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Research Article

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# Modeling the Desorption Isotherms of Starking Delicious Apples for Optimizing Storage Conditions

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## Abstract

This study examines the desorption isotherms of starching delicious apples using the static gravimetric method at two temperatures: 25 °C and 40 °C, chosen respectively to represent ambient storage conditions and higher thermal environments influencing water desorption. Hygroscopic equilibrium was reached after 23 and 20 days, respectively. The experimental data revealed sigmoidal desorption isotherms (Type II), typical of sugar-rich fruits. As temperature increased, equilibrium moisture content decreased significantly. The sorption data were modeled using three mathematical equations: Guggenheim-Anderson-de Boer (GAB), Brunauer, Emmett and Teller (BET), and Langmuir. Among these, the BET model provided the best fit, with high correlation coefficients (r = 0.9975 at 25 °C and r = 0.9992 at 40 °C) and low standard errors (SE = 0.0426 and 0.0158, respectively). The ranges of optimal water activity for safe storage and microbiological stability were identified as 0.74 - 0.45 (at 25 °C) and 0.67 - 0.47 (at 40 °C). These results provide valuable information to optimize post-harvest handling and storage strategies for apples in controlled humidity environments.

## Keywords

Starking delicious, Desorption isotherm, Water activity, Storage stability, Moisture sorption

## Introduction

In Morocco, apple cultivation plays a significant role in the agricultural economy, particularly in the Midelt and Ifrane regions, which together contribute a large share of national production. Apples are cultivated in approximately 33,000 hectares, with an annual production exceeding 600,000 tons. This sector contributes substantially to rural employment and income generation, especially in mountainous and semi-arid areas. Among the numerous apple varieties grown in Morocco, starking delicious is one of the most popular due to its commercial value, vibrant red skin, and sweet, juicy flesh appreciated by Moroccan consumers. The starking delicious apple is characterized by a medium to large size, with an average fruit weight of around 180 - 220 g. It has a firm and crisp texture, a conical to elongated shape, and a relatively high moisture content, making it sensitive to postharvest deterioration if not properly stored [1].

Water is the most abundant component in food and plays a central role in its preservation, texture, biochemical stability, and microbial safety. During quality assessment, the moisture content and its availability commonly measured as water activity ($a_w$) are critical parameters. Water activity is defined as the ratio between the vapor pressure of water in the food and the vapor pressure of pure water at the same temperature. It reflects the energy status of water in a system

and directly influences chemical, enzymatic, and microbial reactions [2].

Both water activity and temperature govern the moisture behavior in food products. When analyzing how food interacts with environmental humidity at a constant temperature, sorption isotherms are used. These curves represent the equilibrium relationship between the water content of a product and the corresponding water activity. Depending on the initial moisture level, two types of isotherms can be distinguished: Adsorption isotherms, derived from dry samples absorbing moisture; and desorption isotherms, derived from moist samples losing water.

Sorption isotherms are essential tools for designing drying processes, predicting shelf life, optimizing storage conditions, and formulating moisture-safe packaging. They provide insight into the hygroscopic behavior of foods and allow estimation of the monolayer moisture content ($X_m$), where food is most stable [3].

Over the past few decades, various mathematical models have been developed to describe sorption isotherms, ranging from theoretically based models (e.g., BET and GAB) to empirical ones (e.g., Langmuir). These models are widely used to fit experimental data and extract key thermodynamic parameters that inform industrial drying, packaging, and storage protocols [4].

Although sorption behavior has been widely studied in various fruits, limited information is available for starking delicious apples under controlled temperature conditions, particularly concerning desorption behavior. Given their relatively high moisture content and sensitivity to environmental changes, understanding their water sorption properties is crucial to reduce postharvest losses and maintain quality during storage and distribution.

In this context, the main objective of this work is to experimentally determine the desorption of isotherms of starking delicious apples at temperatures of 25 °C and 40 °C, using the static gravimetric method. The study also aims to model these isotherms using three widely recognized mathematical models (GAB, BET, and Langmuir) and to determine key parameters such as monolayer moisture content and net sorption heat. The results will enhance understanding of the hygroscopic behavior of this apple variety and contribute to optimizing its drying, conservation, and storage conditions.

