ORIGINAL ARTICLE

Determination and Modeling Desorption Isotherms of Okra (Abelmoschus esculentus L. Moench) and Sweet Green Pepper (Capsicum annum L. Moench)

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Received: 2 April 2020 / Revised: 21 January 2021 /Accepted: 25 January 2021 / Published online: 17 March 2021 \odot The Korean Society for Agricultural Machinery 2021

Abstract

Purpose The aim of this study was to determine the experimental moisture sorption isotherm of green pepper and okra, assess the performance of literature sorption models describing their behavior, and specify bound water properties.

Methods Isotherms were determined through the static gravimetric method at 30, 40, 50, and 60 °C. Twenty models were studied and fittings were done through nonlinear regression using MATLAB R2015b. GAB and Caurie models were used to determine energy constants and bound water properties respectively. Structural parameters were determined according to Kelvin and Halsey equations.

Results All the experimental isotherm were of sigmoid shape. For both samples, Peleg, Enderby, and Guggenheim Anderson de Boer (GAB) models gave the best validation statistic criteria. R-squared (R^2) values were all greater than 0.926 and root-meansquare error (RMSE) values less than 0.04 for both substrates. The GAB energy constants varied with temperature between 6.00 to 51.75 and 34.23 to 176.78 for C_g constants, and 0.70–0.99 and 0.75–0.93 for K_g constants, respectively, for okra and green pepper. The C_g energy constant globally decreased with increasing temperature. The monolayer moisture content W_m , varied with temperature between (0.0740–0.1044) kg kg⁻¹ and (0.0760–0.1522) kg kg⁻¹ respectively for okra and green pepper. Green pepper bound water property values were globally higher than those of okra and both were successfully modeled according to the equilibrium moisture content and according to the temperature. Analysis based on the IUPAC classification revealed a macroporous structure of the two materials.

Conclusions The hygroscopic equilibriums, physicochemical and microbiological stability conditions of green pepper and okra, were determined, for given environmental temperature values. The results obtained from the present study would serve in understanding the water state and mechanism of water sorption, defining drying and storage conditions of the tested vegetables, as well as designing corresponding dryers and packaging.

Keywords Bound water properties . Green pepper . Modeling . Okra . Sorption isotherm

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Introduction

Okra (Abelmoschus esculentus L. Moench) and sweet green pepper (Capsicum annum L. Moench) are vegetable crops grown in the tropical, subtropical, and warm areas of the world. They are herbaceous plants whose fruits are considered vegetables (Mallikarjunaiah [2009](#page-19-0)). Originated from tropical Africa or Asia, okra is an annual plant of the Malvaceae family (Purseglove [1987](#page-19-0)). Its fruits are rich in fiber, protein, and essential amino acids; they are a good source of minerals for human diet (Ca, Na, Cu, Mn, Zn, Mg, P, Fe, and K) and source of provitamin A, and vitamins B, C, and E (Makhadmeh and Ereifej [2007;](#page-19-0) Olivera et al. [2012](#page-19-0); Kouassi et al. [2013;](#page-19-0)

Petropoulos et al. [2018](#page-19-0)). They are appreciated for their viscosity, and their medicinal properties, but also according to the color or the length of the capsule (Olivera et al. [2012\)](#page-19-0). There is a wide variety of okra around the world and their physicochemical characteristics are significantly influenced by genotype and harvest stage (Makhadmeh and Ereifej [2007](#page-19-0); Olivera et al. [2012](#page-19-0); Saha et al. [2016](#page-19-0); Petropoulos et al. [2018](#page-19-0)). In Cameroon, cultivated varieties are not listed. Regarding green pepper, it is an annual plant of the Solanaceae family, native from South America, then probably domesticated in Mexico. Sweet green pepper is the world's second most important solanaceous vegetable after tomato (Sahu and Tiwari [2007\)](#page-19-0). This vegetable is a great source of fiber, K, Ca, P, Mg, provitamin A, and vitamins B and C; it also presents some medicinal properties (Jancik [1936](#page-18-0); Van Duyn and Pivonka [2000](#page-20-0); Pérez-López et al. [2007](#page-19-0); Po et al. [2018\)](#page-19-0). Several cultivated varieties have been mentioned in the literature (Terry Kelley and Boyhan [2009](#page-20-0)); however, there are no references mentioning the typology of those grown in Cameroon.

In the African and Asian continents, okra and sweet green pepper occupy a prominent place in the human diet. They are eaten raw or cooked, or dried and used in the form of powder for seasonings (Sahu and Tiwari [2007\)](#page-19-0). However, after harvest, these two vegetables deteriorate relatively quickly (few days) due to their intrinsic properties and especially climatic and environmental conditions not always favorable (Charrier et al 1997; Shivhare et al. [2000;](#page-19-0) Heard [2002](#page-18-0)). Indeed, their moisture contents vary between 88 and 94% and they are usually, after harvest, stored at room temperature around 25– 35 °C and in an environment with relative humidity between 70 and 100% (Heard [2002](#page-18-0)). In Africa in general, and in Cameroon in particular, their post-harvest conservation remains a permanent problem, as the artisanal techniques employed lead not only to a significant loss of their nutritive values, but also to their instability over time and to economic losses. The annual production of okra in Cameroon rose from 34,120 tons in 2002 to 60,384 tons in 2010 and 90,780 tons in 2016 (INS [2015;](#page-18-0) INS [2017](#page-18-0)). As for pepper, Cameroon's annual production rose from 7,982 tons in 2002 to 37,307 tons in 2012 and to 58,903 tons in 2016 (INS [2015](#page-18-0); INS [2017\)](#page-18-0). Given the ever-growing production of these two vegetables, it is important to master the techniques of their conservation in order to give an added value when marketing.

Regarding conservation techniques, several authors have shown the need to determine the sorption isotherm of food materials (Al-Muhtaseb et al. [2002;](#page-18-0) Martinez-Monteagudo and Salais-Fierro [2014](#page-19-0); Polachini et al. [2016\)](#page-19-0). Indeed, they are experimental curves that show the evolution of the equilibrium water content of the product as a function of the relative humidity of the air surrounding the product, at constant temperatures. They give information on the mechanism of water sorption, the intensities of interactions between food components and water, and the distribution of water

molecules as well as their functional availability in biochemical and biological substances (Touati [2008](#page-20-0); Ahmat et al. [2014\)](#page-18-0). The exploitation of sorption isotherm is necessary for the design and optimization of drying equipment, the determination of the drying limit at given air conditions, the estimation of the microbiological and physico-chemical storage stability, and the determination of the product moisture changes that may occur during storage or the choice of conditioning material (Erbas et al. [2005](#page-18-0); Simal et al. [2007](#page-19-0); Vega-Gálvez et al. [2007](#page-20-0); Moreira et al. [2009](#page-19-0)).

Several models of fruit and vegetable sorption isotherm are cited in the literature and differ essentially in the number of parameters involved and in the empirical, semi-empirical, or theoretical nature of the model (Chirife and Iglesias [1978;](#page-18-0) Touati [2008;](#page-20-0) Wanjiru Gichau et al. [2019](#page-20-0)). These models make it possible to predict the hygroscopic behavior, the states and characteristics of the water in the product under consideration, depending on the progress of drying or during storage. They also give an indication of the evolution of the structure of the product through the variation of the pore radius and the bound water monolayer thickness (Ahmat et al. [2014](#page-18-0)).

Although green pepper and okra are vegetables of considerable economic value, their processing has not received due attention. Moreover, experimental moisture sorption isotherm as well as empirical, semi-empirical, or theoretical models to describe okra and green pepper behaviors remain limited (Kiranoudis et al. [1993](#page-19-0); Fahrettin and Maskan [1999;](#page-18-0) Shivhare et al. [2000;](#page-19-0) Kaymak-Ertekin and Sultanoglu [2001\)](#page-19-0). Some studies are conducted with temperatures not more than 50 °C (Fahrettin and Maskan [1999;](#page-18-0) Vega-Gálvez et al. [2007](#page-20-0)); therefore, they do not involve the usual ranges of drying temperatures. Other studies are conducted on pretreated or transformed materials (Shivhare et al. [2000](#page-19-0); Sahu and Tiwari [2007\)](#page-19-0). From all these past studies, information relative to the properties of bound water are limited, while several authors have mentioned the need to study the influence of temperature on the material characteristic quantities such as the number of monolayers, the percentage of bound water, the water content of the monolayer, the density of sorbed water and the specific surface area of sorption (Sahu and Das 2010 ; Choudhury et al. [2010;](#page-18-0) Ngono Mbarga et al. [2017\)](#page-19-0). These parameters help to understand the moisture behavior in a particular material under different storage conditions. To our knowledge, no literature has been published on okra or green pepper from Cameroon, mentioning the behavior of their equilibrium moisture content according to environmental conditions. Therefore, the objectives of this work were to determine the experimental sorption isotherm of Cameroon okra and sweet green pepper at 30, 40, 50, and 60 °C, to evaluate the performance of literature sorption models, to classify them based on statistical parameters and to determine the bound water properties of these materials.

