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Drying kinetics and quality changes during drying of red pepper

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Abstract

A mathematical model is proposed to simulate the process of drying of individual pieces of red pepper under constant external conditions and to predict changes in some nutritional and organoleptic attributes of the product. The model was solved numerically to obtain moisture content and temperature as well as ascorbic acid and carotenoids concentration in the product as a function of time. A good agreement between predictions and experimental data at different drying temperatures was obtained.

Water sorption isotherms of red pepper were determined in the range 20–50 °C and represented by two different sorption equations. Drying kinetics were represented by a diffusive model, the effective moisture diffusivity ranging from 5.01 to $8.32 \times 10^{-10}\,\mathrm{m^2/s}$ with an activation energy of 23.35 kJ/mol. Degradation kinetics for ascorbic acid and total carotenoids were measured in the range 50–70 °C and modelled as first-order reactions. The rate constants increased with temperature and product moisture content. Average activation energies for carotenoids and vitamin C degradation were 50.1 and 26.9 kJ/mol, respectively.

Keywords: Drying; Sorption isotherm; Ascorbic acid; Carotenoids; Red pepper

1. Introduction

The increasing demand for high-quality shelf-stable dried vegetables requires the design, simulation and further optimization of the drying process with the purpose of accomplishing not only the efficiency of the process but also the final quality of the dry product. During drying, vegetables undergo physical, structural, chemical, organoleptic and nutritional changes that cause quality degradation (Crapiste, 2000).

Red pepper (*Capsicum annuum* L.), as other vegetables, is a good source of antioxidant substances such as carotenoids (provitamin A) and vitamin C, which confer protection against carcinogenic components and delay the aging process (Howard, Smith, Wagner, Villalon, & Burns, 1994; Simonne, Simonne, Eitenmiller, Mills, & Green, 1997). Dried red pepper or paprika is one of the most important vegetable spices, its quality being determined mainly by colour (Mínguez-Mosquera, Jarén Galán, & Garrido-Fernández, 1992; Nagle, Villalon, & Burns, 1979). Carotenoids are responsible for the colour (Davies, Matthews, & Kirk, 1970; Mínguez-Mosquera & Hornero-Méndez, 1993; Reeves, 1987) and their contents are related to varietal and technological factors (Biacs, Czinkotai, & Hoschke, 1992; Carbonell, Piñaga, Yusá, & Peña, 1986; Mínguez-Mosquera, Pérez-Galvez, & Garrido-Fernandez, 2000).

Some previous research has been presented in the literature on the dehydration of red pepper. Turhan, Turhan, and Sahbaz (1997), Ramesh, Wolf, Tevini, and Jung (2001) and Doymaz and Pala (2002) studied the drying kinetics of red pepper under different pretreatments and drying conditions. Other authors reported the influence of drying on various quality parameters such as carotenoids and non-enzymatic browning (Lee &

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Nomenclature

A	ascorbic acid/carotenoids concentration
a,b,c	constants in CR equation
a_v	surface area to volume ratio (m^2/m^3)
a_w	water activity
C, K	constants in GAB equation
Cp_s	specific heat of product (J/g °C)
D_{oeff}	pre-exponential factor in Eq. (4) (m^2/s)
D_{eff}	water diffusivity (m^2/s)
E_a	activation energy for reaction (kJ/mol)
E_d	activation energy for diffusion (kJ/mol)
h_g	external heat transfer coefficient ($W/m^2 K$)
k	reaction rate constant (s^{-1})
k_0	pre-exponential factor in Eq. (6) (s^{-1})
K_i	parameters of rate constant in Eq. (6) ($i = 1, \ldots, 4$)
L	sample thickness (m)
Nu	Nusselt number
n_w	drying rate (kg water/m^2 s)
R	universal gas constant (8.314 J/kg mol)
Re	Reynolds number
t	time (s)
T_a	air temperature (°C)
T_s	product temperature (°C)
X	moisture content, dry basis (kg water/kg dry matter)
X_e	equilibrium moisture content, dry basis (kg water/kg dry matter)
X_o	initial moisture content, dry basis (kg water/kg dry matter)
X_m	monolayer moisture content, dry basis (kg water/kg dry matter)
W	moisture content, wet basis (kg water/kg product)
ΔH_v	heat of vaporization (kJ/kg)
σ	standard deviation
ρ_s	product density (kg/m^3)

Kim, 1989), colour, L-ascorbic acid and sugar retention in green pepper (Sigge, Hansmann, & Joubet, 1999) or colour (Carbonell et al., 1986; Doymaz & Pala, 2002).

