

The Adsorption-Desorption Hysteresis Effect on Pistachio Nuts

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ABSTRACT

The equilibrium moisture content is an important parameter for several post-harvesting operations for pistachio nuts, such as drying processes and storage. In this research the adsorption and desorption equilibrium moisture content were determined for two major varieties of Iranian pistachios at 11 to 85 percent relative humidities and a constant temperature of 50°C. A significant hysteresis effect between the adsorption and desorption processes was observed statistically. For predicting the adsorption and desorption EMC, the Halsey model was found the most proper equation for adsorption processes for two varieties (Ohadi and Kaleghochi), whereas the Oswin and Smith models were most appropriate for Ohadi and Kaleghochi for desorption processes, respectively, at constant a temperature of 50°C.

Keywords: Adsorption, Desorption, Hysteresis, Pistachio.

INTRODUCTION

The name 'Pistachio' derives from the Persian name 'pisteh' or 'pesteh'. Existing documents show that pistachio (*Pistacia vera* L.) has been cultivated in Iran since 3,000-4,000 years ago and was introduced into Mediterranean Europe at approximately the beginning of the Common Era (12).

Drying pistachio nuts is one of the most important unit operations in any pistachio processing plant. The improper operation of pistachio drying may cause severe damage to the whole nut product both qualitatively and quantitatively.

For any hygroscopic material, Equilibrium Moisture Content (EMC) may be defined as the moisture content of the material in equilibrium with a particular environment (temperature and relative humidity) (7). Knowledge of the equilibrium moisture content of agricultural products at various temperatures would allow us to specify the progress of the drying process (desorption) and the storage

conditions (adsorption) for that product (10). The plot of the equilibrium moisture content of a material versus the relative humidity of the environment at a given temperature is referred to as the adsorption or desorption isotherm, depending on whether the material is being made wet or dried. It has been established that in hygroscopic materials the adsorption-desorption isotherms are sigmoid in shape and show a marked hysteresis. In these curves, at any given relative humidity, the moisture content reached from a drier state (on the desorption isotherm) is higher than that reached from a wetter one (on the adsorption isotherm). In other words, the amount of water held by these materials is not only dependent upon the equilibrium relative vapor pressure, but also on upon the direction from which equilibrium is approached (14).

Hysteresis can have a significant effect on the chemical reaction of foodstuffs (5, 7). Several explanations have been proposed for the hysteresis phenomenon for hygroscopic materials. The most favored one is that

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given for cellulosic materials. This phenomenon is justified by the theory of change in active polar sites for the bonding of water molecules. Following this theory, in the original wet condition, the polar sites in the molecular structure of the material are almost entirely satisfied by the absorbed water. Upon drying and shrinkage, the molecules and their water-holding sites are drawn closely enough together to satisfy each other. This reduces the water-holding capacity of the material upon subsequent absorption. In other words, due to the fact that dehydration is never as complete as the original hydration, for any given relative vapor pressure, the material shows a higher moisture content along the desorption curve than it does along the adsorption curve, (9).

The other approach introduces connectivity and pore blocking effects into the picture. The simplest version of this approach is the so called 'ink-bottle' mechanism of hysteresis. The idea here is that, if there is a single cavity connected to the vapor phase with a narrow channel (ink-bottle pore), it is assumed that the evaporation of the liquid from the cavity should be delayed due to the pore blocking. In other words, liquid can evaporate from a pore only if it has direct access to the vapor phase. Otherwise there is a kinetic barrier to the evaporation and hysteresis occurs. This idea together with percolation theory has been applied to more complex three dimensional networks of pores and cavities. These results have been used in the interpretation of experimental data. However, the validity of the pore blocking assumption and the range of the conditions where this effect may be observed is not fully explored (2, 11).

Several mathematical, empirical and semi-empirical models have been proposed to describe the relationship between the equilibrium moisture content and the surrounding air relative humidities for agricultural products such as: the modified Henderson; Chang and Pfost; GAB, Halsey, Smith and Oswin equations. Most of these take into account the effect of temperature (2). The modified Halsey, Smith and Oswin equa-

tions were reported to be the most appropriate models for predicting the EMC values for high oil content kernels, such as pistachio nuts (16).

