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# MODELS OF SORPTION ISOTHERMS FOR FOOD: USES AND LIMITATIONS

## MODELOS DE ISOTERMAS DE SORCION PARA ALIMENTOS: USOS Y LIMITACIONES

Ricardo D. ANDRADE P.[1,2*], Roberto LEMUS M.[3], Carmen E. PÉREZ C.[2]

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## ABSTRACT

Moisture sorption isotherms describe the relationship between moisture content and water activity in food. This work presents basic concepts related to the sorption thermodynamics of water, the classification of isotherms, "uses and limitations of the models", and measurement of sorption isotherms for food materials. The most commonly used models in food are Brunauer-Emmett-Teller and Guggenheim-Anderson-de Boer. The success of the Brunauer-Emmett-Teller model is rather qualitative, considering that almost all cases are linear only in a limited rank of water activity from 0.05 to 0.45, as its main applicability is the estimation of surface areas. And, the use of the Guggenheim-Anderson-de Boer model is generalized by its theoretical bases, mathematical simplicity, and ease to interpret; but it is not frequently used when the water activity greater than 0.93.

**Keywords:** Isotherm, mathematical model, food processing, drying, diffusivity.

## RESUMEN

Las isotermas de sorción describen la relación entre el contenido de humedad y la actividad de agua de un alimento. Este trabajo presenta los conceptos básicos relacionados con la termodinámica de la sorción de agua, clasificación de las isotermas, "usos y limitaciones de los modelos", y la medición de las isotermas de sorción de materiales alimenticios. Los modelos más utilizados en los alimentos son los de Brunauer-Emmett-Teller y Guggenheim-Anderson-de Boer. El éxito del modelo de Brunauer-Emmett-Teller es más bien cualitativo, considerando que en la mayoría de casos sólo es lineal en un rango limitado de actividad de agua de 0,05 a 0,45, por lo que su aplicabilidad principal es la estimación de áreas de superficies y el modelo de Guggenheim-Anderson-de Boer su uso es generalizado por su bases teóricas, simplicidad matemática y fácil interpretación, pero se desvía a actividad de agua superior a 0,93.

**Palabras clave:** isoterma, modelo matemático, procesamiento de alimentos, secado, difusividad.

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[1] Departamento de Ingeniería de Alimentos. Facultad de Ciencias Agrícolas, Universidad de Córdoba. Cra. 6 Nº 76-103. Monteria, Colombia.

[2] Facultad de Ingeniería, Universidad Santiago of Chile. Santiago, Chile.

[3] Departamento de Ingeniería de Alimentos, Universidad de La Serena. La Serena, Chile.

* Corresponding author: randrade@sinu.unicordoba.edu.co

# INTRODUCTION

The water contained in food appears in different forms based on the interactions that exist between the components of food and water molecules (1). The concept of water activity ($a_w$) comes from a series of thermodynamic considerations that entail the chemical potential mathematical expression of the component i, which constitutes the tendency of a component to escape the system. It can also be defined as the ratio of water vapour pressure in the system (food) and the pure water vapour pressure at a constant value of pressure and temperature. Another possible definition is the equilibrium relative humidity of the air surrounding the food at the same temperature (2, 3), and it can be expressed as described in equation 1.

$$a_{w,f} = a_{w,v} = \frac{p_v}{p_{v,sat}} \qquad \textbf{Equation 1.}$$

where f: food; v: vapour; v,sat: pure water vapour pressure.

Thus, the water activity of food equals the relative humidity of the air above it divided by 100, which means that an equilibrium has been reached, constituting a form of measurement of the water amount available in food for a reaction series of biochemical and microbiological nature (3-5).

## Sorption isotherms

The food sorption isotherm describes the thermodynamic relationship between water activity and the equilibrium of the moisture content of a food product at constant temperature and pressure. The knowledge and understanding of sorption isotherms is highly important in food science and technology for the design and optimization of drying equipment, design of packages, predictions of quality, stability, shelf-life and for calculating moisture changes that may occur during storage. Several preservation processes have been developed in order to prolong the shelf-life of food products by lowering the availability of water to micro-organisms and inhibiting some chemical reactions (2, 6-10). The typical shape of an isotherm reflects the way in which the water binds the system. Weaker water molecule interactions generate a greater water activity, thus, the product becomes more unstable. Water activity depends on the composition, temperature and physical state of the compounds (11).

