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Adsorption Isotherm Modeling of Pistachio (*Pistacia vera* L.) and its Role in Storage Stability Assessment

Mohamed Sami[1*], Morad Oubouali[2], Morad Kaddouri[2], Soufiane Ghanimi[2], Fatima Ezzahra Atmani[1], Reda Elkacmi[1], Abdelali Bouali[1] and Aziz Hasib[1]

[1]*Laboratory of Agro-industrial & Environmental Processes, Faculty of Science and Technology, University of Sultan Moulay Slimane, Beni Mellal, Morocco*

[2]*Laboratory of the Engineering and Applied Technologies, Higher School of Technology of Beni Mellal, University of Sultan Moulay Slimane, Beni Mellal, Morocco*

[*]Correspondence to:
Mohamed Sami
Laboratory of Agro-industrial & Environmental Processes,
Faculty of Science and Technology,
University of Sultan Moulay Slimane,
Beni Mellal, Morocco.
E-mail: sammimoh95@gmail.com

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Abstract

Pistachio nuts (*Pistacia vera L.*) are highly sensitive to ambient humidity, and understanding their hygroscopic behavior is essential for optimizing storage and preserving quality. This study investigated the water adsorption properties of pistachio kernels at three temperatures (25 °C, 35 °C, and 45 °C) through experimental testing, utilizing the static gravimetric method. Hygroscopic equilibrium was reached after 11, 9 and 20 days, respectively. The obtained isotherms were classified as type III, high-sugar or high-oil products typically show minimal moisture absorption at low water activity (a_w) levels, followed by a sharp increase in water uptake as the a_w approaches higher values. The adsorption data generated provides essential information for defining optimal storage conditions and preventing quality deterioration during handling, packaging, and distribution. The adsorption data were modeled using three mathematical equations: Guggenheim-Anderson-de Boer model (GAB), Brunauer-Emmett-Teller model (BET), and Langmuir. Among these, The GAB model provided the most accurate fit, showing strong correlation coefficients (R^2 = 0.995 at 25 °C, R^2 = 0.999 at 35 °C, and R^2 = 0.996 at 45 °C). The optimal a_w range that ensures microbiological stability and preserves the quality of pistachio nuts consistently across all three temperatures was between a_w = 0 and 0.2. These findings offer valuable insights for optimizing pistachio storage strategies in controlled humidity environments.

Keywords

Pistachio, Water activity, Adsorption isotherms, Guggenheim-Anderson-de Boer model, Water content

Introduction

Species within the genus (*P. vera L.)* are classified under the family *Anacardiaceae*, which also encompasses other economically and ecologically significant plants, including *Anacardium* species, such as the cashew (*Anacardium occidentale*), mango, as well as different species of sumac. Among them, *P. vera L.* is the sole species capable of producing edible dried fruits of sufficient size for commercial valorization [1], globally the main producers of pistachios are Iran (551,307 tons/year), the United States (447,700 tons/year), Turkey (240,000 tons/year), and China (74,828 tons/year). In comparison, Moroccan production remains very limited, with only 47 tons per year, or about 0.001351 kg per capita [2, 3] Due to its significant nutritional profile and naturally predisposed dehiscence, *Pistacia* species, particularly the pistachio, are gaining prominence as a valuable agricultural commodity, pistachios are enjoyed in many different forms, such as raw, salted, and roasted [4]. The kernel composition per 100 g consists of approximately 53 g of oil, 12 g of carbohydrates, and 27 g of protein, with the remaining fraction

comprising water and mineral constituents [5]. The composition of pistachios varies depending on the cultivar, with the kernel typically comprising approximately 50 to 55% of the total weight, while the shell accounts for 45 to 50%.

Lipid oxidation of pistachios, influenced by seasonality and climatic variations (temperature and relative humidity), leads to a decrease in their quality and shelf life. This process is favored by the natural presence of enzymes. The main factors include lipoxygenase and lipase, as well as exposure to light and the presence of chlorophyll, both of which facilitate lipid oxidation, are factors that contribute to the deterioration of pistachios during storage [6]. The main factors influencing the development of molds and contamination of pistachios by aflatoxins, elements such as temperature, a_w, relative humidity, and changes in the fragile outer shell all contribute to the process [7].