Furthermore, pimentón, which is a spice derived from the red *Capsicum* made up 13.5% of the total spice volume exportations from Argentina (Acerbi, 2005) which implies the research effort to enable producers to compete in the international market in regards to quality requirements.

The aim of this work is to present a simulation model for air drying of red pepper which takes into account the quality deterioration during the process. For that purpose, we determined sorptional behaviour, drying kinetics and ascorbic acid and carotenoids destruction as a function of product moisture content and temperature during drying. Furthermore, the model incorporated the modifications of thermophysical properties and transports coefficients due to solid shrinkage, temperature and moisture content during dehydration.

2. Materials and methods

2.1. Materials

Good-quality fresh red pepper was purchased from a local market (Bahía Blanca, Argentina) and stored in a cabinet at 3 °C and 98% relative humidity until the experiments were carried out. The fruit was washed and, after removing the seeds, were cut into slices of $2 \times 2 \times 0.5$ cm approximately. The initial moisture content of red pepper was 92.4 ± 0.042 g/100 g fresh material.

2.2. Moisture sorption isotherms

Red pepper samples at different moisture contents were obtained by drying the product at low temperatures (20–50 °C) in the laboratory dryer described below. Equilibrium moisture content was determined gravimetrically by drying in a vacuum oven at 60 °C until a constant weight (± 0.001 g) was achieved. Water activity at 20, 30, 40 and 50 °C was measured by duplicate using a Novacina Aw-centre by equilibrating the dried samples against saturated aqueous salts solutions (Rockland, 1960).

2.3. Drying kinetics

A thin layer of pepper samples was dried in a cross-flow laboratory scale dryer with air at 50, 60 and 70 °C, ambient relative humidity, and 0.2 and 1.2 m/s air velocity. The dryer consisted of a closed loop system where the air was partially recirculated by a centrifugal fan, an electrical heater connected to a temperature controller and a drying chamber. Product and air temperatures were measured continuously in the drying chamber with *K*-type thermocouples. Drying curves were obtained by periodic determination of weight and moisture content of pepper samples. Changes in the dimensions of samples due to shrinkage were also measured and used to evaluate density and the surface area to volume ratio.

2.4. Ascorbic acid and total carotenoids determination

Ascorbic acid was determined by a titration method (Pelletier, 1985). Total ascorbic acid was measured as dehydroascorbic acid following oxidation of reduced ascorbic acid with 2,6-dichloro-indophenol and expressed as mg ascorbic acid/100 g vegetable tissue on wet and dry basis. All determinations were carried out in duplicate. The mean value for fresh pepper was 224.4 mg ascorbic acid/100 g fresh product.

Total carotenoids content was determined by measuring the absorbance of a suitable diluted sample (Davies et al., 1970) and expressed as mg carotenoids/100 g vegetable tissue on wet and dry basis. All determinations were carried out in duplicate. The mean value for fresh pepper was 14.26 mg carotenoids/100 g fresh product.

3. Mathematical models

3.1. Sorption isotherms

Sorption isotherms for red peppers were represented by means of the following equations:

GAB (Van den Berg, 1984)

$$X = \frac{X_m K C a_w}{(1 - K a_w)(1 - K a_w + K C a_w)}. \tag{1}$$

CR (Crapiste & Rotstein, 1986)

$$a_w = \exp[-a W^{-b} \exp(-cW)]; \quad W = \frac{X}{1 + X}. \tag{2}$$

Model parameters were estimated by fitting the equations to the experimental data using a non-linear regression routine using the Systat program.

3.2. Drying kinetics

The most widely used theoretical model in drying of individual particles of food products is the diffusive model which puts all the complexity of the problem on an effective transport coefficient and the Biot mass number (Pezzutti & Crapiste, 1997; Ramesh et al., 2001; Turhan et al., 1997). A single diffusive model was adopted to describe isothermal drying of red pepper. When internal mass transfer is the controlling mechanisms and uni-dimensional transport in a slab with constant effective diffusivity can be assumed, the solution of the Fick's second law for the total moisture content is given as (Crank, 1975)

$$\frac{X - X_e}{X_o - X_e} = \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp\left[-\frac{(2i+1)^2 \pi^2}{4L^2} D_{\mathrm{eff}} t\right]. \tag{3}$$

For sufficiently long drying times, the first term ($i = 0$) in the series expansion of Eq. (3) gives a good estimate of the solution. In this case, a linear relationship between logarithm of dimensionless moisture content and time is obtained, which can be used to determine diffusion coefficients.