Materials and Methods

Experimental Device

The desorption isotherm of okra and sweet green pepper were determined by the static gravimetric method, based on the use of saturated salt solutions conferring, for a given temperature and at equilibrium, a precised relative humidity to the environment (Pahlevanzadeh and Yazdani [2005;](#page-19-0) Ahmat et al. [2014\)](#page-18-0). The device used consists of a 53 liters temperature controlled oven (Memmert GmbH, Schwabach, Germany), with temperature range from 20 to 220 °C and absolute uncertainty of 0.5 °C. The tested temperatures were 30, 40, 50, and 60 °C. The 1-l-capacity jars of Bioblock brand used are equipped with a vacuum system creating a partial vacuum to accelerate the sorption process (Fig. 1). The jars were nine in number, providing nine experimental points. Each jar contained a quarter of different saturated salt solution (KOH, LiCl, CH₃COOK, MgCl₂, K₂CO₃, NaBr, CuCl, NaCl, KCl). This group of salts allows the obtention of a wide range of relative humidity, between 5 and 84% (Ahmat et al. [2014\)](#page-18-0). Each jar had a sample holder above the salt solution, on which a cup containing a fresh mass of sample was placed.

Preparation of the Raw Material

Fresh okra and sweet green pepper pods, of uniform maturity, were purchased at the local market of Ngaoundere, in the Adamawa region of Cameroun in the month of July. Fig. [2](#page-3-0) shows a picture of the samples. They were washed with tap water and drained. Using a knife, the stalks were cut and the sepal whorls hand-removed. Pods with wounds and bruises were discarded. Concerning physical characterization, they were weighed, their length and diameter measured using a Mitutoyo digital caliper, and their moisture content determined. These physical quantities were, respectively, for okra and green pepper pods, $(17.64 \pm$ 5.35) and (67.25 \pm 17.67) g for their weight; (7.11 \pm 1.12) and (4.86 ± 1.20) cm for their length; (1.73 ± 0.40) and (4.86 ± 0.78) cm for their diameter; and (94.2 ± 0.2)

and (92.0 \pm 0.2) % wet basis for their moisture content. Values are means \pm standard deviations of measurements from 50 fruits. Pods were sliced (7–10 g each) and placed in a plastic cup. The mass of the sample was small enough to have a very weak influence on the hygrometric conditions of the atmosphere (almost stable saturation of the solution), but large enough for their mass to be measured, once equilibrium was reached, with the weighing scale whose precision was $1/100$. The plastic cup was then placed on a grid disposed about 15 mm above the surface of the salt solution in order to avoid the immersion of the sample in the salt solution, as suggested by Trujillo et al. ([2003](#page-20-0)). To avoid mold growth in the medium, samples were treated in a 10% (m/V) sodium benzoate solution. Three samples of the tested product were placed in each cup in order to obtain an average mass at equilibrium.

Monitoring of Sorption Experiments

The monitoring of the sorption in the experimental device was carried out by weighing the samples (without removing them from their cup and taking into account the weight of the tare) using a Sartorius electronic balance (precision at 1/100), every 24 h, until equilibrium. This was considered attained when the difference between two consecutive measurements of the mass of the sample was less than or equal to 0.01 g. At equilibrium, the water activity (a_w) of the sample is identical to the relative humidity of the air (Eq. (1)).

$$
a_{\rm w} = \frac{P_{\rm vp}}{P_{\rm vs}} = \frac{\rm HR(\%)}{100} \tag{1}
$$

The dry masses (M_s) were obtained after desiccation of the samples resulting from the desorption process, in an oven at 105±0.5 °C for 24 h. The equilibrium moisture content of the product was calculated as presented by Eq. (2).

$$
X_{\rm e} = \frac{M_{\rm he} - M_{\rm s}}{M_{\rm s}}\tag{2}
$$

All samples were run in triplicate.

Fig. 1 (a) A view of the thermostated oven used for experiments. (b) From Ahmat et al. [\(2014](#page-18-0)) A schematic diagram of the sorption jar

Fig. 2 Okra (a) and sweet green pepper (b) samples

Determination of the Biochemical Composition of Okra and Green Pepper

The total moisture and ash content were determined using the AOAC method (AOAC [1990](#page-18-0)). Protein content and total nitrogen were determined by mineralization of samples according to the Kjeldahl method (AFNOR [1982](#page-18-0)) and thereafter, nitrogen was assayed by the method of Devani, described by Sáez-Plaza et al. ([2013](#page-19-0)). The total sugar content was determined by spectrophotometric method of Dubois et al. ([1956\)](#page-18-0) and total lipid content was determined by the Russian method described by Bourely ([1982](#page-18-0)) based on the extraction of lipids using Soxhlet by hexane. The vitamin C content of substrates was determined using the 2,6-dichloro-indophenol titrimetric method (AOAC [2007](#page-18-0)). All samples were run in triplicate.

Modeling Sorption Curves

Numerous sorption models, empirical, semi-empirical, or theoretical, have been successfully used to describe water sorption isotherm of various food materials in a given range of water activity (Chirife and Iglesias [1978;](#page-18-0) Erbas et al. [2005](#page-18-0); Ngono Mbarga et al. [2017](#page-19-0)). As several different mechanisms that depend on the material structure and composition are involved during sorption of water, sorption isotherm may be described by many different equations (Chirife and Iglesias [1978;](#page-18-0) Al-Muhtaseb et al. [2002\)](#page-18-0). The experimental equilibrium moisture content (X_e) data for okra and green pepper were adjusted by testing twenty different models found in the literature (Table [1\)](#page-4-0), among which eight models involving two parameters, ten other models having three parameters and the last two models involving four parameters. Eight of these models involve the effect of temperature. However, there is usually no scientific basis to justify the inclusion of the temperature effect in those models (Aguirre-Loredo et al. [2017\)](#page-18-0). The aim was to determine the models that best describe the

sorption isotherm of our products. For the adjustments, a tenth point (a_w, X_e) at the origin (1E-05, 1E-05) was added to the experimental data, to take into account the absence of moisture in the product at equilibrium with a virtual zero-vapor pressure in the environment (Kouhila et al. [2002;](#page-19-0) Mayor et al. [2005](#page-19-0)).

Determination of the Properties of Bound Water

Caurie model (Caurie [1981\)](#page-18-0) named Caurie2 in this work (Eq. (3)), based on monomolecular adsorption, allows the determination of some characteristics of bound water and the specific surface area of sorption (Singh et al. [2006](#page-20-0)). Similarly, the parameters of the GAB isotherm model (Eq. (4)) have a physical meaning in terms of the sorption processes (Timmermann et al. [2001](#page-20-0)).

$$
X_e = k_1 \cdot k_2 \cdot \left(\frac{a_w}{1 - a_w}\right)^{(2 \cdot k_1 / k_2)}\tag{3}
$$

$$
X_e = \frac{k_1 \cdot k_2 \cdot k_3 \cdot a_w}{(1 - k_2 \cdot a_w) \cdot [1 - k_2 \cdot a_w + k_2 \cdot k_3 \cdot a_w]}
$$
(4)

Several authors (Menkov et al. [1999;](#page-19-0) Ayranci and Duman [2005;](#page-18-0) Erbas et al. [2005;](#page-18-0) Ahmat et al. [2014;](#page-18-0) Ngono Mbarga et al. [2017](#page-19-0)) use the linear form of isotherm equations to determine the properties of bound water. The linear model constants are then obtained through linear regression. For Caurie2, the linear form is generally expressed as presented in Eq. (5), where C and X_0 correspond respectively to k_1 and k_2 of Eq. (3) and are respectively the constant related to the density of sorbed water and the monolayer moisture content.

$$
\ln\left(\frac{1}{X_e}\right) = -\ln(C \cdot X_0) + 2 \cdot \frac{C}{X_0} \cdot \ln\left(\frac{(1 - a_w)}{a_w}\right) \tag{5}
$$

For GAB model, the linear form is generally written as presented in Eq. (6), which necessitates the introduction of the correct value of K_{φ} .