Moisture sorption isotherms depict the connection between a material's equilibrium moisture content and its a_w, held constant at a specific temperature and pressure. These curves provide valuable data on the material's capacity to absorb and hold moisture. In the case of food products, they provide valuable information on sorption mechanisms as well as on interactions between food biopolymers and water content and its temperature [8]. An adsorption isotherm is depicted as a curve at a specific temperature, moisture sorption isotherms describe how a material's moisture content correlates with its a_w, or equilibrium relative humidity, under controlled environmental conditions. They provide a detailed overview of the material's water retention properties at various a_w (X) levels, compared to its equilibrium a_w, exhibiting distinct regions that can be characterized based on the sorption behavior:

- An adsorption isotherm is experimentally determined by subjecting a dried product to controlled moisture adsorption under specified conditions.
- A desorption isotherm is determined through experimentation by exposing a water-saturated material to controlled drying conditions, throughout this process. The connection between the material's moisture content and its a_w is observed throughout the drying process [9].

Adsorption isotherms are essential tools for improving food storage and preservation strategies, providing important insights into how food materials retain moisture under varying environmental conditions [10, 11].

Effectively managing the moisture-absorbing qualities of pistachios is essential for preserving their freshness and ensuring they stay in top condition throughout storage and transport, as it plays a key role in moisture control and preventing deterioration. *P. vera* is highly valued for its unique sensory characteristics and significant commercial worth.

However, research on the water adsorption characteristics of pistachios is quite limited, particularly under varying temperature conditions. Several studies have addressed this topic. For instance, several studies have investigated the water sorption behavior of pistachios under different conditions. Yanniotis and Zarmboutis [12] studied the water absorption isotherms of pistachio nuts (Aegina variety) at 15 °C, 25 °C, and 45 °C [12]. Similarly, Yazdani et al. [4] investigated the sorption isotherms of pistachio (*Pistacia terebinthus L.*) and its protein isolates at 15 °C, 25 °C, and 35 °C [4]. Karatas and Battalbey [13] also analyzed the moisture sorption isotherms of pistachio (Gaziantep variety) at 20 °C. In addition, Denizel et al. [14] investigated both adsorption and desorption isotherms of pistachios, including the shell and husk, using gravimetric and manometric techniques to assess moisture uptake and release behavior.

In recent years, numerous mathematical models have been developed to describe sorption isotherms, ranging from theoretical approaches such as the BET and GAB models to empirical ones like the Langmuir model. These models are widely used to fit experimental data and to determine key thermodynamic parameters. Which plays a vital role in optimizing industrial processes like drying, packaging, and storage [15].

This study focuses on experimentally analyzing the adsorption isotherms of *P. vera L.* at 25 °C, 35 °C, and 45 °C using the static gravimetric method. The results are expected to provide a deeper understanding of the moisture adsorption behavior and hygroscopic properties of this pistachio variety. The sorption isotherms will then be modeled using three widely recognized mathematical models (GAB, BET, and Langmuir). This approach will deepen the understanding of the hygroscopic behavior specific to *P. vera L.*, while providing crucial data for optimizing storage conditions, thereby enhancing the preservation of the product post-drying and packaging.

Materials and Methods

Experimental procedure

Roasted and salted pistachio, sold in bulk at sales outlets in the Fez-Meknes region, Morocco, and imported from the United States, were used for experimentation. The sample studied was collected during the campaign of the year 2024.

In this study, the samples were considered lightly salted (typical commercial levels generally below 1 - 2% sodium chloride, w/w); therefore, the influence of salt on the overall adsorption behavior was expected to remain limited compared with the effect of temperature and the intrinsic composition of pistachio kernels, especially their high lipid content.

The equilibrium moisture content (X) is determined using the equation below:

$$X = \frac{Humid\ mass - Dry\ mass}{Dry\ mass} \quad (1)$$

The pistachios pits have been dissociated from their envelopes and were cut into thin strips of 3 mm in length and 2 - 3 mm thick. Approximately 10 g of the sample was placed in a pre-weighed stainless-steel capsule and then introduced into a glass container containing sulphidic acid solutions of varying concentrations (25% to 85%) to regulate the a_w of the environment. The container was subsequently sealed airtight and placed in an oven (Figure 1) for the experimental procedure [16].

