Original Research Article

Development of Moisture Sorption Isotherm and Mathematical Modeling of Finger Millet (Eleusine coracana)

Abstract

In the literature, only a limited number of studies have explored the sorption characteristics of finger millet-based products.Moisture sorption isotherms provide information on the interaction between food and the storage environment. The sorption isotherms of finger millet based food product were studied with dynamic vapor sorption method, isopiestic Method and static gravimetric methods at different temperatures ranging from $25–70^{\circ}$C with humidity ranges from 5-100%. Additionally, no research has been conducted on whole grains concerning their storage for further processing. This study deals with the sorption properties of whole finger millet grains. Methodically, the equilibrium moisture content of whole finger millet grains was determined by the dynamic humidity chamber method. The Guggenheim–Andersen–de Boer (GAB), Brunauer–Emmett–Teller (BET), Henderson, and Halsey sorption models were applied to describe the relationship between detected water activity and equilibrium moisture content. The study was conducted at three different temperature levels of 25°C, 30°C, and 35°C. The relative humidity ranged from 10% to 90%, with an increment of 10%. The value of average R^2 for each model is 0.9103, 0.7226, 0.9123 and 0.8853, respectively. Furthermore, a new mathematical model incorporating exponential and power-law (nonlinear) relationships was developed, achieving an average R^2 value of 0.9720. Furthermore, this study validates the developed mathematical model for fitting sorption isotherms across different millet varieties and temperature levels. Experimental data from EX-BORNO millet were utilized for model validation. The results demonstrate high accuracy, with the coefficient of determination R^2 values for adsorption at 30 ℃, 40 ℃, 50 ℃, 60 ℃, and 70 ℃ recorded as 0.976, 0.968, 0.963, 0.951, and 0.977, respectively. Similarly, the R^2 values for desorption at these temperatures were 0.978, 0.970, 0.963, 0.954, and 0.963. These findings confirm the robustness of the developed model in capturing moisture sorption behavior, providing a reliable tool for optimizing storage and processing conditions for millet. The developed mathematical model enhances the accuracy of moisture equilibrium predictions, facilitating the development of improved storage systems and drying strategies. These findings contribute to extending the shelf life and optimizing the processing efficiency of finger millet grains in the food industry. Additionally, this study offers a comprehensive analysis of the moisture sorption behavior of whole finger millet grains.

Keywords: Adsorption, Desorption, Finger Millet, Moisture Content, Modeling [1mm]

1 Introduction

Finger millet (*Eleusine coracana*), commonly known as raagi in India, is a highly nutritious cereal crop predominantly cultivated in India and Africa. It serves as a rich source of dietary fiber, complex carbohydrates, and essential amino acids such as methionine and tryptophan, contributing to its

significant role in food security and nutrition [Devi et al., 2014]. Moreover, finger millet is naturally gluten-free, making it an ideal alternative for individuals with celiac disease or gluten sensitivity [Shobana and Malleshi, 2007]. The grains of finger millet are typically ground into flour and utilized in various culinary applications, including porridges, flatbreads, and baked goods.

Moisture content is a critical factor influencing the stability, quality, and shelf life of food materials. It refers to the presence of water in a substance in different forms, including liquid, vapor, or absorbed water. Controlling and measuring moisture levels are crucial in various industries such as food production, pharmaceuticals and agriculture, as excessive or insufficient moisture can affect product quality and microbial stability [Barbosa-Cánovas et al., 2020]. In food systems, moisture affects textural properties, enzymatic reactions, and microbial growth, requiring precise moisture regulation to prevent spoilage and ensure longevity. Sorption is a collective term encompassing both adsorption and desorption processes. Adsorption refers to the adhesion of molecules onto the surface of a material, whereas desorption describes the release of molecules from a material into the surrounding environment [Iglesias and Chirife, 1976]. Understanding these processes is vital for assessing the moisture interactions in food and biomaterials.

A sorption isotherm graphically represents the equilibrium moisture content of a material as a function of water activity at a constant temperature [Labuza, 1984]. Moisture sorption isotherms are widely used to determine the optimal storage conditions for food products, preventing spoilage, mold growth, and other deterioration factors [Van den Berg and Bruin, 1978]. This knowledge enables the development of effective packaging strategies to maintain product quality and extend shelf life. Water activity, an essential indicator of food stability, helps assess microbial growth potential, oxidative rancidity, and nonenzymatic reactions, ultimately determining the shelf stability of food products [Chirife and Iglesias, 1978].

Sorption isotherm modeling has also been widely utilized to predict moisture behavior in food systems. Traditional models such as BET and GAB have been applied to various grains, including rice [Toğrul and Arslan, 2006] and pearl millet [Goneli et al., 2010], where equilibrium moisture content decreased with increasing temperature. Advanced computational techniques, such as artificial neural networks (ANNs), have been employed to predict moisture sorption behavior in cereals and legumes, offering a robust alternative to complex iterative solutions [Al-Mahasneh et al., 2014]. Additionally, moisture sorption characteristics have been linked to storage stability and product quality in extruded food products, where the isotherms exhibited Type-II behavior at varying temperatures [Sahu and Patel, 2020]. The findings from above studies contribute significantly to optimizing food storage conditions, enhancing product stability, and developing improved food packaging materials.