Table 1 Isotherm models used for experimental data fitting, in alphabetical order

Entitled	Model	Parameters
BET (Brunauer et al. 1938)	$X_e = \frac{k_1 \cdot k_2 \cdot a_W}{(1 - a_W) \cdot [1 + (k_2 - 1) \cdot a_W]}$	k_1, k_2
BET Modified (Menkov et al. 1999)	$X_e = \frac{(k_1 + k_2 \cdot T_a) \cdot k_3 \cdot a_W}{(1 - a_W) \cdot 1 - a_W + k_2 \cdot a_W}$	k_1, k_2, k_3
Caurie1 (Caurie 1970)	$X_e = exp(k_1 + k_2 \cdot a_w)$	k_1, k_2
Caurie ₂ (Caurie 1981)	$X_e = k_1 \cdot k_2 \cdot \left(\frac{a_w}{1-a_w}\right)^{(2 \cdot k_1/k_2)}$	k_1, k_2
Chung-Pfost (Chung and Pfost 1967)	$X_e = k_1 - k_2 \cdot ln(-(T_a + k_3) \cdot ln(a_W))$	k_1, k_2, k_3
Enderby (Popovski and Mitrevski 2004)	$X_e = \left[\frac{k_1}{1-k_2\cdot a_W} + \frac{k_3}{1-k_4\cdot a_W}\right]\cdot a_W$	k_1, k_2, k_3, k_4
GAB (Timmermann et al. 2001)	$X_e = \frac{k_1 \cdot k_2 \cdot k_3 \cdot a_W}{(1 - k_2 \cdot a_W) \cdot (1 - k_2 \cdot a_W + k_2 \cdot k_3 \cdot a_W)}$	k_1, k_2, k_3
Hailwood and Horrobin Modified (Aviara and Igbeka 2015)	$X_e = \left[T \cdot \left(\frac{k_1}{a_w} + k_2 \right) - \frac{k_3 \cdot a_w}{T^6} \right]^{-1}$	k_1, k_2, k_3
Halsey (Halsey 1948)	$X_e = \left[\frac{k_1}{\ln(1/_{aw})}\right]^{\left(1\right)}\left(1/_{k_2}\right)$	k_1, k_2
Halsey Modified (Iglesias and Chirife 1976)	$X_e = \left[\frac{-\ln(a_w)}{\exp(k_1 + k_2 \cdot T)}\right]^{(-1/k_3)}$	k_1, k_2, k_3
Harkins & Jura (Harkins and Jura 1944)	$X_e = \left[\frac{k_1}{(k_2 - ln(a_w))}\right]^{(\frac{1}{2})}$	k_1, k_2
Henderson Modified (Thompson et al. 1968)	$X_e = \left[\frac{\ln(1-a_w)}{-k_1\cdot(T+k_2)}\right]^{(1/k_3)}$	k_1, k_2, k_3
Langmuir (Langmuir (1916) cited by Touati 2008)	$X_e = \frac{1}{\left[k_1 + k_2 \cdot a_w^{(k_3-1)}\right]}$	k_1, k_2, k_3
LESPAM (Mghazlia et al. 2016)	$X_e = k_1 \cdot \exp(\frac{k_2 \cdot a_W}{T}) + k_3$	k_1, k_2, k_3
Luikov Modified (Simo Tagne 2011)	$X_e = \frac{k_1 \cdot T + k_2}{[1 - k_3 \cdot \ln(a_w)]}$	k_1, k_2, k_3
Oswin (Oswin 1946)	$X_e = k_1 \cdot \left(\frac{a_w}{1-a_w}\right)^{k_2}$	k_1, k_2
Oswin Modified (Goneli et al. 2010)	$X_e = (k_1 + k_2 \cdot T) \cdot \left[\frac{a_w}{1 - a_w}\right]^{(1/k_3)}$	k_1, k_2, k_3
Peleg (Peleg 1993)	$X_e = k_1 \cdot (a_W)^{k_2} + k_3 \cdot (a_W)^{k_4}$	k_1, k_2, k_3, k_4
Smith (Smith 1947)	$X_e = k_1 - k_2 \cdot ln(1 - a_w)$	k_1, k_2
White and Eyring (1947) cited by Popovski and Mitrevski (2004)	$X_e = \frac{1}{(k_1 + k_2 a_w)}$	k_1, k_2

$$
\frac{a_w}{X_{e} \cdot (1 - K_g \cdot a_w)} = \frac{1}{W_m \cdot K_g \cdot C_g} + \frac{(C_g - 1)}{W_m \cdot C_g} \cdot a_w \tag{6}
$$

In this equation, W_m , K_g , and C_g respectively correspond to k_1 , k_2 , and k_3 in Eq. [\(4](#page-3-0)) and are respectively the monolayer moisture content and energy constants. They are exponential functions of the inverse absolute temperature as presented in Eqs. (7)–(9) (Gabas et al. [2007\)](#page-18-0).

$$
W_m = W_0 \cdot \exp\left(\frac{\Delta H}{RT}\right) \tag{7}
$$

$$
K_g = K_0 \cdot \exp\left(\frac{\Delta H_2}{RT}\right) \tag{8}
$$

$$
C_g = C_0 \cdot \exp\left(\frac{\Delta H_1}{RT}\right) \tag{9}
$$

where W_0 is a constant and K_0 and C_0 are the entropic accommodation factors. The heats of sorption of the monolayer (h_m) and of the multilayer (h_n) were calculated as given in Eqs. (10) and (11).

$$
\Delta H_1 = h_m - h_n \tag{10}
$$

$$
\Delta H_2 = L_v - h_n \tag{11}
$$

where L_v is the average of the pure water enthalpy of vaporization, in the temperature range 30 to 60 $^{\circ}$ C. The average value is 43.12515 kJ mol⁻¹, calculated using Popiel and Wojtkowiak [\(1998\)](#page-19-0) table.

Each regression method uses a specific algorithm leading to some differences in model parameters values (Al-Mahasneh et al. [2012](#page-18-0)). In our calculations, statistical parameters associated to nonlinear regressions were always better than those obtained through linear regressions. Consequently, in the present work, the statistical criteria were privileged in the choice of the regression model. The parameters were therefore estimated by nonlinear regression as presented in the following section.

The number of monolayers of sorbed water, N, was directly calculated for each temperature (Eq. (12)) using the Caurie2 (Eq. ([3\)](#page-3-0)) parameters k_1 and k_2 , estimated by nonlinear regression.

$$
N = \frac{X_0}{C} = \frac{k_2}{k_1}
$$
\n(12)

The percentage of bound water (bw) was calculated as shown in Eq. (13) . The specific surface area of sorption, A, was calculated as presented in Eq. (14), assuming that the magnitude of k_1 in the Caurie's model is equivalent to the density of sorbed water in the monolayer (Singh et al. [2001](#page-20-0)).

$$
bw(\%) = k_2 \cdot N \tag{13}
$$

$$
A = \frac{V}{d} = \frac{k_2 \cdot 10^{-8}}{k_1 \cdot d} = \frac{N \cdot 10^{-8}}{d} = 27.2257 \cdot N \tag{14}
$$

where $d = 3.673 \cdot 10^{-10}$ m is the diameter of water molecules.

The Kelvin equation (Eq. (15)) allows the determination of the critical pore radius r_c (nm). This equation applies primarily to the condensation region of the isotherm (Singh et al. [2001](#page-20-0); Miyata et al. [2003](#page-19-0)):

$$
r_{\rm c} = \frac{-2 \cdot \sigma \cdot V_m}{R \cdot T_a \cdot \ln(a_w)} \cdot 10^9 \tag{15}
$$

However, the Kelvin equation does not take into account the thickness of layers formed on the porous surface prior to condensation. In order to describe the thickness of the precondensation film on the pore walls, the Halsey equation (Eq. (16)) can be used to predict the thickness of the layer, t (nm), formed on the porous surface at a given water activity (Singh et al. [2001;](#page-20-0) Miyata et al. [2003](#page-19-0)).

$$
t = 0.354 \cdot \left(\frac{-5}{\ln(a_w)}\right)^{1/3} \tag{16}
$$

Therefore, pore radius R_p (nm) is calculated as presented in Eq. (17) (Singh et al. [2001](#page-20-0)).

$$
R_{\rm P} = r_{\rm c} + t \tag{17}
$$

Statistical Analysis

The modeling of sorption isotherm requires the statistical methods of regression analysis and correlation. The model parameters were estimated by nonlinear regression using Newton's least squares method to minimize the sum of squares of the residuals between experimental and predicted equilibrium moisture contents (X_{exp} and X_{pre} respectively). In literature, the statistics used to compare models vary from one author to another, which makes it difficult to compare values among several authors. To cover the maximum statistics used in literature and allow further comparisons, the models in this work were compared based on two-dimensional statistics, namely the root-mean-square error (RMSE) which measures the standard deviation of the residuals and the mean absolute error (MAE), and five nondimensional statistics, namely the

mean relative error (MRE), the coefficient of determination $(R²)$ which measures the proportion of variability in the response explained by the regression model, the adjusted Rsquared $(R_{adj}²)$ which takes into account the effects of the number of model parameters, the percentage of deviation (Pd), and the normalized root-mean-square error (NRMSE) expressed as a percentage (Willmott et al. [1985\)](#page-20-0). They were calculated using MATLAB R2015b software as presented by Eqs. (18)–(24). A model was considered to be acceptable if, for all the tested temperatures, the RMSE and MAE values were close to zero, the R-squared (R^2) and adjusted R-squared $(R²_{adj})$ values greater than 0.9, and the MRE, Pd, and NRMSE values below 10% (Kaymak-Ertekin and Gedik [2004;](#page-19-0) Ahmat et al. [2014](#page-18-0)). Moreover, the model should fit the experimental points in the range of tested water activity and present an acceptable shape.

