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Research Paper / Araştırma Makalesi

Color and Ascorbic Acid Degradation Kinetics of Red Pepper (*Capsicum annuum* L.) Slices during Vacuum Drying

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ABSTRACT

Red pepper slices were dried in a vacuum dryer at three different temperatures (45, 55 and 65°C) and two absolute pressures (21.5 kPa and 48.0 kPa). Drying temperature and absolute pressure significantly influenced drying time. Degradation kinetics of ascorbic acid in red pepper slices during vacuum drying followed a first-order kinetic model. The highest ascorbic acid retention occurred in the samples dried the combination of 45°C and 21.5 kPa. In addition to the temperature effect, the drying absolute pressure was effective on the loss of ascorbic acid. The activation energy values for ascorbic acid under both absolute pressure of 48.0 kPa and 21.5 kPa were calculated as 70.85 kJ/mol and 81.43 kJ/mol, respectively. The sample surface color degradation after drying was also determined. The color values (Hunter *L*, *a* and *b*) decreased, while *ΔE* (The color difference) increased during drying. Mathematical modeling of color degradation kinetics indicated that both the zero-order and first-order kinetic model were found to describe the Hunter *L*, *a* and *b* values. However, *ΔE* followed zero-order kinetic model.

Keywords: Red pepper, Vacuum drying, Ascorbic acid, Color, Degradation

Kırmızıbiber (*Capsicum annuum* L.) Dilimlerinin Vakumla Kurutulması Sırasında Renk ve Askorbik Asidin Bozunma Kinetiği

ÖZ

Kırmızı biber dilimleri vakumlu bir kurutucuda üç farklı sıcaklıkta (45, 55 ve 65°C) ve iki mutlak basınçta (21.5 kPa ve 48.0 kPa) kurutulmuştur. Kurutma sıcaklığı ve mutlak basınç kuruma süresini önemli ölçüde etkilemiştir. Askorbik asitin, vakumla kurutma sırasında kırmızıbiber dilimlerindeki bozunma kinetiği, birinci dereceden bir kinetik modele uyduğu belirlenmiştir. En yüksek askorbik asit miktarı, 45°C ve 21.5 kPa kombinasyonunda kurutulmuş örneklerde belirlenmiştir. Kurutma sıcaklığının etkisine ek olarak, kurutma mutlak basıncının da askorbik asit kaybı üzerinde etkili olduğu saptanmıştır. Askorbik asit için hem 48.0 kPa hem de 21.5 kPa mutlak basınç altında yapılan kurutma işleminde, aktivasyon enerji değerleri sırasıyla 70.85 kJ/mol ve 81.43 kJ/mol olarak hesaplanmıştır. Çalışmada ayrıca kurutma sırasında örneklerin yüzey renginin bozulması da incelenmiştir. Renk değerleri (Hunter *L*, *a* ve *b*) azalırken, ΔE değerinin kurutma sırasında arttığı belirlenmiştir. *Hunter L*, *a* ve *b* değerlerinin renk bozulması kinetiğinin matematiksel modellemesi yapılmış ve hem sıfırıncı hem de birinci dereceden kinetik modele uyduğu saptanmıştır. Bununla birlikte, ΔE değerinin sadece sıfırıncı dereceli kinetik modele uyduğu belirlenmiştir.

Anahtar Kelimeler: Kırmızıbiber, Vakumla kurutma, Askorbik asit, Renk, Bozulma

INTRODUCTION

Red pepper is an excellent source of phytochemicals and essential nutrients such as ascorbic acid and tocopherols [1]. Ascorbic acid is an important component of our nutrition and reportedly reduces the risk of cardiovascular diseases and some forms of cancer because of its antioxidant capacity. However, ascorbic acid is one of the most labile vitamins. It is easily oxidized by air, heat and oxidizing enzymes [2]. It is generally observed that if ascorbic acid is well preserved, the other nutrients are also well retained [3]. Color is one of the most important qualities of red pepper, which effects the consumers' preferences. The color of red pepper is controlled by several carotenoids (capsanthin, capsorubin, and xanthophyllys for the red color) [4,5].

Red peppers are usually dried in greenhouse dryers or by spreading them on the ground under open atmosphere (namely, open sun drying) in the most part of the world [5,6]. However, sun drying requires a long drying period, affected by daily weather conditions making it rather difficult to control the moisture content of the sample [7]. In addition, the products may be degraded during sun drying due to wind-borne dirt and dust, infestation by insects, rodents, and other animals [8]. The color retention of red pepper dried either under open atmosphere or green house dryers can be challenging since necessary drying time is considerably long in either case and the browning reactions occur in red pepper [6,9].

