Experimental evaluation of sorption isotherms of chili pepper: an Ethiopian variety, Mareko Fana (*Capsicum annum* L.)

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Abstract: Moisture sorption isotherms of chili peppers of Ethiopian variety, “Mareko Fana” ,were determined at three different temperatures (30℃, 50℃ and 70℃) and relative humidity between (10%-90%), using the standard static, gravimetric method. The modified Halsey, GAB, Oswin, and Henderson sorption models were tested to fit the experimental data. A nonlinear regression analysis method using SPSS 16.0, and Sigma Plot 11.0 software were used to evaluate the constants of sorption models, to select the best equation and to plot graphs. The net isosteric heats of sorption isotherms were determined from the equilibrium data. The models were evaluated statistically by calculating mean bias errors (MBE), mean relative deviations (MRD), root mean square errors (RMSE) and coefficient of determination (R^2). The ranking of statistical errors for each model were done by calculating the average grade. High coefficient of determination and the lowest average grade of statistical errors (1.3 for desorption and 1.0 for adsorption) were obtained from the GAB model indicating that it fits the best to the experimental data followed by modified Halsey’s equation. The worst results were obtained from Henderson’s equation. The value*s* of constant a, b and c of “Mareko Fana” were within the ranges recommended by other researchers (Bell and Labuza, 2000). The results also showed hysteresis indicating that “Mareko Fana” cannot adsorb the same quantity of water vapour as it released during desorption process. The net isosteric heat of sorption were determined from the experimental data where the energy requirements for drying processes as well as design of drying equipment be obtained.

Keywords: chili pepper, equilibrium moisture content, water activity, mathematical models, net isosteric heat of sorption

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1 Introduction

Moisture sorption isotherms describe the relationship between water activity (a_w) and an equilibrium moisture content of the system at a given temperature and pressure. It can also be again described thermodynamically in terms of chemical potential from which equilibrium conditions of multiple phases is determined. A detailed theoretical understanding of water activity is necessary so that sorption isotherms can better be analyzed.

Water activity instruments measure the amount of free (sometimes referred to as unbound or active) water present in a sample. A portion of the total water content presented in a product is strongly bound to specific sites on the chemicals on which the product was comprised of. These sites may include the hydroxyl groups of polysaccharides, the carbonyl and amino groups of proteins, and other polar sites. Hydrogen bonds, ion-dipole bonds, and other strong chemical bonds bound water tightly. Some water is bound less tightly, but is still not available (as a solvent for water-soluble food components). Many preservation processes attempt to eliminate spoilage by lowering the availability of water to microorganisms. Reducing the amount of free or unbound water also minimizes other undesirable chemical changes that occur during storage. Controlling the moisture content during the processing of foods is an ancient method of preservation. This is achieved by either removing water, or binding it so that food becomes

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stable to both microbial and chemical deterioration (Labuza, 1980). Water activity is an important property for food quality, stability and safety. It is widely utilized in the food industries for quality assurance. Both water activity and moisture sorption isotherms are important for new product development, ingredient research, shelf-life estimation, and to fully understanding the moisture within a product (Fennema, 1981). The relationship between the total moisture content and water activity of the food, over a range of values at a constant temperature and under equilibrium conditions, yields a moisture sorption isotherm when expressed graphically (Al-Muhtaseb et al., 2004). Besides, thermodynamics of water sorption has been used to explain the behavior and the structure of water at the surface and inside the foods (Beristain et al., 1990).

The relationship between water content and water activity is a complex phenomenon. An increase in water activity is usually accompanied by an increase in the water content, but in a nonlinear trend. This non-linear relationship between water activity and moisture content at a given temperature and pressure is the moisture sorption isotherm. Sorption isotherms are classified according to their shapes and processes in to five types (Brunaur et al., 1938). Type I: Langmuir and/or similar isotherms, where as water activity increases, the moisture content also increases and the curves are convex upward. These are applicable in filling water monomolecular layer at the internal surface of the material. Type II: These are sigmoidal isotherms where the curves are concave upward. Here, existence of multilayer at internal surface of the material is considered. Type III: These isotherms are known as Flory-Huggins isotherm. These are applicable for solvents or plasticizers above the glass temperature. Type IV: These are isotherms that describe the adsorption of a swellable hydrophilic solid until a maximum of site hydration is reached. Type V: The Brunauer-Emmett-Teller (BET) multilayer sorption isotherm, which is related to type II and III (Blahovec and Yanniotis, 2009; Basu et al., 2006; Mathlouthi and Rogé, 2003). Usually these curves are determined experimentally. For most foods, these curves are sigmoidal in shape, and a moisture sorption isotherm prepared by adsorption will not necessarily be the same as an isotherm prepared by desorption. This phenomenon of different water activity versus moisture values by the two methods is a moisture sorption hysteresis and is exhibited by many foods. Hysteresis represents the difference in water activity between adsorption and desorption isotherms.

