Effect of maturity on the moisture sorption isotherm of chili pepper (Mareko Fana variety)

Eshetu Getahun a,b,c, Nigus Gabbiye c, Mulugeta A. Delele c,⁎, Solomon W. Fanta c, Mekonnen Gebreslasie Gebrehiwot b, Maarten Vanierschot b

a Bahir Dar Energy Center, Bahir Dar Technology Institute, Bahir Dar University, Ethiopia
b KU Leuven, Mechanical Engineering Technology Cluster TC, Group T Leuven Campus, A. Veesiastraat 13, B-3000 Leuven, Belgium
c Faculty of Chemical and Food Engineering, Bahir Dar Technology Institute, Bahir Dar University, Ethiopia

ARTICLE INFO

Keywords:
Food science
Food technology
Glycerol water mixture
Chili
Mareko Fana
Sorption model
Heat of sorption

ABSTRACT

The moisture sorption isotherm at three maturity levels of the Mareko Fana chili pepper variety (red, brown and green) has been studied in this paper. The sorption isotherm was determined based on the standard static gravimetric method using a glycerol-water mixture in a relative humidity range of 10–92% at three temperature levels and nonlinear regression analysis was used to select suitable sorption models. The Clasius - Clapeyron equation was implemented to determine the isosteric heat of sorption of the chili pepper using the experimental equilibrium moisture content at different sorption temperature levels. The results showed that the GAB model was well fitted for green chili pepper, while the OSWIN model described well the brown and red chili variety. There was a difference in net isosteric heat between the adsorption and desorption isotherm of chili pepper maturity. For green chili, the maximum value of the net isosteric heat was 18 kJ mol⁻¹ and 20 kJ mol⁻¹ for adsorption and desorption isotherms, respectively and it decreased exponentially as moisture content increased. The desorption heat was higher than the adsorption heat for each maturity of chili pepper which indicated the existence of hysteresis in the sorption process. In comparison to literature data reported for different chili varieties, Mareko Fana has a lower heat of sorption and monolayer moisture content.

1. Introduction

Chili pepper is largely harvested all over the world except on Antarctica and is ranked as the world's second most valuable condiment vegetable next to tomatoes (Gobie, 2019). Chili peppers are most widely cultivated and consumed in different countries, such as Ethiopia, India, Myanmar, China, Peru, Thailand, Pakistan, Bangladesh, Indonesia, Mexico and Sri Lanka (Peter, 2006). Chili peppers (Capsicum annuum L.) are substantially used as curry and cash crop throughout the world which have a huge potential on national and international markets. Red chili is an important source of digestible carbohydrates, minerals, antioxidants, fibers, and vitamins, particularly it is rich in vitamins A, C and E (Demissie et al., 2010; Hailu and Derbew, 2015). The green, brown and fully dried and grounded chili peppers are important ingredients in the preparation of stew and curry due to their color, flavor and pungency attributes. It is indispensable in most kitchens of societies, especially in Ethiopian ones. Besides, several studies indicate the wide range of medicinal applications of chili peppers (Giuffrida et al., 2014; Popovich et al., 2014; A Omolo, 2014; Olaes et al., 2020). There are numerous kinds of species cultivated and consumed as food, to serve as medicinal application or used as industrial ingredients worldwide. In Ethiopia, the species that are commonly harvested are Capsicum annuum L. and Capsicum frutescens L. (Samira et al., 2013). Mareko Fana and Bako Local (both belonging to Capsicum annuum L.) are the major cultivars amongst others which have been developed through research (Samira et al., 2013). Mareko Fana chili variety is a conical type of fruit that matures to a dark red color and has a high extractable color intensity. Bako Local has a lengthened fruit shape and becomes red in the mature state.

Production of chili has been increased from year to year in Ethiopia. According to the central statistics agency (CSA), 453,608.8 ha of land was used in Ethiopia with an annual production rate of over 18 million quintals and amongst these productions, red chili accounted for about 70.93% (CSA, 2016). Moreover, according to the FAOSTAT (2017) report, the estimated production of peppers in Ethiopia was 64,041 tonnes from 10,000 ha of land for the green form and 306,703 tons of dried pepper from an area of 162,849 ha (Food and Agriculture...
Organization of the United Nations, 2017). However, post-harvest losses of chili peppers are significantly high just like for other vegetables and fruits in Ethiopia. Drying is a primary and suitable preservation technique of chili products to minimize mold development before storage. Molds are the main cause of quality deterioration of chili peppers (Calado et al., 2014).

Full understanding of the behavior of the moisture sorption isotherm of chili pepper is important information for the design and optimization of the drying process, packaging, and storage of the product and to control moisture migration of the products (Kaymak-Ertekin and Sultanoglu, 2001; Singh and Prasad, 2015; Aviara, 2020). Different chili pepper varieties throughout the world have been described using different sorption isotherm models (Table 1). In this aspect, understanding the sorption characteristics of new varieties, like the Mareko Fana species, is very essential to determine the drying characteristics and energy requirement and to identify the optimum drying parameters such as temperature and relative humidity to design the most optimal chili dryer. To maintain the required quality of dried chili, its drying, packaging, and storage should be conducted at optimal conditions. The important parameters such as color, texture, drying rate, storage life, and structure of a dried chili pepper also depend on the sorption characteristics (Mehta and Singh, 2006).