Vacuum drying provides an alternative to conventional atmospheric drying. It allows the removal of moisture under low pressure. Vacuum expands air and water vapor present in the food and creates a frothy or puffed structure, providing a large area-to-volume ratio for enhanced heat and mass transfer [10]. Consequently, with vacuum drying it is possible to have a higher drying rate, lower drying temperature, and an oxygen deficient processing environment [11]. The objective of this experiment is to determine the kinetics of ascorbic acid and color degradation during vacuum drying of red peppers.

MATERIALS AND METHODS

Materials

Fresh red pepper (*Capsicum annuum* L.) samples were purchased from a local market in Denizli, Turkey. They were taken in polyethylene packages and stored at 4 ± 0.5°C in a refrigerator until drying. Moisture content of the samples was determined in a vacuum oven (Model JSVO-60T, JSR, Gongju-City, Korea) at 70°C for 24h [12].

Methods

Vacuum Drying

A laboratory type vacuum oven (Model JSVO-60T, JSR, Gongju-City, Korea) was used for carrying out drying experiments. The temperature of a vacuum oven had a sensitivity of 1°C, with a maximum temperature of 250°C. The internal dimensions of the vacuum oven were 40 × 42 × 35 cm. The oven consisted of an analogous vacuum-meter. Six different temperature – absolute pressure combinations were obtained in vacuum drying by combining three different drying temperatures (45, 55 and 65°C) and two different absolute pressure values (21.5 kPa and 48.0 kPa). The vacuum drying of red pepper studies were carried out under the combinations of 45°C–21.5 kPa, 45°C–48.0 kPa, 55°C–21.5 kPa, 55°C–48.0 kPa, 65°C–21.5 kPa, 65°C–48.0 kPa. The washed red peppers were sliced into 4 cm wide, 7.0±2.0 cm length and 0.6±0.1 cm thickness using a stainless steel knife. In vacuum drying studies about 700 g of red pepper slices were used. The sliced samples were spread in a single layer on the tray. Moisture losses of samples were recorded at 30 min intervals by a digital balance of 0.01 g accuracy (Model TP-3002, Denver, Gottingen, Germany). The vacuum was broken and restored before and after the weight measurements and each process took less than 30 s. The vacuum drying was applied until the weight of sample reduced to moisture content of about 15 g/100 g. All vacuum drying experiments were replicated three times at each temperature – absolute pressure combination and the average values were used.

Ascorbic Acid Analysis

The ascorbic acid content was determined in both fresh and dried red pepper samples following the HPLC (LC-20AD, Shimadzu, Kyoto, Japan) analytical procedure outlined by Demiray et al. [13]. Fresh or dried red pepper samples were mixed with metaphosporic acid solution (1%, v/v) at the ratio of 1:10 (w/v), and the mixture was blended in a Waring blender. Samples were transferred into polypropylene centrifuge tubes and centrifuged at 11000 × g for 20 min at 4°C. Supernatants were filtered using a 0.45 µm PVDF syringe filters (Minisart, Sartorius, Gottingen, Germany). The content of ascorbic acid was measured by using HPLC equipped with a quaternary pump system (LC-20A), a 20 µL loop injector, a photodiode array detector (SPD-M20A), a degasser (DGU-20A) and a column oven (CTO-20A). The ascorbic acid fraction was separated on an ACE 5 C18 column (250 × 4.6 mm, ID, 5 µm) isocratically at 35 ˚C using the mobile phase of ultra-pure water at pH 3 (adjusted with H3PO4) and the flow rate of 0.5 mL min-1. Eluents were monitored at 254 nm.

Color Measurements

The colors of red pepper samples were measured both before drying and at different predetermined periods during drying by a Hunter Lab MiniScan XE colorimeter (Hunter Associates Laboratory, Reston, VA, USA). Before performing color measurements, MiniScan XE colorimeter device was calibrated with white and black standard calibration plates.

Color measurements were made from 3 different points and averaged of these values. The color values were expressed as L (whiteness/darkness), a (redness/greenness) and b (yellowness/blueness) at any time, respectively. And also, the color difference (ΔE) was calculated from the Hunter L, a, b values, according to Eq. (1).