Determination and detail knowledge of sorption isotherm enable researchers to solve various problems in food technology and engineering. These can be summarized as:

1) Determination of the shelf-life and stability of food in food preservation;

2) Modeling of moisture content changes during drying;

3) Problems relating to packaging;

4) Design and optimization of processes and equipment;

5) Ingredient mixing predictions, etc. (Spiess and Wolf, 1983; Gal, 1987)

2 Models for prediction of sorption isotherms

Many mathematical models were proposed by researchers for prediction of data fitting of sorption isotherms of foods. Most of them are empirical and semi-empirical and theoretical models. These expressions are developed based on two, three, four or more parameter models. Due to complex nature of foods, no single model is fully enough to represent all the sorption isotherms of foods.

Many investigators had reported moisture sorption data for different vegetables and fruits at various temperatures (Kiranoudis et al., 1993; Iglesias and Chirife, 1982; Lomauro et al., 1985; Timmerman and Chirife, 1991; Wang and Brennan, 1991; Rapusa et al., 1993). Most of them reported how sorption isotherms depend on temperature variations, determination of the net isosteric heats of sorption and development of new mathematical models to represent sorption isotherms. Chirife and Iglesias (1978) reviewed 23 equations existing in the literature for fitting moisture sorption isotherms of foods and food products. Later, Boquet et al. (1978) evaluated eight equations for 39 deferent foods. Van den Berg and

Bruin (1981) collected and classified 77 such equations. Among these equations, Brunauer Emmett Teller (BET) and the Guggenheim Anderson de Boer (GAB) equations were the most commonly used models in prediction of sorption isotherms. It was reported that the drawback of BET's equation was that, the result obtained from this model was valid only up to water activity of 0.45. The GAB equation was applied successfully to various foods (Van den Berg, 1985) and it was recommended by the European project group, COST 90 on physical properties of foods (Wolf et al., 1985).

A detailed research of literature review showed that moisture sorption isotherms of fruits and vegetables can be described by more than one sorption model (Lomauro et al., 1985). The criteria used to select most appropriate sorption model were the degree of fit to the experimental data and the simplicity of the model. Boquet et al. (1978) and Lomauro et al. (1985) reported that the isotherms for vegetables were best described by the GAB model, followed by the Oswin's and Halsey's equations. Since the majority of mathematical models do not fit the experimental data towards higher water activity range, Schuchmann et al. (1990) proposed a three parameters empirical equation. The authors reported that the equation fits the sorption very well up to $a_W = 0.9-0.99$.

Chili pepper (*Capsicum annum* L.) is particularly an important agricultural product in Ethiopia but there is no published information on sorption isotherms and the net isosteric heats of sorption for "Mareko Fana", an Ethiopian variety.

The objectives of this research work were:

1) To determine experimental adsorption and desorption data for chili pepper of Ethiopian variety "Mareko Fana" at temperatures of 30℃, 50℃ and 70℃;

2) To select the best fit sorption model for prediction of their sorption behaviors among the well known equations, to evaluate constants of the models;

3) To calculate the net isosteric heats of sorption isotherms from the experimental data to determine the energy requirements for chili pepper processing.

Four widely used models were selected for fitting the experimental data of adsorption and desorption isotherms of red chili. All are two and three parameters equations and the parameters of the models were estimated by using Statistical Package for Social Science (SPSS 16.0) and SigmaPlot 11.0 software. The models selected were presented in Table 1.