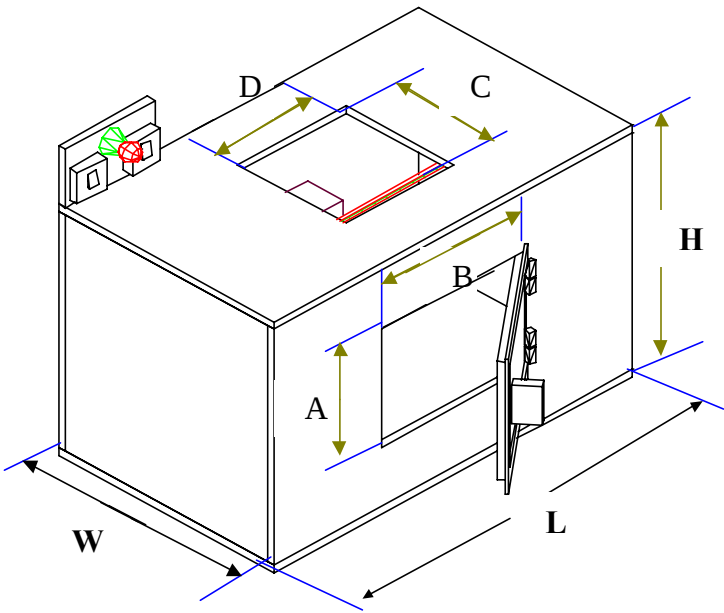
In 1967, Young and Nelson (15) developed an equation for explaining the hysteresis effect on biological materials. In this equation, the equilibrium moisture content was related not only to the temperature and relative humidity but also to the previous moisture content (moisture history) of the biological material. However, due to many parameters involved in the equation, its applicability is limited.

The objectives of this study were:

- 1- To determine the desorption EMC values for Iranian pistachio nuts at relative humidities of 85 down to 11 percent at 50 ° C.
- 2- To determine the adsorption EMC values for the same samples at relative humidities of 11 up to 85 percent at the same temperature.
- 3- To establish the hysteresis loop for the experimental values.
- 4- To find the best fit equation for the desorption and adsorption data.

MATERIALS AND METHODS

Two main varieties of Iranian pistachio nuts, namely Ohadi and Kolehghochi, were selected for the desorption-adsorption experiments. These experiments were conducted at a constant temperature of 50°C for shelled (dehulled) freshly harvested pistachio nuts using two identical environmental chambers. The chambers (0.6×0.6×1.0 m.) were made of pressed wood with thin aluminum foil sheets for inside lining and were insulated effectively (Figure 1). A wire mesh floor was provided inside the chamber on which the samples, thermostat (Honeywell T 6060 A.B.C), thermometer (wet and dry-bulb) and hygrometer were kept. A fan and a 1,000 W heater (in one unit) were hooked against the chamber wall. The fan was used to agitate the inside air continuously and the heater was employed to maintain the inside temperature thermostatically ($\pm 1.0^{\circ}\text{C}$). Dif-



A=30; B=40; C=30; D=30; L=100; W=60, and H=60 cm.

Figure 1. Sketch of the environmental chamber and its dimensions.

ferent relative humidities were maintained by using known saturated salt solutions at 50 °C at seven levels, Table 1 (2, 7, 11, 12, and 17). The saturated salt solutions were placed in several shallow large trays inside each chamber with a total surface area of 0.512 m².

The hygrometer was only used to show the relative humidity fluctuations, and the actual relative humidity inside the chamber was determined by reading the dry and wet bulb temperatures of the air inside the chamber

through the transparent window at the top of the chamber. Each variety of pistachio in four replications was put under experimentation in each chamber at one time. Samples were spread in four wire mesh basket containers maintaining thin-layer depths. An electronic balance (Sartorius, 2354, ±0.001 g) was used for weighing the samples. Equilibrium was acknowledged when three consecutive weight measurements showed a difference of about 0.001 g. The moisture content of each of four samples was deter-

Table 1. Saturated salt solutions.

Salts	Maintained relative humidity, decimal	Salt weight for making saturated solution with 100 g of distilled water, g
LiCl	0.11	117
KC ₂ H ₃ O ₂	0.23	222
CaCl ₂	0.36	177
MgNO ₃	0.49	225
NaNO ₂	0.62	115
NaCl	0.75	40
KNO ₃	0.85	72



mined gravimetrically using an electric oven (24 h. at $105 \pm 1^\circ\text{C}$) (1).

Among the most proper RH/EMC models for predicting the EMC values, the modified Halsey equation was adopted to describe the relation between EMC and relative humidities for the adsorption process and Oswin and Smith models for the desorption process at a constant temperature of 50°C (6, 16):

$$RH = \exp\left[(-\exp A) M_e^{-B}\right] \quad (\text{Halsey}) \quad (1)$$

$$1 - RH = \exp[(A - M_e)/B] \quad (\text{Smith}) \quad (2)$$

$$M_e = A \left(\frac{RH}{1 - RH} \right)^B \quad (\text{Oswin}) \quad (3)$$

where

RH= Relative humidity of the air inside the chamber,

M_e = Equilibrium moisture content, and

A and B are constants.