Chili peppers are harvested at different maturity levels (green, brown, and red). Therefore, it is important to know the sorption isotherm behaviors at different maturity levels for proper drying, packaging, and storage of the chili peppers. To the authors’ knowledge, there was no published information on the sorption characteristics of Mareko Fana chili pepper variety based on the maturity levels. This information is important to identify the problems that are associated with the drying and storage of this product and to fulfill the quality standards of the international market. Therefore, the objective of this study was to investigate the adsorption and desorption isotherm characteristics of Ethiopian chili pepper, more specific the Mareko Fana variety, based on its maturity level using a wide range of temperature (30 °C–65 °C) and relative humidity ranges (10–92%), to determine the sorption heat and to recommend the best sorption isotherm model.

2. Materials and methods

2.1. Materials

Chili peppers (Mareko Fana variety, Figure 1) at three maturity levels (green, brown, and red color), were obtained from the Worera province in the Amhara region, Ethiopia. The colors of the chili pepper based on the maturity level were measured using a spectrophotometer (KONICA MINOLTA, CM-600d, Japan). The stage of maturity depends on the harvesting indices of the chili pepper, resulting in a green (25%), brown (50%) or red (100%) color (Noichinda et al., 2016). The average chili pepper surface color values for the freshly harvested chili pepper used in this study was: green (L* = 38, a* = 2.5 & b* = 23.3), brown (L* = 36.6, a* = 3.8 & b* = 9.5) and red (L* = 26, a* = 4.6 & b* = 2.1). Freshly harvested chili samples were collected from July to December 2019 during the regular harvesting season. Samples were kept in cold storage at 4 °C with 80–95% relative humidity until usage. The safe storage moisture content of chili pepper ranges from 10% to 13% on a wet base (Sahar et al., 2015). Freshly harvested chili pepper was used in the desorption experiments while dried samples (with a moisture content of 12% on a wet base) using a hot air oven at 60 °C for 24 h were used in the adsorption experiments. This drying temperature is below the maximum allowable drying temperature of chili pepper (65 °C), so that the

![Figure 1](image_url)

**Figure 1.** Maturity levels of chili peppers used in the experiment. a) Green pepper, b) Brown pepper c) Red pepper.

| Isotherm | Chili pepper varieties | Best model | Sorption type | Monolayer moisture | Country | Reference |
|----------|------------------------|------------|---------------|-------------------|---------|-----------|
| Desorption | Lamuyo | BET | type II | 0.072-0.100 | Spain | Vega-Gálvez et al., 2007 |
|           | Black peppercorns | GAB | type III | 0.030-0.050 | Sri Lanka | Yoganدرajab et al., 2015 |
|           | Sweet peppers | OSWIN | type II | 0.030-0.040 | India | Sahu and Tiwari, 2007 |
|           | Polyester | Modified OSWIN | type II | 0.190 | India | Kaleemullah and Kailappan, 2004 |
|           | Bursa | Halsey | type II | 0.040–0.101 | Turkey | Kaymak-Ertekin and Sultanoglu, 2001 |
|           | Aji | Andrade | type II | 0.270 | Brazil | Andrade et al., 2017 |
|           | Bico | GAB | type II | 0.060–0.080 | Brazil | Santos et al., 2015 |
| Adsorption | Lamuyo | BET | type II | 0.070–0.10 | Spain | Vega-Gálvez et al., 2007 |
|           | Black peppercorns | GAB, Peleg | type III | 0.040–0.050 | Sri Lanka | Yoganدرajab et al., 2015 |
|           | Sweet peppers | OSWIN, Halsey | type II | 0.100–0.110 | India | Sahu and Tiwari, 2007 |
|           | Polyester | Modified Halsey | type II | 0.290 | India | Kaleemullah and Kailappan, 2004 |
|           | Bursa | Halsey | type II | 0.050–0.080 | Turkey | Kaymak-Ertekin and Sultanoglu, 2001 |
|           | CH-1 | modified Oswin | type II | 0.210 | India | Mehta and Singh, 2006 |
The adsorption and desorption experimental set up is shown in Figure 2. The sorption experimental set up consists of an electrically heated hot air oven (bottom heated) with the temperature and airflow controlled and seven glass jars were used to hold the glycerol-water mixture to maintain the desired relative humidity inside the jar. For both adsorption and desorption experiments, sample chili peppers were placed above the glycerol-water mixture inside the jar.

The adsorption and desorption isotherms were determined by the standard static, gravimetric method using a glycerol water mixture solution prepared as recommended in Forney and Brandl (1992) at temperatures of 30 °C, 55 °C and 65 °C. Different glycerol-water mixture ratios were used to maintain the relative humidity (RH) in the range of 10–92 % at seven levels as shown in Table 2. The jar containing a glycerol-water mixture and chili sample was placed inside the electrical hot air oven. The temperature of the glycerol-water mixture has an insignificant effect on the equilibrium relative humidity and thus all mixtures were prepared at 30 °C. In this experiment, by taking into account the biological variability of the individual chili, maximum effort was put to get a more or less constant sample weight. The duplicate chili pepper sample weights were 2.5 ± 0.24 g for the adsorption and 16.5 ± 0.35 g for the desorption experiments.