Table 1 Mathematical models used to describe the sorption isotherms of red chili

Model	Equation	Reference
Henderson	$1-a_w = \exp(aX_e^b)$	(Henderson, 1952)
Oswin	$X_e = a(\frac{a_w}{1-a_w})^b$	(Oswin, 1946)
GAB	$X_e = \frac{abca_w}{(1-ba_w)(1+(c-1)ba_w)}$	(Van den Berg, 1985)
Modified Halsey	$X_e = a+b(\frac{a_w}{1-ba_w})$	(Iglesias and Chirife, 1981)

Where, *a*, *b*, and *c* were constants of mathematical models; *a* also described the monolayer moisture content (dry basis) and *c* was the energy term in GAB's equation where both can be explained theoretically; X_e was the equilibrium moisture content (dry basis).

The net isosteric heat of sorption or enthalpy of sorption (q_{st}) is defined as the difference between the total heat of sorption (Q_{st}) and the heat of vaporization of water. It can be determined from Equation (1), which is derived from the Clausius-Claperyon's equation.

$$\left[\frac{\partial(\ln(a_w))}{\partial(\frac{1}{T})}\right]_{X_e} = \frac{Q_{sr}-\lambda}{R} = -\frac{q_{st}}{R} \tag{1}$$

Isosteric heat of sorption is a differential molar quantity derived from the isotherm temperature dependence and its application requires the measurement of sorption isotherms at two or more temperatures (Mclaughlin and Magee, 1998).

At three different temperatures (T_1 and T_2) and constant equilibrium moisture content, equation of a straight line can be obtained as Equation (2), where the slope was equal to q_{st}/R.

$$\ln\left[\frac{a_{w2}}{a_{w1}}\right]_{X_e} = -\frac{q_{st}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \tag{2}$$

An empirical exponential relationship between the isosteric heat of sorption and moisture content, as proposed by Tsami (1991) can be fitted to these quantities, according to Equation (3):

$$q_{st} = q_o \exp\left(\frac{X_e}{X_o}\right) \tag{3}$$

where, a_{w2} and a_{w1} were water activities at T_1 and T_2, respectively; q_{st} was the net isosteric heat of sorption, kJ/kg; R was the universal gas constant, kJ/(kg K)$^{-1}$; X_e was equilibrium moisture content; X_o and q_o were constants to be determined.

3 Materials and methods

3.1 Materials

Fresh chili (*Capsicum annum* L.), variety of “Mareko Fana”, was harvested from the field of local farmers around Bure, North West of Ethiopia. Fully ripened chilies of a purely red color were used. Samples were initially sorted for maturity level, color, and size. Chili free of mechanical damage and disease were washed and surface air dried. Samples were kept in cold storage at 5℃ and 80%-90% relative humidity until usage for five days. Fresh and dried chili peppers were used in desorption and adsorption experiments, respectively. A cabinet dryer with relative humidity and temperature controller were used. Samples for both desorption and adsorption process were weighed and put in an aerobic dish with an internal diameter of (24.0±0.1) cm and height of (25.2± 0.1) cm.

The average initial moisture content of chilies was 3.76 kg of water per kg of dry chili. Chilies with an average length of 8.5 cm and diameter of 0.65 cm were used. Throughout this experiment, an electronic weighing balance with a precision of ±0.0001 g was used to measure the weight loss of samples. Duplicate measurements were taken for each case. Samples used in adsorption isotherms were cut into 1 mm length and dried in an oven dryer at 105℃ for 24 h.

3.2 Experimental procedure and methodology

Data for desorption and adsorption isotherms were determined by the standard static, gravimetric method (Spiess and Wolf, 1983; Labuza, 1984) at temperatures of 30℃, 50℃, and 70℃. Duplicate samples each of 3 g (±0.0001 g) for desorption and 0.3 g (±0.0001 g) for adsorption were weighed into glass bottles and placed in 5 little anaerobic jar containing saturated salt solutions prepared as recommended by Labuza (1984) and the COST 90 project (Wolf et al., 1985). The saturated salt solutions used and their corresponding water activities at different temperatures were determined using Equation (4) for the given constants. For all test atmospheres with relative humidity greater than 50%, a small bottle containing about 5 mL of toluene was placed in each anaerobic jar to prevent fungal activity (Labuza, 1984; Wolf et al., 1985; Rapusa et al., 1993). Anaerobic jars were kept in temperature and relative humidity controlled drying cabinet which were set at 30℃, 50℃ and 70℃ and relative humidity between 10%-90%. The cabinet temperatures were controlled at a temperature accuracy of ±1℃. Two replications of the same experiment were carried out. Samples were equilibrated for three weeks or less to reach a constant weight (0±0.0001 g). The equilibrium moisture content was determined using an oven dryer at 105℃ for 24 h.