Sorption isotherms can be generated from an adsorption process or a desorption process; the difference between these curves is defined as hysteresis, as it is shown in figure 1. Water adsorption by food products is a process in which water molecules progressively and reversibly mix together with food solids via chemisorption, physical adsorption, and multilayer condensation. An isotherm can be typically divided into three regions; the water in region A represents strongly bound water, and the enthalpy of vaporization is considerably higher than the one of pure water. The bound water includes structural water (H-bonded water) and monolayer water, which is sorbed by the hydrophilic and polar groups of food components (polysaccharides, proteins, etc.). Bound water is unfreezable and it is not available for chemical reactions or as a plasticizer. In region B, water molecules bind less firmly than in the first zone, they usually present in small capillaries. The vaporization enthalpy is slightly higher than the one of pure water. This class of constituent water can be looked upon as the continuous transition from bound to free water. The properties of water in region C are similar to those of the free water that is held in voids, large capillaries, crevices; and the water in this region loosely binds to food materials (12-15). Moreover, hysteresis is related to the nature and state of the components of food, reflecting their potential for structural and conformational rearrangements, which alters the accessibility of energetically favourable polar sites. The presence of capillaries in food results in considerable decrease in water activity. The explanation for the occurrence of moisture sorption hysteresis comprises the ink bottle theory, the molecular shrinkage theory, the capillary condensation, and the swelling fatigue theory (16).

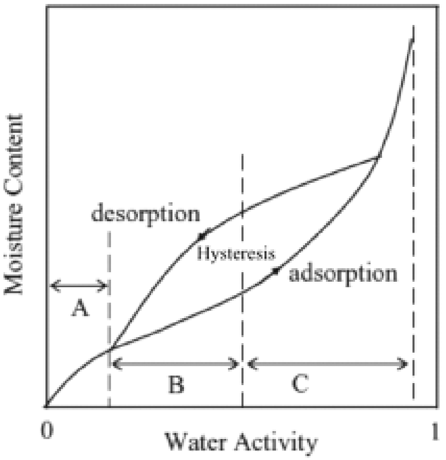

**Figure 1**. Sorption isotherm for a typical food product, showing the hysteresis.

## Classification of sorption isotherms

Brunauer *et al.*, 1940 (17) classified sorption isotherms according to their shape and processes, establishing five different types; as it is shown in figure 2. Type 1: Langmuir and/or similar isotherms that present a characteristic increase in water activity related to the increasing moisture content; the first derivative of this plot increases with moisture content and the curves are convex upwards. This type of sorption isotherm is typically applicable in the process of filling the water monomolecular layer at the internal surface of a material. Type 2: sigmoidal sorption isotherms, in which the curves are concave upwards; it takes into account the existence of multilayers at the internal surface of a material. Type 3: known as the Flory-Huggins isotherm, it accounts for a solvent or plasticizer such as glycerol above the glass transition temperature. Type 4: it describes the adsorption of a swellable hydrophilic solid until a maximum of site hydration is reached. Type 5: the Brunauer-Emmett-Teller (BET) multilayer adsorption isotherm, it is the one observed in the adsorption of water vapour on charcoal and it is related to the isotherms type 2 and 3. The two isotherms most frequently found in food products are the types 2 and 4 (18-20).