The equilibrium moisture contents (EMC) based on the maturity levels of the chili pepper on a dry base, were determined using Eq. (1):

\[ M_e = \frac{M_{eq} - M_{dry}}{M_{dry}} \times 100 \]  

where \( M_e \) is the EMC on a dry basis, \( M_{eq} \) is the weight of chili after achieving equilibrium, and \( M_{dry} \) is the weight of chili after attaining equilibrium moisture content in the oven at 60 °C for 24 h (Hellevang, 1995).

### 2.3. Sorption isotherm modeling

The criteria used to choose the most suitable sorption model were the degree of fit to the experimental data and the easiness of the model. Lomauro et al. (1985), Boquet et al. (1978) and Yan et al. (2008) reported that the vegetable sorption isotherms are mostly described by the GAB model followed by the Oswin and Halsey models. Thus, in this study, four sorption isotherm models were tested, as shown in Table 3, where, \( K, C \) and \( n \) are model constants, \( a_w \) is the water activity, \( M_e \) is the equilibrium moisture content and \( M_a \) is the monolayer moisture content (both on a dry basis).

### 2.4. Heat of sorption

The isosteric heat of sorption is defined as a measure of solid-water binding and interaction energy of food products like chili peppers (Fasina et al., 1997). The net isosteric heat of sorption can be used to analyze the presence of binding energy or the availability of polar sites to

### Table 2. The water activity at different glycerol-water mixture ratios and temperatures.

| Glycerol-water ratio | Specific gravity | Temperature (°C) |
|----------------------|-----------------|-----------------|
|                      |                 | 30              | 55              | 65              |
| 100:1                | 1.262           | 0.100           | 0.110           | 0.115           |
| 25:1                 | 1.248           | 0.220           | 0.230           | 0.236           |
| 6:1                  | 1.231           | 0.350           | 0.360           | 0.367           |
| 10:3                 | 1.197           | 0.560           | 0.570           | 0.574           |
| 11:8                 | 1.159           | 0.720           | 0.730           | 0.738           |
| 2:3                  | 1.109           | 0.860           | 0.870           | 0.875           |
| 3:10                 | 1.077           | 0.920           | 0.930           | 0.934           |

### Table 3. Sorption models applied to the chili pepper experimental data.

| Model name          | Model equation | Reference       |
|---------------------|----------------|-----------------|
| GAB                 | \[ M_e = \frac{M_{eq} - M_{dry}}{M_{dry}} \times 100 \] | (Van den Berg, 1985) |
| Oswin               | \[ M_e = C \times \frac{a_w}{1 - a_w} \] | (Oswin, 1946) |
| Modified Halsey     | \[ M_e = M_a + K \left( \frac{a_w}{1 - a_w} \right) \] | (Halsey, 1948) |
| BET                 | \[ M_e = \frac{M_{eq} - C \times a_w}{(1 - a_w) + (C - 1) \times a_w} \] | (Brunauer et al., 1938) |

Figure 2. Chili sorption isotherm experimental set up: 1- Temperature and air speed controller, 2- suction air fan, 3- chili sample for sorption analysis placed above glycerol-water mixture, 4- heat resistant sealed glass jar to hold glycerol-water mixture to maintain constant relative humidity, 5- oven opening gate, 6- oven tray.
water vapor in which sorption takes place and it is obtained from the Clasius-Clapeyron equation Eq. (2) (Moreira et al., 2008; Tsami, 1991).

\[
\frac{\partial \ln(a_w)}{\partial (1/T)} = \frac{Q_{sr} - \Delta H_{vap}}{R} - q_s \frac{1}{R}
\]  

(2)

By simple re-arrangement the net isosteric heat of sorption of chili pepper was given by Eq. (3):

\[
q_s = - R \frac{\partial \ln(a_w)}{\partial (1/T)}
\]

(3)

where \( a_w \) is the water activity, \( q_s \) is the net isosteric heat of sorption (kJ·mol\(^{-1}\)), \( Q_{sr} \) is the isosteric heat of sorption (kJ·mol\(^{-1}\)), \( H_{vap} \) is the heat of vaporization (kJ·mol\(^{-1}\) water), \( R \) the universal gas constant (kJ·mol\(^{-1}\) K\(^{-1}\)) and \( T \) is the absolute temperature (K). The sorption isotherm was plotted as ln (\( a_w \)) against 1/\( T \) for a specific moisture content of a material and the slope of the line was equal to \( -q_s/R \), the slope was used to determine \( q_s \). Tsami (1991) proposed an empirical-exponential model for \( q_s \) determination using Eq. (4):

\[
q_s = q_o \exp \left( \frac{-M_i}{M_o} \right)
\]

(4)

where \( q_o \) is the sorption heat of the first water molecule in chili pepper (kJ·mol\(^{-1}\)).