Table 2 shows the type of saturated salts used during experimental data collection. Water activity is a function of temperature and this relationship generally can be described by the following empirical equation:

$$\ln a_w = \frac{k_1}{T} - k_2 \tag{4}$$

where, k_1 and k_2 were constants, different for each salt; T was absolute temperature, K.

Table 2 Experimentally determined values of k_1 and k_2 for various salt solutions

Salt solutions	k_1	k_2	Mean relative error/%
LiCl	10.8233	2.2193	0.2040
CH_3COOK	333.9001	2.6185	1.1647
K_2CO_3	503.7970	2.3320	0.0046
$Mg(NO_3)_2$	84.6993	2.2670	0.3413
NaCl	23.1092	0.3607	0.1631
KCl	157.0587	0.6967	0.0289
KNO_3	192.0886	0.7183	0.6177

Table 3 gave the values for a range of salts based on experimental data previously published by Labuza et al. (1985).

In this research work water activities of the salt solutions were not determined experimentally. The required data of water activities were calculated using the values given in Table 2 and Equation (4) at temperatures of 30℃, 50℃ and 70℃ (Table 3).

Table 3 Relative humidity (decimal) of the salt solution calculated using Equation (1) and Table 2 at temperatures of 30℃, 50℃ and 70℃

Salt solutions	Temperature /℃		
	30	50	70
LiCl	0.1130	0.1130	0.1130
CH_3COOK	0.2194	0.2049	0.1929
K_2CO_3	0.4320	0.4320	0.4320
$Mg(NO_3)_2$	0.5116	0.4616	0.4215
NaCl	0.7524	0.7489	0.7458
KCl	0.8364	0.8100	0.7874
KNO_3	0.9188	0.8835	0.8534

3.3 Comparison methods

The suitability of the models was evaluated in terms of statistical errors given below (Sun and woods, 1994; Rehman, 1998):

$$MBE = \sum_{1}^{n}\left(\frac{X_e - X_p}{n}\right) \tag{5}$$

$$MRD = \frac{1}{n} abs\left(\frac{X_e - X_p}{X_p}\right) \tag{6}$$

$$RMSE = \sqrt{n\sum_{1}^{n}\left[\frac{(X_e - X_p)^2}{n}\right]} \tag{7}$$

where, X_p was predicted equilibrium moisture content (dry basis) calculated from different models; n was the number of data points. MBE was a mean biased error and represents the systematic error. A positive value shows over estimation and a negative value indicates under estimation. The value of root mean square error (RMSE) shows the fitting ability of the modeling related to the number of data points. The goodness of fit of the model was described by mean relative deviation (MRD). A model is considered as good if coefficient of determination (R^2) is high, and all error terms are minimum.

4 Results and discussion

In this work, four commonly used models, GAB's, Modified Halsey's, Henderson's and Oswin's models, were applied. The results were summarized below from Table 4 to Table 7. Table 4 and 5 showed the mathematical models applied and statistical data for the selection of the best model that fits experimental data at temperatures of 30℃, 50℃ and 70℃ for desorption and adsorption isotherms, respectively. The data were generated using none linear regression method with SPSS 16.0 software. Each of the statistical data shown in the Table 4 to 7 was the average values determined at these three temperatures.

In Table 4, all four selected models were evaluated statistically by calculating mean bias errors (MBE), mean relative deviations (MRD), root mean square errors (RMSE) and coefficient of determinant (R^2). The average grades of the three statistical errors were calculated for each model. In the case of GAB's model the average rankings of 1.3 and 1.0 were obtained for desorption and adsorption isotherms, respectively. These results showed high coefficient of determination and the lowest average grade of statistical errors indicating that the GAB model fits well to the experimental isotherm data. Therefore, within the range of 0.1-0.9 water activities, GAB's model was the best equation that fits experimental data which was in agreement with the results obtained by other researchers. At values of a_w > 0.9 there was a deviation between the predicted values of the GAB model and the experimental values.