RMSE =
$$
[MSE]^{\frac{1}{2}} = \left[\frac{SSE}{(n-p)}\right]^{\frac{1}{2}}
$$

$$
= \left[\frac{1}{(n-p)} \cdot \sum_{i=1}^{n} (X_{i,exp} - X_{i,pre})^2\right]^{\frac{1}{2}}
$$
(18)

This statistic is also known as the standard error of the estimate, where p is the model number of parameters. It is defined as the square root of the mean square error (MSE).

$$
\text{MAE} = \frac{1}{n} \cdot \sum_{i=1}^{n} \left| X_{i,\text{exp}} - X_{i,\text{pre}} \right| \tag{19}
$$

$$
MRE = \frac{1}{n} \cdot \sum_{i=1}^{n} \left| \frac{X_{i, \exp} - X_{i, \text{pre}}}{\left(\frac{1}{n} \cdot \sum_{i=1}^{n} X_{i, \exp}\right)} \right| \tag{20}
$$

$$
R^{2} = \frac{\text{SSR}}{\text{SST}} = \frac{\sum_{i=1}^{n} (X_{i,\text{exp}} - X_{i,\text{pre}})^{2}}{\sum_{i=1}^{n} (X_{i,\text{exp}} - (\frac{1}{n} \cdot \sum_{i=1}^{n} X_{i,\text{exp}}))^{2}}
$$
(21)

$$
R_{\text{adj}}^2 = 1 - \frac{n-1}{n-p} \cdot (1 - R^2) = 1 - \frac{n-1}{n-p} \cdot \frac{\text{SSE}}{\text{SST}}
$$
(22)

$$
\text{Pd} = 100 \cdot \sqrt{\frac{1}{n} \cdot \left[\sum_{i=1}^{n} \left(\frac{X_{i,\exp} - X_{i,\text{pre}}}{(X_{e,\text{max}} - X_{e,\text{min}})} \right)^2 \right]}
$$
(23)

$$
NRMSE = 100 \cdot \frac{RMSE}{\left(X_{e,\text{max}} - X_{e,\text{min}}\right)}\tag{24}
$$

Three decision criteria, C_{max} , C_{min1} , and C_{min2} , calculated as shown in Eqs. (25) – (27) , were used to assess the performance of sorption isotherm models and classify them. C_{max} is non-dimensional and takes into account the statistics which contribute positively to the description of data by the model, whereas C_{min1} (having the dimension of X_e) and C_{min2} (nondimensional) involve terms that quantify the errors committed using the model. The statistical parameters involved in these three equations are average values over the tested temperatures. The models were first ranked by the value of C_{max} , secondly by the value of C_{min1} , and thirdly by the value of C_{min2} . The best model being the one with the highest value of C_{max} and the lowest values of C_{min1} and C_{min2} .

$$
C_{\text{max}} = \overline{R^2} + \overline{R_{\text{adj}}^2}
$$
 (25)

$$
C_{\text{min1}} = \overline{\text{RMSE}} + \overline{\text{MAE}} \tag{26}
$$

$$
C_{min2} = \overline{\text{MRE}} + \overline{\text{NRMSE}}/100 + \overline{\text{Pd}}/100 + \left(1 - \overline{R^2}\right) + \left(1 - \overline{R_{adj}^2}\right) \qquad (27)
$$

Results and Discussion

Physico-chemical Characterization of Biological **Materials**

The physico-chemical compositions of okra and green pepper are presented in Table 2. This table shows that these two vegetables are rich in water with a dry matter mainly composed of carbohydrates (66.2% and 70.0% respectively), followed by lipids (17.9% and 12.8% respectively) and ash (9.8% and 11.4% respectively). Protein occupies the last place of macronutrients, with a dry matter content of 5.9% and 5.6% respectively. Vitamin C plays a vital role in the human health, as it is involved in many physiological processes in the body. It is the consumption of fruits and vegetables that allow people to cover their daily vitamin C requirements. The results show that this vitamin is present in both vegetables. However, its concentration in okra samples is almost three times higher than that in pepper samples, thus attributing better antioxidant properties to okra. Globally, the obtained results show a

Table 2 Biochemical composition of okra and green pepper

Constituents	Okra $(g/100 g$ wet basis)	Green pepper $(g/100 g$ wet basis)
Moisture content	94.20 ± 0.20 ^{d,B}	92.00 ± 0.20 ^{f,A}
Ash content	$0.57 \pm 0.06^{\text{a,A}}$	$0.91 \pm 0.13^{\rm a,b,B}$
Total protein content	$0.34 \pm 0.06^{\text{a,A}}$	$0.45\pm0.03^{\mathrm{a,B}}$
Total lipid content	$1.04 \pm 0.01^{a,b,A}$	$1.02 \pm 0.01^{\text{d},B}$
Total carbohydrate content	$3.84 \pm 0.40^{b,A}$	$5.60 \pm 0.37^{\rm c,B}$
Soluble sugar content	$2.89 \pm 0.06^{a,b,B}$	$1.88 \pm 0.04^{b,A}$
Vitamin C content *	$85.71 \pm 4.35^{\text{c},B}$	$30.52 \pm 1.30^{\rm e,A}$

Values are presented as mean \pm standard deviation

On the same column, data having the same lowercase superscript are not significantly different at the 5% level. On the same line, data having different uppercase superscript present a statistically significant difference at the 95.0 % confidence level. *(mg/100 g wet basis)

statistically significant difference at the 95.0% confidence level, on each of the nutrient contents of the two substrates.

The multiple comparison test applied to sweet green pepper shows that the ash and protein contents are not significantly different at a 5% level. The results obtained are different from those presented by Faustino et al. ([2007](#page-18-0)) whose lipid and ash fractions, based on the dry matter of the green pepper samples, are approximately two times lower than our respective values. The dry matter of their sample contains three times more protein than ours; however, the sugar contents are almost identical. Similar trends are observed with Jancik ([1936](#page-18-0)) results. Carbohydrate, fat, and ash contents of our samples are double that of Po et al. [\(2018\)](#page-19-0), whereas the protein and vitamin C contents are twice lower than theirs. Our sample's vitamin C contents are also lower than the results presented by Topuz and Ozdemir [\(2007\)](#page-20-0) and Zoran Ilić et al. [\(2014\)](#page-20-0), whose vitamin C levels in green pepper vary between 63 and 147 mg/100 g Several authors (Jancik [1936](#page-18-0); Martinez et al. [2007;](#page-19-0) Pérez-López et al. [2007;](#page-19-0) Zoran Ilić et al. [2014\)](#page-20-0) reported that the variety, the growing conditions, and the stage of maturity as well as the postharvest storage conditions of green sweet pepper affect the fruit quality parameters and bioactive compounds.

The multiple comparison test applied to okra shows that ash, protein, lipid, and soluble sugar levels are not significantly different at a 5% level. The total sugar and ash contents of our okra sample are similar to those presented by Makhadmeh and Ereifej [\(2007](#page-19-0)) on seven varieties of okra and by Kouassi et al. [\(2013](#page-19-0)) on two varieties of okra. However, contrary to our samples, the protein contents of the samples of these two authors are on average seven times higher than their lipid contents. Similar trends are observed with EL-Nahry et al. ([1978](#page-18-0)) and Nwachukwu et al. [\(2014](#page-19-0)) results. Petropoulos et al. ([2018\)](#page-19-0) reported that fruit size has a genotype-dependent impact on the chemical composition and nutritional value of okra pods. Al-Wandawi ([1983\)](#page-18-0) and UdayasekharaRao [\(1985](#page-20-0)) reported that the okra seed is a rich source of proteins, and these contents depend on the cultivar. Knowing that okra lipids and proteins are mainly localized at the grain level, the observed deviations from results obtained from literature, in the contents of these two constituents, could be due to the differences in cultivars used, climatic conditions, quality of the soil, and degree of maturity of the fruits (Mallikarjunaiah [2009\)](#page-19-0). These latter could also explain the vitamin C contents four times higher in our samples, compared to those reported by Bergeret and Masseyeff [\(1958](#page-18-0)) on a variety of okra from Cameroon.

Experimental Desorption Curves

The experimental desorption curves of okra and pepper are presented in Fig. [3.](#page-7-0) The isotherms of the two substrates are all of type II. This one is the sigmoid form of isotherm, which present three zones and an asymptotic tendency when the

Fig. 3 Experimental equilibrium moisture content of okra (a) and green pepper (b), with respect to the equilibrium relative humidity of air above saturated salt solutions (equal to the product water activity), at different temperatures: diamond (30 °C), + (40 °C), square (50 °C), and x (60 °C)

water activity tends towards 1. This type is observed for very dispersed porous structure with condensation in the pores (capillary condensation) occurring before saturation of the material (Kouhila et al. [2002\)](#page-19-0). The three zones, 1, 2, and 3, of type II isotherm, correspond respectively to the adsorption of monomolecular film of water, the adsorption of additional layers of water over the monolayer, and the zone where water is condensed into the pores of the material, followed by dissolution of the soluble material present (Aguirre-Loredo et al. [2017\)](#page-18-0). According to IUPAC (International Union of Pure and Applied Chemistry) classification, there is a progressive thickening of the adsorbed layer characterizing a multimolecular adsorption (Brunauer et al. [1938](#page-18-0); Wanjiru Gichau et al. [2019\)](#page-20-0). According to several authors, most of agri-food product, and medicinal and aromatic plant isotherms, also exhibit this sigmoidal form of isotherm (Iglesias et al. [1986](#page-18-0); Menkov et al. [1999;](#page-19-0) Kouhila et al. [2002;](#page-19-0) Goneli et al. [2010](#page-18-0)).

