



## Comparative Modelling, Sensitivity Analysis and Thermodynamics Study of the Adsorption Characteristics of Dried *Nauclea latifolia* Medicinal Leaves

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**Abstract:** The adsorption characteristics of *Nauclea latifolia* medicinal leaves were examined across selected temperatures (30–50°C) and water activity levels (0.044–0.900) to assess its storage stability. Both univariate semi-empirical and multivariate statistical models were comparatively employed to represent and predict the observed adsorption characteristics. Additionally, sensitivity analysis was conducted to evaluate the dependence of the adsorption characteristics (that is, equilibrium moisture content (EMC (g/g d.b.)) on temperature and water activity storage factors. The net isosteric heat and entropy of adsorption were also determined alongside compensation theory values. The results indicated that EMC decreased with increasing temperature and increased with rising water activity. The minimum and maximum EMC values of 0.015 and 0.221 g/g d.b. were observed at 50°C. The safe moisture content for storing dried *Nauclea latifolia* medicinal leaves was 12.6 g/g d. at 30 to 40 °C and 9 g/g d.b. at 50°C. Amongst the models tested, the Peleg model demonstrated best performance, with its  $R^2$  values ranging from 0.9897 to 0.994 and RMSE values between 0.0039 and 0.0129. Sensitivity analysis revealed that EMC is more sensitive to water activity than to temperature. The net isosteric heat and entropy of adsorption decreased with increasing EMC, indicating that the process was enthalpy-driven. In conclusion, the findings underscore the importance of environmental management in maintaining the storage properties of *Nauclea latifolia* medicinal leaves. The results of the models are useful in guiding the optimal storage conditions and the design of tailored storage facilities for *Nauclea latifolia* medicinal leaves.

**Keyword:** *Nauclea latifolia* Medicinal Leave, Adsorption, Modelling, Sensitivity Analysis, Storage.

### 1. INTRODUCTION

*Nauclea latifolia* is a medicinal plant that is extensively used in traditional African medicine due to its diverse pharmacological properties [1]. Its leaf has been indicated for effectiveness in treating various ailments such as cough, jaundice, stomach disorders, malaria fever, and cancer [2]. Other traditional uses included managing fever, pain, dental caries, septic mouth, dysentery, and as an antipyretic and antinociceptive agent [3 - 4]. In post-harvest handlings, drying of *Nauclea latifolia* leaves enhances preservation, concentration of bioactive compounds, ease of transportation, and shelf stability; making it more suitable for medicinal, culinary, and related applications [5]. Hence, a complementary storage characteristic of *Nauclea latifolia* leaf after drying is essential for sustainable utilization and conservation. Such investigation entails its hygroscopic behaviour in storage and it the main focus in this study.

The adsorption characteristics of food, drug and herb focus on examining their interactions with environmental moisture, which is crucial to resource management and environmental impact such as resource efficiency for optimized storage conditions, spoilage and waste reduction [6]. Hence, optimized moisture absorption practices would promote low environmental impact such as microbial growth and enzymatic reactions, thereby reducing the need for chemical preservatives and additives [7], and also minimize the release of harmful substances into the environment; thus promoting ecological sustainability. Implementing optimal storage conditions can also lead to energy savings by reducing the need for excessive refrigeration or re-drying processes [8]. Most importantly, adsorption of moisture under various conditions (that is, sorption isotherm), provides insights into storage stability, quality preservation, and shelf life prediction [6] [9].

It has been established that the sorption isotherms serve an important quantitative indicator [7]. These isotherms represent the correlation between equilibrium moisture content and relative humidity and offer insights into the distribution and intensity of water molecule connections within products and their hygroscopic equilibrium [10]. Amongst the methods available for sorption isotherms interpretation, mathematical models have been emphasized to enhance the description of these isotherms, with a little less than a hundred equations comprising two or more parameters proposed [7]. Other

complimentary mathematical model indices such as isosteric heat integral and differential of sorption, compensation theory, amongst others have also remained crucial indicators that deepen the understanding of storage and drying processes. These parameters signify the energy released during adsorption/desorption process, and the energy required to disrupt the intermolecular forces between water vapour molecules and the adsorbent surface [6]. Mathematical models play a major role in process control and management.

Presently, varied modelling techniques such as empirical/semi-empirical, physics, statistical, artificial intelligence amongst others are currently in use; however, empirical models are classical, traditional and simple to implement, and are therefore widely utilized [11]. Although empirical models do not necessarily consider the underlying physical or chemical mechanism of a process, however, they offer good predictive power and flexibility [6]. Notably, a potent deficiency of empirical models is the limitation to one-dimensionality. Going forward, statistical mathematical models describe the relationship between variables (multi-dimensionality) in a dataset. Statistical models encompass both the structure of the relationship and the associated uncertainty. Statistical models can range from simple linear regression models to complex hierarchical models, depending on the nature of the data and the research question [12]. It therefore means that statistical models have capability for modelling multidimensional data, and capture possible factors interaction and uncertainties, which is impossible for an empirical model. Despite the advantages and disadvantages, modelling efficiency (coefficient of determination, root means square error and others) remains topmost in determining the successful utilization of a model. Therefore, comparing the model efficiencies of adsorption characteristics of *Nauclea latifolia* medicinal leave between empirical and statistical models is a co-focus in this study.

Sensitivity analysis is such an important post modelling technique to assess the impact of variations in input parameters or assumptions on the outputs of a model. It helps to identify which input factors have the most significant influence on the model's predictions or outcomes [13]. Sensitivity analysis is essential for modelling the adsorption characteristics of biological material, as it will help to identify key parameters, optimize experimental design, quantify uncertainty, assist process control, on-line controller design and enhance model interpretation.