Modified Halsey's equation was found to be the next best model for the whole range of water activity. The worst results were obtained from the two parameter Henderson's equation for both desorption and adsorption isotherms.

Table 4 Estimated errors of the data determined from various models for desorption isotherms of red chili

Model	MBE	MRD	RMSE	G_{ave}	R^2
GAB	0.0465^1	0.0595^2	2.86^1	1.3	99.1
Henderson	0.3180^4	0.1618^4	5.95^4	4.0	95.1
Modified Halsey	0.0561^2	0.0540^1	3.16^2	1.7	99.1
Oswin	0.1878^3	0.0903^3	4.22^3	3.0	98.1

Note: superscripts 1, 2, 3 and 4 indicated rankings of statistical errors of each model. G_{ave} was average grade.

Table 5 Estimated errors of the data determined from various models for adsorption isotherms of red chili

Model	MBE	MRD	RMSE	G_{ave}	R^2
GAB	0.0134^1	0.0626^1	0.9921^1	1.0	99.7
Henderson	0.4451^4	0.2215^4	3.9063^4	4.0	96.9
Modified Halsey	0.0461^2	0.0745^2	1.3565^2	2.0	99.6
Oswin	0.1875^3	0.1145^3	2.1764^3	3.0	99.0

Note: superscripts 1, 2, 3 and 4 indicated rankings of statistical errors of each model.

Table 6 and 7 showed the models used and their coefficients determined using non-linear regression method with SPSS 16.0 software for desorption and adsorption isotherms, respectively. The non-linear method may not always provide the best results for all models because the results do not always converge to a unique solution. Schuchmann et al. (1990) reported that unique solutions were not always guaranteed in non-linear regressions, especially when three or more parameters were involved in the model function like the GAB model. For example, constant *b*, for adsorption of red chili at 70℃ estimated by the method was greater than 1.0 indicating some unexpected errors involved with the experimental data. In order to avoid such problems encountered when applying the non-linear regression method, Schuchmann et al.(1990) recommended repeating the regression procedure with several different initial values of the parameters and different upper and lower limits on their magnitude, until stable and reproducible values are reached.

For most selected models, these constants were only numbers without theoretical backgrounds. But in the GAB equation it can be explained theoretically and this is one of the advantages obtained from this model. Constant *a* was the moisture content of monolayer corresponding to formation of a monomolecular layer on the internal surface of the samples; *c* is the Guggenheim constant related to the energy of sorption of the adsorbed monolayer water molecules; and *b* is a factor corresponding to properties of the multilayer molecules with respect to the bulk liquid.

Table 6 and 7 showed the values of constant *c* of "Mareko Fana" were within the ranges ($c > 5.67$) as recommended by other researchers. On the contrary, except for some points, the values of the parameter *b* (a factor related to interaction energies between multilayer molecules with respect to bulk liquid) were within the reported limits for foods and biopolymer products (Bell and Labuza, 2000). To guarantee a relatively good description of the sigmoidal isotherms and to assure calculated monolayer moisture content, *a*, within ±15.5% from the true monolayer capacity (Lewicki, 1997) stated that the constants should be in the ranges $0.24 \le b \le 1$ and $5.67 \le c \le \infty$.

Table 6 Mathematical models and their coefficients determined using SPSS 16.0 software for desorption isotherms

Coefficients	Models			
	GAB	Henderson	Modified Halsey	Oswin
	30℃			
a	0.0920	1.1210	1.6150	0.1480
b	0.8740	5.4280	0.0330	0.4490
c	24.2530			
	50℃			
a	0.0770	1.4800	1.6850	0.1480
b	0.9030	10.6540	0.0200	0.4490
c	43.1680			
	70℃			
a	0.0570	1.3090	1.4680	0.1250
b	0.9660	9.5500	0.0300	0.5130
c	100.0970			

Table 7 Mathematical models and their coefficients determined using SPSS 16.0 software for adsorption isotherms

Coefficients	Models			
	GAB	Henderson	Modified Halsey	Oswin
	30℃			
a	0.0350	0.6860	1.1840	0.0630
b	0.9840	5.1330	0.0270	0.7300
c	22.6490			
	50℃			
a	0.0340	1.0590	1.2810	0.0650
b	0.9720	11.8040	0.0190	0.6050
c	13.3200			
	70℃			
a	0.0360	0.8110	1.0660	0.0680
b	1.0140	6.0490	0.0380	0.7450
c	8.7620			

The monolayer moisture content of the samples in this work was within the range of 0.057 g to 0.097 g water/g solid. The value of the monolayer moisture content, *a*, indicates the amount of water that is strongly adsorbed to specific sites at the food surface, and this is a value that must be reached in order to assure food stability. Below this value, rates of deteriorative reactions are minimal (Choudhurya, et al., 2011).

