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EQUILIBRIUM MOISTURE CONTENT AND EQUATIONS FOR FITTING SORPTION ISOTHERMS OF *CAPSICUM ANNUUM*

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Abstract
In this paper, we report on the water activity and moisture contents of *Capsicum annuum* in different saturated salt solutions. The sorption isotherms of *Capsicum annuum* were determined within the range of 10-98% relative air humidity at three different temperatures (30 °C, 45 °C and 60 °C), using static gravimetric method. The moisture content of the product was used as in the marketing standard, assuming that no microbial spoilage would occur below a certain moisture level. The best equation was predicted for the experimental data at each temperature using non-linear regression technique. Hence, this correlation between equilibrium moisture content (EMC) and equilibrium relative humidity (ERH) can be given as a new model. Consequently, the experimental data were fitted in several models such as Oswin, GAB, Modified Henderson, Halsey and Modified Halsey. In order to compare these models, three statistical error parameters were used and the best fitted models between sorption isotherms were studied. GAB was the best model to describe the sorption isotherm adequately, over entire temperature range among the others. Besides, a new model which can be considered as better than GAB model, taking into account the experimental results for three temperatures, was proposed.

Keywords: *Capsicum annuum*, equilibrium moisture content, non-linear regression, sorption isotherms

CAPSICUM ANNUUM'UN DENGE NEM İÇERİĞİ VE SORPSİYON İZOTERMLERİNE UYGUN DENKLEMLERİ

Özet
Bu çalışmada, *Capsicum annuum* tipi biberin farklı doymuş tuz çözeltilerindeki su aktivitesi ve nem içerikleri incelenmiştir. *Capsicum annuum*'un sorpsiyon izotermleri, üç farklı sıcaklıktaki (30 °C, 45 °C ve 60 °C), %10 ile %98 arasındaki bağıl hava neminde gravimetrik yöntem kullanılarak belirlenmiştir. Ürünün, nem içeriği satış standartlarında olduğu gibi kullanılmış ve bu belirli nem değerinin altında mikrobiyel bozunmanın olmadığı kabul edilmiştir. Her bir sıcaklıktaki deneysel veriler için, lineer olmayan regresyon tekniği kullanılarak en iyi bağıntı belirlenmiştir. Böylece, bu denklem denge nem içeriği (EMC) ve bağıl denge nemi (ERH) arasındaki bu bağıntı yeni bir model olarak verilebilir. Daha sonra, bu deneysel veriler Oswin, GAB, Modified Henderson, Halsey ve Modified Halsey gibi bazı modellere uygulanmıştır. Bu modellerin birbiriyle karşılaştırılması için istatistiksel parametreler kullanılmış ve bu sorpsiyon izotermleri arasında en iyi uyan model araştırılmıştır. GAB modeli verilen sıcaklık aralığında sorpsiyon izotermi en iyi tanımlayan modeldir. Ayrıca, deney sonuçları göz önünde bulundurularak GAB modelinden daha iyi bir model önerilmiştir.

Anahtar kelimeler: *Capsicum annuum*, denge nem içeriği, lineer olmayan regresyon, sorpsiyon izotermleri

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INTRODUCTION

Capsicum annuum is a general name for plants coming from *Capsicum* species, also known as bell pepper or sweet pepper. Turkey is the third largest producer of pepper after China and Mexico (1) and pepper is the most important crop among vegetables. It is eaten raw or cooked and used as spice. Besides, peppers are consumed as vegetable and condiments and are good sources of vitamins A and C.

Water activity and moisture content are the most important characteristics of dried foods for stability. The nature of sorption isotherms is unique for each food materials. There is a relation between moisture sorption isotherms and water activity and moisture content which is used as one of the input parameters in order to improve drying process while decreasing the drying costs. Sorption isotherms are also important to improve the conditions of several food processes as dehydration, packing or storage and in design and optimizations of unit operations such as preservation, drying and mixing. An isotherm obtained by exposing wet material to air of increasing humidity is termed the adsorption isotherm; while that obtained by exposing the material to air of decreasing humidity is known as the desorption isotherm (2).

