MOISTURE SORPTION ISOTHERMS AND ISOSTERIC HEAT OF SORPTION OF DRY PERSIMMON LEAVES

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ABSTRACT

Moisture sorption isotherms of persimmon leaves were determined at 20, 30 and 40ºC using the standard gravimetric static method over a range of relative humidity from 0.06 to 0.9. The experimental sorption curves were fitted by seven equations: Henderson, Halsey, Smith, Oswin, BET, GAB and Caurie. The Halsey, Smith, GAB and BET models were found to be the most suitable for describing the sorption curves. The isosteric heat of sorption of water was determined from the equilibrium data at different temperatures. It decreased as moisture content increased and was found to be a polynomial function of moisture content.

Keywords: Persimmon leaves; Equilibrium moisture content; Isosteric heat of sorption; Modelling; Sorption isotherms

1. INTRODUCTION

Persimmon crops have grown exponentially over the last decade to double their cultivated area as a result of the profitability of farming and the process of conversion of citrus and other fruit trees (Llácer & Badenes, 2002). Demand has increased significantly in Germany, the United Kingdom, France, Italy and Russia, as well as new emerging markets (the United States, Canada and Brazil).

Persimmon leaves, which are well-known in Japan, are infused with hot water and are used traditionally due to their healing properties (treatment of paralysis, frostbite, burns and to stop bleeding) (Matsuo *et. al*, 1978). Their principal compounds are flavonoid oligomers, tannins, phenols, organic acids, chlorophyll, vitamin C and caffeine (Matsuo *et. al*, 1978; Jo *et al*., 2003). Additionally, good knowledge of their water sorption properties will facilitate their incorporation into food products such as beverages, biscuits, etc.

It has been reported that equilibrium moisture content (EMC) plays a particularly important role at the end of the drying stage (Temple and van Boxtel, 1999). The properties and quality of persimmon leaves preserved by drying depends to a great extent on their physical, chemical and microbiological stability. This stability is determined by the relationship between the EMC of a leaf and its corresponding water activity at a given temperature (Myhara et al., 1998), which is called sorption isotherm. Among the factors that influence the shape and characteristic of water sorption isotherms are the composition, physical state of the components and temperature (Leung, 1986). Food groups (starch products, protein foods, vegetables, fruits, etc.) generally presented isotherms with a similar trend. The physical state (crystalline, amorphous) in which the food components are found significantly affects water retention and depends largely on the technological treatments the foodstuffs have been subjected to. Due to the exothermic character of the phenomenon of adsorption, an increase in temperature results in a loss of product moisture in equilibrium with a given relative humidity. In general, the effect of temperature is most significant for intermediate and low values of water activity.

There is no reported research on the moisture sorption characteristics of persimmon leaves even though they are commonly consumed in Japan in infusions. Moisture sorption isotherms are important for predicting stability during storage and selecting an appropriate packaging material. Once the sorption isotherms at different temperatures have been measured, it is possible to evaluate heat sorption, which determines the interaction between an adsorbent and adsorbate. Water availability in food degradation reactions depends both on water content and the properties of the diffusion surface (Al-Muhtaseb et al., 2004).

Equilibrium moisture content data can be determined using two different techniques: (a) manometric or hygrometric techniques based on direct determination of the vapour pressure or the relative humidity of the interface of a solid with a known moisture content, (b) techniques based on the determination of moisture content of the sample after it has reached equilibrium in a gas environment with a known relative moisture content. This last procedure can be carried out by static or dynamic means. The static gravimetric method is the most commonly used in food engineering, and a large amount of experimental EMC data reported for many plants with medicinal and therapeutic properties was mainly found by employing the gravimetric method. Literature reported experimental EMC for bitter orange leaves (Mohamed et al., 2004), chenopodium ambrosioides (Jamali et al., 2004), citrus reticulate leaves (Jamali et al., 2005), garden mint leaves (Park et al, 2001), green tea in powder and granules (Arslan & Togrul, 2006; Sinija & Mishra, 2007), leaves and stems of lemon balm (Argyropoulos et al., 2012), mate leaves (Zanoelo, 2005), olive leaves and Tunisian olive leaves (Bahloul et al., 2008; Nourhène et al., 2008) and orange peel and leaves (Citrus sinensis) (Kammoun et al., 2012). The numerous studies carried out evidence the importance of the characterization of EMC for predicting the stability and shelf-life of agricultural products. There are four common specific areas of practical application of isotherms related to food processing: drying (in order to save energy and establish the optimal processing conditions), mixing (to determine the water activity of the mixture from the isotherms of each component), packaging (to determine the permeability of the packing) and storage (to lengthen the shelf-life of foods) (Labuza, 1980; Gal, 1983).