In this work, the monolayer moisture content (Table 6) decreased with increase in temperature, but Table 7 does not follow this trend. Such a decrease with temperature may also be attributed to the fact that the binding of water molecules become less stable at increased temperature and break away from water binding sites of the sample. But, there is no general agreement among scientists about effects of temperature on monolayer values. Some authors have obtained similar results for different foods in which it was observed that the monolayer moisture content is nearly constant and independent of temperature, (Gabas, et al., 2007). Whereas other authors have observed that constant *a* depends on the temperature (Simal et al., 2007).

The curve shows desorption isotherms at temperatures of 30℃, 50℃ and 70℃ (Figure 1). The graphs were drawn, using equilibrium moisture content (%, dry basis) as a function of water activity (decimal) using SigmaPlot 11.0 software. The sorption isotherms of the samples exhibit typical sigmoid-shaped curves which belong to Type II isotherm as classified by Brunauer et al. (1938), and Bell and Labuza (2000). Equilibrium moisture content increased slowly with increasing water activity. The equilibrium moisture content of the samples increased with the rise in a_w when temperature was kept constant, and decreased with the increase in temperature at constant a_w. This may be attributed to a change in the total number of active sites for water binding caused by temperature-induced physical changes in the sample (Moreira et al., 2008). The mobility of water molecules also increased at increased temperatures making them to become less stable and to break away from water binding site, thus decreasing the equilibrium moisture content of the films at the same a_w (Rhim and Lee, 2009).

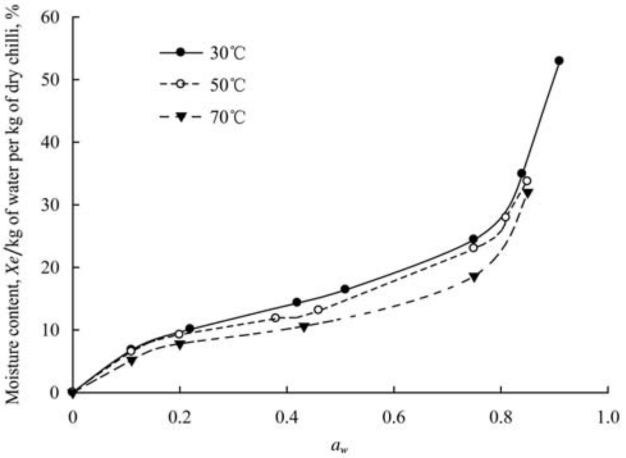

Figure 1 Plots of equilibrium moisture content as functions of water activity at temperatures of 30℃, 50℃ and 70℃ for desorption isotherms

Figure 2, 3 and 4 showed plots of experimental and predicted equilibrium moisture content as a function of water activity for desorption and adsorption isotherms at temperatures of 30℃, 50℃ and 70℃, respectively. At each temperature, the predicted equilibrium moisture contents were calculated using GAB"s model. The graphs were drawn using SigmaPlot 11 software. On each graph, experimental and predicted equilibrium moisture contents were compared for desorption and adsorption isotherms at all temperatures. In all cases the data predicted by GAB's equation were better approached by experimentally determined equilibrium moisture content between the ranges of 0.1-0.9 water activities.