Sorption isotherms are useful tools for understanding the changes in the water activity during heating process for some fruits such as prunes and raisins (3) and are also used for prediction of temperature dependence during storage of sugar-rich fruits (4). Some researchers have studied the equilibrium moisture content of some medicinal and aromatic plants (5). In addition, more data on sorption isotherms of grapes, apricots, apples, soybean, red chili, sugar beet root and *Beauveria bassiana* (Balsamo) Vuillemin have been reported (6-11).

In order to determine the moisture sorption isotherms, some tools such as a water vapor pressure capacitance manometer (12) and experimental apparatus for the sorption isotherms measurement (13) as well as some methods such as examination of water activity of high porosity model food at, above and sub-freezing temperature (14) were employed. Number of works to predict equations for fitting water sorption isotherms has been reported by researchers (6, 7, 11, 15-17).

Drying process of peppers was carried out by hot air provided from flat plate solar air heating collectors. Temperature elevations during drying process were between 30 and 60 °C in summer season. For this reason; obtained data from experiment at least three different temperatures can meet our needs for next stage of drying process of peppers. The aim of this study was to determine EMC/ERH equations for 30 °C, 45 °C and 60 °C. Subsequently, five EMC/ERH equations were compared on their ability to fit data for *Capsicum annuum*.

MATERIALS AND METHOD

All samples used for the experiment were produced in Turkey and obtained as fresh commercial sweet peppers from local market in Izmir. They are selected in uniform size and shape and without any defect on visual inspection. Samples were washed in cold water to remove soil and dust particles. The method used for determination of sorption isotherms was the static gravimetric method. The experimental apparatus consisted of a thermostatically controlled water bath accurate to ± 0.5 °C and six air-tight vacuum glass jars called sorption containers. Sorption containers are simple preserving jars which can be tightly sealed against water vapor by means of plastic seal rings and glass lids (Figure 1). Each Sorption container contained different saturated salt solution such as LiCl, $MgCl_2$, K_2CO_3, NaBr, NaCl, $BaCl_2$ and K_2SO_4 to provide defined constant relative humidity which varies from 10% to 97% inside the sorption container.

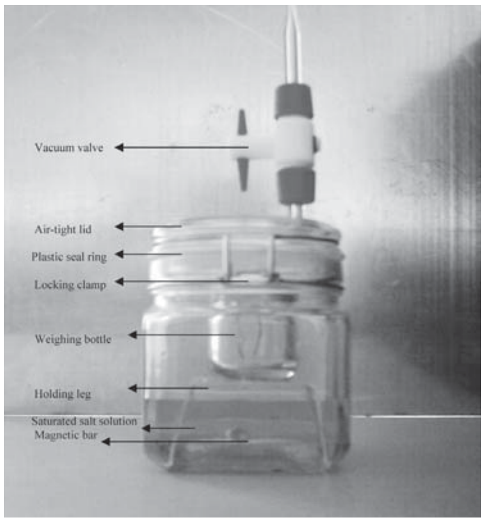

Figure 1. Sorption container

Samples were placed on small bottles (weighing bottle) above the saturated salt solution and suspended over saturated salt solution of known concentrations during fourteen days. The values of their equilibrium relative humidities at different temperatures are given in Table 1 (6, 7, 11, 18).

Table 1. Selected saturated salt solutions and corresponding air relative humidities

Salt	Equilibrium Relative Humidity (%)		
	30 °C	45 °C	60 °C
LiCl	11.15	11.00	11.30
$MgCl_2$	32.73	31.50	29.30
K_2CO_3	43.80	41.00	43.20
NaBr	57.70	51.50	49.70
NaCl	75.32	75.32	74.50
$BaCl_2$	90.26	88.00	84.00
K_2SO_4	97.30	96.00	95.00

The experimental apparatus utilized are shown in Figure 2. Temperature control sorption containers should be placed in thermostatically controlled water bath. During the sorption experiments, the water bath was covered with plastic film to prevent vapor leakage. Sorption containers are immersed in a thermostated water bath adjusted to a fixed temperature for 5 hours so as to bring the salt solution to a constant temperature.