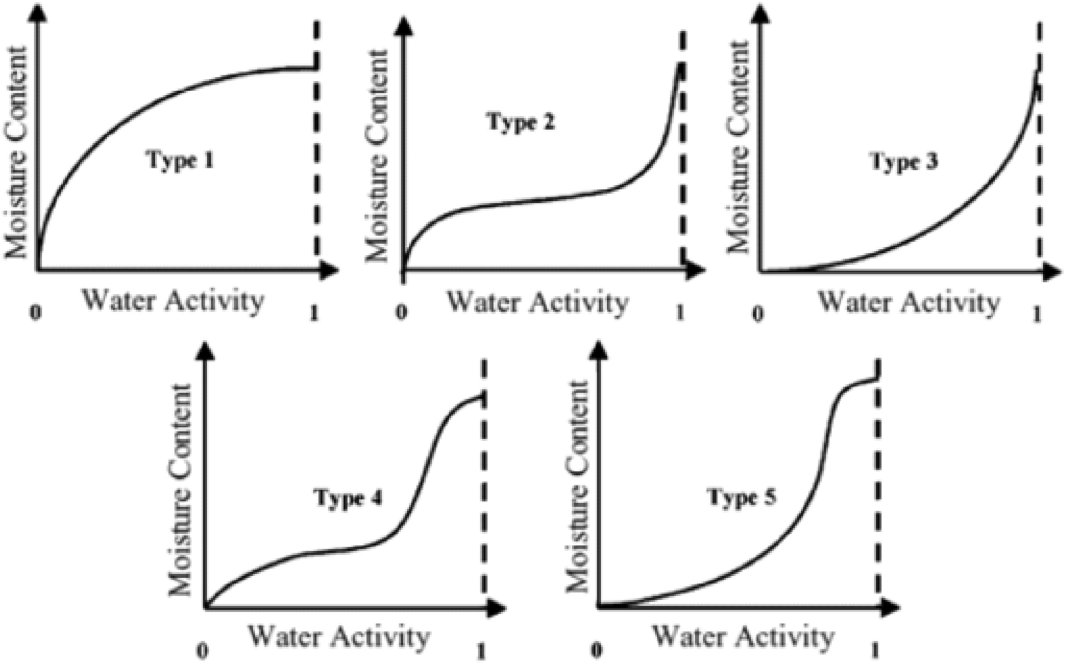

**Figure 2.** Types of isotherms described by Brunauer (Mathlouthi & Rogé, 2003 (20)).

Van den Berg and Bruin (16) classified the 77 most important models into three groups: theoretical, partially theoretical, and fully empirical. A new classification system proposed by Blahovec and Yanniotis (18) applies for 115 sorption isotherms (given in the literature) mainly for different agricultural products and/or food products. The sign of the initial slope (at $a_w = 0$) of the transformed isotherm ($D_{10}$), and the ratio of the final slope (at $a_w = 1$) of the same isotherm to the initial one ($R_{fi}$) determines the isotherm class, as it is shown in table 1: Type I, Langmuir- like (Brunauer's class I, for positive both $D_{10}$ and $R_{fi}$); type II, miscellaneous Guggenheim-Anderson-de Boer (GAB), GAB-like (Brunauer's class II, for positive $D_{10}$ and negative $R_{fi}$); and type III, solution-like (Brunauer's class III, for negative $D_{10}$ and positive $R_{fi}$), where $D_{10}$ is the first derivative of $a_w/w$ at $a_w = 0$; $R_{fi}$ is the ratio of the first derivative of the $a_w/w$- $a_w$ plot at the final value ($a_w = 1$) to the first derivative at the initial value ($a_w = 0$); $X_4$ is the parameter, determined by equation 2.

$$\frac{a_w}{w} = X_1 + (X_2 + X_1 X_4) a_w - (X_3 + X_2 X_4 - X_1 X_4^2) \frac{a_w^2}{1 + X_4 a_w}$$

**Equation 2.**

**Table 1.** Basic characteristics of sorption isotherms of different types.

| Parameter type | $D_{10}$ | $R_{fi}$ | $a_{wm}$ | $X_4$ |
|---|---|---|---|---|
| I Langmuir-like | Positive | Positive | - | Positive |
| II GAB-like | | | | |
| IIa | Positive | Negative | 0-1 | $-0.1<X_4<0.1$ |
| IIb | Positive | Negative | 0-1 | < -0.1 |
| IIc | Positive | Negative | 0-1 | > 0.1 |
| III solution-like | Negative | Positive | - | Negative |

## Measurement of sorption isotherms

For food products, the sorption isotherm can be measured by means of three different measuring techniques: gravimetric, manometric or hygrometric, according to Iglesias and Chirife, 1978 (21). In the gravimetric methods, the weight of the sample is measured with a balance. In the manometric methods, the vapour pressure of water is measured when it is in equilibrium with a sample at given moisture content. In the hygrometric methods, the equilibrium relative humidity with a sample at a given moisture content is measured. Two examples of more modern techniques to measure the concentration in a sample are the impedance spectroscopy technique and the light reflection and/or attenuation technique, such as the infrared spectroscopy (22).

## Mathematical models of sorption isotherms

Aiming to mathematically express the relation between the water activity of food and its moisture content, diverse models have been developed suc as nonlinear, linear, regressional models, constituted in their parameters by two, three, four and six partial regression coefficients, which explain each one of the three zones that the isotherm of sorption of humidity conforms. In many cases, the model that is suitable for certain food product is not suitable for a different one, what is more, the model only exhibits a suitable predictive ability for certain moisture activity ranges.

Several mathematical models have been proposed to describe sorption isotherms. Some of them were developed with a theoretical basis to describe adsorption mechanisms (15, 23); whereas the others are just empirical or a simplification of more elaborate models. In some ranges of water activity, sorption isotherms can be approximated to linear equations (24).

There are some semi-empirical equations with two or three fitting parameters to describe moisture sorption isotherms. The most common equations that are used for describing sorption in food products are the Langmuir equation, the BET equation, the Oswin model, the Smith model, the Halsey model, the Henderson model, the Iglesias-Chirife equation, the GAB model, and the Peleg model (2).