2.5. Data analysis

The drying rate constants and coefficients of all chili pepper sorption models were estimated using non-linear least square regression analysis, which was performed using the SPSS (Statistical Package for Social Science), Version 20 software package. The selection of the model with the best fit to the experimental data was conducted by comparing the coefficient of determination \( R^2 \), the chi-square value \( \chi^2 \) and the root mean square value (RMSE). The model with the best fit has the highest coefficient of determination \( R^2 \), and lowest root mean square error (RMSE), and chi-square \( \chi^2 \) values (Gbaha et al., 2007; Akpinar and Bicer, 2008), which are determined using Eq. (5), Eq. (6) and Eq. (7) respectively.

\[
R^2 = \frac{\sum_{i=1}^{N} (M_{exp,i} - \bar{M}_{exp})^2}{\sum_{i=1}^{N} (M_{exp,i} - \bar{M}_{pre})^2}
\]

(5)

\[
\text{RMSE} = \sqrt{\frac{\sum_{i=1}^{N} (M_{exp,i} - M_{pre,i})^2}{N}}
\]

(6)

\[
\chi^2 = \frac{\sum_{i=1}^{N} (M_{exp,i} - M_{pre,i})^2}{N - z}
\]

(7)

Figure 3. Equilibrium moisture content of chili based on maturity level at different temperatures in desorption isotherms (% of dry base): a) 30 °C, b) 55 °C c) 65 °C.
where $M_{\text{exp},i}$ and $M_{\text{pre},i}$ are experimental and predicted equilibrium moistures, respectively; $N$ is the number of samples; $z$ is the number of drying constants; $M_{\text{exp},i}$ and $M_{\text{pre},i}$ are the average values of experimental and predicted equilibrium moistures respectively.

3. Results and discussions

3.1. Effect of maturity on desorption and adsorption isotherms of chili peppers

The experimental equilibrium moisture content (EMC) of green, brown and red chili pepper at different water activities ($a_w$) and temperatures are presented in Figures 3 and 4 and these values represent the mean value of the replicates at each water activity and temperature. The standard deviations of the EMC of chili pepper at each experimental point were found in the range of 0.2–6.

Maturation indicates the fruit and vegetable physiological and metabolic changes that terminates with a maximum accumulation of dry matter and is characterized by biochemical, physical, morphological and physiological parameters, including moisture content, age and fruit colors (Dos Santos et al., 2020). It was observed that pre-mature chili pepper had a high moisture content and fully matured chili pepper had a low moisture content. Due to this physiological change of chili pepper during the maturation stage, the color value of chili pepper also

Figure 4. Equilibrium moisture content of chili pepper based on maturity level at different temperatures in adsorption isotherms at: a) 30 °C, b) 55 °C, c) 65 °C.

Figure 5. Hysteresis in desorption and adsorption isotherms of red chili pepper. a) Effect of temperature on red chili hysteresis, b) Red chili average hysteresis at 65 °C.
| Temperature (°C) | Chili Maturity | Model parameter | Model | GAB | OSWIN | BET | Modified Halsey |
|-----------------|----------------|-----------------|-------|-----|-------|-----|----------------|
|                 |                | Coefficients    |       |     |       |     |                |
| 30               | Green chili    | Mo              | 0.045 | 0.046 | 0.079 |
|                 |                | C               | 9.5376754.570 | 8.883 | -2159585.000 |
|                 |                | K               | 0.981 |       | 1.132 |
|                 |                | N               |       | 0.662 |       |
|                 |                | Comparison criteria |       |       |       |
|                 |                | R²              | 0.995 | 0.978 | 0.995 |
|                 |                | RMSE            | 1.747 | 5.89  | 1.747 |
|                 |                | χ²              | 1.747 | 5.89  | 1.747 |
| 55               | Green chili    | Mo              | 0.035 |       | 0.035 |
|                 |                | C               | 27.759 | 8.817 | 27.253 |
|                 |                | K               | 0.990 |       | 0.728 |
|                 |                | N               |       | 0.631 |       |
|                 |                | Comparison criteria |       |       |       |
|                 |                | R²              | 0.995 | 0.981 | 0.995 |
|                 |                | RMSE            | 1.747 | 5.130 | 1.747 |
|                 |                | χ²              | 4.373 | 25.85 | 4.387 |
| 65               | Green chili    | Mo              | 0.025 |       | 0.025 |
|                 |                | C               | 157863143.7 | 4.875 | 2144441441.000 |
|                 |                | K               | 0.977 |       | -56258822.960 |
|                 |                | N               |       | 0.655 |       |
|                 |                | Comparison criteria |       |       |       |
|                 |                | R²              | 0.996 | 0.982 | 0.996 |
|                 |                | RMSE            | 0.45  | 1.818 | 0.494 |
|                 |                | χ²              | 0.494 | 1.818 | 0.494 |
| 30               | Brown chili    | Mo              | 0.067 |       | 0.071 |
|                 |                | C               | 20.294 | 12.560 | 17.971 |
|                 |                | K               | 0.938 |       | -0.188 |
|                 |                | N               |       | 0.553 |       |
|                 |                | Comparison criteria |       |       |       |
|                 |                | R²              | 0.992 | 0.991 | 0.992 |
|                 |                | RMSE            | 3.026 | 2.744 | 3.026 |
|                 |                | χ²              | 3.026 | 2.744 | 3.026 |
| 55               | Brown chili    | Mo              | 0.064 |       | 0.069 |
|                 |                | C               | 6.854 | 10.492 | 5.766 |
|                 |                | K               | 0.902 |       | -0.386 |
|                 |                | N               |       | 0.542 |       |
|                 |                | Comparison criteria |       |       |       |
|                 |                | R²              | 0.988 | 0.990 | 0.988 |
|                 |                | RMSE            | 3.101 | 2.272 | 3.101 |
|                 |                | χ²              | 3.102 | 2.272 | 3.102 |
| 65               | Brown chili    | Mo              | 0.041 |       | 0.044 |
|                 |                | C               | 19.139 | 7.472 | 16.466 |
|                 |                | K               | 0.924 |       | -0.357 |
|                 |                | N               |       | 0.518 |       |
|                 |                | Comparison criteria |       |       |       |
|                 |                | R²              | 0.974 | 0.977 | 0.974 |
|                 |                | RMSE            | 3.765 | 2.755 | 3.765 |
|                 |                | χ²              | 3.768 | 2.756 | 3.765 |