In addition to these, the graphs showed the hysteresis of desorption and adsorption isotherms. It can be seen that at all temperatures and constant water activity, the equilibrium moisture content of desorption isotherms was

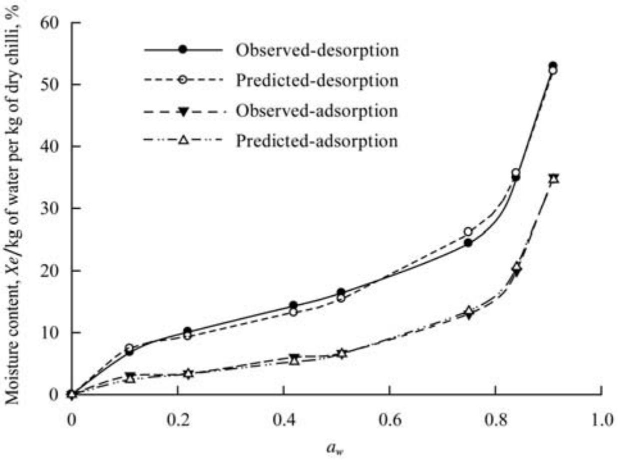

Figure 2 Experimental and predicted desorption and adsorption isotherms using GAB equation for red chilli at 30℃

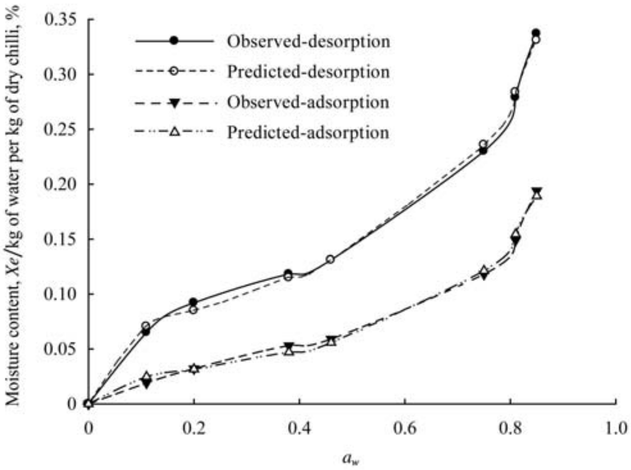

Figure 3 Experimental and predicted desorption and adsorption isotherms using GAB equation for red chili at 50℃

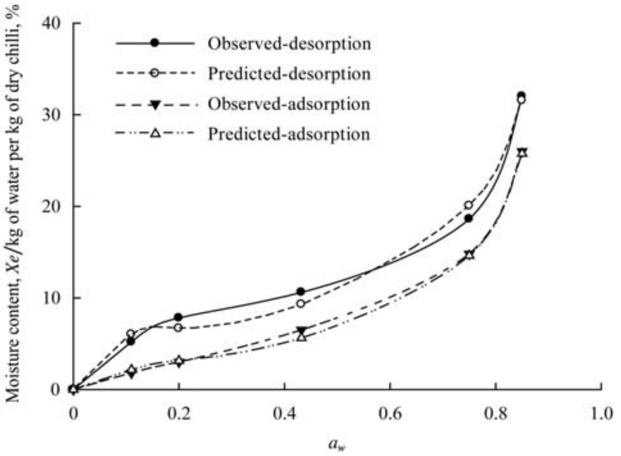

Figure 4 Experimental and predicted desorption and adsorption isotherms using GAB equation for red chili at 70℃

greater than adsorption isotherms. This showed that chili pepper cannot absorb the same quantity of water vapor that was released during desorption process due to deformation and other physico-chemical changes of the food material.

Figure 5 showed a plot of natural logarithm of water activity as a function of the inverse of the three absolute temperatures for selected equilibrium moisture contents between 0.1-0.4 kg of water per kg of dry chili. For each case water activities were determined using GAB equation. At constant equilibrium moisture content, slopes and intercepts were determined using Equation (2) for three water activities and three temperatures from which the net isosteric heat of sorption was determined. From the graph it can be seen that as the equilibrium moisture content increases, the slopes decreases resulting in a decrease of net isosteric heat of sorption isotherms.