Hysteresis, a common phenomenon observed in sorption isotherms, occurs when the adsorption and desorption curves do not coincide, resulting in a loop in the graphical representation. This behavior is particularly evident in porous materials due to the complex interactions between adsorbate molecules and the adsorbent surface [Lowell et al., 2012]. The International Union of Pure and Applied Chemistry (IUPAC) classifies hysteresis into four types:

a H1 Type Hysteresis: Characterized by a closed loop with a sharp transition between adsorption and desorption.

b H2 Type Hysteresis: Features a gradual desorption branch that does not entirely retrace the adsorption path.

c H3 Type Hysteresis: Exhibits a wide loop with a desorption branch at higher relative pressures.

d H4 Type Hysteresis: Presents a narrow loop where the desorption branch partially follows the adsorption path [Sing, 1985].

. Hysteresis occurs due to differences in the energy required for adsorption (moisture uptake) and desorption (moisture release), often influenced by material structure, pore size, and interactions between water molecules and the material [Van der Sman, 2023, Caurie, 2007, YORK, 1981, Yang et al., 1997].

H1 hysteresis is characterized by a narrow, steep loop in the moisture sorption isotherm. This type of hysteresis is typically observed in materials with uniform, cylindrical pores, such as well-ordered mesoporous materials like Spray-dried dairy powders. The adsorption and desorption branches of the loop are nearly parallel, indicating minimal pore network effects [Cychosz and Thommes, 2018]. This suggests that the material has a relatively simple and consistent pore structure, allowing for a more predictable and reversible moisture sorption process.

H2 hysteresis exhibits a broader loop with a steep desorption branch. It is commonly found in materials with complex pore networks viz. Starch-based foods . In these materials, desorption is delayed due to pore blocking, which leads to a sharp drop in moisture content at a specific relative humidity (RH). This behavior is a result of the intricate pore structure, where narrower pore openings can trap moisture, causing a lag in desorption compared to adsorption [Shimizu and Matubayasi, 2024].

H3 hysteresis features a gradual, sloping loop without a clear plateau. This type of hysteresis is often observed in materials with non-rigid aggregates or slit-shaped pores, such as dehydrated fruits/vegetables or layered structures [Schiller et al., 2018]. The absence of a distinct plateau and the sloping nature of the loop reflect weaker interactions between water and the material. This indicates that the material's structure does not facilitate strong or uniform moisture retention, leading to a more gradual change in moisture content with varying RH [Hong et al., 2018].

H4 hysteresis is exemplified by protein-rich foods such as casein or soy protein isolates. These materials typically possess a combination of microporous and mesoporous structures. At low RH , moisture primarily fills the micropores, resulting in a narrow hysteresis loop. As the RH increases, capillary condensation occurs in the larger mesopores, leading to a broader loop. This dual behavior, characterized by a narrow loop at low RH and a broader loop at higher RH, is a hallmark of H4 hysteresis [Toncón-Leal et al., 2021].

Finger millet grains are susceptible to moisture, which can lead to spoilage, mold growth, and nutrient loss [Nickhil et al., 2024]. Sorption isotherm studies aid in determining the appropriate storage conditions (humidity levels, temperature, and packaging) to maintain the quality and prevent spoilage during storage [Gichau et al., 2020]. Different foods have specific moisture content ranges where they are more stable and less prone to spoilage or deterioration. For Finger millets, knowing the range of moisture content at different humidity levels can help in preserving its nutritional value, taste, texture, and overall quality during storage and processing [Balasubramanian and Viswanathan, 2010].

Studies on various finger millet-based foods as well other millets, including extruded products and probiotic milk powder, have shown Type II or Type III isotherms [Yadav and Mishra, 2023]. The GAB and BET models have been found to best fit the sorption data [Timmermann, 2003]. The sorption isotherms of millet grains exhibit a sigmoidal shape (type II) and are influenced by temperature and relative humidity [Alamri et al., 2018]. Various mathematical models, including GAB, BET, and modified Henderson, have been used to describe the sorption behavior of millet grains and flours [Sharma et al., 2018, Corrêa et al., 2006, Acurio et al., 2024].

Understanding sorption isotherms and hysteresis behavior in finger millet is crucial for optimizing storage conditions, improving food processing techniques, and ensuring product stability. This study aims to characterize the moisture sorption behavior of finger millet and evaluate the hysteresis effect using a DTH-controlled chamber. In this study, a dynamic temperature-humidity (DTH) controlled chamber was employed to measure the water sorption isotherm of finger millet. The temperature and relative humidity within the DTH chamber were controlled within the range of 25°C to 35°C and 10% to 90%, respectively. This approach allows for precise measurement of water activity at various conditions with high reproducibility. It also helps to design appropriate packaging materials and storage conditions to prevent moisture uptake or loss during transportation and storage, ensuring the product

remains safe and maintains its quality.