(continued on next page)
significantly varied. These color variations during physiological maturation indicated that as maturity increased, $L^*$ (luminosity) and $b^*$ (yellowness) values decreased, however, the $a^*$ (redness) value increased. As can be observed in Figures 3 and 4, EMC was decreased as the maturity levels of chili pepper increased from green to red in the desorption-adsorption isotherm. Thus, green chili appeared to be more susceptible to water loss as compared to brown and red chili since immature chili pepper has a high moisture content to be lost. At the same water activity level, red chili has the highest equilibrium moisture content whereas green chili has the lowest EMC, while the EMC value of brown chili was found in between the red and green peppers. This study showed that EMC of chili pepper at all maturity levels in the temperature (Yan et al., 2008). The mean value of the hysteresis curve of the desorption-adsorption isotherms decreased as water activity increased. Reports revealed that when the water activity starts to increase, the dissolution of soluble components in the product increase and maximize the moisture contents (Dalgç et al., 2012). The equilibrium moisture content suddenly increased at water activities higher than 0.85 for all maturity levels of chili peppers in both desorption and adsorption isotherms. A similar report was found in the work of Kaymak-Ertekin and Sultanoglu (2001), for the Bursa chili pepper variety. As can be observed, the variation of equilibrium moisture content showed sigmoidal shape (Type II, as classified by Brunauer et al. (1938)) for all maturity stages of the chili (Figures 3 and 4). It is common to see such sigmoidal shape in most fruit and vegetable sorption curves.

### 3.2. Hysteresis on the desorption and adsorption isotherms

The sorption isotherms of chili pepper, Mareko Fana variety, indicated that the adsorption and desorption isotherms have hysteresis in which the equilibrium moisture content was higher at a particular water activity for the desorption curve compared to the adsorption curve (Figure 5). Various studies report the occurrence of hysteresis in chili pepper sorption isotherms. Hysteresis is detected in most chili pepper varieties and at all maturity stages (Al-Muhtaseb et al., 2002). This could be due to a change in porosity and structure/morphology in chili peppers during the adsorption and desorption process (Yogendrarajah et al., 2015). However, the nature of hysteresis is different from variety to variety and depends also on the stage of maturity. The hysteresis of the sorption isotherms of chili pepper was detected over the entire range of water activity due to some thermodynamically irreversible processes (Al-Muhtaseb et al., 2002). The effect of temperature on the hysteresis level is shown in Figure 5a. As can be seen in the figure, maximal hysteresis was obtained at water activities of about 0.59 and 0.92 and at temperatures of 55 °C and 30 °C, respectively. It was observed that the value of hysteresis was lower at 65 °C than 30 °C and 55 °C in the range of 0–0.7 water activity, probably due to the high elasticity capillary walls and hydrogen bonds between the chili pepper and water at high temperature (Yan et al., 2008). The mean value of the hysteresis curve of the chili pepper was depicted in between the adsorption and desorption curves as shown in Figure 5b. The value of hysteresis increased with water activity. Similar phenomena were reported for mango skin (Souza et al., 2015) and red chili (Kaleemullah and Kailappan, 2004).

### 3.3. Fitting of sorption models to the experimental sorption data

The sorption data of chili peppers were fitted to four well-known sorption isotherm models. The experimental results of the nonlinear regression model constant and comparison criteria are presented in Tables 4 and 5. The GAB and BET models were the best sorption models to fit experimental data for green chili with a high value of $R^2$ (0.976–0.996) and a low value of RMSE (0.450–3.401) for all sorption isotherms as shown in Tables 4 and 5. The OSWIN model was capable of...
Table 5. Estimated sorption model constants and comparison criteria of equilibrium moisture content for green, brown and red chili pepper in adsorption isotherm process.