## Langmuir equation

Langmuir proposed the following physical adsorption model on the basis of unimolecular layers with identical and independent sorption sites, and which is expressed as it is shown in equation 3:

$$a_w\left(\frac{1}{M_w}-\frac{1}{M_o}\right)=\frac{1}{C\,M_o}$$ **Equation 3.**

where $M_w$ is the equilibrium moisture content (kg water/kg dry matter), $M_0$ is the monolayer sorbate content (kg water/kg dry matter) and C is a constant.

The value of the monolayer ($M_0$) is of particular importance because it indicates the amount of water that is strongly adsorbed in specific sites, and it is considered to be the value at which a food product is the most stable.

Langmuir's isotherm is the most crucial equation among the theoretical models, which is based on the forces acting between the product surface and the water condensed from the vapour as a monomolecular layer. The extensions of the Langmuir's underpinning idea on multi-molecular layers result in the BET and GAB isotherms, which are able to describe sigmoidal shaped isotherms commonly observed in the case of food and other materials of biological origin (25). Values of the various coefficients and regression coefficient ($R^2$) for Langmuir equation, are presented on table 2.

**Table 2** Estimated parameters of the Langmuir equation for some foods.

| Product | Temp. °C | $M_0$ | C | $R^2$ | Type | Reference |
|---|---|---|---|---|---|---|
| Pear osmotic dehydration | 40 | 1015.778 | 0.000593 | 0.79 | A | Park *et al.*, 2001 (26) |
| Pear | 40 | 1596.919 | 0.00038 | 0.83 | D | Park *et al.*, 2001 (26) |
| Garden mint leaves | 30 | 5.748 | 0.055 | 0.93 | D | Park *et al.*, 2002 (27) |
| Garden mint leaves | 40 | 9.248 | 0.029 | 0.98 | D | Park *et al.*, 2002 (27) |

D: desorption; A: adsorption.

### Brunauer-Emmett-Teller (BET) equation.

The BET equation (equation 4), which is the most widely used model in food systems, was first proposed by Brunauer, Emmett and Teller (23). It represents a fundamental milestone in the interpretation of multi-layer sorption isotherms, particularly the types II and III. It is also an effective method for estimating the amount of bound water in specific polar sites of dehydrated food systems (2, 28).

$$M_w = \frac{M_0\, C\, a_w}{(1-a_w)\,(1+(C-1)a_w)} \qquad \textbf{Equation 4.}$$

where $M_0$ is the monolayer moisture content, which represents the moisture content at which the water attached to each polar and ionic groups starts to behave as a liquid-like phase. And, C is the energy constant related to the net heat of sorption; it is related to the difference between the molecules that sorb energy of the first layer and the other remaining layers. These constants are also the constant characteristic of the isotherm of sorption of monolayer of Langmuir. Almost in all cases, the deviation of the linearity of these graphs indicates that, at high vapour pressures, the amount adsorbed by the sorbent is lower than the one predicted by the isotherm (2, 29).

The BET equation represents a basis in the interpretation of isothermal sorption multilayers and it has been applied in gas adsorption and porous steam in surfaces and solids, as well as in water, especially in steam absorption, by homogenous polymers and other materials. Nevertheless, the considerable success of the isotherm is rather qualitative that quantitative. If we considered the linearized forms of the equations of isotherms as the estimation of the applicability rank that they own in its linear sections, it can be observed that, in almost all cases, BET graphs are linear only in a limited range of water activity from 0.05 to 0.45. This difficulty in the process of fitting the experimental dates on the totality of the range of relative pressure application determined that the main application of the BET equation is the one related to the estimation of surface areas (29).

The theory behind the development of the BET equation has been questioned due to the assumptions that (a) the rate of condensation on the first layer is equal to the rate of evaporation from the second layer; (b) the binding energy of all of the adsorbates on the first layer is same; and (c) the binding energy of the other layers is equal to the one of pure adsorbates. The assumptions of an uniform adsorbent surface and the absence of lateral interactions between adsorbed molecules are incorrect, considering the heterogeneous food surface interactions. Nevertheless, the theoretical basis that provided this isotherm stimulated the investigation for developing alternatives that broaden the scope of the BET equation, or for reformulating the model to find new physical approaches (18, 30).

The BET equation can be considered to be the most useful for determining the optimum moisture conditions for good storage stability, especially for dehydrated food products (31). The parameters of the BET equation for different food products are listed on table 3.