2 Materials and Methods

Moisture sorption isotherms were determined using a controlled temperature-humidity chamber with 25°C, 30°C and 35°C of temperature levels and 10-90 % relative humidity levels. Samples were equilibrated under different humidity conditions, and the equilibrium moisture content was measured. The sorption data were analyzed using mathematical models to characterize the adsorption-desorption behavior and hysteresis effects.

2.1 Material selection and Pre-processing

The GN8 variety of finger millet as shown in figure 1 was used in the experimental study. All foreign materials, such as dust, stones, chaff, immature and broken seeds, as well as bad seeds, were removed by winnowing and picking. Four replicates, each consisting of 5-gram samples, were measured using an analytical weighing balance (Model No. MS-105, METLER TOLEDO, Readability-0.01 mg;Repeatability-0.015 mg). A hot air oven (ModelNo. BTI 336, BIOTECHNOLOGIES INC., Temperature Sensitivity and accuracy- 0.5 $^{\circ}$C) was used to measure the initial moisture content of the finger millet grain.

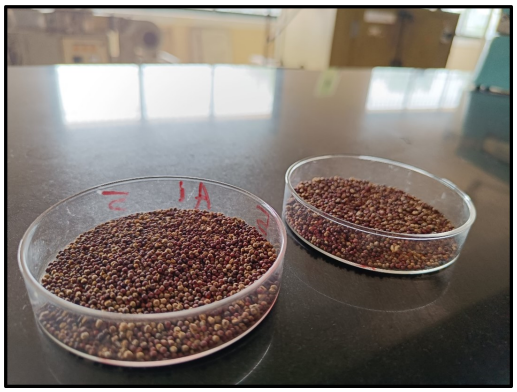

Figure 1: GN8 variety of Finger Millet

Figure 2: Dynamic temperature-humidity chamber

A humidity control chamber was used to create a controlled environment with temperatures of 25°C, 30°C, and 35°C, along with humidity levels of 10, 20, 30, 40, 50, 60, 70, 80, and 90% to study the water sorption capacity of the samples. Desiccators were used to store samples during weighing.

A water activity meter was used to measure the water present in the samples when they attained Equilibrium Moisture Content (EMC).

2.2 Moisture Content Determination

Initial moisture content of the sample was measured in quadruplicates by drying samples at 105℃ for 24 h in a hot air oven. Three trials were conducted and statistical averaging taken to determine the initial moisture content present in the sample. Moisture content was determined using equation 2.1.

$$Mc = (W_w - W_d)/W_d * 100 \tag{2.1}$$

where:

- Mc = moisture content (dry basis)
- W_w = weight of materials before oven drying
- W_d = weight of material after oven drying

2.3 Determination of Isotherms

In this developed method, a dynamic temperature-humidity (DTH) chamber (Model No. 106RP92C, EIE INSTRUMENTS PVT. LTD.) as shown in figure 2 was used to measure the sorption isotherm. DTH has preheating technology and a unique heating system that ensures homogeneous air and temperature distribution inside a chamber. At the same time, this technology ensures fast recovery of the humidity and temperature after opening and closing. In this technology, water spray in a premixing chamber and mix with air (i.e., desire relative humidity) and then circulate to the humidity chamber at a specified relative humidity. The air relative humidity and temperature are automatically controlled by the system. The temperature and humidity of the chamber can be controlled in the range of 22℃ to 70℃ and 10 to 95 %, respectively. Finally, weight of the samples were recorded at time interval of 3 hours until equilibrium state achieved.

Initially, the DTH chamber was set to a temperature of 25°C with 10% relative humidity. The samples, each weighing 5 grams, were placed inside the chamber only after it had stabilized at the set conditions. The samples were uniformly distributed in four petri dishes. The weight of each samples were recorded at 3 hours of intervals until equilibrium was reached. Subsequently, the relative humidity of the chamber was increased to 20% while maintaining the temperature at 25°C, and the weight of samples were recorded every 3 hours until equilibrium reached. This process was repeated by incrementing the relative humidity by 10% steps up to 90% for the adsorption process. At each equilibrium condition the water activity was measured.

Table 1 represents the adsorption isotherm data at different temperature levels 25°C, 30°C and 35°C with the corresponding EMC and water activity at various RH.

For isotherm measurements at different temperatures (30°C and 35°C), the same procedure was followed. For the desorption process, the relative humidity of the chamber was reduced in 10% decrements from 90% to 10% at temperatures of 25°C, 30°C, and 35°C, following the same methodology. Table 2 represents the desorption isotherm data at different temperature levels 25°C, 30°C and 35°C with the corresponding EMC and water activity at various RH.