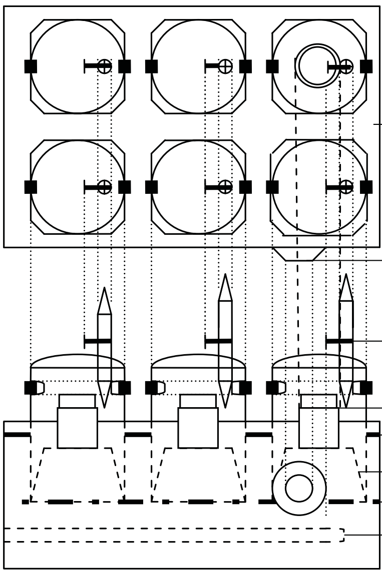

Figure 2. Experimental apparatus

Initial moisture content of fresh samples was determined according to TSE Standard 1129 (19) as 94% on the wet basis. Subsequently, equilibrium moisture contents were studied. Samples with quantities changing between 4.9 gram and 5.9 gram were weighed into small bottles they were placed on the saturated salt solution within the range of 10-97% relative air humidity. When moisture content of the sample reached the desired value at the end of the equilibration time (approximately 14 days), sample weights were measured (accuracy of balance, ±0.001). Experiment procedure was repeated three times for each temperature (30, 45 and 60 °C). As a result, equilibrium moisture contents were calculated as a mean value of each temperature and diagrams of sorption isotherms for each temperature were drawn for moisture content versus water activity (a_w). Thus a mathematical model for prediction of their sorption behavior as a function of water activity was suggested for temperatures 30 °C, 45 °C and 60 °C. In order to determine the mathematical model for temperatures of 30 °C, 45 °C and 60 °C, non-linear regression analysis method was used.

Numerous mathematical models for the description of the moisture sorption behavior of foods are available in literature. Some of them have been developed theoretically while the others are empirical or semi-empirical. In this study, the experimental data are fitted in several models (Oswin, GAB, Modified Henderson, Halsey and Modified Halsey). In order to compare the results three statistical error parameters namely, residual sum of squares (RSS), standard error of estimate (SEE) and coefficient of determination (R^2), were used. Equations 1, 2, 3 for Oswin model, equations 4, 5, 6 for Halsey model, equations 7, 8, 9 for modified Henderson model, equations 10, 11, 12, 13, 14 for modified Halsey model, equation 15 for GAB model are given below:

1- $h_r = (M/a)^{1/b} / [1 + (M/a)^{1/b}]$ (17)

2- $M = a [A_w / (1- A_w)]^n$ (15)

3- $M = k \times (a_w / (1 - a_w)^n$ (11)

4- $h_r = \exp(-a / M^b)$ (17)

5- $a_w = \exp(-k / M^n)$ (16)

6- $A_w = \exp(-a/ R \times T \times (M / M_m)^r)$ (15)

7- $h_r = 1\text{-}\exp[-a \times (T + b) \times M^c]$ (17)

8- $a_w = 1\text{-} \exp[-a \times (T + b) \times M^c]$ (6)

9- $M= [\ln (1 - a_w) / (-k \times (T + c))]^{1/n}$ (11)

10- $h_r = \exp[-(a + b \times T) \times M^{-c}]$ (17)

11- $A_w = \exp[-\exp(b \times T + c) \times M^{-r}]$ (15)

12- $a_w = \exp[-\exp(a + b \times T) \times M^{-c}]$ (6)

13- $a_w = \exp[-\exp(k \times T + c) \times M^{-n}]$ (11)

14- $M = [-\exp(a \times T_k + c) / \log RH]^{1/b}$ (7)

15- $M = (a \times b \times c \times h_r)/[(1-b \times h_r) \times (1-b \times h_r+b \times c \times h_r)]$ (17)

where; h_r, a_w, A_w, Water activity (%); M, Equilibrium moisture content (% d.b.); RH, Relative humidity; T, Temperature (°C); T_k, Temperature (°K); M_m, Mono layer moisture content ; a, b, c, k, n, r and R are constants.