The experimental curves of the isotherm of okra and green pepper (Fig. 3) show that at a given water activity, the equilibrium moisture content increases with decrease in temperature. Similar results have been reported by several authors (Kouhila et al. [2002;](#page-19-0) Choudhury et al. [2010](#page-18-0)). Erbas et al. [\(2005\)](#page-18-0) suggest that at lower temperatures, water molecules have a lower kinetic energy which is not enough to overcome the corresponding sorption energy. The effect of temperature on isotherm is more marked in pepper than in okra. For a given temperature and water activity in zones 1 and 2 of the sorption isotherm, the equilibrium water content observed for okra is always lower than that obtained with green pepper. The gap is even more marked at low temperatures. This phenomenon could be related to the difference in structure of the two materials and to the change in sorption properties of the material constituents during the sorption process, due to physical and chemical interactions induced by heating (Chirife and Iglesias [1978\)](#page-18-0). Modeling experimental curves would allow for better understanding of the phenomenon.

Modeling and Classification of Desorption Isotherm

The twenty models of sorption isotherm presented in Table [1](#page-4-0) were used to assess their ability to represent the experimental results of the desorption isotherm of okra and green pepper obtained at four different temperatures (30, 40, 50, and 60 °C). The classification of the twenty sorption isotherm models, based on the statistical parameters and the method previously described in the statistical analysis section, indicates that the four-parameter models occupy the first places. The first three models, in order of merit, are the Peleg, Enderby, and GAB models for okra and the Enderby, Peleg, and GAB models for green pepper (Table [3\)](#page-8-0). These three models are compared to the experimental points in Fig. [4.](#page-9-0) It appears that for all the tested temperatures, the behavior of okra and pepper can suitably be described by these three models. Of the twenty tested models, in addition to these first three models, ten other models meet the acceptability criteria, these are the Caurie2, modified Hailwood and Horobin, Halsey, modified Halsey, Lespam for okra/Harkins and Jura for green pepper, modified Henderson, Langmuir, modified Luikov, Oswin, and modified Oswin models (Table [3](#page-8-0)). For each tested temperature, the statistical parameters of the validated models are presented in Tables [4](#page-10-0) and [5](#page-11-0), respectively, for okra and green pepper. The Lespam and Harkins & Jura models for the two substrates are also shown. The model constants are presented in Table [6](#page-12-0) for both substrates.

In literature, the Peleg model has adequately described the moisture sorption isotherm of several food products (Kaya and Kahyaoglu [2005](#page-18-0); Ouafi et al. [2015\)](#page-19-0). However, unlike the GAB model, the Peleg model is a purely empirical model without a theoretical background. Several authors have

Rank	Okra					Green pepper				
	Cmin1	Cmin2	Cmax	Models	Cmin1	Cmin2	Cmax	Models		
$\mathbf{1}$	0.0212	0.1804	1.9559	Peleg	0.0432	0.3460	1.8818	Enderby		
2	0.0220	0.1863	1.9537	Enderby	0.0449	0.3583	1.8798	Peleg		
3	0.0265	0.2291	1.9421	GAB	0.0435	0.3593	1.8761	GAB		
4	0.0261	0.2353	1.9389	Hailwood & H. Mod.	0.0461	0.3868	1.8702	Oswin		
5	0.0307	0.2553	1.9349	Langmuir	0.0461	0.3868	1.8702	Caurie ₂		
6	0.0308	0.2688	1.9289	Luikov	0.0461	0.3967	1.8603	Oswin Mod.		
7	0.0310	0.2697	1.9279	Caurie ₂	0.0439	0.3861	1.8596	Hailwood & H Mod.		
8	0.0310	0.2697	1.9279	Oswin	0.0498	0.4229	1.8525	Halsey		
9	0.0310	0.2752	1.9224	Oswin Mod.	0.0510	0.4254	1.8515	Langmuir		
10	0.0341	0.3243	1.9039	Halsey	0.0491	0.4211	1.8514	Luikov Mod.		
11	0.0377	0.3306	1.9025	Lespam	0.0498	0.4340	1.8413	Halsey Mod.		
12	0.0366	0.3284	1.8985	Henderson Mod.	0.0515	0.4476	1.8386	Harkins & Jura		
13	0.0341	0.3316	1.8966	Halsey Mod.	0.0526	0.4726	1.8214	Henderson Mod.		
14	0.0405	0.3769	1.8818	Smith	0.0593	0.5295	1.7969	Smith		
15	0.0365	0.3706	1.8786	Harkins & Jura	0.0613	0.5403	1.7922	Lespam		
16	0.0429	0.4058	1.8682	Caurie1	0.0600	0.5422	1.7886	Caurie1		
17	0.0409	0.4541	1.8265	BET	0.0642	0.6282	1.7382	Chung-Pfost		
18	0.0401	0.4649	1.8138	BET Mod.	0.0666	0.6441	1.7148	BET		
19	0.0507	0.5766	1.7655	White & Eyring	0.0689	0.6776	1.7036	White & Eyring		
20	0.0592	0.6415	1.7351	Chung-Pfost	0.0659	0.6641	1.6932	BET Mod.		

Table 3 Classification of isotherm models according to their statistical performances to describe experimental data of okra and green pepper

mentioned that the GAB model is well suited to describe the sorption isotherm of most fruits and vegetables (Timmermann et al. [2001](#page-20-0)). It is therefore frequently used to determine important parameters which are useful in physicochemical descriptions, including the moisture content in the monolayer, which represents the amount of water required to form a monolayer on the surface, as well as energy constants (Timmermann et al. [2001\)](#page-20-0). Fahrettin and Maskan ([1999](#page-18-0)) successfully applied GAB model to describe the behavior of okra adsorption isotherm at temperatures between 10 and 30 °C. However, contrary to our results, they observed that the monolayer moisture content k_1 (or W_m) decreases with increase in temperature and that the energy constants k_2 (or K_{φ}) and k_3 (or $C_{\rm g}$) increase with temperature. Taking into account their range of tested temperatures, this result would indicate the presence of an extremum around 30 °C. Kaymak-Ertekin and Sultanoglu ([2001](#page-19-0)) showed that the GAB and the Oswin models are satisfactory in predicting the equilibrium moisture content of peppers, with orders of magnitude and evolution with the temperature of the constants k_1 and k_2 , similar to our results. These authors also observed, with the red pepper, the presence of a maximum for the evolution of k_3 (C_g) with temperature. However, our C_g values are on average ten times higher than theirs. The GAB model monolayer moisture contents obtained with red bell pepper by Vega-Gálvez et al. [\(2007\)](#page-20-0) ranged from 0.07 to 0.10 (g g^{-1} db), similar to our results with sweet green pepper. Swami et al. ([2005](#page-20-0)) attributed the decrease in the monolayer moisture content k_1 (W_m) with the increase in temperature, to the decrease in the number of active sites, or total sorption ability of the material, due to physical and chemical changes induced by temperature.

According to Van Den Berg [\(1991\)](#page-20-0), most dried food products are empirically observed to display their greatest stability at moisture contents comparable to the monolayer moisture content. According to the GAB model, the monolayer moisture contents vary with temperature between 7.40 and 10.44 $(g/100 g db)$ for okra and between 7.60 and 15.22 $(g/100 g db)$ for green pepper. Therefore, these two vegetables have an identical critical water activity value of 0.35 corresponding to an average moisture content of 7.5 (g/100 g db). Beyond this value, their stability would be compromised. This value is less severe than the average values of 3.7 (BET) and 4.9 (GAB) (g/100 g db) obtained by Sahu and Tiwari ([2007](#page-19-0)) on osmotically dehydrated sweet pepper. The water content range for green pepper stability observed in literature varies between 7.0 and 45.0 (g/100 g db) (Kiranoudis et al. 1993 ; Zhang et al. [1996](#page-20-0); Kaymak-Ertekin and Sultanoglu [2001](#page-19-0)) for temperatures between 10 and 60 °C. Vega-Gálvez et al. [\(2007\)](#page-20-0) obtained a moisture content of the monolayer between 7.0 and 10.0 (g water/100 g db) with red bell pepper (Var

Fig. 4 Adjustment of Peleg (a), Enderby (b), and GAB (c) models to okra (left side) and green pepper (right side) experimental data. Experimental points: diamond (30 °C), + (40 °C), square (50 °C), and x (60 °C). Models: solid line (30 °C), dotted line (40 °C), dashed line (50 °C) and mixed line (60 °C)

Lamuyo), for temperatures between 10 and 30 °C. They observed no direct dependence on temperature.