2.4 Different Models of Sorption Isotherm

The collected isotherm data was analyzed and assessed using various well-established sorption isotherm models that are commonly applied in moisture sorption studies. These models include the GAB model, the Brunauer-Emmett-Teller (BET) model, the Henderson and the Halsey model. Each of

Table 1: Adsorption data at 25°C, 30°C and 35°C

	25°C		30°C		25°C	
RH (%)	EMC(%db)	Water Activity(a_w)	EMC(%db)	Water Activity(a_w)	EMC(%db)	Water Activity(a_w)
10	4.38	0.251	3.17	0.281	5.49	0.153
20	6.03	0.278	5.36	0.282	6.43	0.206
30	7.27	0.312	7.07	0.296	7.22	0.264
40	7.95	0.360	7.45	0.319	7.71	0.324
50	8.75	0.411	8.17	0.379	7.75	0.396
60	9.55	0.485	8.89	0.447	8.06	0.466
70	10.59	0.540	9.90	0.485	10.24	0.533
80	12.08	0.627	11.17	0.601	10.65	0.620
90	14.21	0.716	12.48	0.708	11.85	0.703

Table 2: Desorption data at 25°C, 30°C and 35°C

	25°C		30°C		35°C	
RH (%)	EMC(%db)	Water Activity(a_w)	EMC(%db)	Water Activity(a_w)	EMC(%db)	Water Activity(a_w)
10	2.08	0.239	2.33	0.282	5.86	0.084
20	4.19	0.272	4.44	0.284	6.39	0.162
30	6.33	0.313	6.35	0.301	7.02	0.240
40	7.95	0.360	7.50	0.321	7.70	0.319
50	9.85	0.423	7.97	0.389	7.73	0.392
60	11.45	0.475	8.93	0.459	8.05	0.472
70	12.33	0.554	10.0	0.500	8.97	0.554
80	12.96	0.628	11.79	0.606	10.41	0.621
90	14.19	0.715	12.48	0.789	11.81	0.703

these models was evaluated to determine its suitability in accurately describing the moisture sorption behavior of the finger millet.

2.4.1 GAB (Guggenheim-Anderson-de Boer) Model

The GAB model is best suited for food products, including grains and millets, as it accounts for monolayer moisture content, multilayer sorption, and sorption at higher water activities. It provides good accuracy over a wide range of water activity (0.10-0.90). GAB model can be express as below:

$$M = \frac{M_0 C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)} \tag{2.2}$$

where: - M = equilibrium moisture content (g water/g dry matter) - M_0 = monolayer moisture content - C = Guggenheim constant - K = factor correcting for multilayer adsorption - a_w = water activity

2.4.2 BET (Brunauer-Emmett-Teller) Model

The BET model is good for moisture sorption at low water activity (0.05-0.50) but underestimates sorption at higher RH. BET model is expressed mathematically as:

$$M = \frac{M_0 C a_w}{(1 - a_w)(1 + (C - 1) a_w)} \tag{2.3}$$

where: - M = equilibrium moisture content (g water/g dry matter) - M_0 = monolayer moisture content - C = BET constant

2.4.3 Henderson Model

The Henderson model is an empirical equation commonly used for grains and food products due to its simplicity in fitting experimental data. The Henderson model for moisture sorption isotherms is given by:

$$[-\ln(1 - a_w)]^n = kT^{-1}M \tag{2.4}$$

where: -a_w = water activity -M = equilibrium moisture content -T = temperature in Kelvin -k, n = model constants

2.4.4 Halsey Model

The Halsey model is suitable for high RH conditions and is frequently used in cereals and grains and millets.

$$M = A\left(\ln\frac{1}{a_w}\right)^B \tag{2.5}$$

where: a_w = water activity M = equilibrium moisture content A, B = model constants

To analyze the sorption behavior of finger millet, experimental data were fitted to various widely used adsorption isotherm models, including GAB, BET, Henderson, and Halsey. The adsorption parameters for each model were estimated at different temperatures ($25°C$, $30°C$, and $35°C$). Table 3 presents the computed model parameters, monolayer moisture content, and the corresponding goodness-of-fit measures, including the coefficient of determination (R^2), mean squared error (MSE), and mean absolute error (MAE). These parameters help in evaluating the accuracy and applicability of each model in predicting equilibrium moisture content under different temperature conditions.

Table 3: Adsorption Parameters for Different Models at Various Temperatures

Temperature (°C)	Model	Monolayer Moisture	Constants	R^2	MSE	MAE
25	GAB	21.04	[21.04, 0.3171, 3.588]	0.97204	0.22922	0.39293
25	BET	4.4883	[4.488, 8.243e+05]	0.87423	1.03100	0.88004
25	Henderson	–	[12.38, 0.6292]	0.96565	0.28160	0.36283
25	Halsey	–	[7.516, 0.6141]	0.93328	0.54697	0.58871
30	GAB	135.61	[135.6, 0.1373, 0.9476]	0.79966	1.46270	1.05080
30	BET	4.2601	[4.26, 4.147e+05]	0.68270	2.31660	1.36310
30	Henderson	–	[11.62, 0.6025]	0.82256	1.29550	0.88858
30	Halsey	–	[7.2, 0.5831]	0.76857	1.68970	1.06870
35	GAB	6.4026	[6.403, 0.6807, 34.16]	0.95924	0.15896	0.31118
35	BET	4.2529	[4.253, 2.954e+06]	0.61109	1.51680	1.03910
35	Henderson	–	[10.77, 0.3789]	0.94886	0.19946	0.34426
35	Halsey	–	[7.76, 0.4235]	0.95431	0.17819	0.34823

Table 4 presents model parameters, monolayer moisture content, and goodness-of-fit measures (R^2, MSE, MAE) to assess the accuracy of each model in predicting equilibrium moisture content at different temperatures for desorption behaviour.