Storage study and sorption isotherm modelling of leaves, just like any other biological material, is crucial for understanding the moisture sorption behaviour, which is essential for various applications such as processing, pharmaceuticals, and agro-forestry. In relevant literatures, Vasileva *et al.* [14] examined the moisture sorption characteristics of white mulberry (*Morus alba*) as a natural alternative to sugar and modelled the observed experimental data. Sobowale *et al.* [15] focused on determining the sorption isotherms and heat of sorption of *Moringa oleifera* leaves, providing insights into the moisture sorption behaviour. However, a study on sorption isotherm of *Nauclea latifolia* medicinal leave, development of alternative multi-dimensional statistical model and post modelling sensitivity analysis are scarce in the literature. Therefore, the aim of this study was to fill these notable gaps in study.

## 2. MATERIALS AND METHODS

### 2.1 Procedure

*Nauclea latifolia* leaves were obtained from a farmland in Ogbomoso Township (8.133°N latitude and 4.245°E longitude), Oyo state, Nigeria during raining season (20<sup>th</sup> July, 2023). A digital weighing balance (accuracy of ±0.000 g) and Stangas (SG-9052G, Stangas Luxury Modern Appliances, Italy) oven and glass jars were used for measurements, drying purposes and equilibration of samples, respectively. Physically sound leaves were utilized for the experiment. The leaves (1 kg) were washed in distilled water and air-dried in the laboratory environment (27 – 30°C) for 1 h prior to oven drying at 70°C for 10 h. The dried leaves were then packed and stored in a glass bottle for one day until the next experimental phase.

### 2.2 Investigation of Adsorption Characteristics

The equilibrium moisture content of *Nauclea latifolia* leaves at 30, 40, and 50°C were determined using a gravimetric technique in accordance with the method of Heras *et al.*, (2014) [16]. This method relies on saturated salt solutions to maintain a constant relative humidity in the surrounding air. Six saturated salt solutions (KOH, MgCl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, NaNO<sub>3</sub>, KCl, and BaCl<sub>2</sub>) were prepared by dissolution in distilled water at a higher temperature (50°C) to ensure saturation upon cooling (29°C). Glass jars (1 litre each) with insulated lids were utilized for the experiment. Each jar was filled one-quarter full with a prepared saturated salt solution, maintaining a layer of solid salts throughout the equilibration period. A tripod was placed in each jar to hold *Nauclea latifolia* leaves samples. These solutions provided a range of water activity from 0.07 to 0.89. Leaf samples (0.005 g ±0.001 g) were weighed and placed in the jars with the saturated salt solutions. The jars were tightly sealed and placed in the oven at specified temperatures (30, 40, 50°C) for equilibration. Samples were weighed daily until no further mass change occurred (7 days). The equilibrated samples were then brought out of the jar and oven dried at 105°C for 24 h. The difference in mass before ( $m_b$ ) and after ( $m_a$ ) oven drying allowed calculation of the moisture content ( $m_e$ ) at hygroscopic equilibrium with Equation 1.

$$m_e = \frac{m_b - m_a}{m_a} \quad (1)$$

**2.3 Univariate Empirical Modelling of Sorption Kinetic**

Univariate modelling refers to the analysis and modelling of data that consists of observations on a single characteristic or attribute [17]. Empirical models are univariate and are generally less computationally demanding. This allows for faster model development and analysis, particularly when dealing with datasets of limited size [18]. In this study, four semi-empirical models with independent characteristic of time (*t*) and parameters/constants were utilized to understand, represent and explain the adsorption characteristics of *Nauclea latifolia* leave. The model names and their respective mathematical composition are represented in Table 1. The univariate empirical modelling was implemented in Matlab R2014a software.

Table 1: Model utilized for experimental data fitting

Model Name	Model Representation	Equation Number	Reference
GAB	$m_e = \frac{abca}{(1-ac)(1-ac+acb)}$	(2)	[19]
Henderson – Thompson	$m_e = \left[ \frac{\ln(1-\alpha)}{-a(d+c)} \right]^{1/b}$	(3)	[16]
White and Eiring	$m_e = \frac{1}{(a+b\alpha)}$	(4)	[16]
Smith	$m_e = a - b(\ln(1 - \alpha))$	(5)	[19]
Peleg	$m_e = a(\alpha)^b + c(\alpha)^d$	(6)	[19]
Caurie	$m_e = \exp(a + b\alpha)$	(7)	[9]

*a, b, c* and *d* are the model parameters of the empirical models, while *α* is the water activity

**2.4 Multivariate Modelling of Sorption Kinetics**

Multivariate modelling is an indispensable tool in various academic disciplines due to its ability to analyze complex datasets with multiple interacting variables [20][21]. Compared to univariate approaches that focus on single variables, multivariate models offer understanding of factors interaction that deepens relationship understanding and identification of latent variables [22]. In this study, multi-linear regression modelling was implemented in Design Expert 6 software. Multi-linear regression is a powerful tool used to model the relationship between a continuous dependent variable and two or more independent variables [23].

The multivariate model is represented by Equation (8)

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \dots + \beta_n X_n + \epsilon \tag{8}$$

Where: the dependent variable (*Y*) is expressed as a linear combination of the independent variables (*X*<sub>1</sub> to *X*<sub>*n*</sub>) along with an error term (*ε*). The coefficients (*β*) represent the regression coefficients, which quantify the individual effect of each independent variable on the dependent variable, holding all other variables constant [20]. The error term (*ε*) accounts for unexplained variance in the data, which could be due to random error, measurement inaccuracies, or the influence of other variables not included in the model [23].

**2.5 Modelling Efficiency**

The efficiency of the models were determined using statistical indicators, including the sum of squared error (SSE), coefficient of determination (*R*<sup>2</sup>) and, root mean square error (RMSE). A lower SSE and RMSE with a higher *R*<sup>2</sup> (usually ranged from 0 to 1) indicate a better fit and their respective mathematical representations are depicted in Equation. (9) – (11) [24][25].

$$SSE = \sum_{i=1}^n (\text{Pred}, i - \text{Exp}, i)^2 \tag{9}$$

$$R^2 = 1 - \left( \frac{\sum_{i=1}^n (\text{Pred}, i - \text{Exp}, i)^2}{\sum_{i=1}^n (\text{Pred}, i - \text{AverageExp})^2} \right) \tag{10}$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (\text{Exp}, i - \text{Pred}, i)^2}{N}} \tag{11}$$

Where: *Pred, i* is the *i*<sub>*th*</sub> predicted value, *Exp, i* is the *i*th experimental value and *AveragedExp* is the average of all the experimental value. *n* represents the number of observations.