RESULTS AND DISCUSSION

Desorption isotherms of *Capsicum annuum* were studied at three different temperatures (30 °C, 45 °C, and 60 °C). The weight of each sample (sample with weighing bottle) was recorded at 12 hours intervals by taking out the sample from the container very fast and then replacing it in the container. The weight recording period was about 15-20 seconds. This procedure was continued until the weight was constant. Approximately 7-14 days were required for equilibrium of the sample with the environment maintained by saturated salt solution.

Equilibrium moisture contents decreased with increasing temperature at constant water activity and increased with increasing water activity at constant temperature. These results are similar with the findings of McLaughlin and Magee (20). Experiment results are examined for two different purposes.

Firstly, in order to model the sorption curves, several equations were proposed for the correlation of the equilibrium moisture content with the equilibrium relative humidity of their surrounding for vegetables. For this reason, experimental data were compared with the given model equations such as Oswin, Modified Oswin, GAB, Modified Henderson, Halsey for each temperature.

In order to find the best fitting sorption models to experimental data for each temperature, all sorption models were examined for the same temperature. Data Fit 8.0 was also used to determine the best fitting curve and equation. The comparisons of these models at 30 °C, 45 °C and 60 °C isotherm temperatures can be seen at Figure 5, Figure 6 and Figure 7, respectively. As a result, the values of R^2 obtained from fitting curve varied between 0.8430 and 0.9133 at 30 °C, 0.7578 and 0.8662 at 45 °C, 0.8222 and 0.9182 at 60 °C and calculation constants (a, b, c, d and T) were given Table 3. In this manner, GAB model can be used for three temperatures, while Modified Henderson model for 30 °C, GAB model for 45 °C and 60 °C has the ability to accurately describe the EMC/ERH relationship.

Secondly, a new model can be proposed taking into account the coefficient of determination (R^2). The values of this model are given in Table 2. The most accurate equation were obtained from the results of these experiments for three temperatures (data without curves are presented in Figure 3). In order to model the best sorption curves, nonlinear regression analysis was used. Thus, the best fitting equations and appropriate curves for experimental data could be identified. Equation of experimental data and best fitting curves which were obtained from curve fitting software called Data Fit 8.0 for this equation are given in Figure 4. The values of R^2 obtained from fitting curve varied between 0.895 and 0.981. These values for three temperatures (30 °C, 45 °C and 60 °C) suggest acceptable result for the same equation. Therefore, only one equation for sorption models can be given below. Besides, model equation and their statistical parameters and calculation constants (a, b and c) are given in Table 2.

$$M = a . b^{x} . x^{c}$$

where; M, equilibrium moisture content; x, water activity (a_w), and a, b, c are constants.

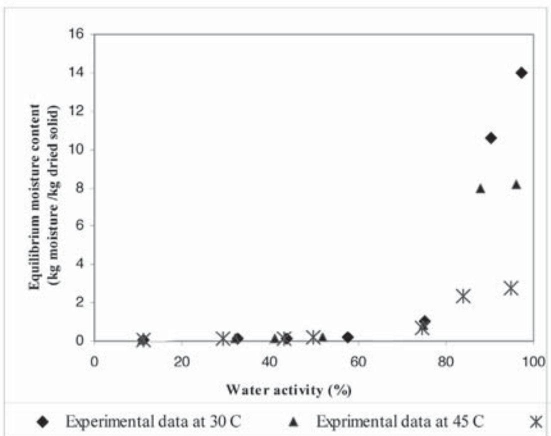

Figure 3. Experimental data at 30 °C, 45 °C, 60°C

Table 2. The best fitting equations for experimental data

Models	Statistical Parameter	Constants		
30 °C Model	R^2	a	b	C
a . b ^{x}. x ^{c}	0.98116307	0.056158154	1.0860687	-0.537943
45 °C Model	R^2	a	b	C
a . b ^{x}. x ^{c}	0.85623002	164.471911	0.06701573	7.49634573
60 °C Model	R^2	a	b	C
a . b ^{x}. x ^{c}	0.935486	0.543122736	1.077570883	-1.173615863