# Materials and Methods

## Sample preparation

The samples used in this study consisted of starking delicious apples harvested at commercial maturity from the Aghbala region in the Béni Mellal–Khénifra province of Morocco. The degree of maturity was determined based on the characteristic red skin coloration, an average firmness of 65 ± 2 N, and a soluble solids content of 13.8 ± 0.3 °Brix. Each apple was carefully sliced into thin, uniform sections to enhance the desorption process. A mass of 30.000 ± 0.002 g of apple slices was accurately weighed using an analytical balance. The initial moisture content of the fresh samples was 84.6 ± 0.4 g water/g (wet basis). To inhibit fungal growth during the experiment, 0.512 ± 0.002 g of thymol crystals were added to each sample.

## Experimental setup

Approximately 30 g of sample were placed in pre-weighed stainless-steel capsules and introduced into sealed glass desiccators containing sulfuric acid solutions of known concentrations to establish controlled water activity environments. The sealed containers were then placed in an oven, as illustrated in figure 1. The samples were weighed every 24 h until the mass became constant. Equilibrium was considered to be reached when the difference among three consecutive weight measurements was less than 0.001 g. To minimize the influence of ambient conditions, each weighing was completed within 30 s.

The final moisture content is determined by drying the samples in an oven at 105 °C. The desiccators were then placed in a temperature-controlled oven set at 25 °C. The mass of the samples was monitored periodically until equilibrium was reached, defined as no significant change in mass between successive measurements (±0.002 g). Once mass stability was achieved, the samples were removed and oven-dried at 105 °C for 48 h to determine their dry mass ($M_s$). The difference between the wet and dry masses was used to calculate the equilibrium moisture content of each sample. The equilibrium moisture content ($X_m$) was determined using the following equation [5]:

$$X_{eq} = \frac{(M_h - M_s)}{M_s}$$

Where, $M_h$ is the mass of the sample at equilibrium (g) and $M_s$ is the dry mass of the sample (g).

After completing the experiment at 25 °C, the same procedure was repeated at a second temperature of 40 °C. Each condition was performed in triplicate, and the reported values correspond to the meaning of the three replicates.

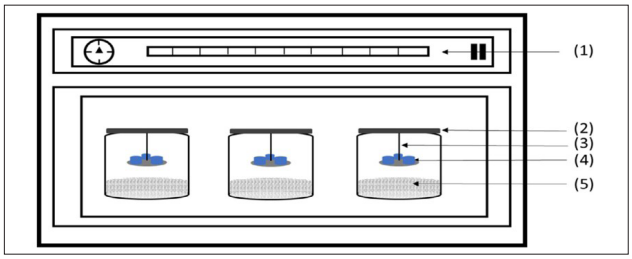


**Figure 1:** Experimental apparatus for the sorption isotherm: **(1)** thermostatic bath; **(2)** sample jars; **(3)** sample holders; **(4)** date samples; and **(5)** sulphidic acid solutions.

## Modeling tools

The three mathematical models presented in table 1 were selected to describe the desorption isotherms obtained experimentally in this study. These models GAB, BET, and Langmuir are widely used in the literature for modeling sorption phenomena in food products. The parameters of the GAB equation ($X_m$, C, K), BET ($X_m$, C), and Langmuir ($X_m$, C) were determined using Curve Expert Professional 2.7.0 software based on experimental data. A nonlinear least squares regression method was applied to fit the models to the measured equilibrium moisture content, minimizing the sum of squared differences between the experimental and predicted values.

**Table 1:** Mathematical equations of the three models GAB, BET, and Langmuir.

| Model | Equation | Variables |
|---|---|---|
| GAB [6] | $X=\frac{Xm*aw*C*K}{(1-aw*K)(1+aw*C*K-aw*k)}$ | $X_m$<br>C<br>K |
| BET [7] | $X=\frac{Xm*aw*C}{(1-aw)(1-aw+aw*C)}$ | $X_m$<br>C |
| Langmuir [8] | $X=\frac{Xm*aw*C}{(1+aw*C)}$ | $X_m$<br>C |

**Note:** $X_m$ is the water content corresponding to the monomolecular layer expressed on a dry basis (g water/g dry matter, g/g db), C is the GAB constant or BET constant or Langmuir constant, K is the GAB constant, and $a_w$ is the water activity.