**2.6 Net Isothermic Heat of Sorption and Differential Entropy of Sorption**

The thermodynamics properties are generally evaluated from moisture sorption data with the Clausius-Clapeyron equation [19] as represented by Equation (12).

$$[-Ln(\alpha)]_M = \frac{\Delta h_d}{RT} - \frac{\Delta S_d}{R} \tag{12}$$

Where:  $\alpha$  is the water activity, M is the moisture content, R is the gas constant, T is the temperature,  $\Delta h_d$  is the net isosteric heat of sorption and  $\Delta S_d$  is the differential entropy of sorption.

By plotting  $Ln(\alpha)$  versus  $\frac{1}{T}$ , for a given moisture content (M),  $\Delta h_d$  is determined from the slope of Equation (12) i.e.  $\frac{-\Delta h_d}{R}$ , and  $\Delta S_d$  is determined from the intercept of Equation (12) i.e.  $\frac{\Delta S_d}{R}$ .

When this is applied at different moisture contents, the dependence of  $\Delta h_d$  and  $\Delta S_d$  with moisture content can be determined.

### 2.7 Enthalpy – Entropy Compensation Theory

The compensation theory proposes a linear relationship between  $\Delta h_d$  and  $\Delta S_d$  as represented in Equation (13) [10].

$$\Delta h_d = T_\beta X \Delta S_d + \infty \tag{13}$$

Where:  $T_\beta$  is the isokinetic temperature,  $\infty$  is the free energy

In order to validate the applicability of this theory to the thermodynamic properties of *Nauclea latifolia* medicinal leaves, Krug’s method was employed to juxtapose the constant rate temperature  $T_\beta$  with the harmonic average temperature  $T_{hm}$ . If  $T_\beta$  equals  $T_{hm}$ , the theory can effectively elucidate the driving mechanism behind the process. In instances where  $T_\beta$  surpasses  $T_{hm}$ , the adsorption process is primarily driven by enthalpy; conversely, when  $T_\beta$  is less than  $T_{hm}$ , the adsorption process is pre-dominantly entropy-driven. The equation for the harmonic average temperature,  $T_{hm}$ , is delineated in Equation (14) [10].

$$T_{hm} = \frac{N}{\sum_{i=1}^N \frac{1}{T_i}} \tag{14}$$

Where: N is the number of isotherms

### 2.8 Sensitivity Analysis

The sensitivity analysis was implemented in Python 3 using uniform assumption to determine the importance of each input variable for the observed moisture adsorption properties of *Nauclea latifolia* leaf at different storage temperatures and relative humidity. The derived multi-dimensional statistical model assisted in sensitivity analysis.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Adsorption Characteristics

The moisture absorption characteristics of *Nauclea latifolia* leaves in this study are represented in Figure 1.

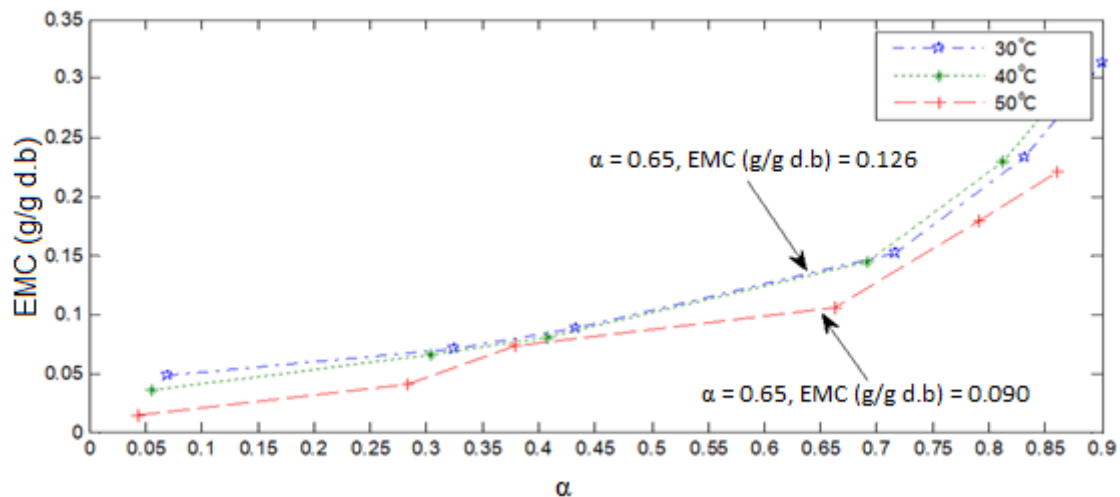


Figure: 1: Moisture adsorption characteristics of *Nauclea latifolia*

The figure showed that the moisture adsorption characteristics of *Nauclea latifolia* leave conforms to the typical type II sigmoidal shaped curve in accordance with Brunauer's classification [19], which is common to food materials. The equilibrium moisture content increased with increment in water activity and reduced with increment in temperature which is also consistent with the observation of Akoy and von Hörsten, (2013) [26]. The least EMC was 0.015 found at 50°C and water activity level of 0.044 while the highest EMC was 0.313 found at 30°C and water activity level of 0.9. The observed increase in equilibrium moisture content as water activity increased is attributed to increased average molecular weight of the mobile water fraction of the solution. Hence, the elevated water activity enhanced the mass transfer driving force between the materials and surrounding water molecules. This effect amplifies the potential for water molecule migration on the material's surface, potentially leading to the phenomenon of multi-molecular layer water adsorption [27].

The decreasing effect of the elevated temperature on the equilibrium moisture content can be attributed to the fact that elevated temperature induces both physical and chemical alterations within the material matrix. This disrupts the established equilibrium between the material's hydrophilic and hydrophobic moieties, leading to a decrease in the number of adsorbed water molecules [15]. Then, the equilibrium moisture content shifted towards a lower water holding capacity. Similar results were documented with persimmon leaves [16].