| Temperature (°C) | Chili Maturity | Model parameter | Model | Comparison criteria |
|------------------|----------------|-----------------|-------|---------------------|
|                  |                | Coefficients    |       |                     |
|                  |                | Mo              |       |                     |
| 30               | Green chili    | 0.058           | -     | 0.046               |
|                  |                | 2.590           | -     | 3301.000            |
|                  |                | 0.937           | -     | 1.060               |
|                  |                | 0.665           | -     |                     |
|                  |                | Comparison criteria |     |                     |
|                  |                | R²              |       | 0.993               |
|                  |                | RMSE            |       | 1.961               |
|                  |                | χ²              |       | 1.961               |
| 55               | Green chili    | 0.046           | -     | 0.048               |
|                  |                | 4.240           | -     | 3.762               |
|                  |                | 0.923           | -     | 1.037               |
|                  |                | -               | -     |                     |
| 65               | Green chili    | 0.029           | -     | 0.031               |
|                  |                | 51.223          | -     | 43.81               |
|                  |                | 0.923           | -     | -2.641              |
|                  |                | -               | -     |                     |
| 30               | Brown chili    | 0.084           | -     | 0.083               |
|                  |                | 1.952           | -     | 1.759               |
|                  |                | 0.892           | -     | 1.057               |
|                  |                | -               | -     |                     |
| 55               | Brown chili    | 0.045           | -     | 0.047               |
|                  |                | 9.495           | -     | 8.885               |
|                  |                | 0.939           | -     | 0.425               |
|                  |                | -               | -     |                     |
| 65               | Brown chili    | 0.032           | -     | 0.034               |
|                  |                | 55.703          | -     | 48.873              |
|                  |                | 0.935           | -     | -2.378              |
|                  |                | -               | -     |                     |

(continued on next page)
Table 5 (continued)

| Temperature (°C) | Chili Maturity | Model parameter | Model |
|------------------|----------------|-----------------|-------|
|                  |                | Coefficients    |       |
|                  |                | Mo              | 0.077 |
|                  |                | C               | 4.073 |
|                  |                | K               | 0.923 |
|                  |                | N               | 0.602 |
|                  |                | R²              | 0.993 |
|                  |                | RMSE            | 2.818 |
|                  |                | χ²              | 2.818 |
|                  |                | GAB             | 0.080 |
|                  |                | OSWIN           | -     |
|                  |                | BET             | 3.624 |
|                  |                | Modified Halsey | 1.061 |
| 30               | Red chili      | K               | 0.923 |
|                  |                | N               | 0.602 |
|                  |                | R²              | 0.993 |
|                  |                | RMSE            | 2.818 |
|                  |                | χ²              | 2.818 |
| 55               | Red chili      | Mo              | 0.052 |
|                  |                | C               | 8.862 |
|                  |                | K               | 0.932 |
|                  |                | N               | 0.568 |
|                  |                | R²              | 0.983 |
|                  |                | RMSE            | 4.130 |
|                  |                | χ²              | 4.130 |
| 65               | Red chili      | Mo              | 0.035 |
|                  |                | C               | 57.329|
|                  |                | K               | 0.933 |
|                  |                | N               | -     |
|                  |                | R²              | 0.966 |
|                  |                | RMSE            | 3.899 |
|                  |                | χ²              | 3.899 |

Figure 6. Comparison of experimental data with predicted values of red chili based on different models during desorption isotherm. a) at 30 °C, b) at 55 °C, c) at 65 °C.
describing the sorption isotherm well just like the GAB model but somehow insufficient for green chili. However, brown and red chilies were sufficiently well explained by the OSWIN model since this model had a high value of $R^2$ (0.972–0.993) and a low RMSE (1.827–4.948), respectively. Thus, the OSWIN model provided the best fit to experimental data for brown and red chili pepper maturities for a wide range of water activities (0.11–0.92).

It was also observed that as the temperature of the sorption isotherm increased, the correlation coefficient slightly decreased in the OSWIN model for brown and red chili peppers. Moreover, as can be seen in Figures 6 and 7, the four sorption models such as GAB, OSWIN, BET and modified Halsey were fitted to the experimental data for both the desorption and adsorption isotherm. It was observed that the modified Halsey model did not show a good fit over the entire range of water activity, for all maturity levels of chili peppers and for all desorption and adsorption isotherms. It has been reported that the modified Halsey model describes well the sorption behavior of food products that contain starch. Chili pepper does not have a large amount of starch since it contains mainly vitamins and minerals (Andrade et al., 2011).

The validation of the best desorption and adsorption models of red chili pepper was confirmed by comparing the correlation of the predicted moisture ratio with the experimentally obtained moisture ratios. The comparison of the predicted EMC with the experimental EMC of red chili at desorption and adsorption is shown in Figures 8 and 9 respectively at a temperature of 55 °C. It was observed from these figures that the OSWIN model was best fitted to the experimental data for both desorption and adsorption isotherms. The predicted EMC data followed a straight line which validated the suitability of the selected best model.

3.4. The monolayer moisture content of chili peppers

The characteristics of monolayer moisture content indicated that 0.4 is the maximum limit of water activity in most fruits and vegetables to minimize microbial growth and chemical and enzymatic reactions in order to get a good storage stability (Vega-Gálvez et al., 2007). Investigating the monolayer moisture amount (Mo) is an important parameter to design the chili pepper dryer for best performance. The monolayer moisture content of chili pepper was calculated during desorption and adsorption isotherms. It was observed from these figures that the OSWIN model was best fitted to the experimental data for both desorption and adsorption isotherms. The predicted EMC data followed a straight line which validated the suitability of the selected best model.