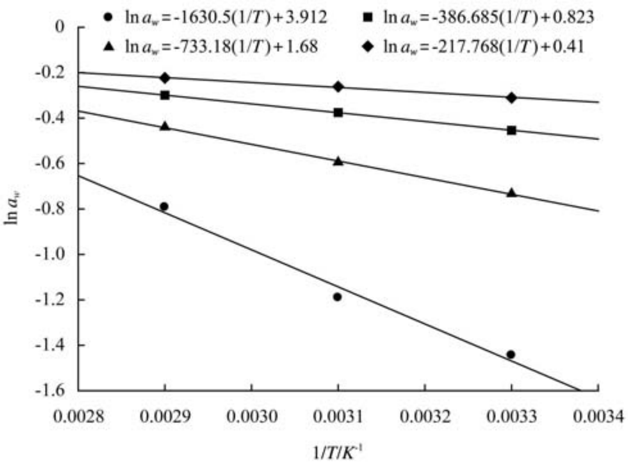

Figure 5 Plots of natural logarithms of water activity as a function of the inverse of absolute temperatures for selected equilibrium moisture contents

Figure 6 showed a plot of the net isosteric heat of sorption as a function of equilibrium moisture content. The graph was draw using paired temperatures of 30℃, 50℃ and 70℃ were used. The net isosteric heats of sorption were taken from the slopes of Figure 5 multiplied by the universal gas constant (*R*). The graph was drawn using SigmaPlot 11.0 software, but it can also be described mathematically with help of Equation (3). After determination of constants of Equation (3), q_o and X_o, with SPSS 16.0 software, Equation (8) were obtained below. From this equation it can be seen that as the moisture content increases the net isosteric heat of sorption decreases exponentially.

$$q_{st} = 3189\exp\left(\frac{-X_e}{0.069}\right) \quad (R^2 = 99.7) \tag{8}$$

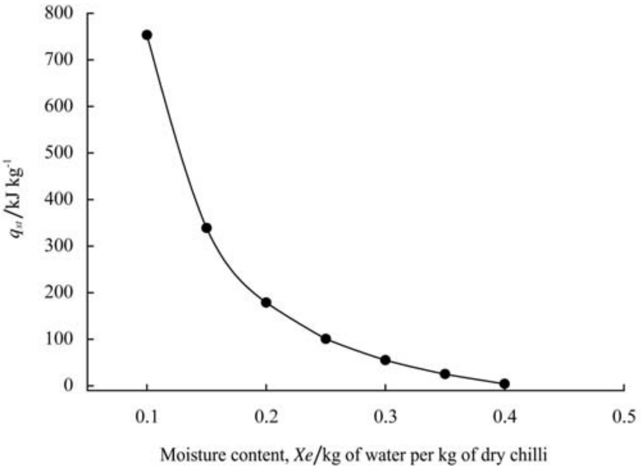

Figure 6 Plot of the net isosteric heat of sorption (q_{st}) as a function of equilibrium moisture content

The elevated net heats of sorption of water at low moisture contents are an indication of strong water-food interactions in the fruit. As the moisture content increases, the available sites for sorption of water reduced, resulting in lower values of q_{st} (Telis et al., 2000). This is in agreement with the work of (Telis-Romero et al., 2005) for mangoes. According to Wang and Brennan (1991), the decrease in the isosteric heat with higher amounts of sorbed water can be quantitatively explained by considering that initially sorption occurs on the most active available sites, giving rise to high interaction energy. As these sites become occupied, sorption occurs on the less active ones, resulting in lower heats of sorption. For very low moisture contents, the values q_{st}

are highly negative, which means that sorption is a compulsive reaction. According to (Tsami, 1991), the more negative the value of q_{st}, the higher the degree of binding of water on the food surface.

5 Conclusion and recommendation

For the evaluation of parameters of the selected models, a non-linear regression method was applied. Calculated values of constants *c* and *b* of GAB's model were within the ranges (*c*>5.67) and between 0.87-1.0, respectively and both were within the reported limits for food products. The values of monolayer moisture content, *a*, are between 0.057 g and 0.097 g water/g solid and this result was within the reported range. GAB's model fits the best to the experimental isotherm data since average grades of 1.3 and 1.0 obtained were the minimum values of statistical errors. Modified Halsey's equation was found to be the next best model for the whole range of water activity. The worst results were obtained from the two parameter Henderson's equation.

"Mareko Fana", an Ethiopian variety of chili pepper showed hysteresis at all temperatures. In this work the net isosteric heat of sorption of isotherms of chili pepper were determined from the experimental data. The result showed that as the equilibrium moisture content decreased the net isosteric heat of sorption increased which was an indication of availability of strong water-food interactions in the fruit. As the moisture content increases, the available sites for sorption of water reduced, resulting in lower values of q_{st}. Based on these results, the energy requirements of drying processes for chilli pepper and the design of a dryer can be realized.

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