In storage, water activity ( $\alpha$ ) is a critical factor governing the reproduction and proliferation of microorganisms. Its value directly influences the quality characteristics and storage stability of food products [10]. Studies, such as the work by Yu et al. (2016) [28], have demonstrated that microbial growth, encompassing bacteria, yeasts, and molds, is significantly inhibited when  $\alpha$  falls below 0.7. Notably, a further decrease in  $\alpha$  to values below 0.6 appears to render most microorganisms within the food matrix incapable of survival. Based on this established knowledge, the present study adopted  $\alpha$  values of 0.65 as reference indices for safe moisture content in dried *Nauclea latifolia*. At this value, the safe moisture content for *Nauclea latifolia* is 12.6 (g/g d.b.) for 30 and 40°C storage temperatures and 9 (g/g d.b.) for 50°C storage temperatures. Ruan et al. (2022) [10] reported a safe moisture content of 18.77 - 15.60%, and the relative safe moisture content of 14.6 - 11.06% for microwave vacuum dried Tilapia, and acknowledged that the finding was critical to deciding the drying endpoint of tilapia and other biological materials and for choosing storage conditions.

**3.2 Univariate Empirical Modelling of the Adsorption Characteristics**

Table 2 presented the fitted empirical equations and their respective derived parameters with model performances.

Table 2: Model parameter and performance

Model Name	Model Parameter	Adsorption Temperature °C		
		30	40	50
GAB	a	0.0527	1.9470	0.0496
	b	77.4700	0.0929	8.2100
	c	0.9253	1.0270	0.9123
	R <sup>2</sup>	0.9991	0.9833	0.9878
	RMSE	0.0039	0.0175	0.0114
White and Eiring	a	19.6000	20.5500	26.1300
	b	-18.2500	-19.6800	-25.2600
	R <sup>2</sup>	0.9980	0.9933	0.9614
	RMSE	0.0050	0.0096	0.0176
Peleg	a	0.1044	0.4171	0.2840
	b	0.2991	5.6080	5.9040
	c	0.3870	0.1072	0.1180
	R <sup>2</sup>	0.9994	0.9997	0.9897
	RMSE	0.0039	0.0024	0.0129
Smith	a	0.0247	0.0166	0.0098
	b	0.1185	0.1291	0.1051
	R <sup>2</sup>	0.9819	0.9828	0.9832
	RMSE	0.0156	0.0154	0.0116
Caurie	a	-3.6850	-3.8090	-4.0000
	b	2.7330	2.9250	2.8720
	R <sup>2</sup>	0.9699	0.9797	0.9791
	RMSE	0.0201	0.0167	0.0129



Based on the performance indicators in the table, Peleg model showed the best efficiency in explaining the experimental data at all studied temperatures due to its highest  $R^2$  and lowest RMSE values while Caurie model showed the least performance. Generally, a model with  $R^2$  value greater than 0.7 within the limit of 0 (zero) – 1 (unity) is considered acceptable [27].

In the study of moisture sorption isotherms and heat of sorption of Algerian Bay leaves (*Laurus nobilis*), Ouafa et al., (2015) [19] also found Peleg model to be the best fitting model for describing the experimentally observed sorption curves.

**3.3 Multivariate Statistical Modelling of the Adsorption Characteristics**

The developed multivariate model developed for the equilibrium moisture content (EMC (g/g d.b.)) in this study is presented in Equation (15)

$$EMC (g/g \text{ d.b.}) = 0.1660 + 0.0575 * \alpha - 0.0119 * B - 0.4071 * \alpha^2 + 1.5878E-004 * B^2 + 1.4328E-003 * \alpha * B \tag{15}$$

Where:  $\alpha$  = Water activity, and B = Temperature (°C)

The model is based on a second-order polynomial regression equation. The intercept of the equation (0.1660), represents the baseline EMC value when both independent variables  $\alpha$  and B are zero. The linear term represents the effect of the variable  $\alpha$  and B on the EMC in a linear fashion. The 0.0575 coefficient for  $\alpha$  indicates the rate of change in EMC per unit change in  $\alpha$ . The -0.0119 coefficient for B suggested that B has a negative effect on EMC, by decreasing EMC with each unit increase in B. The quadratic term represents the nonlinear effect of  $\alpha$  and B on EMC. The negative nonlinear coefficient of  $\alpha$  indicates that the relationship between  $\alpha$  and EMC is concave (relative to x-axis), suggesting diminishing returns. The positive non linear coefficient of B implied a convex (relative to x-axis) relationship, suggesting accelerating effects or sensitivity at higher values of B. The interaction term (1.43283E-003 \*  $\alpha$  \* B) captures the combined effect of  $\alpha$  and B on EMC. The positive coefficient suggests that the presence of one variable enhances the effect of the other on EMC. On the overall, the Equilibrium Moisture Content (EMC) is a critical property of materials such as agricultural products, indicating the moisture level at which the material is in equilibrium with its surrounding environment. Understanding and predicting EMC is crucial for processes like drying, storage, and quality control.

The performance of the multivariate statistical model used in this study is represented in Table 3

Table 3: Analysis of variance of the multivariate statistical model

Source	Sum of Squares	df	Mean Square	F Value	Prob > F	Remark	Value
Model	0.14	5	0.029	55.70	< 0.0001	Significant	
$\alpha$	0.11	1	0.11	217.98	< 0.0001	Significant	
B	2.465E-003	1	2.465E-003	4.82	0.0486	Significant	
$\alpha * B$	2.096E-004	1	2.096E-004	0.41	0.5342	Non- significant	
$\alpha^2$	0.013	1	0.013	25.30	0.0003	Significant	
$B^2$	1.007E-003	1	1.007E-003	1.97	0.1861	Non- significant	
Residual	6.141E-003	12	5.118E-004				
Cor Total	0.15	17					
R-Squared							0.9587
Adj R-Squared							0.9415
Pred R-Squared							0.9096
Adeq Precision							19.898

The Model F-value is a measure of the significance of the overall model. A high Model F-value, such as 55.70 in this case, means that the model is significant, with extended meaning that the variables (water activity and temperature) included in the model have a meaningful impact on the equilibrium moisture content. There is a low (only a 0.01%, that is Prob>F value of 0.0001) chance that a Model F-Value this large could occur due to randomness without any actual relationship between the variables and the response.