The objectives of this study were:

- To determine the effect of temperature on the moisture sorption isotherms of persimmon leaves.
- To analyze the data using seven sorption isotherm equations available in the related literature.
- To find the most suitable model describing the isotherms of persimmon leaves.
- To calculate the net isosteric heat of sorption of water from the experimental data.

2. MATERIALS AND METHODS

2.1. Materials and chemicals

Persimmon leaves (D. kaki, Rojo Brillante var.) were picked from trees in an orchard in Valencia (Spain). Potassium Chloride, Magnesium Chloride 6-hydrate, Potassium Hydroxide, Sodium Chloride, Magnesium Nitrate 6-hydrate, Potassium Carbonate, Lithium Chloride, and Thymol were obtained from Panreac. Ammonium nitrate was obtained from VWR and dehydrated Barium chloride from Scharlab.

2.2 Global chemical analysis

In order to characterize the persimmon leaves, analyses were carried out in accordance with the method proposed by the Association of Official Analytical Chemists (AOAC, 1984). Moisture content was determined using the gravimetric method, oven drying at 150ºC up to constant weight (24 h). Total protein was determined using the Kjeldahl method and protein was calculated using the general factor (6.25) (El-Shurafa et al., 1982). Fat content was determined by the Soxhlet method using petroleum ether (40-60ºC boiling range) as a solvent. Ash content was measured using a muffle at 550ºC up to constant weight (4 h).

The sample weight was measured with a gravimetric balance (Mettler-Toledo) with a precision of 0.0001 g. Moisture content, protein, fat and ash content were expressed in dry basis (g/100 g d.b.). All analytical determinations were performed in triplicate. Values of different parameters were expressed as the mean ± standard deviation.

2.3 Experimental procedure

In a preliminary study, it was demonstrated that subjecting the raw material to hot air drying at 100ºC was the drying method which best preserved the antioxidant properties of persimmon leaves. For this reason, leaves were blanched at 100 ºC for 5 min and then dried at 100ºC for 30 minutes in a convective drier.

The sorption method used was the static gravimetric technique, which involves the use of saturated salt solutions to maintain a fixed relative humidity when equilibrium is reached. The water activity of the food is identical to the relative humidity of the atmosphere at equilibrium conditions and the mass transfer between the product and the ambient atmosphere is assured by natural diffusion of the water vapour. Nine saturated salt solutions (KOH, LiCl, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, NH_4NO_3, NaCl, KCl and $BaCl_2$) were prepared corresponding to a wide range of water activities ranging from 0.0610 to 0.9096 (Hall, 1957). Nine glass desiccators were used for this study. Each desiccator had a small recipient that contained the saturated salt solutions.

A small quantity of Thymol was added to the containers that had saturated salts with water activities higher than 0.6, in order to prevent microbial growth.

For each of these experiments, about 1 g of the dried leaves was placed in the respective weighing bottles. All nine desiccators were placed in an incubator and the gain or loss in weight of the samples in each desiccator was monitored every week. The EMC was acknowledged when three consecutive weight measurements showed a difference of less than 0.001 g. This took about 50-60 days, depending on the temperature inside the incubator. The procedure was carried out in triplicate for each sample and the average values of EMC were measured. The temperature of the incubator was changed, and the same experiment was conducted for the sorption process at 20, 30 and 40 ºC.

2.4 Analysis of sorption data

A large number of models have been proposed in the related literature for sorption isotherms. In the present study, the description of the relationship between EMC, a_w and the temperature of persimmon leaves were verified according to the seven models (Henderson, 1952: Basunia & Abe, 2001; Lahsasni, Kouhila, Mahrouz & Fliyou, 2003; Mohamed, Kouhila, Jamali, Lahsasni & Mahrouz, 2004) as shown in Table 2.

The criterion used to evaluate the quality of the fit was the mean relative deviation modulus:

$$MRE = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{M_{i,exp} - M_{i,pre}}{M_{i,exp}}\right| \quad (1)$$

where, $M_{i,exp}$ is the i^{th} experimental value of EMC; $M_{i,pre}$ is the i^{th} value predicted by the model; and N is the number of data points.