The GAB model is considered one of the most reliable and extensively applied in food science [6]. It is particularly suitable for modeling sorption isotherms over a wide range of water activities (0.05 to 0.95) and is accepted by many European researchers. The GAB model enables the estimation of the monolayer moisture content ($X_m$), as well as the sorption heat associated with the monomolecular and multilayer adsorption [7]. The model parameters $X_m$, C, and K are product and temperature dependent and are determined by fitting to experimental data.

The BET model is also used in this study. Though more limited in scope than GAB, it remains useful for estimating monolayer moisture content in the lower water activity range (typically up to $a_w \approx 0.5$) [8]. The BET constant C provides information on the energy of adsorption relative to that of liquid water.

The Langmuir model, initially developed for gas adsorption, is sometimes applied to food systems and assumes monolayer adsorption on a homogeneous surface. Although less frequently used in food dehydration studies, it still provides valuable insights under certain conditions [9].

Overall, for water activity levels not exceeding 0.90, the GAB model offers a robust fit for desorption isotherms of agri-food products. In contrast, the applicability of the BET model is generally limited to lower water activity ranges.

## Results and Discussion

### Desorption results for starking delicious apples at 25 °C and 40 °C

The experimental values of equilibrium moisture content for the starking delicious apple variety were determined for each water activity level, corresponding to sulfuric acid solutions, at two temperatures: 25 °C and 40 °C. The results are summarized in the following table 2.

Hygroscopic equilibrium was considered to be reached when successive mass measurements, taken at 24 h intervals, showed variations lower than ±0.001 g in the apple samples. The corresponding equilibrium moisture contents for each sulfuric acid solution are reported in table 2. In both cases, the desorption curves exhibit a sigmoidal shape (Type II) [10], typical of fruits rich in carbohydrates [11]. These observations are consistent with previously reported results for various sugar-rich products, including dried apricots (*Prunus armeniaca* L.) [12], figs (*Ficus carica* L.) [13], bananas (*Musa* spp.), mangoes (*Mangifera indica* L.), and pineapples (*Ananas comosus* L.) [14].

**Table 2:** Desorption isotherms of *starking delicious* apples.

| Temperature | Water activity | Water content (%) |
|---|---|---|
| 25 °C | 0.8756 | 1.653 |
| | 0.7493 | 1.209 |
| | 0.6651 | 1.066 |
| | 0.5683 | 1.091 |
| | 0.4588 | 1.053 |
| | 0.3557 | 0.907 |
| 40 °C | 0.8785 | 1.102 |
| | 0.7537 | 0.561 |
| | 0.6742 | 0.440 |
| | 0.5748 | 0.386 |
| | 0.4700 | 0.337 |
| | 0.3669 | 0.242 |

At a constant temperature, the equilibrium moisture content of apples decreases with both water activity and time. For water activity values higher than approximately 0.66 - 0.67, corresponding to the free water zone, a pronounced decrease in moisture content is observed. At 25 °C, the equilibrium moisture content decreases from 1.65 - 1.06 g/g (dry basis), whereas at 40 °C, it drops from 1.10 - 0.44 g/g (dry basis). This reduction is attributed to the weak bonds between water molecules, which are easily disrupted by temperature, and to the decrease in the number of available adsorption sites. In this zone, free water remains highly reactive and available for microbial growth [15], thus favoring mold development [16]. Between water activity levels of approximately 0.74 - 0.45, corresponding to the intermediate zone, water is weakly bound in multilayers. At both temperatures, a gradual reduction in moisture content is observed (from 1.06 - 0.44 g/g db at 25 °C, and from 0.44 - 0.34 g/g db at 40 °C).