The Prob > F value measures the probability of observing an F-value as extreme as the one obtained under the null hypothesis (i.e., no significant relationship), the Prob > F value less than 0.05 suggests that the model terms are significant, while values greater than 0.10 indicate that the model terms are not significant. In this case, the terms  $\alpha$  (water activity), B (equilibrating temperature), and  $\alpha^2$  (square of water activity) are deemed as significant model terms, as their associated Prob > F values are below 0.05. Notably, the insignificance of factor  $\alpha * B$  showed that there was no interaction between the water activity and equilibrating temperature, therefore the two factors affected the equilibrium moisture content differently.

In addition, the R-squared ( $R^2$ ) value is 0.9587 in this study. Comparatively, the  $R^2$  value of this statistical model is lower than the  $R^2$  value of the best performer of the univariate empirical model (that is, Peleg model), however, the model assisted in gaining more insight into the process such as effect of each contributory factor in the linear and non-linear region and possible interaction of factors. Such gain and flexibility are useful in automation, monitoring, sensitivity analysis, and control of the process considering the model's compactness. The Pred R-Squared (Predicted R-Squared) of 0.9096 indicates the proportion of the variance in the response variable that is explained by the predictors in the model, while the Adj R-Squared (Adjusted R-Squared) of 0.9415 adjusts the R-squared value for the number of predictors in the model, providing a more accurate estimate of model fit.

The statement Adeq Precision measures the signal-to-noise ratio, indicating how well the model predicts the response relative to the inherent variability in the data. A ratio greater than 4 is considered desirable, suggesting that the signal (that is, the meaningful information) is much stronger than the noise (that is, random variation). In this result with a ratio of 19.898, the signal-to-noise ratio is high, indicating that the model provides an adequate representation of the relationship between the predictors and the response variable. Therefore, the model is suitable for navigating the design space, implying that it can be reliably used for making predictions or drawing conclusions about the system under study.

The contribution of each factor (that is,  $\alpha$  - water activity, and B - equilibrating temperature) is graphically represented in Figure 2, based on the implication of the statistical model.

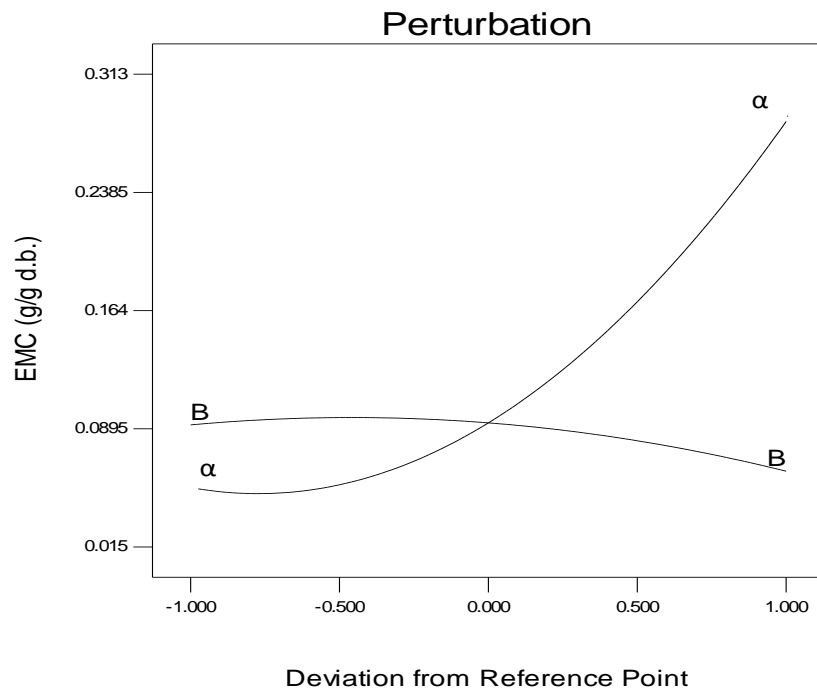


Figure 2: Effect of water activity (factor  $\alpha$ ) and temperature (factor B) on moisture adsorption of *Nauclea latifolia*

The graph complements the observation seeing in Figure 1 where increment in water activity factor increased the equilibrium moisture content significantly. The increment was a little reluctant in the beginning, thereafter, the moisture gain improved drastically. On the contrary, increment in temperature factor had an initial slight increment on the moisture gain before significant decrease in the moisture gain. Comparatively, the effect of water activity increment looked more critical to moisture gain than the effect of temperature increment. Ruan et al., (2022) [10] derived  $R^2$  value of 0.9559 with Mod-BET for 30 °C sorption isotherms of microwave vacuum dried Tilapia fillets.

### 3.4 Model Comparison

Comparing the univariate and multivariate models used in this study, it was observed that both modelling approaches demonstrated strong performance, as evidenced by their statistical metrics, such as the  $R^2$  and RMSE values shown in Tables 2 and 3. The univariate models slightly outperformed the multivariate model in these metrics. However, the multivariate model offers a more compact representation of the process variables by incorporating them simultaneously, whereas the univariate models consider each variable separately. This compactness allows the multivariate model to capture not only the individual effects of the process variables but also their interactive (or combined) effects. Such a compact representation is essential for post-modelling operations, including optimization and effective process controller design, among other applications.

