Klotz method (R2 = 0.9981; SSR = 0.6204), demonstrating a high sensitivity to the vertical transition zone. The Klotz model further provided physical insight into water clustering with a calculated m value of 4.649. These validated correlations provide a robust foundation for the techno-economic assessment and design of mmen-Mg2(dobpdc)-based DAC systems, ensuring humidity effects are accurately represented in large-scale process simulations.

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1. Introduction

Amine-functionalised porous solids are among the most promising adsorbents for direct air capture (DAC) due to their high CO_2 capacity at low partial pressures, strong selectivity, stability, and reversible adsorption behaviour. Compared to liquid amine scrubbing, these solid sorbents also mitigate challenges such as amine volatility and solvent degradation. Among them, mmen-Mg_2(dobpdc) has received particular attention due to its exceptional CO_2 uptake and fast adsorption kinetics. Its characteristic sigmoidal CO_2 isotherm originates from a cooperative insertion mechanism involving reversible polymerisation of CO_2 into ammonium carbamate chains along the pore axis (McDonald et al., 2012). Although CO_2 adsorption in this material is well-documented, the role of water adsorption is often neglected in process modelling (Ghiri et al., 2025). While humidity may not inhibit CO_2 capacity and can even slightly enhance it under both flue gas and DAC conditions (Siegelman et al., 2017; Wu et al., 2022), experimental evidence confirms that water is co-adsorbed, particularly at the lower temperatures required for DAC, and that water uptake decreases only at elevated temperatures above approximately 75 °C (Mcdonald, 2015). Neglecting this water uptake leads to significant errors in mass and energy balances, potentially miscalculating the energy required for thermal regeneration.

To accurately evaluate these effects, a robust mathematical representation of the water adsorption isotherm is necessary. An adsorption isotherm characterises a sorbent's capacity and equilibrium behaviour across varying pressures at a constant temperature. While most water isotherms follow a Type I profile amine-functionalised MOFs frequently exhibit step-like isotherms. These profiles, characterized by an extremely sharp transition zone, present a significant challenge that standard non-cooperative equations cannot adequately address ("Giani de Vargas Bri˜ao," 2022; Trevor Ciha, 2022).

This study addresses this critical gap by identifying the optimal isotherm parameters for the Klotz and Weighted Dual-Site Langmuir (W-DSL) models to accurately represent the water uptake in mmen-Mg_2(dobpdc). By validating these models against experimental data, this work provides a physically consistent foundation for more accurate representation of humidity effects in adsorption-based process simulations and supports improved design and techno-economic assessment of mmen-Mg_2(dobpdc)-based DAC systems.

2. Methodology

To numerically evaluate the effect of humidity on mmen-Mg_2(dobpdc), water adsorption behaviour was modelled using a comparative isotherm-based approach. Experimental water adsorption data were analysed to identify a suitable mathematical representation capable of capturing the sigmoidal shape and steep transition region observed in the isotherm. Based on these characteristics, two models were selected for evaluation: the W-DSL model and the Klotz model. The W-DSL model was employed to account for adsorption site heterogeneity within the framework, allowing different site populations to contribute to water uptake. In contrast, the Klotz model was used to assess the presence of cooperative adsorption effects associated with water clustering at higher relative pressures.

1- Weighted Dual-Site Langmuir

This model which is presented in Equations 1-4 is specifically designed to describe isotherms with abrupt transitions by dividing the adsorption behaviour into two regimes, occurring below and above the step pressure, represented by distinct dual-site Langmuir isotherms n_L and n_U. These regimes are integrated using a weighting parameter, w, governed by a width factor, sigma, which dictates the abruptness of the sigmoidal rise. Temperature-dependent constants for the step pressure, width factor, and site affinities (b_L, and b_U) were parameterized using Equations which are shown in Table 1.

$$q = n_L(1-w) + n_U w \quad (1)$$

$$n_L = \frac{n_{L0} b_L p}{1 + b_L p} \quad (2)$$

$$n_U = \frac{n_{U0} b_U p}{1 + b_U p} + b_H p \quad (3)$$

$$w = \left(\frac{\frac{\exp\left(lnp - lnp_{step}\right)}{\sigma}}{1 + \exp\left(lnp - lnp_{step}\right)}\right)^{\gamma} \quad (4)$$

$$\ln(P) = \frac{\Delta H_{ads}}{RT} + C \quad (5)$$

Table 1. Time dependent parameters of W-DSL isotherm model.

Temperature Dependent Equations	Physical Description
$p_{step} = p_{step,0} \exp\left(\left(\frac{-H_{step}}{R}\right) \times \left(\frac{1}{T_o} - \frac{1}{T}\right)\right)$	pressure threshold for the vertical transition.
$\sigma = X_1 \exp\left(X_2 \times \left(\frac{1}{T_o} - \frac{1}{T}\right)\right)$	Controls the abruptness/slope of the sigmoidal step.
$b_i = b_{i0} \exp\left(\frac{E_i}{RT}\right)$	Represents the adsorption affinity for sites L and U.