Effect of temperature on the moisture diffusion coefficient can be described by an Arrhenius-type equation in the form:

$$D_{\mathrm{eff}} = D_{\mathrm{oeff}} \exp\left[-\frac{E_d}{R T_a}\right]. \tag{4}$$

3.3. Carotenoids and ascorbic acid losses

A pseudo-first-order kinetics was assumed to represent ascorbic acid and total carotenoids destruction in the form:

$$\frac{dA}{dt} = -kA. \tag{5}$$

The reaction rate constant k was expressed as a function of moisture content and temperature of the product as follows:

$$k = k_0 \exp\left[-\frac{E_a}{R T_s}\right], \quad k_0 = K_1 X^{K_2}, \quad \frac{E_a}{R} = K_3 + K_4 X. \tag{6}$$

Kinetics model constants were estimated by fitting the equations to experimental data using a non-linear regression routine (Systat, 1995).

3.4. Drying model

The drying model is based on the differential mass and energy balances for the slice assuming internal control (diffusion) for mass transfer and external control (convection) for heat transfer, and can be expressed as (Crapiste & Rotstein, 1997)

$$\frac{dX}{dt} = -\frac{n_w a_v}{\rho_s} = -\frac{\pi^2 D_{\mathrm{eff}}}{4L^2}(X - X_e), \tag{7}$$

$$\frac{dT_s}{dt} = \frac{a_v}{\rho_s C p_s}[-n_w \Delta H_v + h_g(T_a - T_s)]. \tag{8}$$

These differential equations along with the kinetic equations that describe variations in ascorbic acid and carotenoids concentration and the corresponding initial conditions were integrated as a function of drying time using the MATLAB program (Matlab, 1999).

Knowledge of equilibrium, thermophysical and transport properties is needed as part of the information required for the drying model to be solved. Food size, temperature and moisture content change during drying and this modifies the thermophysical and transport properties of individual particles. Solid density and the surface area to volume ratio were calculated from experimental data by measuring side and thickness of particles with a caliper and correlated as functions of the dimensionless moisture content during drying. The specific heat

Table 1
Thermophysical properties of red pepper

Density (kg/m^3)	
$\rho_s = 2798 \exp[-15.83(X/X_o)] + 845.2 \exp[0.125(X/X_o)]$	$X/X_o \geqslant 0.1$
$\rho_s = 1138 \exp[2.33(X/X_o)]$	$X/X_o < 0.1$
Surface area, a_v (m^{-1})	
$a_v = a_{vo}[5.149 - 18.813(X/X_o) + 28.684(X/X_o)^2 - 14.02(X/X_o)^3]$	
Specific heat, Cp (kJ/kg °C)	
$Cp = 815.4 + 3382X/(X+1)$	

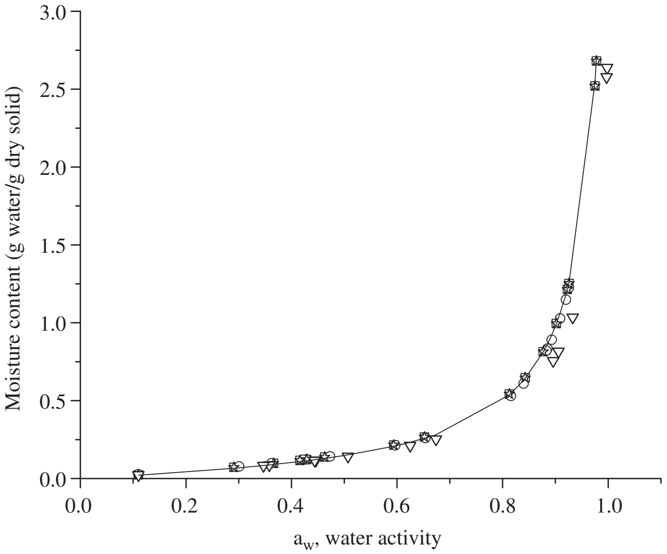

Fig. 1. Desorption isotherm for red pepper in the range 20–50 °C: ▽ ($T = 50\,°C$), ☆ ($T = 40\,°C$), ○ ($T = 30\,°C$), ☐ ($T = 20\,°C$), ---- (CR) and — (GAB).