An observation of the model-ranking Table [3](#page-8-0) shows that the modified Caurie2, Oswin, and modified Oswin models

Table 4 Okra sorption isotherms: model statistical parameters according to temperature

Model	$T(^{\circ}C)$	RMSE	MAE	MRE	Rsq	Rsq- adj	Pd $(\%)$	NRMSE (%)
Peleg	30	0.0086	0.0052	0.0327	0.9971	0.9956	1.4736	1.9024
	40	0.0178	0.0112	0.0872	0.9733	0.9600	5.1427	3.9481
	50	0.0151	0.0084	0.0740	0.9761	0.9641	5.2045	3.3646
	60	0.0113	0.0071	0.0715	0.9830	0.9746	4.4388	2.5109
Enderby	30	0.0105	0.0066	0.0410	0.9956	0.9935	1.8002	2.3241
	40	0.0178	0.0106	0.0824	0.9732	0.9598	5.1529	3.9560
	50	0.0156	0.0084	0.0741	0.9747	0.9620	5.3518	3.4599
	60	0.0115	0.0071	0.0716	0.9824	0.9736	4.5187	2.5561
GAB	$30\,$	0.0166	0.0120	0.0749	0.9872	0.9835	3.0922	3.6959
	40	0.0177	0.0113	0.0876	0.9692	0.9603	5.5289	3.9298
	50	0.0165	0.0103	0.0906	0.9670	0.9575	6.1114	3.6579
	60	0.0126	0.0089	0.0900	0.9754	0.9684	5.3471	2.8003
Hailwood	30	0.0156	0.0120	0.0749	0.9872	0.9835	3.0922	3.4572
$\&$ H.	40	0.0165	0.0113	0.0876	0.9692	0.9603	5.5289	3.6760
Modified	50	0.0154	0.0103	0.0906	0.9670	0.9575	6.1114	3.4216
	60	0.0131	0.0102	0.1023	0.9697	0.9611	5.9288	2.9045
Langmuir	30	0.0281	0.0219	0.1367	0.9633	0.9528	5.2313	6.2526
	40	0.0176	0.0118	0.0919	0.9694	0.9606	5.5079	3.9148
	50	0.0150	0.0096	0.0842	0.9727	0.9649	5.5584	3.3269
	60	0.0112	0.0077	0.0777	0.9807	0.9752	4.7359	2.4802
Luikov	30	0.0262	0.0217	0.1359	0.9637	0.9533	5.2015	5.8154
	40	0.0165	0.0120	0.0934	0.9692	0.9604	5.5224	3.6717
	50	0.0146	0.0101	0.0883	0.9702	0.9617	5.8082	3.2519
	60	0.0125	0.0096	0.0962	0.9725	0.9646	5.6525	2.7691
Caurie2	30	0.0271	0.0214	0.1338	0.9611	0.9563	5.3797	6.0146
	40	0.0168	0.0110	0.0857	0.9681	0.9641	5.6230	3.7385
	50	0.0157	0.0101	0.0890	0.9655	0.9612	6.2466	3.4973
	60	0.0131	0.0087	0.0881	0.9694	0.9656	5.9582	2.9189
Oswin	30	0.0271	0.0214	0.1338	0.9611	0.9563	5.3797	6.0146
	40	0.0168	0.0110	0.0857	0.9681	0.9641	5.6230	3.7385
	50	0.0157	0.0101	0.0890	0.9655	0.9612	6.2466	3.4973
	60	0.0131	0.0087	0.0881	0.9694	0.9656	5.9582	2.9189
Oswin	30	0.0271	0.0214	0.1338	0.9611	0.9500	5.3797	6.0146
Modified	40	0.0168	0.0110	0.0857	0.9681	0.9590	5.6230	3.7385
	50	0.0157	0.0101	0.0890	0.9655	0.9556	6.2466	3.4973
	60	0.0131	0.0087	0.0881	0.9694	0.9607	5.9582	2.9189
Halsey	30	0.0202	0.0164	0.1022	0.9783	0.9756	4.0155	4.4895
	40	0.0197	0.0137	0.1066	0.9562	0.9508	6.5854	4.3784
	50	0.0200	0.0147	0.1290	0.9442	0.9372	7.9449	4.4482
	60	0.0184	0.0131	0.1322	0.9403	0.9329	8.3273	4.0795
Lespam	30	0.0362	0.0253	0.1584	0.9393	0.9219	6.7253	8.0383
	40	0.0222	0.0154	0.1197	0.9512	0.9372	6.9552	4.9435
	50	0.0176	0.0123	0.1083	0.9622	0.9515	6.5347	3.9113
	60	0.0123	0.0095	0.0952	0.9766	0.9699	5.2167	2.7321
Henderson	30	0.0386	0.0301	0.1880	0.9208	0.8982	7.6799	8.5864
Modified	40	0.0192	0.0118	0.0917	0.9584	0.9465	6.4199	4.2683
	50	0.0157	0.0114	0.0998	0.9659	0.9561	6.2139	3.4790
	60	0.0113	0.0084	0.0849	0.9773	0.9708	5.1378	2.5170
Halsey	30	0.0202	0.0164	0.1022	0.9783	0.9722	4.0155	4.4895
Modified	40	0.0197	0.0137	0.1066	0.9562	0.9437	6.5854	4.3784
	50	0.0200	0.0147	0.1290	0.9442	0.9283	7.9449	4.4482
	60	0.0184	0.0131	0.1322	0.9403	0.9233	8.3273	4.0795
Harkins & Jura	30	0.0176	0.0133	0.0834	0.9836	0.9816	3.4926	3.9049
	40	0.0225	0.0149	0.1158	0.9431	0.9360	7.5082	4.9919
	50	0.0230	0.0174	0.1524	0.9261	0.9169	9.1402	5.1174
	60	0.0214	0.0158	0.1588	0.9187	0.9085	9.7223	4.7629

have almost identical statistical results, justified by the identical form of the writing of their respective equations. The only difference lies in the adjusted R^2 of the modified Oswin model, which has a third parameter to be determined, inducing a decrease in its adjusted R^2 value. These three models are thus written, for a given temperature, in the general form presented by Eq. (28).

50 0.0229 0.0153 0.1093 0.9511 0.9371 6.4516 5.6101 60 0.0225 0.0177 0.1471 0.9410 0.9242 7.3758 5.4975

40 0.0414 0.0298 0.1794 0.8792 0.8447 10.8898 10.1233 50 0.0237 0.0171 0.1221 0.9544 0.9414 6.2236 5.7855 60 0.0232 0.0181 0.1499 0.9453 0.9297 7.1029 5.6596

Lespam 30 0.0533 0.0389 0.1818 0.8574 0.8167 10.8919 13.0183

Table 5 Green pepper sorption isotherms: model statistical parameters according to temperature

Model T(°C) RMSE MAE MRE Rsq Rsq-

Pd (%) NRMSE (%)