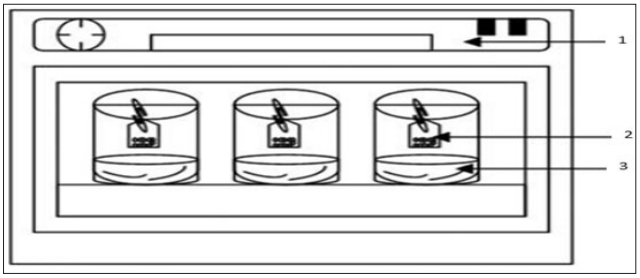

Figure 1: Schematic of the experimental setup used for sorption isotherm measurements: **(1)** thermostatable bath; **(2)** pistachio samples; and **(3)** sulphidic acid solutions [16].

Five samples were tested at three different temperatures 25 ˚C, 35 ˚C, and 45 ˚C. Each sample was weighed every 24 h until it reached equilibrium, a process that required between 7 and 12 days. To reduce the influence of environmental factors, each weighing was completed in about 20 s. At high a_w conditions (a_w > 0.70), especially at 45 ˚C, samples were visually inspected throughout the equilibration period to detect any microbial growth. No visible mold development was observed on the pistachio samples. Therefore, the recorded mass increase was attributed solely to water adsorption. The moisture content was evaluated by drying the samples in an oven at 105 ˚C until a stable weight was reached.

The sample weight was monitored over time, and equilibrium was considered reached when three consecutive measurements exhibited minimal variation, with a difference of less than 0.001 g [10]. The a_w values corresponding to aqueous sulphidic acid solutions at 25 ˚C, 35 ˚C, and 45 ˚C were obtained from the reference data reported by Karatas and Battalbey [13] and Maskan and Göğüş [17].

Modeling tools

The three mathematical models listed in table 1 were selected to fit the adsorption isotherms obtained from the experimental data in this study. The GAB, BET and Langmuir models, known for their effectiveness in describing sorption phenomena in food products, were applied. The parameters associated with the GAB (A, B, C), BET (A, B) and Langmuir (A, C) equations were estimated using CurveExpert Professional 2.7.0 Software, nonlinear regression analysis was used to fit the experimental data, making this process possible.

Results and Discussion

Table 2 displays the adsorption isotherm data for 25 ˚C, 35 ˚C, and 45 ˚C. Figure 2 illustrates the variations in a_w and moisture content at three different temperatures (25 ˚C, 35 ˚C, and 45 ˚C). Table 3 presents the results of the nonlinear regression analysis, which was applied to fit the sorption models to the experimental adsorption data of the pistachio samples.

Table 2: Water adsorption isotherms of pistachio at 25 ˚C, 35 ˚C, and 45 ˚C.

Temperature	a_w	Water content (%)
25 ˚C	0.8202	5.90
	0.5612	3.21
	0.3524	2.16
	0.0483	1.32
	0.0013	1.20
35 ˚C	0.8238	6.61
	0.5713	2.35
	0.3757	1.72
	0.0531	0.94
	0.0016	0.78
45 ˚C	0.8280	6.80
	0.5809	1.44
	0.3757	1.28
	0.0581	0.54
	0.0019	0.26

At 25 ˚C, a_w ranged from 0.0013 to 0.8202, while the moisture content varied between 1.2% and 5.9%. At 35 ˚C, a_w ranged from 0.0016 to 0.8238, and moisture content ranged from 0.78% to 6.61%. At 45 ˚C, the maximum a_w recorded was 0.8280, which corresponded to a moisture content of 6.8%. After this point, both a_w and moisture content started to decline.

Each point on the curve represents the average of five water content values. The adsorption isotherms shown in figure 1 demonstrate that water adsorption by pistachio is minimal at low a_w, but increases significantly as a_w rises.