It is generally considered that MRE values below 10% indicate an adequate fit for practical purposes (Aguerre, Suarez & Viollaz, 1989).

The differences between the measured and predicted EMC values for various water activities were defined as residuals, and these residuals were plotted against predicted values of EMC. A model is considered acceptable if the residual values fall in a horizontal band centered around zero, and displays no systematic tendencies towards a clear pattern. If the residual plot has a clear pattern, the model is not acceptable.

2.5 Determination of net isosteric heat of sorption

The CLAUSIUS-CLAPEYRON equation derived for the vapour-liquid equilibrium (2), applied to temperature-pressure vapour data relating to the product, allows the enthalpy change associated with the sorption process (net isosteric heat of sorption) (3) to be calculated for different levels of humidity. The net isosteric heat of sorption represents the total energy available to do work, while entropy at any temperature is equivalent to lost work and gives a measure of the energy that is not available to perform work. Thus, the energy that is available to do work is the difference between these two quantities (Aviara & Ajibola, 2002).

Differential heat of sorption (ΔH) measures the energy changes that occur during the sorption process and is indicative of the level of attractive or repulsive forces of the system. The Gibb's free energy (ΔG), associated with the spontaneity of the process, may be calculated for the adsorption process (4). Entropy changes (ΔS) may be associated with spatial reorganization occurred at the water-solute interface, which can be calculated by the equation (5).

$$\ln(p) = \frac{\Delta H}{R} \cdot \frac{1}{T} + K \quad (2)$$

$$\Delta H = \Delta H_V + Q_S \quad (3)$$

$$\Delta G = R \cdot T \cdot \ln\left(\frac{P}{P^0}\right) = R \cdot T \cdot ln a_w \quad (4)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (5)$$

where: p is the water vapour pressure in equilibrium with the material at a given temperature (atm); ΔH_v is the heat of water evaporation (-43.96 kJ/mol); Qs is the net isosteric heat of sorption (kJ/mol), aw is the water activity (dimensionless), T is the absolute temperature (K), R is the universal gas constant (kJ/mol K), p^o is the pure water vapour pressure (atm) and K is a constant.

3. RESULTS AND DISCUSSION

Dried persimmon leaves presented a moisture content of about 4.34 ± 0.16% (dry basis), and protein, ash and fat contents of about 3.3 ± 0.2%, 4.7 ± 0.1% and 11.26 ± 0.23%, respectively.

3.1. Sorption isotherms

Many food products exhibit a different behaviour for adsorption and desorption processes. Nevertheless, when a food product is subjected to water content changes in a range that implies water loss or gain, the use of a ‘‘working isotherm”, as suggested by Labuza (1984), may be useful to predict any drying or humidification cycle undergone by the food. In this study, it was of interest to obtain useful data over the whole water content range and consequently, all the experimental EMC–a_w values were considered to construct the ‘‘working sorption isotherm” of dry persimmon leaves (Fig. 1). The sorption isotherm obtained presents a sigmoidal shaped curve, thus reflecting a Type II isotherm (according to Brunauer’s classification) (Brunauer et al., 1940). The behaviour observed was typical of plant products and similar results have been obtained with other leaves such as tea leaves (Arslan & Togrul, 2006; Sinija & Mishra, 2007), olive leaves (Bahloul et al., 2008), orange leaves (Mohamed et al., 2004) and lemon balm leaves (Argyropoulos et al., 2012).

The EMC decreases as temperature increases, at constant water activity (Fig. 1); however, this influence was not noteworthy as it occurs with many food materials. The higher excitation state of water molecules at a higher temperature thus decreasing the attractive forces between them may explain this result (Mohamed et al., 2004). Moreover, at constant temperature, the EMC increases as water activity increases. This is consistent with similar results that have been reported in the related literature for other products (Argyropoulos et al., 2012; Arslan and Togrul, 2006; Bahloul et al., 2008; Basunia and Abe, 2011; Nourhène et al., 2008; Mohamed et al., 2004).