### 3.5 Sensitivity Analysis

Sensitivity analysis of process factors evaluates how changes in independent variables affect a dependent variable within a given set of assumptions. In the context of processes, it assesses the impact of variations in factors such as input parameters, operating conditions, or environmental variables on the output or performance of a process. Through the adjustment of one factor at a time while keeping others constant, sensitivity analysis identifies critical factors influencing process outcomes. This method enhances decision-making by quantifying the degree of uncertainty and helps in optimizing process performance and resource allocation. In this study, the sensitivity analysis of the adsorption characteristics of *Nauclea latifolia* leaf is represented in Figure 3.

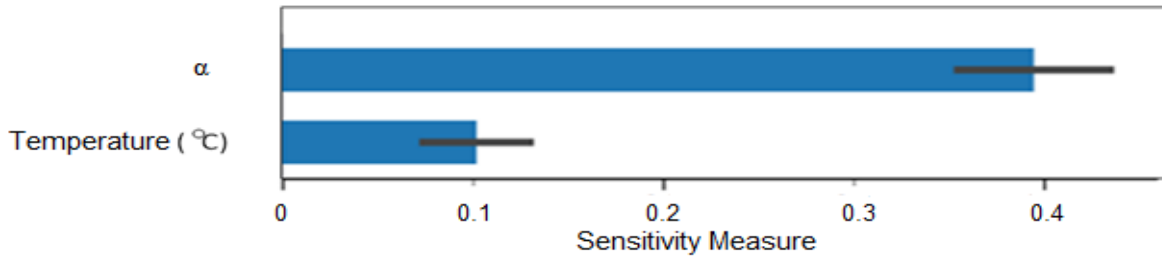


Figure 3: Sensitivity analysis of *Nauclea latifolia* leaf adsorption

The figure showed that temperature has the highest contribution to the variability of the equilibrium moisture content of *Nauclea latifolia* leaf followed by water activity. This is important information for dried *Nauclea latifolia* leaf storage facility design and control. In the study of Adeyi et al. [25] on the sensitivity analysis of the effective moisture diffusivity of fish cracker, it was found out that oven temperature had the highest contribution to effective moisture diffusivity followed by oven air velocity and sample thickness.

### 3.6 Thermodynamics Characterization

The net isosteric heat of sorption ( $\Delta h_d$ ) and differential entropy of sorption ( $\Delta S_d$ ) in this study are represented in Figure 4.

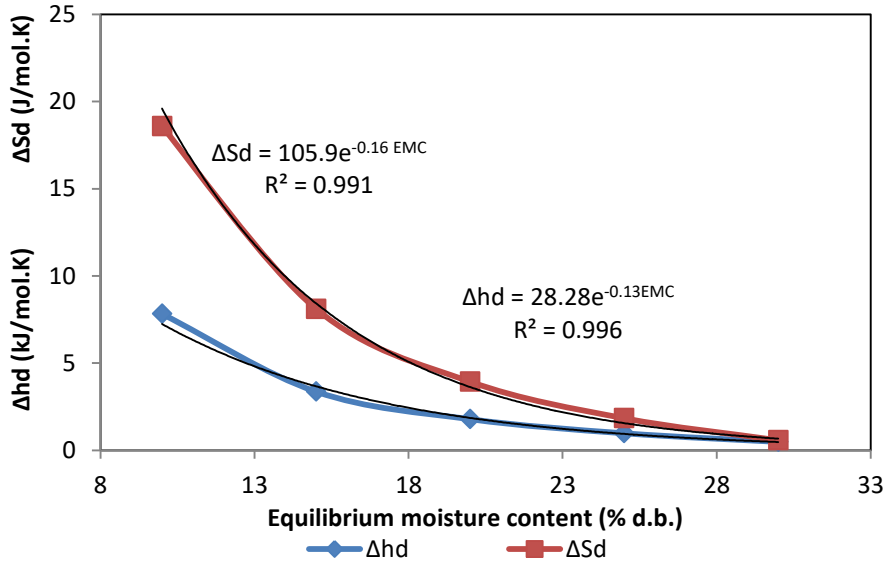


Figure 4: the integral enthalpy and entropy of *Nauclea latifolia* leaves

The net isosteric heat of sorption is a critical thermodynamic parameter essential for understanding the interaction between moisture and food materials. It is also instrumental in analyzing the drying process and assessing the stability of foods under specific storage conditions [29]. As illustrated in Figure 4, the net isosteric heat of sorption (blue line) exhibits an exponential decline with increasing equilibrium moisture content. At low levels of equilibrium moisture content, however, the net isosteric heat of sorption remained high. This phenomenon can be attributed to the abundance of active sites within the *Nauclea latifolia* leave, which results in a strong adsorption force between the *Nauclea latifolia* leave and water molecules. Therefore, at lower moisture content, the material can effectively adsorb water due to the high number of active sites available for adsorption. This means the material has a strong capacity to attract and hold water molecules



when it is relatively dry. As the material becomes more saturated with moisture, its ability to adsorb additional water decreases significantly. The observation is fitted to the exponential model for prediction and the model is represented on Figure 4 with high prediction efficiency of  $R^2 = 0.996$ . These results were close to the report of Ouafa et al. [19].

Furthermore, Figure 4 showed the trend of the differential entropy of sorption (red line) obtained in this study. An increase in the equilibrium moisture content of materials leads to a decrease in the differential entropy. This decrease is related to the presence of numerous adsorption sites in *Nauclea latifolia* leaves at low moisture content, which implied a strong moisture absorption capacity at that state. At higher moisture content levels, few adsorption sites are available and the adsorption shifts to a multi-molecular layer, leading to a reduced moisture absorption capacity. This result reinforces the indication that differential entropy can serve as a reference parameter for quantifying the hygroscopicity of materials during storage. The observation is fitted to the exponential model for prediction and the model is represented on Figure 4., with high prediction efficiency of  $R^2 = 0.991$ . This result conforms to the report of Heras et al. [16].

### 3.7 Enthalpy – Entropy Compensation

The entropy-enthalpy compensation theory is crucial for analyzing the mechanism of water adsorption in material, and for understanding the associated physical and chemical changes. Linear regression fitting of differential entropy and net equivalent adsorption heat in the adsorption test of *Nauclea latifolia* medicinal leaves as presented in Figure 5 yielded a high fitting degree with  $R^2 = 0.999$ , indicating the presence of entropy and enthalpy compensation.