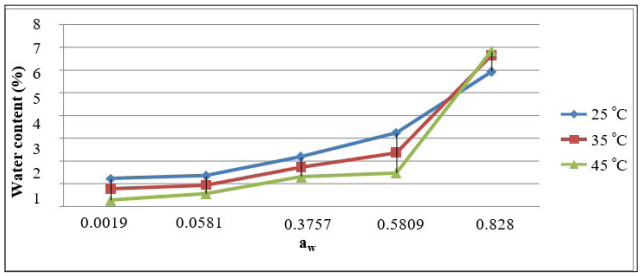

Figure 2: Adsorption isotherms of pistachio at 25 ˚C, 35 ˚C, and 45 ˚C.

Table 1: Mathematical formulations of the GAB, BET, and Langmuir adsorption models.

Model	Model equation	Model parameters
GAB [18]	$X = \frac{X_m * C * K * a_w}{(1 - K * a_w)(1 - K * a_w + C * K * a_w)}$	X_m: monolayer moisture content (g water/g dry matter, dry basis) C: GAB constant related to sorption energy K: constant accounting for multilayer properties
BET [19]	$X = \frac{X_m * C * a_w}{(1 - a_w)[1 + (C - 1)a_w]}$	X_m: monolayer moisture content (g/g dry basis) C: BET constant associated with adsorption energy
Langmuir [20]	$X = \frac{X_m * C * a_w}{1 + C * a_w}$	X_m: maximum adsorption capacity (g/g dry basis) C: affinity constant of the model

Table 3: Estimation of the parameters for the three models at 25 °C, 35 °C, and 45 °C.

Temperature (°C)	Models	A	B	C	n	R^2
25 °C	BET	2.505	-	28.19	0.976	0.902
	GAB	1.475	0.916	3.50×10^3	-	0.995
	Langmuir	1.445×10^3	-	4.65×10^{-3}	-	0.804
35 °C	Langmuir	4.118×10^3	-	1.58×10^{-3}	-	0.786
	GAB	0.981	1.034	2.28×10^3	-	0.999
	BET	1.306	-	8.45×10^2	0.937	0.990
45 °C	GAB	0.580	1.105	3.74×10^2	-	0.996
	BET	0.701	-	2.51×10^2	0.875	0.996
	Langmuir	5.543×10^3	-	1.08×10^{-3}	-	0.704

Typically, the isotherms taken at higher temperatures are lower than those at lower temperatures. In addition, as the temperature rises, the product's equilibrium moisture content tends to decrease. These results are in line with those observed for other dried fruits, such as almonds from Irvingia gabonensis [21], this phenomenon happens because higher temperatures increase the kinetic energy and movement of water molecules, leading to greater molecular motion and more space between molecules. As a result, the water molecules are less tightly bound and can be more easily released from the adsorption sites within the food matrix. This behavior, as noted in earlier study by Arslan-Tontul [22], is associated with a reduction in the number of active binding sites due to the physicochemical changes caused by the temperature [23].

Adsorption isotherms have a characteristic shape of foods rich in sugars, which absorb substantial amounts of water at elevated a_w levels, but remain little when the a_w is low. The water content of the pistachio rises substantially when the a_w exceeds 0.5, a similar result was observed during the study of pistachio nut paste [12].

The adsorption isotherm of pistachio is type III, characteristic of pure crystalline sugars. It is distinguished by low moisture absorption as long as the a_w remains below 0.7 - 0.8, followed by a significant increase beyond this threshold. This can be explained by the fact that water primarily forms hydrogen bonds with the hydroxide ion groups present on the surfaces of crystalline regions, proteins, and polysaccharides [24]. This phenomenon is likely influenced by the high oil content (around 50%) of pistachio. Previous studies have shown a decrease in the number of active sites available for monomolecular adsorption, with similar findings reported in the literature by Arslan-Tontul [22] and Togrul and Arslan [25]. The pronounced increase in the moisture content of pistachio. The behavior observed for a_w values exceeding 0.7 can be attributed to the progressive dissolution of sugars, leading to their complete solubilization. This process is characterized by a shift from a crystalline to an amorphous structure, which leads to a greater number of accessible sorption sites as the biopolymer matrix expands [26]. An increase in temperature facilitates the dissolution of sugars, thereby enhancing water retention within the food matrix. This behavior has been similarly observed by other researchers in various food products [13, 18-20] including fig [21].