**Table 3.** Estimated parameters of the BET equation for various food products.

| Product | Temp.°C | $M_0$ | C | $R^2$ | Type | Reference |
|---|---|---|---|---|---|---|
| Corn flour | 22 | 0.056 | 502.82 | 0.99 | A | Vega *et al.*, 2006 (32) |
| Yam | 45 | 0.706 | 2.908 | 0.91 | D | Montes *et al.*, 2009 (33) |
| Dried potato * | 30 | 0.078 | 7.345 | nr | D | Iguedjtal *et al.*, 2008 (34) |
| Dried potato * | 30 | 0.055 | 9.226 | nr | A | Iguedjtal *et al.*, 2008 (34) |
| Dried tomato | 30 | 0.1624 | 14.06 | nr | A | Goula *et al.*, 2008 (35) |
| Apples ** | 30 | 0.137 | 26.430 | nr | A | Kaymak-Ertekin & Gedik, 2004 (36) |
| Apples ** | 30 | 0.234 | 20.166 | nr | D | Kaymak-Ertekin & Gedik, 2004 (36) |
| *Chhana podo* *** | 35 | 0.04834 | 4.464 | 0.994 | D | Jayaraj *et al.*, 2006 (37) |
| Blueberry | 40 | 0.067 | 5.743 | nr | A | Vega *et al.*, 2009 (38) |
| Blueberry | 40 | 0.100 | 101.45 | nr | D | Vega *et al.*, 2009 (38) |

nr: not reported; D: desorption; A: adsorption.

* $a_w$ range: 0.1–0.5; ** $a_w$ range: 0.11–0.5; *** $a_w$ range: 0.25–0.54.

**Oswin model**: It is an empirical model that consists in a series expansion for sigmoid shaped curves and it was developed by Oswin, 1946 (39, 40). It is described in equation 5:

$$M_w = C\,(\frac{a_w}{1-a_w})^n \qquad \textbf{Equation 5.}$$

where C and n are constants.

The Oswin equation was used to relate the moisture content of fatfree dry milk and freeze-dried tea up to a water activity of 0.5 (39), as well as for various food, as it is shown in table 4.

**Smith model**: In 1947, Smith developed an empirical model to describe the final curved portion of water sorption isotherm of high molecular weight biopolymers. He theorized that there are two fractions of water that are sorbed onto a dry surface; the first fraction exhibits a higher condensation heat than the normal and it would be expected to follow the Langmuir model. Smith based his model on the second fraction, which only can be formed after the first fraction has been sorbed. He considered that the second fraction consists of multilayers of condensed water molecules, which effectively prevent any possible evaporation of the initial layer. He theorized that the moisture content in the second fraction was proportional to the logarithm of the difference between the $a_w$ of the sample and pure water (2, 43). This model can be written as equation 6:

$$M_w = C_1 + C_2 \ln(1 - a_w) \qquad \textbf{Equation 6.}$$

where $C_1$ is the quantity of water in the first sorbed fraction, and $C_2$ is the quantity of water in the multilayer moisture fraction.

This equation could be used in the water activity range from 0.5 to 0.95 in the case of wheat desorption (44) and for various products, as it is shown in table 5.

**Table 4.** Estimated constants of the Oswin model for several food products.

| Product | Temp. °C | C | n | $R^2$ | Type | Reference |
|---|---|---|---|---|---|---|
| Corn flour | 22 | 0.106 | 0.299 | 0.99 | A | Vega *et al.*, 2006 (32) |
| Yam | 45 | 0.353 | 0.495 | 0.991 | D | Montes *et al.*, 2009 (33) |
| Dried potato | 30 | 0.125 | 0.461 | nr | D | Iguedjtal *et al.*, 2008 (34) |
| Dried potato | 30 | 0.103 | 0.548 | nr | A | Iguedjtal *et al.*, 2008 (34) |
| Dried tomato pulp | 30 | 0.303 | 0.441 | nr | A | Goula *et al.*, 2008 (35) |
| Dried cashew apple | 30 | 10.72 | 0.581 | 0.9979 | D | Alcântara *et al.*, 2009 (41) |
| Banana pulp | 20 | 0.164 | 1.122 | 0.9869 | D | Gouveia *et al.*, 2004 (42) |
| Mango pulp | 20 | 0.114 | 0.855 | 0.992 | D | Da Silva *et al.*, 2002 (43) |
| Garlic | 50 | 0.095 | 0.720 | 0.991 | D | Moraes *et al.*, 2008 (44) |
| Apple | 50 | 0.332 | 0.670 | 0.9786 | D | Moraes *et al.*, 2008 (44) |

nr: not reported; D: desorption; A: adsorption.