adj

Table 6 Okra and green pepper isotherm model constants according to temperature

Model	$T(^{\circ}C)$	Okra					Green pepper			
		k1	k2	k ₃	k4	k1	k2	k ₃	k4	
Caurie2	30	0.2132	0.7470			0.1933	1.2449			
	40	0.1761	0.8245			0.1860	1.0189			
	50	0.1689	0.7800			0.1908	0.8340			
	60	0.1604	0.7266			0.1811	0.7650			
Enderby	$\boldsymbol{0}$	1.0718	-7.5548	0.0387	1.0683	2.6328	-12.0579	0.0499	0.9608	
	40	75.1923	-1521.6834	0.1214	0.6846	212.5282	-2447.3023	0.1129	0.7695	
	50	0.1453	0.5327	41.6439	-1201.0875	0.1035	0.8282	141.0186	-2306.8549	
	60	47.4880	-2199.7991	0.1636	0.3718	0.1207	0.7133	143.2380	-3409.2363	
GAB	30	0.0740	0.9890	51.7508		0.1522	0.7508	40.7463		
	40	0.0865	0.8506	20.2420		0.1007	0.8607	176.7757		
	50	0.0906	0.7981	11.2016		0.0806	0.9257	58.1161		
	60	0.1044	0.6977	5.9927		0.0760	0.9056	24.2320		
Hailwood	30	0.0088	0.4328	9.5494E+ 09		0.0072	0.2082	3.5070E+ 09		
&Horobin	40	0.0168	0.2605	3.8285E+ 10		0.0016	0.2454	3.4800E+ 10		
Modified	50	0.0247	0.1814	1.2540E+ 11		0.0046	0.2397	$1.7641E+$ 11		
	60	0.0651	0.0005	5.0000E-01		0.0651	-0.0166	5.0000E-01		
Halsey	30	0.0565	1.3193			0.0279	2.1407			
	40	0.0253	1.6536			0.0275	1.8589			
	50	0.0228	1.6289			0.0364	1.5445			
	60	0.0201	1.5946			0.0323	1.4999			
Halsey	30	-82.9698	2.6699	1.3193		-76.3890	2.4270	2.1407		
Modified	40	-259.5730	6.3974	1.6536		-389.3082	9.6429	1.8589		
	50	300.1249	-6.0781	1.6289		127.4781	-2.6158	1.5445		
	60	260.2386	-4.4024	1.5946		-102.6713	1.6540	1.4999		
Harkins & Jura	30	0.0128	-0.1082			0.0387	0.0511			
	40	0.0121	-0.0470			0.0217	-0.0107			
	50	0.0101	-0.0451			0.0132	-0.0842			
	60	0.0079	-0.0516			0.0100	-0.0903			
Henderson	30	0.2972	-11.7557	1.1504		0.5272	2.1558	2.3198		
Modified	40	-0.4237	-74.3206	1.6185		-0.4465	-76.1682	1.9468		
	50	-0.4015	-90.5543	1.5946		-0.3215	-82.4706	1.5152		
	60	-0.3936	-107.6258	1.5683		-0.3076	-97.2140	1.4521		
Langmuir	30	-802.7141	803.5778	0.9893		-64.8684	66.9509	0.9580		
	40	-165.9940	168.3433	0.9614		-589.2123	591.3745	0.9924		
	50	-33.2614	36.0275	0.8234		-640.7877	642.6405	0.9898		
	60	-11.5840	14.9724	0.5969		-180.8284	182.9298	0.9597		
Luikov	30	0.2504	-74.7446	10.1540		0.2500	-75.2934	1.4349		
	40	0.2499	-77.8207	2.9015		0.2499	-77.8051	2.1052		
	50	0.2498	-80.3424	2.8382		0.2501	-80.2654	3.5892		
	60	0.2498	-82.8643	2.8360		0.2500	-82.7938	3.7011		
Oswin	30	0.1593	0.5710			0.2406	0.3105			
	40	0.1452	0.4271			0.1895	0.3650			
	50	0.1317	0.4330			0.1591	0.4575			
	60	0.1165	0.4414			0.1386	0.4735			
Oswin	30	-7.1113	0.2424	1.7514		-7.1282	0.2456	3.2206		
Modified	40	-9.6780	0.2456	2.3414		-9.6831	0.2468	2.7397		
	50	-12.1841	0.2463	2.3097		-12.1622	0.2464	2.1857		
	60	-14.6924	0.2468	2.2653		-14.6816	0.2470	2.1118		
Peleg	30	1.2488	9.3312	0.2154	0.5131	0.4474	6.4623	0.2917	0.3594	
	40	0.2788	3.0882	0.1348	0.3354	0.1572	0.2078	0.3494	3.1401	
	50	0.2382	2.1711	0.0974	0.2957	0.1241	0.2376	0.3770	3.1361	
	60	0.2107	1.6561	0.0668	0.2874	0.3105	2.3033	0.0832	0.1948	
Lespam	30	0.0090	132.9303	0.0506		9.1466	1.2351	-9.0867		
	40	0.1463	47.3342	-0.1169		0.1355	53.8244	-0.0802		
	50	0.2275	41.4876	-0.2071		0.0750	93.6290	-0.0355		
	60	0.4000	29.6417	-0.3878		0.0944	93.8523	-0.0671		

Figures in bold are monolayer moisture contents predicted by Caurie2 and GAB models

$$
X_e = A \cdot \left(\frac{a_w}{1 - a_w}\right)^B \tag{28}
$$

For the Caurie2 model, $A = k_1 \cdot k_2$ and $B = 2 \cdot k_1/k_2$; for the Oswin model, $A = k_1$ and $B = k_2$ and for the modified Oswin model, $A = k_1 + k_2$. T and $B = k_3$.

Properties of Bound Water: Determination of Energy **Constants**

The models of the okra energy constants obtained, related to the water molecule layers, are presented in Eqs. (29) – (31) :

$$
W_m = 2.71095 \cdot \exp\left(\frac{-9048.90854}{RT}\right) \tag{29}
$$

$$
R2 = 0.9645 \quad \text{RMSE} = 0.0029
$$

$$
K_g = 0.02388 \cdot \exp\left(\frac{9366.28594}{RT}\right)
$$
 (30)

 $R^2 = 0.9806$ RMSE = 0.0207

$$
C_g = 4.89925 \cdot 10^{-8} \cdot \exp\left(\frac{52192.39946}{RT}\right)
$$

\n
$$
R^2 = 0.9674 \quad \text{RMSE} = 3.6994
$$
\n(31)

The results indicate that temperature has a significant effect on the C_g energy constant. On the other hand, the two constants W_m and K_g evolve little with temperature. W_m tends to increase with increase in temperature. This phenomenon could be due to the effect of temperature on the gums and mucilaginous substances of okra, increasing their water retention properties.

Concerning green pepper, the models of the energy constants obtained are presented in Eqs. (32)–(34):

$$
W_m = 2.173800 \cdot 10^{-5} \cdot \exp\left(\frac{22222.32795}{RT}\right)
$$

$$
R^2 = 0.9334 \quad \text{RMSE} = 0.0090
$$
 (32)

$$
K_g = 5.92947 \cdot \exp\left(\frac{-5104.80113}{RT}\right) \tag{33}
$$

$$
R^2 = 0.7658
$$
 RMSE = 0.0463

$$
C_g = 5.53794 \cdot 10^{-5} \cdot \exp\left(\frac{38435.02149}{RT}\right)
$$
\n
$$
R^2 = 0.7352 \quad \text{RMSE} = 41.2198
$$
\n(34)

Here also, the constants W_m and K_g seem to be slightly influenced by the temperature with respective average values of 0.10239 ± 0.03493 (kg kg⁻¹ db) and 0.86069 ± 0.07814 . However, each of these constants evolves in the opposite direction of the variations of these parameters observed with okra. As for okra, the energy constant C_{φ} of green pepper decreases significantly with increasing temperature between 40 and 60 °C. This effect of temperature could be attributed to structural modifications in the substrate, induced by changes in the crystallinity of polymers, cross-linking and denaturation of proteins, or non-enzymatic browning reactions (Iglesias et al. [1986\)](#page-18-0). Since the C_g values are greater than 2, the isotherms are of type II (Taitano and Singh [2012\)](#page-20-0) and confirm the sigmoid form observed above. For the two substrates and in the range of tested temperatures, the constant values related to multilayer properties, K_{α} , also known as the degree of freedom of water molecules (Aguirre-Loredo et al. [2017\)](#page-18-0) were all close to but less than unity and varied between 0.70–0.99 and 0.75– 0.93 respectively for okra and green pepper. These results confirm the particular characteristic of the GAB model (Timmermann et al. [2001](#page-20-0); Taitano and Singh [2012](#page-20-0)). Table 7 presents the average values, over the range of tested temperatures, of W_m and K_g for okra and green pepper.

From Eq. (10) to Eq. (11) (11) , the heat of sorption for the first and subsequent layers of water molecules of okra and green pepper samples were calculated and are presented in Table 7. This table shows that the energy of sorption of water between the monolayer and the multilayer is greater for okra compared to that of green pepper; they are both positive and respectively equal to 52.19 and 38.44 kJ/mol. According to Kiranoudis

Fig. 5 Okra (o) and green pepper (*); sorbed water number of monolayers (N); percentage of bound water (%bw); monolayer moisture content $(k₂)$; sorption surface area (A) according to temperature

et al. [\(1993\)](#page-19-0), ΔH_1 is expected to have a large positive value, due to the exothermic interaction of water vapor with primary sorption site of the material. They obtained estimated values for green pepper of 33.4 kJ/mol relatively close to the value obtained for our green pepper sample.

The removal of water from green pepper requires greater energies as we move from the zone of condensation of pure water to the area of the monolayer bound water. On the other hand, the positive value of the water sorption enthalpy between the condensing zone of the pure water and the upper layer of the okra multilayer (ΔH_2) is linked to the fact that the energy constant, K_{g} , of okra decreases with temperature. This result indicates that the water sorption energy of the upper layers of okra is substantially equal to the latent heat of

Fig. 6 Okra (o) and green pepper (*) density of sorbed water (k_1) according to temperature

vaporization of pure water. In literature, the estimated values of ΔH_2 are found to be positive for vegetables and negative in the case of fruits (Kiranoudis et al. [1993;](#page-19-0) Simal et al. [2007\)](#page-19-0). Therefore, these results indicate that green pepper behaves like a fruit with regard to its sorption characteristics, while okra behaves like a vegetable. These behaviors are also noticed through the ΔH values of the two vegetables.

Modeling Bound Water Properties

The Caurie2 model was used to determine these bound water properties. As illustrated in Fig. 5, the temperature effects on bound water properties are more pronounced with green pepper as compared to okra. In the range of tested temperatures, the number of monolayers is greater than 1 indicating that, for the two substrates, the sorption process is multilayered. Green pepper number of monolayers, percentage of bound water, water content of the monolayer, and specific surface area of sorption are in average higher than those of okra. This phenomenon is more accentuated at low temperatures. This result indicates a difference in structure of the two substrates. From 50 °C and above, these parameters converge to almost identical values, indicating that at high temperature, the bound water properties are not significantly influenced by the nature of the two substrates. The density of sorbed water (Caurie2 constant model, k_1) globally decrease with the increase of temperature, with a more pronounced effect in the case of okra (Fig. 6).