The suitability of the models was evaluated and compared using the Mean Relative Error, P, (MRE, %) and Standard Error of estimate (SEM), (3, 4, 7, 8, 11, 16).

$$SEM = \sqrt{\frac{\sum_{i=1}^N (M_{ai} - M_{mi})^2}{df}} \quad (4)$$

$$MRE = \frac{100}{N} \sum_{i=1}^N \left| \frac{M_{ai} - M_{mi}}{M_{ai}} \right|$$

where

M_{ai} = Experimental value for EMC,

M_{mi} = Predicted value for EMC,

N= Number of experiments,

df= Degree of freedom (number of date point minus number of constant in the model).

RESULTS AND DISCUSSIONS

The experimental desorption and adsorption EMC values at seven levels of relative humidity and at a constant temperature of 50°C for two varieties of Iranian pistachio nuts are given in Tables 2 and 3.

The hysteresis loops for two pistachio varieties at 50°C were shown in Figures 2 and 3. For pistachio nut meat, similar hysteresis loops were reported at 20°C (13).

The hysteresis phenomenon was found to be highly significant for both varieties especially at the middle range of ambient air relative humidity, (Figures 2 and 3; level of significance, $\alpha = 0.01$). This effect seemed to

Table 2. The EMC values (% db.) for desorption and adsorption for the Ohadi variety.

RH (decimal)	Desorption, M_{des}	Adsorption, M_{ads}	$M_{des} - M_{ads}$
0.11	2.25	2.25	0.0
0.23	3.46	2.21	1.25
0.36	3.78	2.48	1.39
0.49	4.62	3.00	1.62
0.62	6.15	5.03	1.12
0.75	7.60	6.60	1.00
0.85	9.27	8.65	0.62

Table 3. The EMC values (% db.) for desorption and adsorption for the Kalehghochi variety.

RH (decimal)	Desorption, M_{des}	Adsorption, M_{ads}	$M_{des} - M_{ads}$
0.11	2.16	2.16	0.0
0.23	2.85	2.14	0.71
0.36	3.55	2.26	1.29
0.49	5.78	3.78	2.00
0.62	7.35	5.56	1.79
0.75	9.18	8.34	0.84
0.85	12.09	11.54	0.55

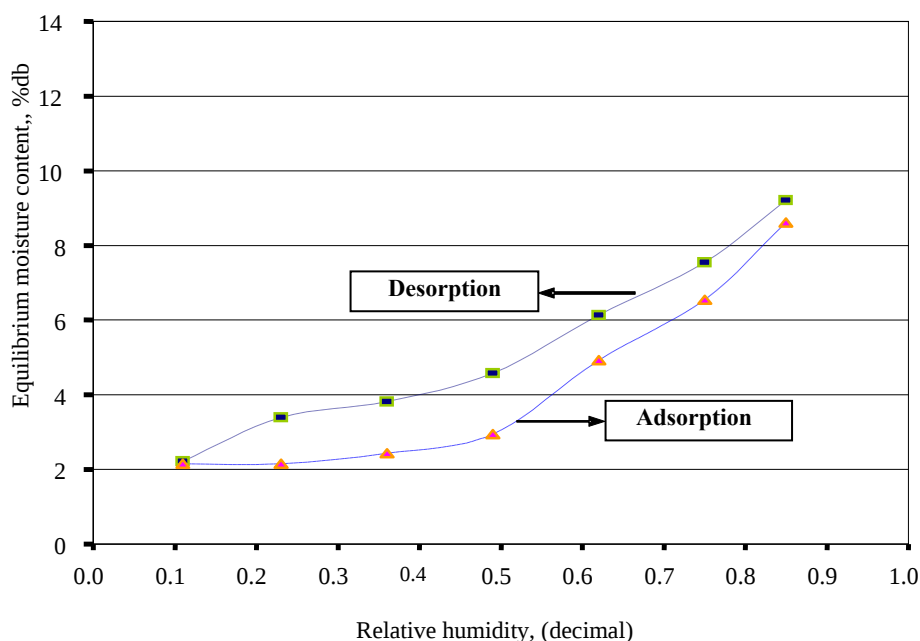


Figure 2. Hysteresis loop of pistachio nuts for the Ohadi variety at 50°C (experimental values).

be different for two varieties. This difference may be attributed to the different size and chemical compositions of the pistachio varieties. The sorption and desorption isotherms have a sigmoid (S-shaped) profile typical for hygroscopic materials. Similar results have been previously reported for many seeds and food materials (8, 9, 10). The one-way analysis of variance showed that the EMC values were significantly dif-

ferent for the two processes (desorption and adsorption) as well as for two varieties of pistachio kernel nuts at constant temperature of 50°C, (Table 3).