Table 2
Estimated sorption model constants for red pepper at 20–50 °C

GAB	CR
$X_m = 0.127$	$a = 0.857$
$K = 0.976$	$b = 0.224$
$C = 1.625$	$c = 4.768$
$r^2 = 0.995$	$r^2 = 0.999$
$\sigma = 0.0614$	$\sigma = 0.0195$

estimation was done based on data reported by Polley, Snyder, and Kotnour (1980).

Heat transfer coefficients were calculated from a specific dimensionless equation for drying of foodstuffs and corrected by shrinkage (Ratti & Crapiste, 1995):

$$Nu = 0.249 Re^{0.64}, \quad h_g = h_{g0}\left(\frac{a_v}{a_{vo}}\right)^{0.36}. \tag{9}$$

4. Results and discussion

The thermophysical properties of red pepper as a function of moisture content are showed in Table 1.

Equilibrium results for red pepper are presented in Fig. 1. Effect of temperature in the range 20–50 °C showed to be negligible, and only one isotherm was drawn for simplicity. This is in agreement with results obtained by Carbonell et al. (1986) for red pepper between 5 and 35 °C. It can be observed that sorption equilibrium shows the characteristic behaviour of high sugar food products. Desorption data at 30 °C for green pepper reported by Kiranoudis, Maroulis, Tsami, and Marinos-Kouris (1993) and Turhan et al. (1997) were found to be higher than those obtained in this work, particularly at low water activities. On the other hand, Carbonell et al. (1986) and Kaymak-Ertekin and Sultanoglu (2001) presented lower equilibrium moisture contents at high water activities for red pepper at 30 °C.

Table 3
Estimated parameters for destruction rate constants

Constants	Ascorbic acid	Carotenoid
K_1	1.082	6320
K_2	0.590	0.483
K_3	3144	5992
K_4	8.990	8.976
r^2	0.980	0.971

Constants are dimensionless.

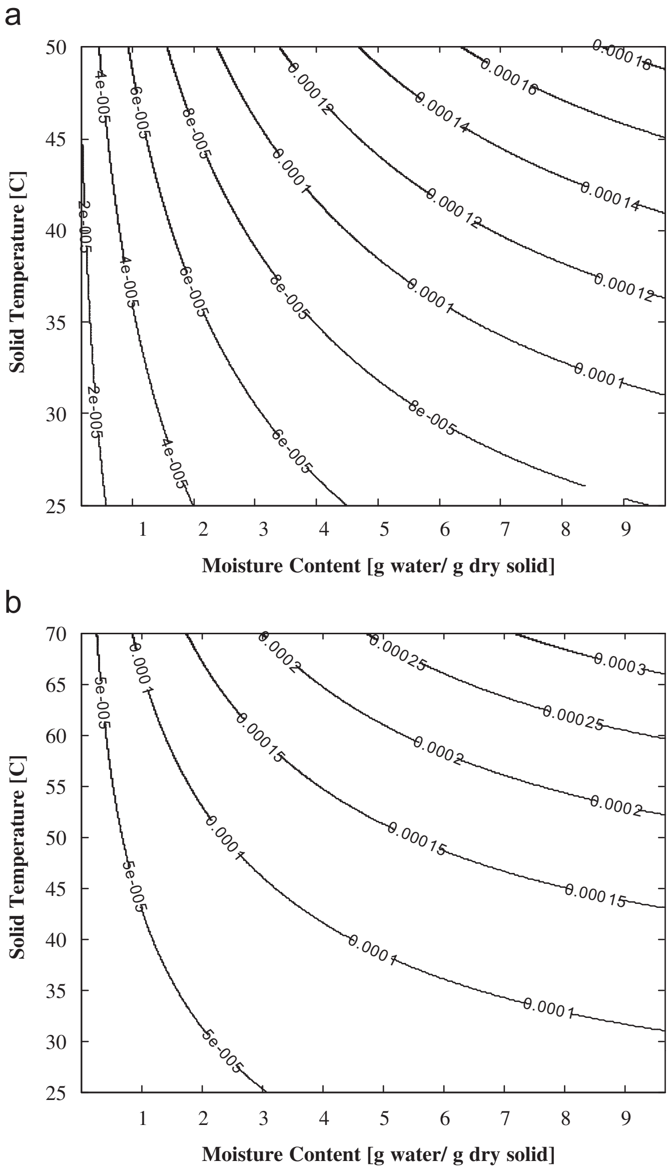

Fig. 2. Contour curves for the reaction rate constant of ascorbic acid lost during drying at (a) 50 °C and (b) 70 °C.