3.5. Interaction energy between chili and water molecules

The sorption parameters such as C, K and n are associated with the interaction energy between chili pepper and water molecules. High values of heat of sorption can be obtained from a high value of the
sorption constant $C$ which indicates a strong food-water molecule interaction matrix (Erbas¸ et al., 2005). The parameter $C$ is the energy constant which can be related to the net heat of sorption. It shows the difference between the first and the other remaining layers of water molecules that absorbs energy. The study indicated that the values of $C$ were significantly high at the three temperature levels in both desorption and adsorption isotherms as shown in Tables 4 and 5 respectively. It is used as an indicator in the Brunauer’s classification of sorption isotherms. When the $C$ value is greater than 2, the sorption isotherm can be categorized as type II, sigmoidal shape (Farahnaky et al., 2009). For this study, the values of $C$ obtained were higher than 2. The interaction energies amongst multilayer food concerning to bulk liquid can be characterized by the $K$ value. The amount of $K$ increases with the solubility of the material. The value of $K$ in this study was around one for all sorption isotherms, especially for the GAB model as shown in Tables 4 and 5. A similar result has been reported by the work of Vega-Gálvez et al. (2007) for red bell chili peppers.

3.6. Heat of sorption

The amount of isosteric heat of sorption ($q_{st}$) of chili peppers, based on different maturity levels, was calculated using Eq. (3) from the EMC of the experimental data at different sorption temperatures. It was estimated using the OSWIN model at constant moisture content. The amount of heat of sorption of chili peppers was affected by the EMC and its variation as a function of moisture content was plotted using Eq. (4) as shown in Figure 8 for desorption and adsorption isotherms. The thermodynamic constants are also presented in Table 6 which were used for Eq. (4). Chili maturity influences the heat of sorption. It was observed that the heat of sorption exponentially decreased with increasing water activity for all chili pepper maturity levels, as shown in Figure 10. It can also be seen that green pepper has a higher isosteric heat of sorption compared to red and brown chili. The highest energy required to remove the entire water content in the product was observed at low moisture content. This phenomenon is probably due to highly active polar sites on the surface of the product and also water-food interaction is stronger in low EMC and becomes weaker with an increase in EMC (Nourhine et al., 2008).

There was a difference in net isosteric heat between the adsorption and desorption isotherm. For instance, for green chili, the maximum value of a net isosteric heat was 18 kJ mol$^{-1}$ and 20 kJ mol$^{-1}$ for adsorption and desorption isotherms, respectively, and decreases exponentially as moisture content increases. Hence, the net heat of sorption needed in the desorption isotherm was higher than the adsorption isotherm for all maturity levels of chili peppers.

3.7. Comparison of Mareko Fana with global chili varieties

The variety has a significant impact on the sorption isotherm characteristics of chili peppers. Different global chili varieties were described using different sorption models, classification type, and monolayer moisture content as presented in Table 1. Most of the chili pepper varieties have sigmoidal shape, type II (S-shape), as classified by Brunauer. However, the black peppercorns chili variety has a type III sorption shape (J-shape). The experimental sorption isotherms of the Ethiopian chili, Mareko Fana, variety were compared to these chili varieties sorption isotherm characteristics. The comparison indicated that the Mareko Fana chili variety has a relatively low value of monolayer moisture content which indicates the maximum limit of water activity during storage to keep it in a safe condition. The monolayer moisture amounts of many food products have been reported to relate to the chemical and physical
Figure 9. Comparison of the red chili experimental EMC with predicted EMC during adsorption isotherm at a temperature of 55 °C. a) GAB model, b) OSWIN model, c) BET model and d) Modified Hasley model.

Table 6. Thermodynamic constants in the determination of heat of sorption as function of chili pepper maturities.

| Isoeestrisk model constant | Chili maturity | Green pepper | Brown pepper | Red pepper |
|----------------------------|---------------|--------------|--------------|------------|
| Adsorption                 |               |              |              |            |
| $q_o$                      | 3183          | 3177         | 3149         |
| $M_o$                      | 0.092         | 0.085        | 0.075        |
| Desorption                 |               |              |              |            |
| $q_o$                      | 3189          | 3179         | 3153         |
| $M_o$                      | 0.095         | 0.088        | 0.078        |

Figure 10. Effect of moisture content on the heat of sorption of chili peppers. a) Desorption, b) Adsorption.
stability of dehydrated food products like chili peppers (Karel, 1973). The Ethiopian chili variety was best fitted to the OSWIN and GAB sorption models which have similar sorption characteristics of bico, lamuyo and sweet pepper varieties. The net heat of sorption for different chili pepper varieties were reviewed and presented in Table 7. As can be observed, the Aji chili pepper variety had higher value of net heat of sorption as compared to the other chili pepper varieties’ heat of sorption. The desorption heat is higher than the adsorption heat for all chili pepper varieties. It was also observed that the Mareko Fana chili variety has a relatively low value of sorption heat as compared to the other varieties which indicated that low energy is needed to remove the moisture from the active site during drying process.

4. Conclusions

The sorption isotherms of an Ethiopian chili pepper variety (Mareko Fana) at different maturity levels (green, brown and red) and different temperatures were investigated by a standard gravimetric method using various glycerol-water mixture ratios. The EMC decreased with increasing sorption temperature at constant water activity for each maturity level. Green chili pepper has a higher EMC than red chili and the EMC of brown chili was found in between. Hysteresis was observed between desorption and adsorption isotherms for each maturity level of chili peppers. The OSWIN, GAB and BET models explained the sorption data of green, brown and red peppers well over the ranges of water activity and temperature. Among those models, the GAB and BET models described green chili pepper well, whereas the OSWIN model described the brown and red chilies. The modified Halsey model was the worst to describe all chili pepper maturities in the given temperature and water activity range. The isosteric heat exponentially decreased as moisture content increased for each maturity level. The experimental sorption results were compared to other different chili varieties which are found in different countries and the Mareko Fana chili variety has a lower heat of sorption and monolayer moisture content. Full understanding of the sorption characteristics of Mareko Fana is highly important to design appropriate solar dryers (on progress) to improve the quality and storability of chili pepper. Besides, the sorption isotherm data is an important information for the development of an appropriate packaging system.