All the selected sorption isotherm models were systematically evaluated, and their validation parameters were thoroughly analyzed in the Results and Discussion section. During the assessment, it was observed that there existed an opportunity to develop a more precise mathematical model

Table 4: Desorption Parameters for Different Models at Various Temperatures

Temperature (°C)	Model	Monolayer Moisture	Constants	R^2	MSE	MAE
25	GAB	327.93	[327.9, 0.2157, 0.2315]	0.87552	1.9318	1.2423
25	BET	5.008	[5.008, 11.42]	0.74284	3.9909	1.7204
25	Henderson	–	[13.23, 0.7531]	0.85591	2.2361	1.2372
25	Halsey	–	[7.334, 0.713]	0.77280	3.5259	1.5894
30	GAB	276.42	[276.4, 0.14, 0.4075]	0.74399	2.4773	1.4069
30	BET	3.5707	[3.571, 6.759e+05]	0.32087	6.5718	2.3508
30	Henderson	–	[10.8, 0.5714]	0.74997	2.4195	1.3240
30	Halsey	–	[6.946, 0.4833]	0.65199	3.3676	1.5319
35	GAB	5.5543	[5.554, 0.7402, 8.321e+04]	0.97327	0.086544	0.24708
35	BET	4.1491	[4.149, 1.313e+07]	0.49280	1.6425	1.1184
35	Henderson	–	[10.17, 0.2836]	0.88305	0.37871	0.5026
35	Halsey	–	[7.803, 0.3633]	0.96406	0.11637	0.30502

with an improved goodness-of-fit compared to the existing models. Consequently, a new exponential-power-based model was formulated specifically for finger millet to better describe its moisture sorption behavior. This newly developed model has the potential to be further validated and extended for application to other grains and millet varieties, ensuring broader applicability in food storage and processing studies.

3 Development of Mathematical Model

Mathematical modeling of moisture sorption isotherms is essential for understanding the equilibrium relationship between water activity and moisture content at different temperatures. Existing models such as GAB, BET, Halsey, and Henderson have been widely used; however, their accuracy varies depending on the material. To achieve a higher goodness-of-fit, a new exponential-power-based model was developed using MATLAB specifically for finger millet. This section presents the formulation of the developed model, its parameter estimation for selected temperature levels, and statistical validation to ensure its applicability in predicting sorption behavior.

The newly formulated mathematical model establishes a quantitative relationship between EMC and a_w across different temperatures. This model is designed to accurately describe the sorption behavior of the material and provide a reliable prediction of moisture equilibrium conditions under varying environmental conditions. The mathematical expression representing this relationship is given as follows:

$$M(T, a_w) = A(T) \cdot e^{B(T) \cdot a_w} + C(T) \cdot a_w^{D(T)} \tag{3.1}$$

where:

- $M(T, a_w)$ = Equilibrium Moisture Content (%db)
- T = Temperature (℃)
- a_w = Water Activity
- $A(T), B(T), C(T), D(T)$ are temperature-dependent coefficients.

3.1 Evaluation of Developed Model

The accuracy and reliability of the developed mathematical model were evaluated by comparing its predictions with experimentally obtained data at three different temperature levels. To assess the model's performance, the experimental moisture sorption data were fitted using the developed

model, and its effectiveness was quantified using statistical validation metrics such as the coefficient of determination (R^2) and the root mean square error (RMSE). The following sections present the fitted models along with their respective efficiency measures, demonstrating the model's suitability for describing the equilibrium moisture content-water activity relationship.

The newly developed mathematical model describing the relationship between equilibrium moisture content (M) and water activity (a_w) at different temperatures is presented as follows:

For a temperature of $\mathbf{25^\circ C}$, the model is given by:

$$M(25^\circ C, a_w) = 4.512 \cdot e^{1.215 \cdot a_w} + 2.157 \cdot a_w^{0.895} \tag{3.2}$$

The accuracy of the model at $\mathbf{25^\circ C}$ was evaluated using statistical parameters. The coefficient of determination (R^2) was found to be **0.9728**, indicating that 97.28% of the variation in equilibrium moisture content is explained by the model. Additionally, the root mean square error (RMSE) was **0.4722**, demonstrating a low prediction error and strong agreement between the experimental and predicted values.