The step pressure P_{step} was identified at the 313 K inflection point as 0.8 mbar, while the isosteric heat of adsorption was calculated as -49.127 kJ/mol via the Clausius-Clapeyron relation (Equation 5). By plotting ln(P) vs 1/T at a constant loading of 1 mmol/g, the thermodynamic consistency of the model was established. Finally, the remaining coefficients were optimized via a non-linear regression solver in Microsoft Excel by minimizing the Sum of Squared Residuals (SSR). This rigorous parameterization allows the W-DSL model to capture the verticality of the water isotherm, providing a reliable basis for comparison with the Klotz method in representing DAC-relevant conditions.

2- Klotz Model

This model which is shown in Equation 6, provides a different approach to modelling step-shaped isotherms by treating adsorption as a multi-stage process. This model has been successfully utilised for Type IV water isotherms in materials such as activated carbons and carbon molecular sieves. The formulation used here (Equation 3) is a modified version of the n-layer BET equation, where the parameter m corresponds to the maximum number of adsorbed layers (Buttersack, 2019).Compared to the W-DSL model, the Klotz model is mathematically simpler and requires fewer fitting parameters. These parameters were determined by employing a non-linear regression via the Excel solver to minimize the discrepancy between the model and experimental data.

$$\theta = \frac{Cq_{max}(1 - (1+m){q_{max}}^{m} + m{q_{max}}^{m+1})}{(1 - q_{max})(1 + (C-1)q_{max} - C{q_{max}}^{m+1})} \quad (6)$$

To ensure the reliability of the identified parameters, the isotherm models were calibrated by validating simulated data against experimental results. This calibration process utilised the Non-linear Least Squares Regression method, implemented via the Data Solver function in Microsoft Excel. The primary objective was to minimise the Sum of Squared Residuals (SSR), as defined by Equation 7. In this expression $q_{i,obs}$ represents the i-th experimental value of q, $q_{i,fit}$ is the i-th value of q calculated by the isotherm model, and m denotes the number of data points. In addition to SSR, the Coefficient of Determination R^2 was employed as a second criterion for validation (Equation 8). The R^2 value was determined by plotting the experimental data against the model-predicted values and calculating the variance explained by the regression trendline. These statistical metrics collectively measure the degree of alignment between the model and the experimental observations. Higher R^2 values, approaching unity, indicate strong agreement and confirm the model's ability to accurately represent the sharp, sigmoidal transition of water adsorption in mmen-Mg_2(dobpdc).

$$SSR = \sum_{i=1}^{m} \left(q_{i,obs} - q_{i,fit}\right)^2 \quad (7)$$

$$R^2 = 1 - \frac{\sum_{i=1}^{m} (q_{i,obs} - q_{i,fit})^2}{\sum_{i=1}^{m} (q_{i,obs} - \bar{q}_{i,obs})^2} \quad (8)$$

Results

Weighted Dual-Site Langmuir Performance

The W-DSL model demonstrated an exceptional ability to capture the complex, sigmoidal water adsorption behaviour of mmen-Mg_2(dobpdc). As illustrated in Figure 1A, the model successfully tracks the sharp vertical transition zone between 2 and 3 mbar. The optimisation process yielded a SSR of 0.4017, indicating a high degree of alignment between the predicted and observed values. The final optimised parameters resulting from this fit are summarised in Table 2. To further validate the model's predictive accuracy, the calculated water equilibrium loading (q_{calc}) was plotted against the experimental measured data (q_{exp}), as shown in Figure 1B. The resulting linear trendline yielded an R^2 value of 0.9988, underscoring the model's robustness in predicting bed adsorption capacity across the entire pressure range.

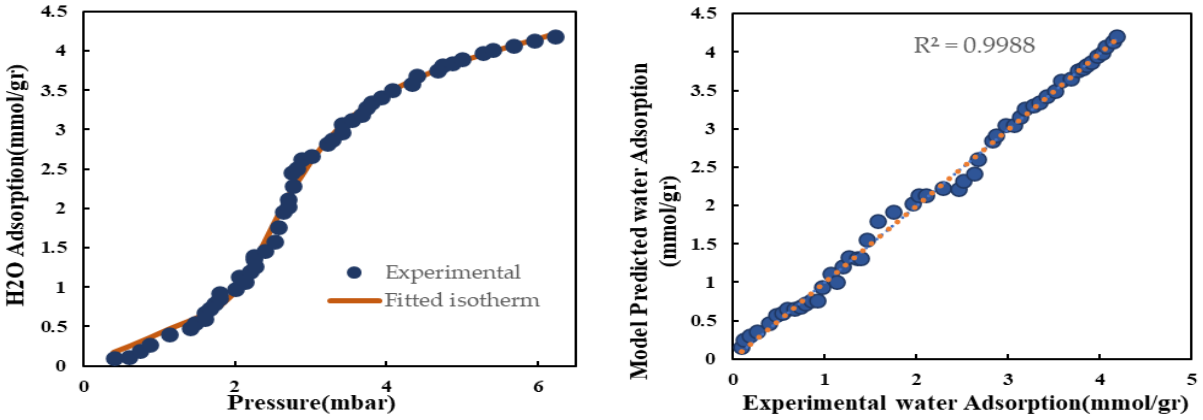

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Figure 1 (A) Fitting of the W-SDL model on water isotherm experimental data, (B) Error estimation between experimental and simulated isotherm points.