**Table 5.** Constants of the Smith model for some food products.

| Product | Temp. °C | $C_1$ | $C_2$ | $R^2$ | Type | Reference |
|---|---|---|---|---|---|---|
| Yam | 45 | 0.106 | 0.356 | 0.992 | D | Montes *et al.*2009 (33) |
| Dried tomato pulp | 30 | 0.049 | -0.754 | nr | A | Goula *et al.*, 2008 (35) |
| Cashew Apple | 30 | 0.7552 | -33.69 | 0.9746 | D | Alcântara *et al.*, 2009 (41) |
| Mango pulp | 20 | -0.018 | 0.213 | 0.979 | D | Da Silva *et al.*, 2002 (43) |
| Walnut kernels | 25 | 1.684 | 4.108 | 0.960 | D | Togrul & Arslan, 2007 (47) |
| Walnut kernels | 25 | 0.617 | 4.325 | 0.9867 | A | Togrul & Arslan, 2007 (47) |
| Blueberry | 40 | -0.848 | -0.083 | nr | A | Vega *et al.*, 2009 (38) |
| Blueberry | 40 | -0.516 | 0.072 | nr | D | Vega *et al.*, 2009 (38) |

nr: not reported; D: desorption; A: adsorption.

**Halsey model:** This model provides an expression for the condensation of multilayers at a relatively large distance from the surface, assuming that the potential energy of a molecule varies as the inverse nth power of its distance from the surface. This equation is a good representation of adsorption data regarding isotherms type I, II, or III. Moreover, this equation described the sorption behaviour of food products that contain starch (30, 48). This model is described as it is expressed in equation 7:

$$M_w = M_o \left( - \frac{A}{RT \ln a_w} \right)^{1/n} \qquad \textbf{Equation 7.}$$

where A and n are constants; R is the universal gas constant; T is the absolute temperature; and $M_0$ is monolayer moisture content.

Since the use of the RT term does not eliminate the temperature dependence of A and n, the Halsey equation was modified by Iglesias and Chirife, 1976 (49) into the following form, as it is described in equation 8:

$$M_w = \left( - \frac{C}{\ln a_w} \right)^{1/n} \qquad \textbf{Equation 8.}$$

where C and n are constants. The Halsey model was used for various food products, as it is shown in table 6.

**Table 6.** Estimated parameters of the Halsey model for various food products.

| Product | Temp. °C | C | n | $R^2$ | Type | Reference |
|---|---|---|---|---|---|---|
| Corn flour | 22 | 0.002 | 2.516 | 0.96 | D | Vega *et al.*, 2006 (32) |
| Pear osmotic dehydration | 40 | 0.178 | 0.666 | 0.99 | D | Park *et al.*, 2001 (26) |
| Pear | 40 | 0.147 | 0.853 | 0.99 | D | Park *et al.*, 2001 (26) |
| Banana pulp | 20 | 0.185 | 0.756 | 0.9871 | D | Gouveia *et al.*, 2004 (42) |
| Blueberry | 40 | 0.108 | 0.890 | nr | A | Vega *et al.*, 2009 (38) |
| Blueberry | 40 | 0.056 | 1.672 | nr | D | Vega *et al.*, 2009 (38) |

nr: not reported; D: desorption; A: adsorption.

**Henderson model:** This is a commonly used model and it can be expressed as it is described in equation 9:

$$M_w = \left( - \frac{\ln(1 - a_w)}{C} \right)^{1/n} \qquad \textbf{Equation 9.}$$

where C and n are constants.

According to this model, a plot of ln (–ln(1 – aw)) versus ln Mw should give as a result a straight line. However, Rockland observed three localized isotherms that did not provide precise information on the physical state of water. The constants of the Henderson model in different food products are listed on table 7.

**Table 7.** Parameters of the Henderson model for various food products.

| Product | Temp. °C | C | n | $R^2$ | Type | Reference |
|---|---|---|---|---|---|---|
| Passion fruit peel | 25 | 2.160 | 0.591 | 0.990 | D | Oliveira *et al.*, 2006 (50) |
| Pineapple peel | 25 | 2.04 | 0.601 | 0.993 | D | Oliveira *et al.*, 2006 (50) |
| Yam | 45 | 0.126 | 0.126 | 0.933 | D | Montes *et al.*, 2009 (33) |
| Dry cashew apple | 30 | 0.0509 | 1.08 | 0.9926 | A | Alcântara *et al.*, 2009 (41) |
| Walnut kernels | 25 | 0.037 | 1.781 | 0.9854 | D | Togrul & Arslan, 2007 (47) |
| Walnut kernels | 25 | 0.123 | 1.267 | 0.9990 | A | Togrul & Arslan, 2007 (47) |

D: desorption; A: adsorption.