In Table 3, the values denoted by similar small and capital letters showed a non-significant difference at level of 99% probabilities.

A nonlinear, least-square regression program was used to fit the models for the ex-

Table 4. Desorption and adsorption EMC comparison for two pistachio varieties at 50°C.

Process→ Variety ↓	Desorption	Adsorption	Mean
Ohadi	5.32 ^b	4.28 ^c	4.80 ^B
Kaleghochi	6.14 ^a	5.06 ^b	5.60 ^A
Mean	5.73 ^A	4.67 ^C	

Table 5. The constants for models for the Ohadi variety at 50°C.

Process	Model	A	B	SEM	MRE
Desorption	Oswin	4.940	0.364	0.208	3.835
Adsorption	Halsey	1.583	1.563	0.404	7.991

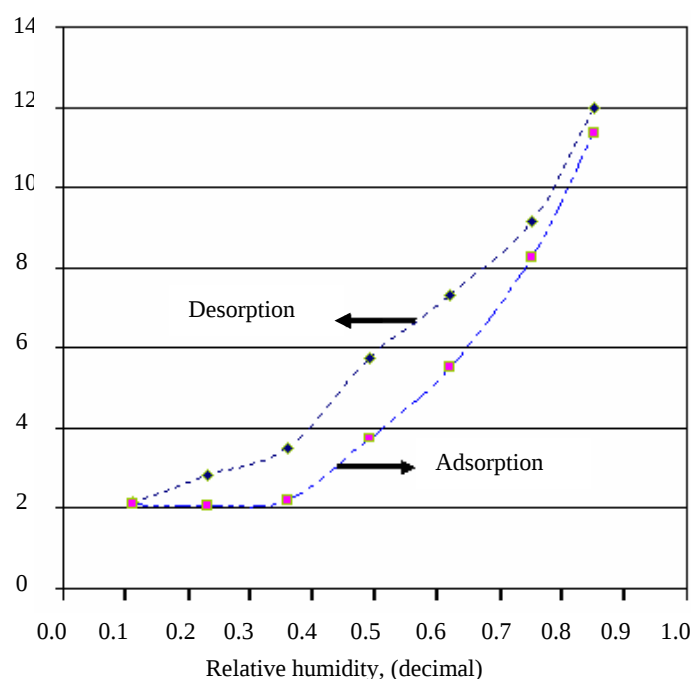


Figure 3. Hysteresis loop of pistachio nuts for the Kalehghoch variety at 50°C (experimental values).

perimental values (11, 13). The values of the two above mentioned errors (SEM and MRE) were calculated and found to have least magnitudes in applying the Halsey model for adsorption and the Smith and Oswin model for desorption processes in comparison to other models (16). The related constants in Halsey, Smith and Oswin equations are given in Tables 4 and 5 for two varieties.

CONCLUSIONS

At a constant temperature of 50°C, the experimental values for adsorption and desorption were determined and the hysteresis effect was found to be very significant for both pistachio varieties especially at ERH of 36 to 75 percent.

For predicting the desorption and adsorption EMC, the Halsey model was found to be the most appropriate model for the adsorption process for both varieties of pistachios at a full range of relative humidities

while the Oswin model was a proper model for the Ohadi and the Smith model for Kalehghochi varieties throughout the desorption processes at a constant environmental temperature of 50°C.

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اثر پدیده پسماند دفعی و جذبی بر روی دانه پسته

ع. زمردیان و ن. ع. توکلی

چکیده

در اکثر پروسه‌های پس از برداشت عامل رطوبت تعادلی نقش مهمی ایفا میکند، نظیر پروسه خشک کردن و انبار کردن. در تحقیق حاضر مقادیر رطوبت تعادلی دو وارسته مهم پسته (اوحدی و کله قوچی) در دو فرایند دفعی و جذبی و در رطوبت‌های نسبی ۱۱ تا ۸۵ درصد و در دمای ثابت ۵۰ درجه سانتیگراد تعیین گردیدند. پدیده پسماند بین دو فرایند دفع و جذب رطوبت بطور کاملاً واضح مشاهده گردید. برای پیش بینی مقدار رطوبت تعادلی مدل هالسی برای وارسته‌های اوحدی و کله قوچی در فرایند جذب بسیار مناسب تشخیص داده شد در حالیکه برای فرایند دفع مدل‌های اوسوین و اسمیت در مورد هر دو وارسته نتایج بهتری را ارائه دادند.