This phase is characterized by moderate dehydration, where water molecules are partially adsorbed on the surface. Under these conditions, microbial proliferation is limited, and product stability improves [17]. In the monolayer zone, between 0.45 and 0.35 (at 25 °C) and 0.47 - 0.37 (at 40 °C), water molecules are strongly bound to the apple matrix through multiple hydrogen bonds, making further dehydration difficult [12, 18, 19]. In this region, water is no longer available as a reactive agent, resulting in enhanced resistance to micro-

bial activity, including mold growth. The overall decline in equilibrium moisture content with decreasing water activity is primarily due to the reduction in adsorption sites and the structural transition of carbohydrates from an amorphous to a crystalline state [15]. Based on these findings, the optimal conditions for effective preservation of starking delicious apples correspond to a water activity range between 0.45 and 0.74, where the product remains microbiologically stable and less prone to degradation.

## Effect of temperature on the desorption isotherm of starking delicious apple

The desorption isotherm curves of starking delicious apples at 25 °C and 40 °C are presented in figure 2. The isotherms obtained at the higher temperature lie below those obtained at the lower temperature. It is observed that, for the same water activity value, the equilibrium moisture content decreases as the temperature increases. This trend is consistent across all water activity levels. The results obtained are consistent with those reported by Benseddik et al. [20]. This behavior is typical of carbohydrate-rich foods and can be attributed to the increase in sorption heat, reflecting stronger water-binding energy.

The rate of water loss increases with rising temperature; at 40 °C, moisture loss occurs more rapidly than at 25 °C. This can be explained by the thermal hydrolysis of hydrogen bonds between water molecules. At elevated temperatures, these molecules become more mobile and dispersed, which enhances their thermal agitation. As a result, more energy is absorbed, facilitating water desorption from the product. In a related study, Adil et al. [21] demonstrated that equilibrium moisture content decreases with increasing temperature. Moreover, the physical state of the material and its water activity were found to significantly influence its water retention capacity. Over time, the material gradually attains hygroscopic equilibrium during storage.

## Modeling results of the apple desorption isotherm at 25 °C and 40 °C

The results of the nonlinear regression analysis for fitting the sorption equations to the experimental desorption data of starking delicious apple samples are presented in table 3 below. The desorption isotherm data of the studied apple variety at 25 °C were modeled using three common sorption isotherm models: GAB, BET, and Langmuir. The models were compared based on their correlation coefficient (r), SE, and estimated monolayer moisture content ($X_m$).

All models demonstrated SE values approaching zero, indicating a good fit with the experimental data. Among these, The BET model showed the best agreement with the experimental data with the highest correlation coefficient (r = 0.9975) and the lowest (SE = 0.0426), making it the most suitable for representing the desorption isotherm of the apple at this temperature.

The BET model estimated a monolayer moisture content ($X_m$) of 1.2440 g/g db, which is notably lower than the values predicted by the GAB model's value of 6.7076 g/g db and the Langmuir models of 3.120 g/g db. Accurate estimation of $X_m$ is important because it represents the moisture level at which