The values of  $T_\beta$  and  $\alpha$  were 407.4 K and 0.192 J/mol, respectively. According to Equation (14), the harmonic average temperature  $T_{hm}$  was 307.78 K. Since  $T_\beta$  and  $T_{hm}$  were not equal, the entropy-enthalpy compensation theory is valid for this experiment, and thus applicable to the adsorption process of *Nauclea latifolia*. Furthermore, since  $T_\beta > T_{hm}$ , it can be concluded that the water adsorption process in *Nauclea latifolia* is enthalpy-driven. In addition,  $\infty > 0$ , implying that the adsorption process is non-spontaneous and requires energy input. Therefore, regulating the environmental energy can reduce the possibility of deterioration, thereby ensuring the quality of the processed and stored products. This result conforms to the report of Silva et al. [9], Ruan et al. [10], and Oyelade et al. [13].

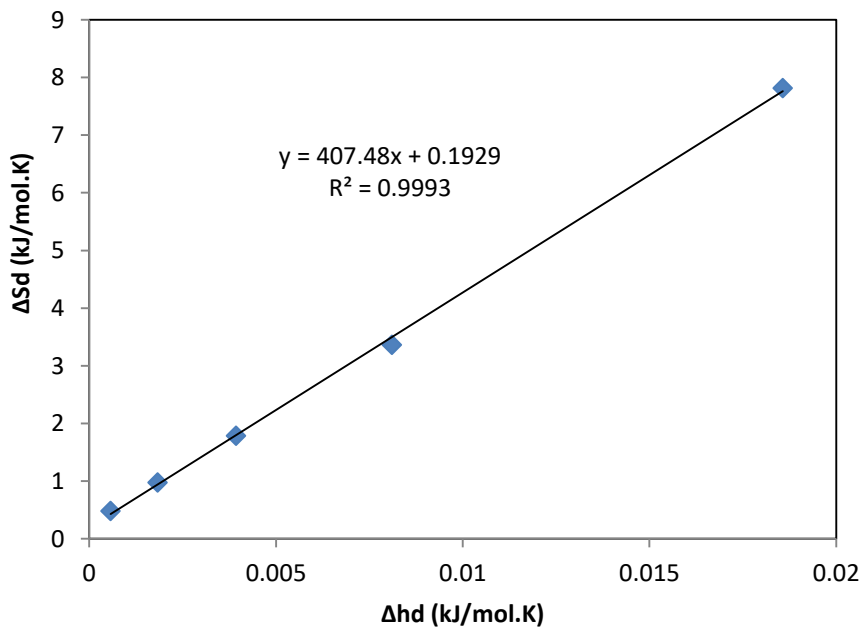


Figure 5: Relationship between differential entropy and net isometric heat (enthalpy) of adsorption

## 4. CONCLUSION

The study focused on the adsorption characteristics of dried *Nauclea latifolia* leave, examining its behaviour across different temperatures and water activity levels to assess shelf stability. Various models, including univariate semi-empirical and multivariate statistical models, were comparatively used to represent and predict the adsorption characteristics. Post modelling sensitivity analysis highlighted the dependence of equilibrium moisture content to water activity. The study also analyzed the net isosteric heat and entropy of adsorption. The Peleg model demonstrated superior performance, with coefficient of determination ( $R^2$ ) values ranging from 0.989 to 0.994. The safe moisture content for storage was determined to be 12.6 g/g d.b. at 30 - 40°C and 9 g/g d.b. at 50°C. The net isosteric heat and entropy of adsorption indicated an enthalpy-driven process. In conclusion, the findings emphasized the importance of environmental management for maintaining proper storage of *Nauclea latifolia* leaves and provided required knowledge for its stable storage condition.