For a temperature of $\mathbf{30^\circ C}$, the model takes the form:

$$M(30^\circ C, a_w) = 3.876 \cdot e^{1.101 \cdot a_w} + 1.995 \cdot a_w^{0.923} \tag{3.3}$$

At $\mathbf{30^\circ C}$, the model exhibited an R^2 value of 0.9934, signifying an excellent fit with the experimental data, while the RMSE was determined to be **0.2189**, further confirming the model's high predictive capability and minimal deviation from observed values.

For a temperature of $\mathbf{35^\circ C}$, the model is expressed as:

$$M(35^\circ C, a_w) = 5.225 \cdot e^{1.089 \cdot a_w} + 1.641 \cdot a_w^{0.812} \tag{3.4}$$

At $\mathbf{35^\circ C}$, the model achieved an R^2 value of 0.9498, reflecting a strong correlation between the predicted and experimental values. The RMSE for this temperature was **0.4427**, indicating an acceptable level of accuracy in predicting equilibrium moisture content at this condition.

These results demonstrate the robustness of the developed model across different temperatures, showing its potential applicability in predicting moisture sorption behavior with high precision.

3.2 Comparison of the Developed Model with Existing Moisture Sorption Models

The developed mathematical model for EMC as a function of water activity (a_w) and temperature (T) is not exactly the same as any standard available model such as BET, GAB, Henderson, Hasley, Peleg, Chung-Pfost, or Oswin models.

The evaluation of the existing sorption isotherm models resulted in average coefficient of determination (R^2) values of **0.9103**, **0.7226**, **0.9123**, and **0.8853**, respectively as indicated by table 3. While these models provided reasonable fits to the experimental data, a newly developed mathematical model exhibited superior performance, achieving an average R^2 value of **0.9720**. This indicates a significant improvement in the predictive accuracy of the moisture sorption behavior, demonstrating the effectiveness and reliability of the developed model for describing equilibrium moisture content at different temperatures.

3.3 Validation of Model with different Dataset

For the validation of the developed mathematical model across different millet varieties and temperature levels, data from Ex-Borno millet was utilized, as reported in the study by [Aviara et al., 2016] as shown in table 5.

Table 5: Equilibrium Moisture Content (EMC) at Different Temperatures and Water Activities (a_w) of EX-BORNO Millet

Temperature	a_w	0.07	0.11	0.22	0.32	0.51	0.61	0.70	0.82	0.89	0.97
30℃	Ads EMC	14.4	17.1	22.0	23.3	23.8	24.0	25.7	27.0	31.6	35.3
	Des EMC	14.4	17.1	22.0	24.2	25.6	26.0	26.5	27.0	31.6	35.3
40℃	a_w	0.07	0.11	0.22	0.32	0.51	0.61	0.71	0.82	0.89	0.98
	Ads EMC	12.8	15.5	19.7	20.8	21.3	21.8	22.7	24.7	27.0	31.1
	Des EMC	12.8	15.5	19.7	22.1	22.9	23.3	23.9	24.7	27.4	31.1
50℃	a_w	0.07	0.11	0.21	0.31	0.50	0.60	0.70	0.81	0.89	0.96
	Ads EMC	10.0	13.4	17.2	17.8	18.2	19.0	19.7	21.5	24.5	27.3
	Des EMC	10.0	13.5	17.2	18.6	19.7	20.6	21.5	24.6	27.3	–
60℃	a_w	0.07	0.11	0.21	0.31	0.50	0.60	0.70	0.80	0.88	0.95
	Ads EMC	8.5	11.5	14.9	16.9	17.0	17.4	17.5	18.7	21.5	25.0
	Des EMC	8.5	11.5	15.9	16.9	17.1	17.5	17.8	18.7	21.5	25.0
70℃	a_w	0.07	0.11	0.20	0.30	0.50	0.60	0.70	0.80	0.88	0.94
	Ads EMC	7.0	10.0	11.5	11.9	12.3	12.7	13.9	16.1	19.2	22.3
	Des EMC	7.0	10.0	12.9	14.0	14.6	15.0	15.5	16.4	19.3	22.3

3.4 Characteristics of Developed Model

The developed mathematical model possesses distinct characteristics, which are discussed in detail below. These features differentiate it from existing models.

1. **Combination of Exponential and Power Law Terms**
   - The model consists of both an **exponential** term ($A(T)e^{B(T)a_w}$) and a **power-law** term ($C(T)a_w^{D(T)}$).
   - Most existing models, such as BET and GAB, rely on thermodynamic principles and do not follow this hybrid functional form.
2. **Temperature-Dependent Parameters**
   - In classical models like the Henderson equation:

$$EMC = \left(-\frac{\ln(1-a_w)}{K}\right)^{\frac{1}{N}}$$

     the parameters K and N are constants for a given material.
   - In the developed model, the parameters $A(T)$, $B(T)$, $C(T)$, and $D(T)$ explicitly depend on temperature, making it more flexible.
3. **Hybrid Model Structure**
   - The first term, $A(T)e^{B(T)a_w}$, captures exponential moisture sorption behavior.
   - The second term, $C(T)a_w^{D(T)}$, accounts for nonlinear water activity dependency, which is often missing in purely empirical models.