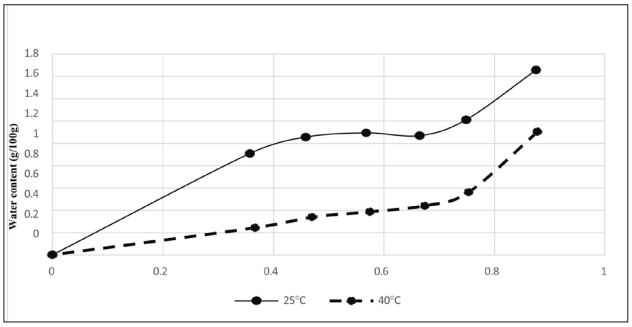


**Figure 2:** Effect of temperature on the desorption isotherm of starking delicious apple variety.

**Table 3:** Parameter estimation of the three models at 25 °C and 40 °C.

| Models | Parameter | Temperature at 25 °C | Temperature at 40 °C |
|---|---|---|---|
| GAB | $X_m$ | 0.671 | 0.145 |
| | C | 0.654 | 0.986 |
| | K | $1.182 \times 10^8$ | –10.884 |
| | S | 0.104 | 0.029 |
| | r | 0.985 | 0.998 |
| | $R^2$ | 0.971 | 0.995 |
| BET | $X_m$ | 1.244 | 1.178 |
| | C | 8.300 | 0.735 |
| | n | 0.996 | 0.990 |
| | S | 0.043 | 0.015 |
| | r | 0.998 | 0.999 |
| | $R^2$ | 0.995 | 0.998 |
| Langmuir | $X_m$ | 3.120 | 622.885 |
| | C | 0.999 | 0.001 |
| | S | 0.143 | 0.183 |
| | r | 0.965 | 0.871 |
| | $R^2$ | 0.931 | 0.758 |

**Note:** S is deviation between experimental data and model-predicted values, r is correlation between experimental data and the model, and $R^2$ is the overall goodness of fit of the model.

the material is most stable and less susceptible to microbial growth or chemical degradation.

Comparable studies support these findings. For example, emphasized the importance of the BET model in describing sorption isotherms for fruits, particularly at moderate water activities, noting its reliability in estimating monolayer moisture content. Similarly, Said et al. [22] found that the BET model provided a good fit for the sorption isotherms of dehydrofrozen-textured apple, reporting correlation coefficients in the range of 0.972 to 0.982 [23] also analyzed dehydrated apples (Golden delicious) and concluded that the BET model produced better fitting results across different temperatures compared to the GAB and Langmuir models, with correlation coefficients exceeding 0.98 and $X_m$ values in comparable ranges. Furthermore Moraes et al. [24], observed that the BET model gave a good fit to experimental data for various apple varieties, especially at water activity levels below 0.5, which is consistent with the current results. These results underline the suitability of the BET model for the studied apple variety at 25 °C, providing both accurate prediction of moisture sorption behavior and realistic parameter values.

The parameter values characterize the apple desorption isotherm at 40 °C, according to the GAB, BET, and Langmuir models. The table 3 presents the parameter values for the GAB, BET, and Langmuir equations, along with the statistical criteria used to select the most appropriate model describing the desorption isotherm of the 'starking delicious' apple variety at 40 °C. The correlation coefficients (r) range from 0.8712 to 0.9993, and coefficients of determination ($R_2$) range between 0.7589 and 0.9985.

Among the three models, the BET model again stood out, achieving the highest correlation (r = 0.9993) and determination ($R_2$ = 0.9985), along with the lowest (SE = 0.0158), indicating superior fit to the experimental data. The monolayer moisture content ($X_m$) estimated by BET is 1.178 g water/g dry matter significantly higher than the GAB estimate (0.145 g/g) and far lower than the extreme Langmuir estimate (622.9 g/g), which appears unrealistic in context.

These findings align well with recent literature. For instance, a study on apples at 40 °C found that although all models delivered $R_2$ > 0.9. The GAB model was preferred over alternatives in most cases, including at 40 °C for apple isotherms supporting the general reliability of multilayer models in fruit products [25]. Another investigation of apples at 40 °C reported the BET model performed best in the water activity range $a_w$ < 0.45, with realistic $X_m$ and strong descriptive capacity consistent with the current results [26].

Thus, based on statistical performance and plausible monolayer moisture estimates, the BET model is confirmed as the most robust and realistic choice for representing the desorption behavior of 'starking delicious' apples at 40 °C.

## Conclusion

This study determined the desorption of isotherms of starking delicious apples at 25 °C and 40 °C using the static gravimetric method. The BET model provided the best fit to the experimental data, accurately describing the moisture–water activity relationship. Equilibrium moisture content decreased with increasing temperature, reflecting the thermosensitive nature of the fruit. The optimal water activity range for safe storage was found to be 0.47 - 0.67, which can help minimize spoilage and preserve fruit quality. Limitations of this study include the investigation at only two temperatures and the absence of adsorption data. These findings can support apple storage operations under controlled relative humidity and provide a basis for future studies on intermediate temperatures and sorption thermodynamics.

## Acknowledgements

None.

## Conflict of Interest

None.

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