Model constants obtained by fitting the equations to experimental data are shown in Table 2. The obtained monolayer moisture content X_o was higher than those reported by Carbonell et al. (1986) and Kaymak-Ertekin and Sultanoglu (2001), 0.0816 and 0.095 kg/kg$_{dm}$, respectively, but significantly lower than that obtained by Kiranoudis et al. (1993), which was 0.212 kg/kg$_{dm}$. Sorption isotherms predicted by the models with the estimated constants are presented in Fig. 1. A very good correspondence between experiments and models is observed for both GAB and CR equations.

Linear relationships were obtained by plotting experimental drying data at different temperatures in terms of logarithm of dimensionless moisture content versus time. The value of r^2 for the linear regression varied between 0.998 and 0.999. This indicates that the entire drying curve can be represented approximately by a diffusion model with a constant effective diffusion coefficient D_{eff}. Effect of the external resistance to mass transfer was analysed according to the method proposed by Pezzutti and Crapiste (1997) and was negligible under the drying conditions studied in this work. Similar results were obtained by Kaleemullah and Kailappan (2006). Obtained values for the diffusion coefficient increased with temperature from $5.01 \times 10^{-10}\,m^2/s$ at 50 °C to $8.32 \times 10^{-10}\,m^2/s$ at 70 °C, with an activation energy of 33.83 kJ/mol. This value compares satisfactorily with similar data for red pepper reported in the literature by Carbonell et al. (1986) and Turhan et al. (1997), 36.6 and 28.4 kJ/mol, respectively.

Experimental data of ascorbic acid and total carotenoids concentration as a function of moisture content and temperature of red pepper during drying time were correlated with the kinetic model given by Eqs. (5) and (6). The model constants for ascorbic acid and total carotenoids destruction are presented in Table 3.

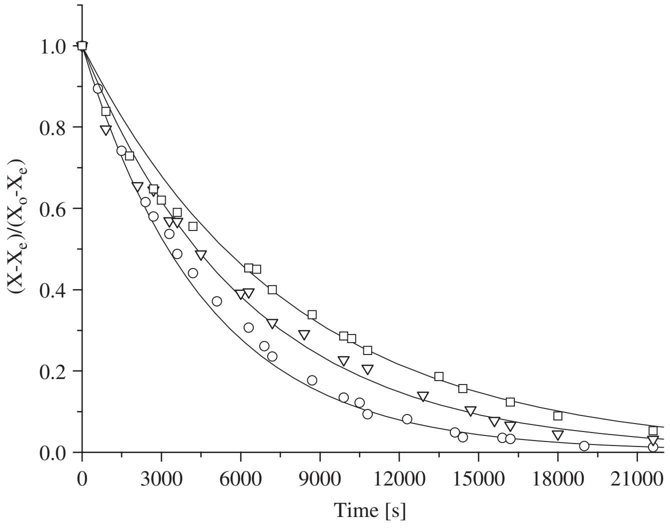

Fig. 3. Air drying curves of red pepper at different temperatures, $Y = 0.0058$ kg/kg. Model (—), ○ ($T = 70$ °C), ▽ ($T = 60$ °C) and □ ($T = 50$ °C).

The reaction rate constants increased with solid temperature and moisture content as can be observed from Fig. 2 which shows the contour curves $k = f(X,T_s)$, for the ascorbic acid at 50 and 70 °C, results on carotenoids are not presented. The mean activation energies for vitamin C and carotenoids destruction were 26.9 and 50.1 kJ/mol, respectively. Lee and Kim (1989) reported activation energies from 32.2 to 114.5 kJ/mol for the decolourization of carotenoids at moisture contents up to 3 kg/kg$_{dm}$.

Fig. 3 shows the drying curves predicted by the model as they compare with experimental drying data obtained with drying air at 50, 60 and 70 °C. Experimental and predicted changes in dimensionless ascorbic acid and total carotenoids retention during drying as a function of air temperature are presented in Figs. 4 and 5. Each experimental point