- This combination allows better flexibility in fitting experimental sorption data.

The developed model is a **new empirical equation** developed by directly fitting to experimental data at different temperatures. It is **not the same** as existing models but shares some general characteristics with traditional moisture sorption models in food engineering.

4 Results and Discussions

The adsorption isotherm at each temperature level is shown in figure 3 for 25°C, figure 4 for 30°C and figure 5 for 35°C. The data points (red circles) represent experimental measurements, while the different curves correspond to various sorption models: GAB, BET, Henderson, and Halsey.

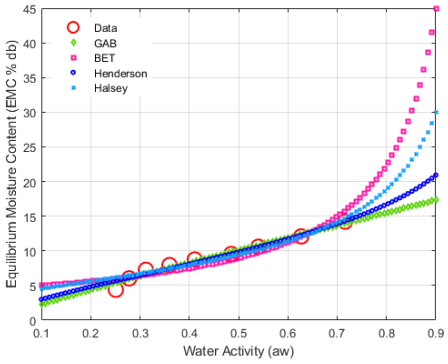

Figure 3: Moisture adsorption isotherm at 25℃

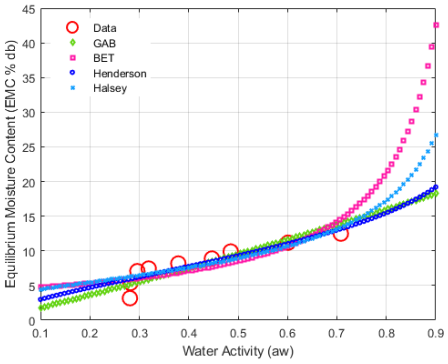

Figure 4: Moisture adsorption isotherm at 30℃

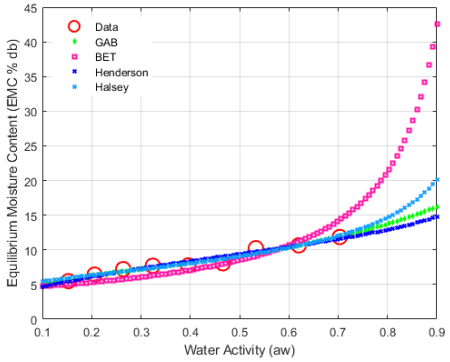

Figure 5: Moisture adsorption isotherm at 35℃

The GAB model (green diamonds) shows good agreement with experimental data across the entire range, while the BET model (pink squares) diverges significantly at higher water activity, overestimating

EMC. The Henderson and Halsey models (blue markers) follow the trend of the experimental data more closely than BET but slightly deviate at higher a_w values.

From the figure 3 to figure 5, there is an improvement in the model fit, particularly for the GAB, Henderson, and Halsey models. The GAB model remains the most accurate, aligning well with the experimental data throughout. The BET model consistently exhibits an exponential rise in EMC at high a_w values, suggesting its limitation for high water activity ranges. The Henderson and Halsey models maintain a reasonable fit but still show some deviation from the data at high a_w.

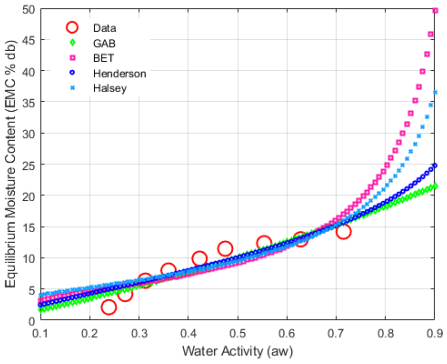

Figure 6: Moisture desorption isotherm at 25℃

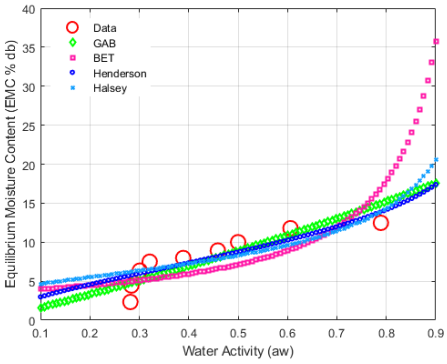

Figure 7: Moisture desorption isotherm at 30℃

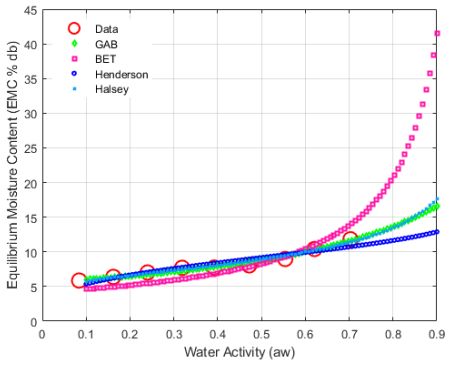

Figure 8: Moisture desorption isotherm at 35℃

The desorption isotherm at each temperature level is shown in figure 6 for 25°C, figure 7 for 30°C and figure 8 for 35°C. The BET model (pink squares) shows a sharp increase at higher a_w, indicating its limitation in accurately representing moisture content beyond monolayer adsorption.