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (1)$$

Kinetic Models of Ascorbic Acid and Color Degradation

The degradation of ascorbic acid and color in red peppers during drying were calculated by using the standard equations for zero and first-order reactions and degradation rate constants were determined by fitting Eqs. (2) and (3) to experimental data.

$$C = C_0 + k_0 t \quad (2)$$

$$C = C_0 \exp(k_1 t) \quad (3)$$

where C is the studied parameter (ascorbic acid content, L, a, b and ΔE) at any given drying time, C_0 are initial values of untreated samples and k_0, k_1 are rate constants. Furthermore, half-life value $t_{1/2}$ of ascorbic acid was calculated by the Eq. (4).

$$t_{1/2} = -\ln(0.5) \times k^{-1} \quad (4)$$

The Arrhenius equation is the most widely accepted method of accounting for the temperature dependence of the rate constant in food systems. The temperature and the rate constant are related according to the Arrhenius equation (Eq. (5)):

$$k = k_a \exp(-\frac{E_a}{RT}) \quad (5)$$

where k is the rate constant at temperature T (K), k_a is the frequency factor, E_a is the activation energy (kJ/mol), and R is the universal gas constant (8.314 J/molK).

The coefficient Q_{10} is another way to characterize the effect of the temperature on the rate of a reaction and it was calculated by the Eq. (6).

$$Q_{10} = (k_2/k_1)^{10/(T_2 - T_1)} \quad (6)$$

where k_1 and k_2 are reaction rate constants at temperatures T_1 and T_2, respectively (h^{-1}).

Statistical Evaluation

Drying experiments were performed in triplicates and the measurements were performed in duplicates. Means ± standard deviations of the experimental results were reported. Statistically significant differences between samples were determined using Microsoft Excel® (Microsoft Office, Washington, USA).

RESULTS AND DISCUSSION

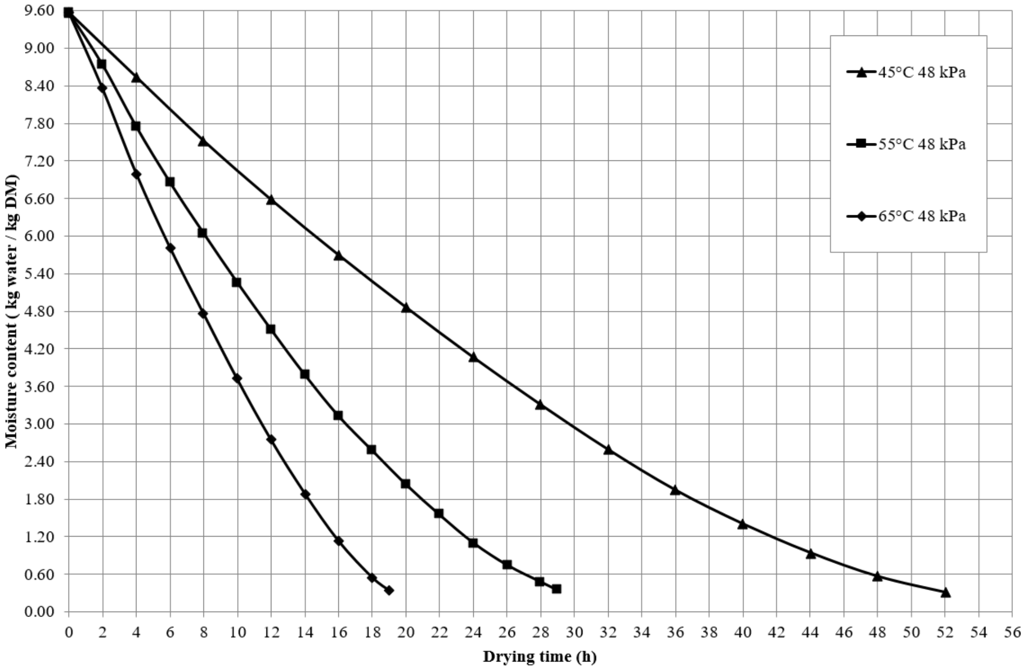
Effect of Vacuum Drying Conditions on Moisture Content

The moisture content of the red pepper slices was reduced from initial value of 9.58 to less than 0.3 kg water/kg dry matter. The effects of drying temperatures and pressures on the vacuum drying process are shown in Fig. 1A and 1B, where the moisture content of the samples at various time intervals was recorded. Fig. 1A and 1B showed that drying pressure had a certain effect on the drying process, the drying time was reduced by decreasing drying pressure. Drying processes at absolute pressure of 21.5 kPa took shorter than expected applications at 48.0 kPa absolute pressure. As a matter of fact, while the moisture content of red peppers at 45ºC at 21.5 kPa absolute pressure drop from 9.58 to 0.3 kg water / kg dry matter value, it took 44 hours, this process was completed in 52 hours at 48.0 kPa absolute pressure at the same temperature. The results were in agreement with several researchers who had also reported a decrease when the drying pressure was decreased during the vacuum drying of some vegetables such as pumpkin [14], carrot [15], mushroom [16]. Also increase in temperature level in vacuum drying had an important effect on the reduction of drying time.