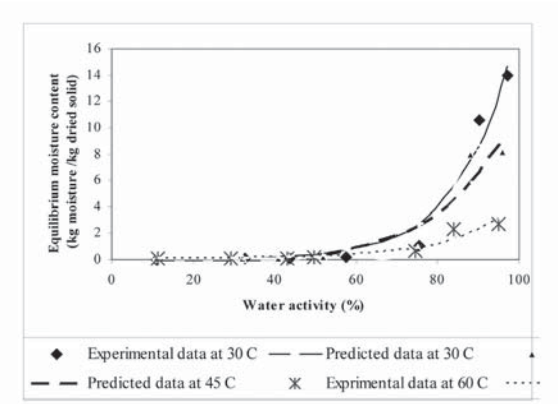

Figure 4. Comparisons of experimental data with data predicted using equations for 30 °C, 45 °C, and 60 °C

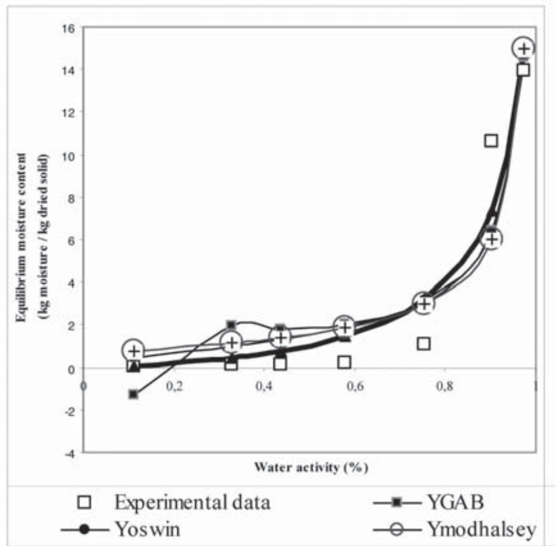

Figure 5. Comparisons of experimental and predicted desorption isotherms of *Capsicum annuum* determined using Oswin, GAB, Modified Henderson, Halsey and Modified Halsey at 30 °C

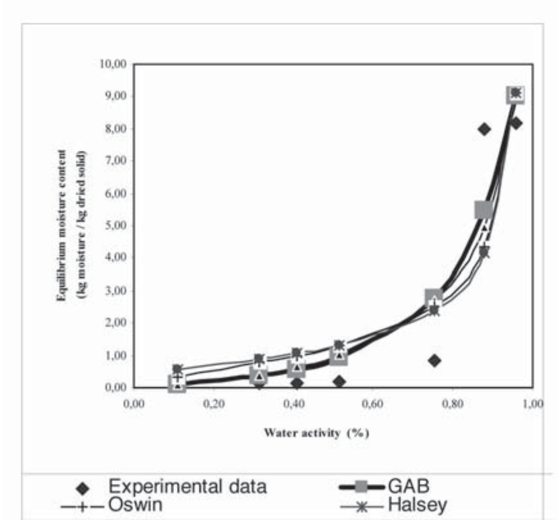

Figure 6. Comparisons of experimental and predicted desorption isotherms of *Capsicum annuum* determined using Oswin, GAB, Modified Henderson, Halsey and Modified Halsey at 45 °C

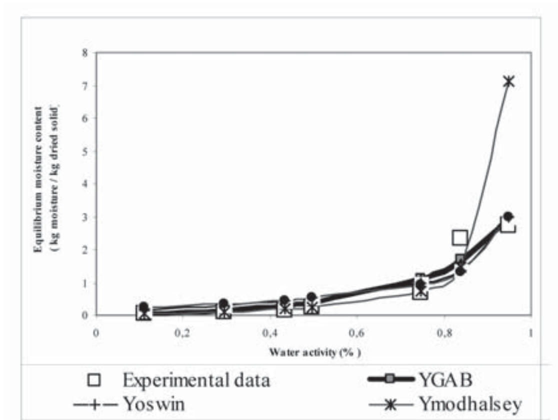

Figure 7. Comparisons of experimental and predicted desorption isotherms of *Capsicum annuum* determined using Oswin, GAB, Modified Henderson, Halsey and Modified Halsey at 60 °C