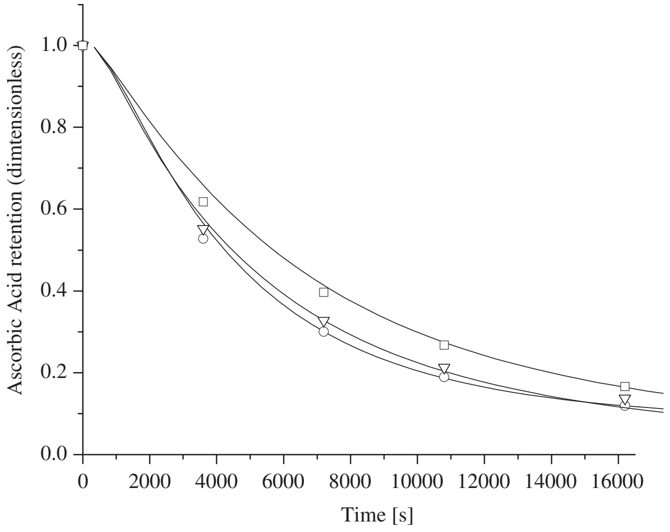

Fig. 4. Change in ascorbic acid retention during drying as a function of air temperature: Model (—), ○ ($T = 70$ °C), ▽ ($T = 60$ °C) and □ ($T = 50$ °C).

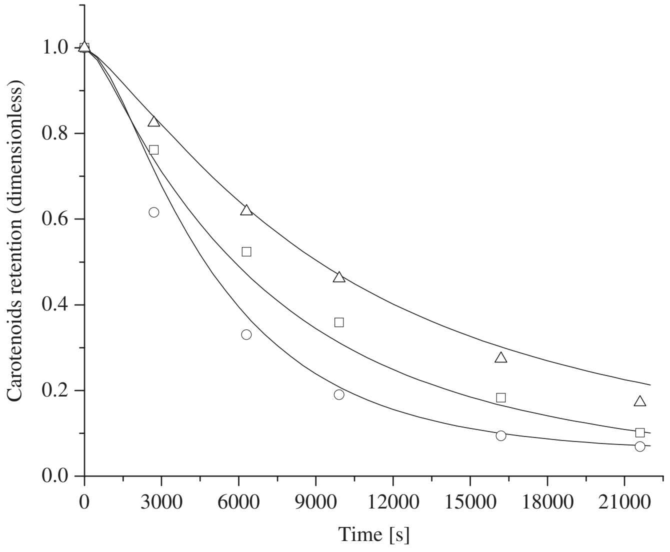

Fig. 5. Change in total carotenoid retention during drying as a function of air temperature: Model (—), ○ ($T = 70$ °C), ▽ ($T = 60$ °C) and □ ($T = 50$ °C).

represents the mean value of two replications. It can be observed that the proposed model predicted satisfactorily the drying kinetics and quality changes in red pepper.

An increase in drying air temperature has a negative effect on quality for both vitamin C and carotenoids. At 50 °C the model predicts higher losses in vitamin C than in colour after 4.5 h of drying ($X = 0.11$ g water/g dry solid) because ascorbic acid retention was 16.8 mg/100 g product (losses of 83.2 mg/100 g product) whilst the product lost 70.5 mg/100 g product of its original colour. At 60 °C the product decolourizes 85 mg/100 g product whilst the losses in vitamin C are 87 mg/100 g product and finally, at 70 °C the percentage of both components losses is higher than 91 mg/100 g product.

Indeed, drying at 60 or 70 °C produced approximately the same nutritional degradation of the product from the ascorbic acid retention standpoint. The destruction rate is higher at high moisture contents than at others stages of drying. In particular for carotenoids, it could be due to solubilization and mobility of catalysts such as copper, peroxidase and the presence of ascorbic acid (Kanner, Mendel, & Budowsky, 1977), which is in agreement with the results obtained by Lee and Kim (1989).

The ascorbic acid retention after drying was in the range 12–18%. Sigge et al. (1999) reported a 25–40% retention of the vitamin C during dehydration of green peppers between 55 and 75 °C, Howard et al. (1994) found 75% losses of vitamin of "pimientos jalapeños" dried at 100 °C, and Daood, Vinkler, Markus, Hebshi, and Biacs (1996) reported 63% losses during drying of red peppers at ambient temperature.

5. Conclusions

A model to simulate the drying of individual pieces of red pepper and to predict some quality changes that undergoes the product during drying was developed and numerically solved with Matlab. Loss of nutritional values and colour during drying was assessed by representing the ascorbic acid and carotenoids destruction with a pseudo-first-order kinetics, the reaction rate constant depending on moisture content and product temperature. Temperature had little effect on water sorption in red pepper at 20–50 °C and the isotherm can be represented adequately by the GAB and CR models. Drying kinetics of red pepper slices can be modelled as a simple diffusive problem, the effect of temperature on the effective diffusion coefficients represented by an Arrhenius-type equation. A good agreement between model predictions and experiments at different drying temperatures was obtained. The results show that the proposed model can be used to optimize the drying process in order to obtain higher quality dried red pepper from a nutritional and organoleptic standpoint.

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