The crossing of the three isothermal curves occurs around water activities greater than about 0.75 (Figure 2). This observation is consistent with the isotherms of many foods' rich in sugar [29]. However, in this case, where the material has a low sugar content, such an intersection of the curves was not anticipated. A similar phenomenon was observed in the isotherms of *P. terebinthus* [4]. However, an inverse effect was observed at high a_w values, where pistachios absorb more water at higher temperatures. The intersection of the three adsorption isotherm curves indicates changes in the sorption properties of pistachios at elevated water activities.

The adsorption isotherm is divided into three distinct regions, each corresponding to a specific range of a_w: zone A (a_w = 0 - 0.2), zone B (a_w = 0.2 - 0.7), and zone C (a_w = 0.7 - 1.0) [25].

In zone A, adsorption corresponded to monolayer adsorption, where water molecules were strongly attached to the polar sites by hydrogen bonds [30]. In zone B, the moisture content reached its critical level, ensuring optimal stability of the pistachios during storage. A strong linear relationship was observed between moisture content and a_w, which is likely attributed to structural changes in the matrix and the interactions of water with its constituent components [22]. Multilayer adsorption occurred in this region, where water molecules interacted to fill the micropores of the matrix. In region A, water existed in a bound state, restricting its involvement in biochemical reactions. In zone C, water penetrated the pores and intercellular spaces, becoming mechanically trapped in voids before eventually condensing into free water. This free water is sufficiently mobile to participate in biochemical processes [31]. When a_w exceeds 0.7, even a small increase leads to a marked rise in water adsorption, indicating that this range is particularly susceptible to deterioration, including the growth of surface mold.

Adsorption isotherms for the pistachio variety were measured at 25 °C, 35 °C, and 45 °C. The experimental data were then fitted to three classic sorption isotherm models BET, GAB, and Langmuir to determine which model best captured the observed behavior. The quality of the fits was evaluated by comparing their correlation coefficients (R^2), this approach allowed for a quantitative assessment of how accurately the models represented the experimental data at each temperature. All three models provided a good fit, with the GAB model showing the highest correlation (R^2 = 0.999 at 35 °C), making it the most suitable for describing the pistachio adsorption isotherm. The monolayer moisture content (X_m) predicted by the GAB model (0.981 g/g dry matter) was lower than the values estimated by the BET model (1.306 g/g) and the

Langmuir model (4.118×10^3 g/g). Accurately determining X_m is crucial for ensuring product stability and reducing microbial and chemical risks. As a result, the GAB model is seen as the most reliable for optimizing storage conditions.

The GAB model has proven to be effective for modeling the moisture adsorption isotherms in various carbohydrate-rich food products. It has been successfully applied to dried apricots [32], dates of different varieties [10], as well as pistachio kernels and shells [33]. Belarbi et al. [33] also reported that this model provides an accurate fit for the adsorption isotherms of Mejhoul dates. In addition, our findings, consistent with these studies, confirm that the GAB model provides an accurate representation of the sorption isotherms of pistachios [17], pistachio paste [26], and whole pistachios [34]. These results, which align with previous studies by Soleimanifard and Hamdami [35] and Zhang et al. [36], validate the use of the GAB model for predicting moisture sorption in pistachio products, as demonstrated in this study.

Conclusion

This study investigated the moisture adsorption isotherms of pistachio (*P. vera L.*) using the static gravimetric method at 25 °C, 35 °C, and 45 °C. Hygroscopic equilibrium was reached after 11, 9, and 7 days, respectively, confirming the strong influence of temperature on equilibrium time. The results indicate that the optimal storage range for maintaining quality and ensuring microbiological stability is at low a_w, between a_w = 0 and 0.2, regardless of temperature. Among the tested models, the GAB model showed the best agreement with experimental data (R^2 = 0.995 - 0.999), making it a reliable tool for predicting moisture behavior and supporting the optimization of pistachio storage conditions.

Acknowledgements

None.

Conflict of Interest

None.

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