**Iglesias-Chirife equation:** Iglesias-Chirife, 1976 (48) proposed the following empirical model, presented in equation 10:

$$\ln\left[M_w + \left(M_w^2 + M_{w,0.5}\right)^{1/2}\right] = C_1 a_w + C_2 \qquad \textbf{Equation 10.}$$

where $M_{w,0.5}$ is the moisture content at the water activity of 0.5; $C_1$ and $C_2$ are constants. This model was found to be suitable for food products with high sugar content, such as fruits among other products as it is shown in table 8.

**Table 8.** Constants of the Iglesias-Chirife equation for some food products.

| Product | T °C | $C_1$ | $C_2$ | $M_{w,0.5}$ | $R^2$ | Type | Reference |
|---|---|---|---|---|---|---|---|
| *Chhana podo* | 35 | 3.658 | 1.076 | nr | 0.943 | D | Jayaraj *et al.*, 2006 (37) |
| Walnut kernels | 25 | 1.807 | 1.415 | nr | 0.944 | D | Togrul & Arslan, 2007 (47) |
| Walnut kernels | 25 | 2.328 | 0.911 | nr | 0.995 | A | Togrul & Arslan, 2007 (47) |
| Grapes | 30 | 1.674 | -0.843 | 0.290 | nr | D | Kaymak-Ertekin & Gedik, 2004 (36) |
| Grapes | 30 | 1.760 | -1.923 | 0.240 | nr | A | Kaymak-Ertekin & Gedik, 2004 (36) |

nr: not reported; D: desorption; A: adsorption.

**Guggenheim-Anderson-de Boer (GAB) model:** The term GAB model comes from the names Guggenheim, Anderson and De Boer, who independently derived the equation in 1966, 1946 and 1953, respectively (25). This model has many advantages over the others, such as having a viable theoretical background since it is a refinement of Langmuir and BET theories of physical adsorption. This model postulates that the state of sorbate molecules in the second layer is identical to the one in superior layers, but different from those of the liquid state. These authors introduced a second sorption stage of the molecules of a sorbate that was differentiated as a good sorbate. This isotherm necessarily contains a third constant, k, which measures the difference of the chemical potential standard between the molecules of this second stage and those of the pure liquid state. The GAB model is expressed as it is expressed in equation 11:

$$M_w = \frac{M_0\, C\, K\, a_w}{(1-K\, a_w)(1-K\, a_w + C\, K\, a_w)}$$ **Equation 11.**

where $M_0$ is the monolayer moisture content; C and K are the adsorption constants, which are related to the energies of interaction between the first and the further sorbed molecules at the individual sorption sites. They can be theoretically expressed as it is expressed in equation 12 and equation 13:

$$C = c_0 \exp(\frac{H_0 - H_n}{RT})$$ **Equation 12.**

$$K = k_0 \exp(\frac{H_n - H_l}{RT})$$ **Equation 13.**

where $c_0$ and $k_0$ are the entropic accommodation factors; $H_0$, $H_n$, and Hı are the molar sorption enthalpies of the monolayer, the multilayers on top of the monolayer, and the bulk liquid, respectively. R is the ideal gas constant and T is the absolute temperature. Note that when K is 1, the GAB model becomes the BET equation. The GAB model is divided into two additive terms, the first one describes the classical mono-molecular layer expression in Langmuir's adsorption isotherms, and the second term describes the multilayer adsorption corresponding to Raoult's law, as it is presented in equation 14:

$$\frac{M_w}{M_0} = \frac{(C-1)Ka_w}{(1-Ka_w+CKa_w} + \frac{Ka_w}{(1-Ka_w)}$$ **Equation 14.**

The GAB model has been used due to its theoretical bases, it describes the sorption behaviour in a wide range of $a_w$ (0 - 0.9). Thus, it was found to be suitable for analysing more than 50% of fruits, meat and vegetables, as it is shown in table 9. Furthermore, the use of the GAB equation has been recommended by the European COST 90 project (24, 35, 50). The major advantages of the GAB model are the following: it has a viable theoretical background since it is a further refinement of Langmuir and BET theories of physical adsorption; it provides a good description of the sorption behaviour of almost every food product (aw < 0.9); its parameters ($c_0$, $k_0$, $H_0$, $H_n$, and Hı) have a physical meaning in terms of the sorption processes; and it describes most of the temperature effect on isotherms by means of Arrhenius type equations (45, 51).