Table 3. Equation coefficients and statistical values of five different equations

Sorption Isotherms at 30 °C		Equation Coefficients					
Model	Equation	R^2	a	b	c	D	T
Modified Henderson	$M = (Ln(1-a_w)/(-a.(b+c)))^d$	0.9133	0.7013	0.1494	0.8174	1.6158	
Oswin	$M = a.(a_w/(1-a_w))^c$	0.8645	1.5412		0.6339		
Modified Halsey	$M = (-Ln(a_w)/Exp(a+b.T))^{(1/c)}$	0.8497	1.7700	-0.3162	-1.4536		4.5424
Halsey	$M = (-a/ln(a_w))^b$	0.8497	1.3963	0.6879			
GAB	$M = (a.b.c.a_w)/((1-b.a_w).(1-b.a_w+c.a_w))$	0.8430	0.7614	0.9749	-4.8233		
Sorption Isotherms at 45 °C		Equation Coefficients					
Model	Equation	R^2	a	b	c	D	T
GAB	$M = (a.b.c.a_w)/((1-b.a_w).(1-b.a_w+c.a_w))$	0.8662	52.3881	0.7732	0.0163		
Modified Henderson	$M = (Ln(1-a_w)/(-a.(b+c)))^d$	0.8326	0.8143	0.3764	0.4971	1.4646	
Oswin	$M = a.(a_w/(1-a_w))^c$	0.7775	1.2543		0.6243		
Modified Halsey	$M = (-Ln(a_w)/Exp(a+b.T))^{(1/c)}$	0.7578	-37.7063	2.7075	-1.4488		13.9278
Halsey	$M = (-a/ln(a_w))^b$	0.7578	1.0036	0.6902			
Sorption Isotherms at 60 °C		Equation Coefficients					
Model	Equation	R^2	a	b	c	D	T
GAB	$M = (a.b.c.a_w)/((1-b.a_w).(1-b.a_w+c.a_w))$	0.9182	20.3690	0.7133	0.0235		
Modified Henderson	$M = (Ln(1-a_w)/(-a.(b+c)))^d$	0.8929	0.8045	0.9856	0.6236	1.2937	
Oswin	$M = a.(a_w/(1-a_w))^c$	0.8446	0.5206		0.5922		
Modified Halsey	$M = (-Ln(a_w)/Exp(a+b.T))^{(1/c)}$	0.8222	0.1976	0.1871	-0.7700		-8.8392
Halsey	$M = (-a/ln(a_w))^b$	0.8222	0.2642	0.6662			

CONCLUSION

The sorption curves provide valuable information about the equilibrium moisture content of pepper. They present a clear idea on the stability of the plant after drying, as well as information on the different kind of water in the product. So, these curves are valuable for storage and conservation of pepper.

Sorption isotherms of *Capsicum annuum* were determined by experiment and then modelled. The saturated salt method can be successfully used for experimental determination of the equilibrium moisture content of *Capsicum annuum*. It can be concluded from the results that equilibrium moisture content increases with increasing water activity and decreasing temperature at constant relative humidity (water activity). Result of five equation fitted to the experimental data at 30 °C are plotted at Figure 5 and the best fitted equation was found to be the modified Henderson equation given in Table 3. In spite of the best fitting at 30 °C, for 45 °C and 60 °C, the best equation was found to be GAB equation when five equations were compared to experimental data in Table 3. Besides, approximation to GAB model was realized with temperature increases. The best fitted coefficient and values for R^2 for equations predicted as acceptable to fit the experimental data are shown at Table 3. In order to eliminate differences between models at various temperatures, a new model was developed instead of modified Henderson and GAB.

This study represents preliminary stage of the study on convective drying of *Capsicum annuum* in solar drier with auxiliary device.

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