The Henderson and Halsey models (blue markers) offer reasonable approximations but deviate significantly at high a_w levels.

The results highlight the superiority of the GAB model for predicting moisture sorption behavior, especially for food materials where water activity extends across a wide range. The BET model is only

suitable for lower a_w values, as it significantly overestimates EMC beyond 0.6 a_w. The Henderson and Halsey models provide a moderate fit but are not as reliable as GAB.

The model's effectiveness has been evaluated with experimental data at three temperature levels (25°C, 30°C, and 25°C), with corresponding equations explicitly stated. The statistical validation, including R^2 and RMSE values, confirms the model's capability, with an average R^2 of 0.9720, significantly outperforming existing models such as BET, GAB, and Henderson. The R^2, demonstrated through model evaluation across different temperatures, highlights its reliability in accurately describing equilibrium moisture content.

To validate the developed mathematical model for various millet varieties and temperature levels, the study utilized data from EX-BORNO millet, as reported by [Aviara et al., 2016]. The validation results, as illustrated in figure 9, indicate that for different temperatures, namely $30^\circ C$, $40^\circ C$, $50^\circ C$, $60^\circ C$, and $70^\circ C$, the coefficient of determination (R^2) values for adsorption are 0.976, 0.968, 0.963, 0.951, and 0.977, respectively, while for desorption, the corresponding R^2 values are 0.978, 0.970, 0.963, 0.954, and 0.963 for EX-BORNO millet.

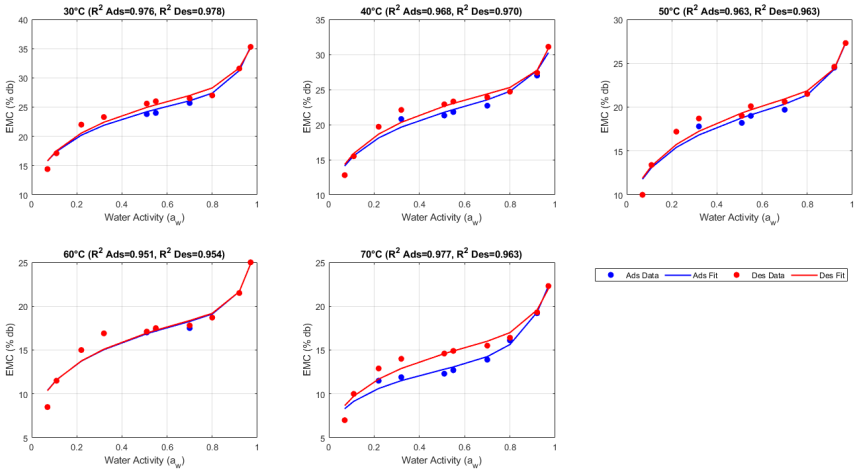

Figure 9: Validation of developed mathematical model with different temperature for EX-BORNO millet

Comparisons with traditional models reinforce the originality of this study, as the developed model uniquely integrates exponential and power-law terms, making it distinct from standard moisture sorption equations. These findings emphasize the importance of selecting the appropriate model when analyzing sorption behavior in food products.

5 CONCLUSIONS

The study confirms the superiority of the GAB model in predicting moisture sorption behavior, particularly for food materials with a wide range of water activity. While the BET model performs well at lower a_w values, it significantly overestimates EMC beyond 0.6 a_w, limiting its applicability. The Henderson and Halsey models offer a moderate fit but lack the reliability of the GAB model, making them less suitable for accurate moisture sorption predictions.

The developed model introduces a hybrid approach to predict EMC by combining exponential and power-law terms. Unlike conventional models such as BET and GAB, which are based on thermodynamic principles, this model incorporates temperature-dependent parameters for improved flexibility. The exponential term accounts for moisture sorption behavior, while the power-law term captures nonlinear water activity effects. This structure enables better adaptability to experimental data, making the model more versatile in describing moisture sorption characteristics across different temperature conditions.

The evaluation of existing sorption isotherm models yielded average R^2 values of 0.9103, 0.7226, 0.9123, and 0.8853 for GAB, BET, Henderson and Halsey models, respectively. While these models provided reasonable fits, the developed model outperformed them with an average R^2 of 0.9720, demonstrating superior accuracy and reliability in describing moisture sorption behavior across temperatures.

The validation results, based on an external dataset, demonstrate a strong correlation between predicted using developed model and experimental values considered for EX-BORNO millet. The coefficient of determination R^2 for adsorption at different temperatures ($30^\circ C$, $40^\circ C$, $50^\circ C$, $60^\circ C$, and $70^\circ C$) are 0.976, 0.968, 0.963, 0.951, and 0.977, respectively. Similarly, for desorption, the corresponding R^2 values are 0.978, 0.970, 0.963, 0.954, and 0.963. These results confirm the accuracy and reliability of the proposed mathematical model across varying temperature conditions and for different millets.

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