## REFERENCE

- [1] Iheagwam, F.N., Israel, N., Kayode, K.O., DeCampos, O.C., Ogunlana, O.O, & Chinedu, S.N. (2020). *Nauclea latifolia* Sm. Leaf Extracts Extenuates Free Radicals, Inflammation, and Diabetes-Linked Enzymes.Oxidative Medicine and Cellular Longevity. 9 (2020), 1 - 13 Doi: 10.1155/2020/5612486.
- [2] Balogun, M.E., Besong, E.E., Obu, D.C., Obu, M.S.U., & Djobbissie, S.F.A. (2016). *Nauclea latifolia*: A Medicinal, Economic and Pharmacological Review. International Journal of Plant Research, 6(2), 34-52. DOI: 10.5923/j.plant.20160602.03
- [3] Ademola, I.O., Fagbemi, B.O.& Idowu S.O., (2007). Anthelmintic efficacy of *Nauclea latifolia* extract against gastrointestinal nematodes of sheep: in vitro and in vivo studies. Afr. J. Trad. 4(2), 148 – 156.
- [4] Ajayi, O.S., Aderogba, M.A., Akinkunmi, E.O., Obuotor, E.M., & Majinda, R.R.T. (2020). Bioactive compounds from *Nauclea latifolia* leaf extracts. Journal of King Saud University, 32(4), 2419-2425. DOI: 10.1016/j.jksus.2020.03.031
- [5] Okonkwo, C.E., Olaniran, A.F, Adeyi, O., Adeyi, A.J., Ojediran, J.O., Adewumi, A.D., Iranloye, Y.M.& Erinle, O.C. (2021). Drying characteristics of fermented – cooked cassava chips used in the production of complementary foods: Mathematical and Gaussian process regression modeling approach. Journal of Food Process Engineering. 44(1), 1 – 14. <https://doi.org/10.1111/jfpe.13715>.
- [6] Sridhar, A., Ponnuchamy, M., Kapoor, A., & Prabhakar, S. (2022). Valorization of food waste as adsorbents for toxic dye removal from contaminated waters: A review. Journal of Hazardous Materials 424(Pt B):127432. DOI: 10.1016/j.jhazmat.2021.127432.
- [7] Onuoha, J. N., & Abu, J. O. (2021). Moisture Adsorption potentials and energy models of *Gongronema latifolium* leaf grits. Food Science & Nutrition, 9(12), 6142–6153. <https://doi.org/10.1002/fsn3.2616>
- [8] Rahman, S., & Kalapathy, U. (2018). A case study on water activity and moisture sorption isotherm of food products. Emerging Technologies in Food Science. 34 (2). 25–45. [https://doi.org/10.1007/978-981-13-2324-5\\_2](https://doi.org/10.1007/978-981-13-2324-5_2)
- [9] Silva, A. C., Maia, G. A., & Nascimento, R. S. (2019). Moisture sorption isotherm and shelf life prediction. Journal of Food Engineering, 264 (3), 109–115. <https://doi.org/10.1016/j.jfoodeng.2019.04.009>
- [10] Ruan, J., Li M., Liu Y., Ye B., & Ling C. (2022). Adsorption isotherm and thermodynamic properties of microwave vacuum dried tilapia fillets. LWT - Food Science and Technology 166(2022), 113766. <https://doi.org/10.1016/j.lwt.2022.113766>.
- [11] Zhou, Y., Song, Y., & Yang, L. (2023). Investigating Adsorption-Based Atmospheric Water. Sustainability, 14(19), 12582. <https://doi.org/10.3390/su141912582>.
- [12] Borsboom, D., Mellenbergh, G. J., & van Heerden, J. (2004). The concept of validity. Psychological Review, 111(4), 1061–1071. <https://doi.org/10.1037/0033-295X.111.4.1061>.
- [13] Oyelade, O.J., Tunde-Akintunde T.Y., Igbeka J.C., Oke, M.O., & Raji O.Y. (2008). Modelling moisture sorption isotherms for maize flour. 44(2), 179–185. doi:10.1016/j.jspr.2007.10.005
- [14] Vasileva, A., Durakova A., Petrova T., & Choroleeva K. (2024). Moisture sorption characteristics of white mulberry (*Morus alba*) as a natural alternative to sugar. Journal of Hygienic Engineering and Design. 39(1), 1 – 10.
- [15] Sobowale, S.S., Oke M.O., Odunmbaku L.A. & Adebo O.A. (2017). Equilibrium sorption isotherms of *Moringa oleifera* leaves at different temperatures.. African Journal of Science, Technology, Innovation and Development, 9(1), 61–68. doi:10.1080/20421338.2016.1263435.
- [16] Heras, M.R., Heredia, A., Castelló, M.L., & Andrés, A. (2014). Moisture sorption isotherms and isosteric heat of sorption of dry persimmon leaves. Food Bioscience, 7(2), 88–94. doi:10.1016/j.fbio.2014.06.002
- [17] Sohil, F., Sohali, M.U., & Shabbir, J. (2021). An introduction to statistical learning with applications in R. Statistical Theory and Related Fields, 6(1), 87–87. <https://doi.org/10.1080/24754269.2021.1980261>
- [18] Venables, W.N., Ripley, & B.D.. (2002). [Statistics and Computing] Modern Applied Statistics with S., Fourth Edition. doi:10.1007/978-0-387-21706-2
- [19] Ouafa, N., Moghrani, H., Benaouada, N., Yassaa, N., Maachi, R., & Younsi, R. (2015). Moisture Sorption Isotherms and Heat of Sorption of Algerian Bay Leaves (*Laurus nobilis*). Maderas. Ciencia y tecnología 17(4), 759 – 772. DOI:10.4067/S0718-221X2015005000066.
- [20] Zeitler, D.W. (2015). Applied Multivariate Statistics with R. Journal of Statistical Software. 1<sup>st</sup> Edition. Doi: 10.18637/jss.v071.b02
- [21] Fabrigar, L.R., Wegener, D.T., MacCallum, R.C., & Preacher, K.J. (1999). Evaluating the use of exploratory factor analysis in psychological research. Psychological Methods, 4(2), 272-280. doi:10.1037/1082-989x.4.3.272
- [22] Cohen, J., Cohen, P., West, S.G., & Aiken, L.S. (2002). Applied multiple regression/correlation analysis for the behavioral sciences . 3<sup>rd</sup> Edition. <https://doi.org/10.4324/9780203774441>
- [23] Hair, J.F., Black, W.C., Babin, B.J., & Anderson, R.E. (2019). Multivariate data analysis. 8<sup>th</sup> Edition. Pearson Education
- [24] Adewale, O.O., Afam, I.O.J., & Patrick, F.K. (2015). Drying Kinetics of Banana (*Musa spp.*), Inerciarca 40(6), 374-380.
- [25] Adeyi, A.J., Adeyi, O., Oke, E.O., Okonkwo, C.E & Ogunsola, A.D. (2021). Effective moisture diffusivity of *Sierrathrisa leonensis* cracker: optimization, sensitivity and uncertainty analyses. Scientific African 12(1), 1 – 9. <https://doi.org/10.1016/j.sciaf.2021.e00807>.

- [26] Akoy, E.O.M., & von Hörsten, D. (2013). Moisture sorption isotherms of mango slices. *International Journal of Agricultural and Food Science*.
- [27] Kane, C.S.E, Kouhila, M., Lamharrar, A., Idlimam, A. & Mimet, A. (2008). Moisture sorption isotherms and thermodynamic properties of tow mints: *Mentha pulegium* and *Mentha rotundifolia*. *Journal of Renewable Energies* 11(2). 75 – 89. DOI: 10.54966/jreen.v11i2.67.
- [28] Yu, L., Na, L., Wenjiang, W., & Chunyan, H. (2016). Research on adsorption isotherms and the net isosteric heat of dried products of *Benincasa hispida*, *06 Journal of Light Industry*, 31(1), 24–30.
- [29] Zhang, Z, Li, X., Jia, H, & Liu, Y. (2022). Moisture sorption isotherms and thermodynamic properties of tiger nuts: An oil-rich tuber. *Food Science and Technology*. 167. <https://doi.org/10.1016/j.lwt.2022.113866>.