Experimental data were fitted to seven different models (Table 1); the BET equation being the only one that stems from a thermodynamic approach to the sorption process (Iglesias and Chirife, 1976). The parameters obtained have a physical meaning, $W_{o,}$ corresponding to the amount of water needed to surround the food surface with just one layer of water molecules and C, relating to the heat liberated in the monolayer sorption process. The concept of monolayer water content was found to be a reasonable guide for various aspects of interest in dried foods, relating to the limit from which the rate of deteriorative reactions began to increase significantly. Nevertheless, this equation is not adequate at high water activity levels, when dissolution phenomena become more important than sorption. The GAB model (Table 1) has been used successfully by many researchers to fit sorption data over a wide range of a_w.

The experimental results obtained from the sorption isotherm of dry persimmon leaves were used to estimate the parameters of the different sorption models (Table 1) and the results are shown as mean values, regression coefficient (r^2) and mean relative error (MRE) in Table 2. According to the figures obtained for both assessment criteria, r^2 and MRE, all models can be grouped into three sets: the Halsey, Smith, Gab and BET models could be considered to best describe experimental data, since all of them reached high values of r^2 and MRE lower than 10%; the Herderson model yielded the worst results according to the two criteria chosen; and the Oswin and Caurie models would be in the middle. Figure 2 shows the comparison between experimental and calculated (GAB model) data of sorption isotherms of persimmon leaves obtained at 20, 30 and 40 ºC. The GAB model appears to be one of the most suitable for describing the relationship between water content, water activity and temperature throughout the intervals considered. On the other hand, a model whose parameters have a physical meaning is highly interesting because it provides a link with physical phenomena and allows comparisons with other materials. Thus, the GAB model was found to be the best model to describe sorption isotherm of dry persimmon leaves. The values of monolayer moisture for dry persimmon leaves from the GAB model at different temperatures were similar to those obtained for mate and tea leaves (Zanoelo, 2005; Arslan & Togrul, 2006).

3.2. Isosteric heat of sorption and sorption entropy

The differential heats of sorption, ΔH, were calculated from the slope of the plot between the values of ln (p) and 1/T for moisture content ranging from 0.5 % to 14% as shown in Fig. 3; ΔG and ΔS were calculated according to equations 4 and 5 and the variation of ΔH, ΔG and ΔS with moisture content is shown in Fig. 4. The moisture level for which ΔH and ΔS are at their maximum approximately fits with the BET monolayer value (Brunauer et al., 1938), which represents the product moisture corresponding to a situation where the primary adsorption sites are saturated by water molecules. When the most accessible points are saturated, the water vapour is adsorbed at primary points of the less accessible areas, thus the associated heat of sorption is the greatest just before the completion of the monolayer (Fig. 4).

The net isosteric heats of sorption were estimated from equation 3 and their correlation with the moisture content can be expressed mathematically as a function of moisture content (Mohamed et al., 2004):

$$Q_{st} = 0.7397M^2 - 18.162M + 90.451 \quad (r = 0.9962) \qquad (6)$$

This mathematical relationship can be a useful tool for calculating the heat of sorption of dry persimmon leaves for other moisture contents. The net isosteric heat decreases as leaf moisture increases; similar results for many plants and food materials such as withered leaves, black and green tea have been reported in the related literature (Lahsasni et al., 2003). The rapid increase in the heat of sorption at low moisture content is related to the existence of highly active polar sites on the surfaces of the food material, which are covered with water molecules forming a mono-molecular layer (Lahsasni et al., 2003).

4. CONCLUSIONS

The equilibrium sorption isotherm for dry persimmon leaves has been obtained at 20, 30 and 40ºC using the static gravimetric method. Temperature only slightly influences water activity and the curves presented a sigmoid shape and belong to type II according to BET classification. Of the seven models used, the Halsey, Smith, Gab and BET models provided the best fit to experimental data according to the previously chosen criteria. By applying the Clausius-Clapeyron concept, the net isosteric heats for sorption were evaluated and an empirical equation was established to describe these variations between 0.5% and 14% (d.b.). Net isoteric heat was found to be a polynomial function of moisture content.

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Figure captions:

Figure 1. Equilibrium moisture content (EMC) vs. water activity (aw) at 20, 30 and 40 ºC for persimmon leaves

Figure 2. Adsorption isotherms of persimmon leaves fitted with seven models

Figure 3. ln(p) vs. 1/T graphs for calculating the heat of sorption of persimmon leaves

Figure 4. Variation of ΔH differential, ΔG and ΔS for the water vapour adsorption depending on the moisture