Table 1. Fitting parameters for W-SDL isotherm model.

Parameters	Value	Parameters	Value
n_{L0}	1615.359(Mole/Kg)	b_{H0}	2.2e-1(Mole/(Kg.Mbar)
b_{L0}	2.49e-4(1/Mbar)	E_H	16.84(KJ/Mole)
E_L	60.07(KJ/Mole)	X_1	0.227
n_{U0}	2.87(1/Mbar)	X_2	10(1/k)
b_{U0}	1.04e-1	ϒ	174
E_U	57.28(kJ/Mole)		

Klotz Model Performance

Following a parallel optimisation approach, the Klotz model was fitted to the experimental data, as shown in Figure 2A, resulting in fitted parameters of C = 0.0685, m = 4.649, and q_{max}= 0.591mmol/gr, where the magnitude of, m, reflects the cooperative nature of water uptake responsible for the sigmoidal isotherm. This model achieved a minimum SSR value of 0.6204, and validation using a parity plot (Figure 2B) resulted in an R^2 value of 0.9981. While the Klotz model accurately represents the general trend of the isotherm, its SSR is approximately 54% higher than that of the W-DSL model.

Comparison of the two models shows that the W-DSL formulation achieved a lower SSR (0.4017) than the Klotz model (0.6204), indicating slightly better numerical agreement with experimental data, while both produced very high R^2 values. Despite this, the Klotz model provides a physically meaningful representation of cooperative water adsorption and clustering, which underlies the sigmoidal isotherm. Thus, while W-DSL offers marginally higher fitting accuracy, the Klotz formulation is preferred for process-level modelling due to its mechanistic consistency.

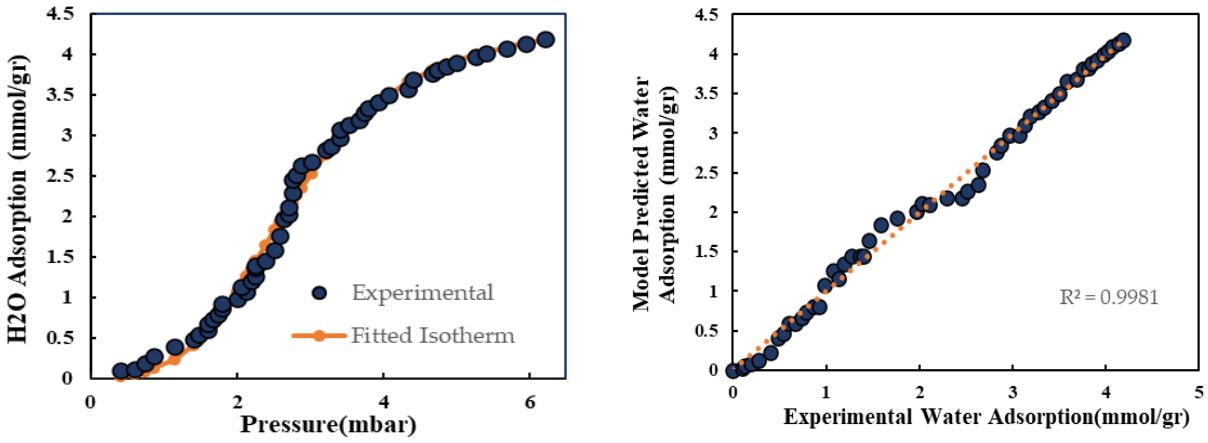

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Figure 2. (A) Fitting of the Klotz model on water isotherm experimental data, (B) Error estimation between experimental and simulated isotherm points.

Conclusion

In this study, two isotherm models were evaluated to describe water adsorption in mmen-Mg_2(dobpdc): the W-DSL model and the Klotz model. The W-DSL model successfully captured the sigmoidal adsorption behaviour with slightly better numerical agreement (SSR = 0.4017) compared to the Klotz model (SSR = 0.6204), while both models achieved very high R^2 values, indicating excellent predictive accuracy. The W-DSL model reproduces the sigmoidal shape by representing adsorption on two distinct site populations, effectively capturing the uptake phenomenologically but without explicitly describing cooperative water-water interactions. In contrast, the Klotz model provides a physically meaningful representation of clustering and cooperativity, reflecting the underlying adsorption mechanism. Therefore, despite the marginally higher SSR, the Klotz formulation is preferred for process-level modelling under DAC-relevant conditions, where mechanistic consistency is critical for accurate design and optimisation.

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