**Table 9.** Estimated parameters of the GAB model for various food products.

| Product | T °C | $M_0$ | C | K | $R^2$ | Type | Reference |
|---|---|---|---|---|---|---|---|
| Corn flour | 22 | 0.082 | 23.23 | 0.622 | 0.98 | A | Vega *et al.*, 2006 (32) |
| Passion fruit peel | 25 | 0.094 | 2.488 | 1.015 | 0.997 | D | Oliveira *et al.*, 2006 (50) |
| Pineapple peel | 25 | 0.445 | 0.310 | 0.896 | 0.999 | D | Oliveira *et al.*, 2006 (50) |
| Yam | 70 | 0.136 | 0.448 | 2.111 | 0.90 | D | Montes *et al.*, 2009 (33) |
| Dried tomato pulp | 30 | 0.2102 | 8.85 | 0.823 | nr | A | Goula *et al.*, 2008 (35) |
| Pear dehydration | 40 | 0.072 | 13.276 | 1.125 | 0.99 | A | Park *et al.*, 2001 (26) |
| Banana pulp | 20 | 0.142 | 1.251 | 1.052 | 0.9879 | D | Gouveia *et al.*, 2004 (42) |
| Mango pulp | 20 | 5.838 | 0.029 | 0.637 | 0.994 | D | Da Silva *et al.*, 2002 (43) |
| Walnut kernels | 25 | 0.03729 | 3.135 | 0.752 | 0.9999 | A | Togrul & Arslan, 2007 (47) |

nr: not reported; D: desorption; A: adsorption.

The GAB model underestimates the moisture content values at high water activity levels (aw > 0.93). The discrepancy underlines two facts: this type of model is unsuitable for a high humidity range, and the saturated salt solution method does not provide sufficient information to get a complete sorption curve (19).

**Peleg model:** This model is a purely empirical equation without a theoretical background. It presents the same or even a better suitability than the

GAB model. It is a four-parameter model described in equation 15:

$$M_w = C_1 a_w^{C_3} + C_2 a_w^{C_4} \qquad \textbf{Equation 15.}$$

where $C_1$, $C_2$, $C_3$, and $C_4$ are constants; $C_3 < 1$ and $C_4 > 1$. The model does not have a monolayer incorporated in it.

The Peleg model adequately described the moisture sorption isotherms of pestil (52) and other food products as it is shown in table 10.

**Table 10.** Constants of the Peleg model for various food products.

| Product | T.°C | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $R^2$ | Type | Reference |
|---|---|---|---|---|---|---|---|---|
| Yam | 45 | 2.609 | 0.507 | 7.372 | 0.635 | 0.9957 | D | Montes *et al.*, 2009 (33) |
| Instant green tea | 20 | 1.7266 | 3.8739 | 1.5540 | 16.545 | 0.9984 | A | Sinija & Mishra, 2008 (53) |
| Green tea granules | 20 | 3.8765 | 1.7269 | 16.555 | 1.5544 | 0.9984 | D | Sinija & Mishra, 2008 (53) |
| Dried potato | 30 | 0.225 | 0.327 | 0.783 | 9.030 | nr | A | Iguedjtal *et al.*, 2008 (34) |
| Walnut kernels | 25 | 7.820 | 5.809 | 1.013 | 6.191 | 0.9995 | A | Togrul & Arslan, 2007 (47) |
| Walnut kernels | 25 | 8.791 | 12.07 | 0.718 | 15.26 | 0.9943 | D | Togrul & Arslan, 2007 (47) |
| Pistachio nut | 20 | 81.782 | 2.9602 | 8.3281 | 0.2008 | 0.9918 | D | Hayoglu1 & Faruk, 2007 (54) |
| Pistachio nut | 4 | 56.468 | 1.8775 | 6.7588 | -0.227 | 0.9835 | D | Hayoglu1 & Faruk, 2007 (54) |

nr: not reported; D: desorption; A: adsorption.

## CONCLUSIONS

Water sorption isotherms are important thermodynamic tools for predicting the interactions between water and food components. The models that are used the most in food products are BET and GAB models. The BET model presents the obstacle that only provides good results in $a_w$<0.45, and its application is reduced to the estimation of surface areas. Finally, in the case of the GAB model, its use is generalized by its theoretical bases, mathematical simplicity, and ease to interpret since its parameters have a physical meaning; but it is not frequently used when $a_w$>0.93, that is why some modifications have been performed to it.

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