For green pepper, the values of specific surface area of sorption, number of monolayers, percentage of bound water, and water content of the monolayer decrease with the increase in temperature and tend to attain a constant value at high temperatures. Similar results were found by Sahu and Das

Table 8 Second order polynomial models of bound water properties according to the absolute temperature in K ($Y = a_1 \cdot T_a^2 + a_2 \cdot T_a + a_3$)

	Okra					Green pepper				
Model parameters N		bw	A	k ₁	k2	N	bw	А	k ₁	k ₂
a_1	-0.00317	-0.00389	-0.08636	0.00007	-0.00033	0.00203	0.00505	0.05540	-0.00001	0.00039
a ₂	2.04865	2.49261	55.77597	-0.04731	0.20726	-1.37230	-3.37720	-37.36181	0.00343	-0.26586
a_3	-325.96296	-395.49530	-8874.56995	7.96078	-31.99117	235.51936	567.64725	6412.17998	-0.30643	45.79328
Statistical parameters										
R^2	0.92041	0.87890	0.92041	0.96999	0.88364	0.98110	0.99635	0.98110	0.59076	0.99798
R^2 adj	0.88061	0.81835	0.88061	0.95499	0.82546	0.97165	0.99452	0.97165	0.38615	0.99697
RMSE	0.19267	0.22904	5.24549	0.00495	0.01786	0.17494	0.16189	4.76277	0.00422	0.01182

[\(2010\)](#page-19-0) and Choudhury et al. [\(2010\)](#page-18-0) on other substrates. On the contrary, the increase in temperature has a slightly positive effect on the okra's specific surface area of sorption and on the sorbed water number of monolayers. However, the temperature effects on the other bound water properties are negligible. These results indicate that, for a better efficiency, the desorption process of okra substrates would require higher temperatures compared to those necessary for green pepper. Moreover, during desorption, it would be wise to find a compromise between high sorption surface area, low energy expenditure, and product quality.

Models of variation of bound water properties according to temperature have been determined (Table 8). These results are well-adjusted by second-order polynomial functions. However,

Fig. 7 Okra (left side) and green pepper (right side) pore radius (a) and bound water monolayer thickness (b) according to the equilibrium moisture content, at different temperatures (diamond: 30 °C; +: 40 °C; square: 50 °C; and x: 60 °C)

Table 9 Second order polynomial model parameters for the variation with equilibrium moisture content of critical pore radius, bound water monolayer thickness, and pore radius $(Y = a_1 \cdot X_e^2 + a_2 \cdot X_e + a_3)$

Model	Okra				Green pepper				
	30 °C	40 °C	50° C	60 °C	30 °C	40 °C	50 °C	60 °C	
	Critical pore radius.								
a_1	10557.0061	56106.7519	61762.2886	95095.6654	44692.48740	26081.34657	45882.99590	55767.67023	
a_2	13854.2126	5685.5452	5823.5557	1384.4429	-2144.06590	8262.87478	3338.30387	2679.73678	
a_3	-269.0395	31.1425	69.1485	233.3754	171.08141	-261.19492	125.24828	223.27981	
R^2	0.9794	0.9342	0.9093	0.9206	0.88552	0.85611	0.99301	0.95514	
R^2 -adj	0.9735	0.9154	0.8834	0.8980	0.85281	0.81500	0.99101	0.94232	
RMSE	533.3488	533.3488	533.3488	533.3488	$4.01E + 02$	$4.01E + 02$	$4.01E + 02$	$4.01E + 02$	
	Bound water monolayer thickness								
a_1	-3.0192	-2.7396	-3.6802	-3.2049	0.50238	-2.03666	-1.62802	-2.84634	
a_2	3.2118	3.4340	3.7740	3.8330	1.68275	2.92767	2.85258	3.31584	
a_3	0.2612	0.2623	0.2710	0.2934	0.26259	0.22951	0.27829	0.28931	
R^2	0.9867	0.9751	0.9710	0.9682	0.91614	0.92729	0.97429	0.95264	
R^2 -adj	0.9829	0.9680	0.9627	0.9591	0.89218	0.90652	0.96694	0.93911	
RMSE	0.0458	0.0458	0.0458	0.0458	5.59E-02	5.59E-02	5.59E-02	5.59E-02	
Pore radius									
a_1	10553.9869	56104.0123	61758.6084	95092.4607	44692.98979	26079.30991	45881.36789	55764.82387	
a ₂	13857.4244	5688.9792	5827.3297	1388.2758	-2142.38315	8265.80246	3341.15646	2683.05262	
a_3	-268.7784	31.4048	69.4195	233.6688	171.34401	-260.96541	125.52656	223.56912	
R^2	0.9794	0.9342	0.9093	0.9206	0.88552	0.85612	0.99301	0.95514	
R^2 -adj	0.9735	0.9154	0.8834	0.8980	0.85282	0.81502	0.99101	0.94232	
RMSE	533.3929	533.3929	533.3929	533.3929	401.06684	401.06684	401.06684	401.06684	

with respect to Caurie2 constants with low values, such as k_1 for green pepper and k_2 for okra, a better adjustment could be obtained by third-order polynomial functions. Figs. [5](#page-14-0) and [6](#page-14-0) present the model fitting to the data.

Fig. [7](#page-15-0) shows the evolution of the pore radius and the thickness of the bound water monolayer of the two substrates, as a function of the equilibrium water content of okra and green pepper. The ranges of variation of these two quantities are practically the same for the two plants and vary respectively from 300 to 8000 nm and from 0.4 to 1.1 nm. According to the IUPAC classification, we are in the presence of macropores. Since the thicknesses of the bound water monolayers are very small, less than 1.2 nm, the curves of the critical radius are similar to those of the pore radius for each substrate. Velázquez-Gutiérrez et al. ([2015](#page-20-0)) reported that the pore radius of the mucilage extracted from chia seeds ranged from 0.87 to 6.44 nm. It can be seen from Fig. [7](#page-15-0) that the pore radius and the thickness of the bound water monolayer of the two substrates increase with the equilibrium moisture content according to a second-order polynomial model, the parameters of which are presented in Table 9. Model parameters for the bound water monolayer thickness are also presented in the same table. The coefficients of determination of these models vary between 0.909–0.987 and 0.856–0.993 respectively for okra and green pepper. Hence, during desorption, there is a tightening of the pores of the substrate indicating a possible reduction in the volume of the material during drying. For a given equilibrium moisture content and for a given temperature, the pore radius and the thickness of the okra monolayer are always slightly higher than those of green pepper. Globally for both plants, for a given equilibrium water content, the increase in temperature causes a magnification of the pore radius and an increase in the thickness of the monolayer of bound water. Similar pore radius behaviors have been reported by Singh et al. ([2001](#page-20-0)) and Igbeka and Blaisdell [\(1982\)](#page-18-0) on meat products. However, in zone 1 of the sorption isotherm and in the case of okra, these quantities seem independent of the temperature and vary linearly with the equilibrium moisture content. The effect of temperature on the pore radius is more marked in zones 2 and 3 of the sorption isotherm, where for a given equilibrium moisture content, an increase in temperature induces an increase in pore radius and the thickness of the monolayer of bound water. This may be due to physical and/ or chemical changes in the product induced by temperature. The difference in behavior between the two substrates would be closely related to their composition. The presence of mucilage and gums in okra is a key factor (Gunsanee [2011](#page-18-0)). The observed narrowing (shrinkage) suggests that prior to drying,

a pretreatment of the substrates should be considered, to avoid severe shrinkage during drying.

Conclusion

The desorption isotherm curves of okra and green pepper were experimentally determined at four temperatures (30, 40, 50, and 60 °C) and were of type II, indicating a high hygroscopicity of the materials. Peleg, GAB, and Enderby models presented the best fits of the twenty tested models. The evaluation of the water content of the monolayer showed that the physicochemical and microbiological stability of okra and green pepper are obtained at equilibrium moisture content of 8 and 10 $(g/100 \text{ g db})$, respectively, corresponding to an optimal water activity of 0.35 for both vegetables. Bound water properties were determined and showed that substrate constituents play a key role in water sorption mechanism. The calculated energy constants indicate that okra has the characteristics of vegetables, while green pepper has those of fruits. The pore radius was found to decrease with decreasing moisture content for a given temperature, and to decrease with decreasing temperature for a given moisture content and for a particular product. For a given moisture content, okra's pore radius were found to be slightly higher than those of green pepper. The determination of these parameters is of fundamental importance for good preservation of the product through drying, as well as the design of equipment for post-harvest preservation.

Acknowledgements The authors thank the French Embassy through the Cooperation and Cultural Action Service (SCAC) program for the financial support.

Declarations

Conflict of Interest The authors declare no competing interests.

Abbreviations

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