Declarations

Author contribution statement

Eshetu Getahun: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Nigus Gabbiiye, Solomon W. Fanta, Mekonnen Gebreslasie Gebrehiwot, Maarten Vanierschot, Mulugeta A. Delele: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Funding statement

This work was supported by Bahir Dar University, Institute of Technology, Bahir Dar Energy Center.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

Reference

A Omolo, M., 2014. Antimicrobial properties of chili peppers. J. Infect. Dis. Ther. 2 (4), 2-145.
Akpinar, E.K., Bicer, Y., 2008. Mathematical modelling of thin layer drying process of long green pepper in solar dryer and under open sun. Energy Convers. Manag. 49 (6), 1367-1375.
Ali-Muhtaseb, A.H., McMinn, W.A.M., Magee, T.R.A., 2002. Moisture sorption isotherm characteristics of food products: a review. Food Bioprod. Process. Trans. Inst. Chem. Eng. Part C. 80 (2), 118-128.
Andrade, E.T., Figueira, V.G., Teixeira, L.P., Taveira, J.H., Boem, F.M., 2017. Determination of the hygroscopic equilibrium and isosteric heat of aji chili pepper. Rev. Bras. Eng. Agríc. Ambient. 21 (12), 865-871.
Andrade, R.D., Lemus, R.M., Perez, C.C., 2011. Models of sorption isotherms for food: uses and limitations. Vitae, Rev. La Fac. Química Farm 18 (3), 325-334.
Aviara, N.A., 2020. Moisture sorption isotherms and isotherm model performance evaluation for food and agricultural products. In: Sorption in 2020s, p. 1-45.
Baguet, R., Chirife, J., Iglesias, H.A., 1978. Equations for fitting water sorption isotherms of foods: II. Evaluation of various two-parameter models. Int. J. Food Sci. Technol. 13 (4), 319-327.
Brunaure, S., Emmett, P.H., Teller, E., 1938. Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 60 (2), 309-319.
Calado, T., Venancio, A., Abrunhosa, L., 2014. Irradiation for mold and mycotoxin control: a review. Compr. Rev. Food Sci. Food Saf. 13 (5), 1049-1061.
CSA, R., 2016. The federal democratic republic of Ethiopia central statistical agency report on area and production of major. Stat. Bull.
Dalgic, A.C., Pekmez, H., Bellabgh, K.B., 2012. Effect of drying methods on the moisture sorption isotherms and thermodynamic properties of mint leaves. J. Food Sci. Technol. 49 (4), 439-449.
Demiriste, T., Ali, A., Zerufu, D., 2010. Availability and consumption of fruits and vegetables in nine regions of ethiopia with special emphasis to vitamin A deficiency. Ethiop. J. Health Dev. 23 (3), 216-222.
Dos Santos, R.F., Gomes-Junior, F.G., Marcos-Filho, J., 2020. Morphological and physiological changes during maturation of okra seeds evaluated through image analysis. Sci. Agric. 77 (3).
Erba, M., Ergüat, M.F., Cetel, M., 2005. Moisture adsorption behaviour of semolina and farina. J. Food Eng. 69 (2), 191-198.

Table 7. Effect of variety on the net sorption heat of chili peppers.

| Isotherm  | Chili pepper Varieties | EMC (dry base) | Net isosteric heat of sorption (kJ mol⁻¹) | Reference |
|----------|------------------------|----------------|------------------------------------------|-----------|
| Desorption | Lamuyo 0.050 0.060 | 0.700-74.200 | (Vega-Gálvez et al., 2007) |
| Black peppercorns | 0.020-0.700 | 0.500-73.310 | (Yogendrarajah et al., 2015) |
| Sweet peppers | 0.050-0.380 | 14.000-50.000 | (Sahu and Tiwari, 2007) |
| Bursa 0.080-0.450 | 0.7000-38.000 | (Kaymak-Ertekin and Sultanoglu, 2001) |
| Aji 0.070-0.550 | 145.220-202.270 | (Andrade et al., 2017) |
| Bico 0.100-0.750 | 10.270-47.500 | (Santos et al., 2015) |
| Mareko Fana 0.050-0.550 | 0.003-20.000 | Current study |
| Adsorption | Lamuyo 0.050-0.800 | 0.700-36.900 | (Vega-Gálvez et al., 2007) |
| Black peppercorns | 0.040-0.700 | 0.800-28.060 | (Yogendrarajah et al., 2015) |
| Polyster | 0.110-0.860 | 25.000-45.000 | (Kaleemullah and Kailappan, 2004) |
| Bursa 0.060-0.350 | 0.006-20.000 | (Kaymak-Ertekin and Sultanoglu, 2001) |
| Mareko Fana 0.030-0.350 | 0.030-17.000 | Current study |