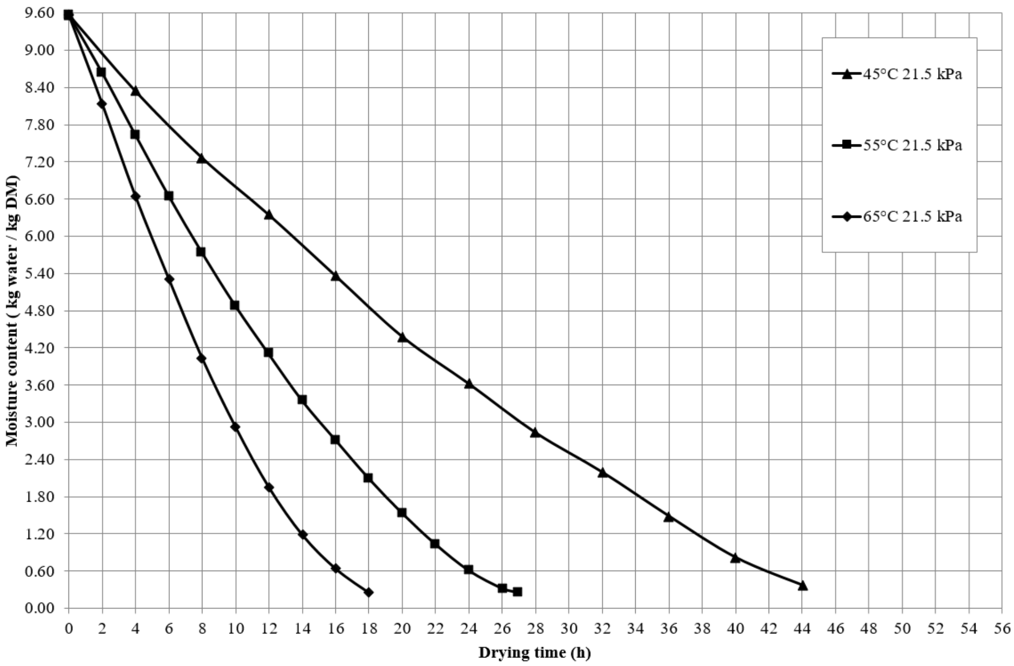
Degradation Kinetics of Ascorbic Acid

Degradation in ascorbic acid during vacuum drying of red pepper slices followed a first-order reaction. The concentration of ascorbic acid in samples with two different drying pressures (21.5 and 48.0 kPa) dried at three different temperatures (45, 55 and 65°C) for different time periods was measured and the plots of natural logarithm of ascorbic acid content of red pepper slices against time were prepared. Fig. 2A and 2B shows the achieved values of natural logarithm of ascorbic acid content of red pepper slices against time and temperature for two drying pressure.

The kinetic parameters of ascorbic acids degradation during vacuum drying at selected drying conditions are shown in Table 1. The rate constant increased at higher drying temperatures. This could be explained by the assumption that accelerated the ascorbic acid degradation [17]. As found by Di Scala and Crapiste [17], drying temperature had a strong influence on the degradation of ascorbic acids in red peppers. Increasing drying temperature from 50 to 70°C increased the degradation rate constants of ascorbic acids. Also, Marfil et al. [18] indicated that degradation of tomato ascorbic acids follows first-order reaction. In addition to the temperature effect, it has been determined that the drying pressure is also effective on the loss of ascorbic acid. Thus, after drying at 45˚C under 48.0 kPa absolute pressure, the amount of ascorbic acid in the samples was determined as 377.17±2.30 mg / 100 g dry matter, whereas at 21.5 kPa absolute pressure and again at 45°C 643.69±3.16 mg / 100 g dry matter were determined as dry matter. This result shows that the loss of ascorbic acid is further reduced by decreasing the drying pressure. The main reason for this is the decrease in the amount of oxygen in the drying chamber due to the vacuum effect. Ascorbic acid is a vitamin which can be easily oxidized. Ascorbic acid oxidation reactions are also slowing down by decreasing the amount of oxygen in the drying chamber. Results of this present study were in good agreement with the data reported in the literature. As a matter of fact, Methakhup et al. [19] purined after pitting of Indian gooseberries and dried by vacuum drier at 65 and 75°C under absolute pressure of 7, 10 and 13 kPa. They reported that as a result of the ascorbic acid analyzes, the loss of ascorbic acid was also increased by increasing the absolute pressure of the drying chamber.

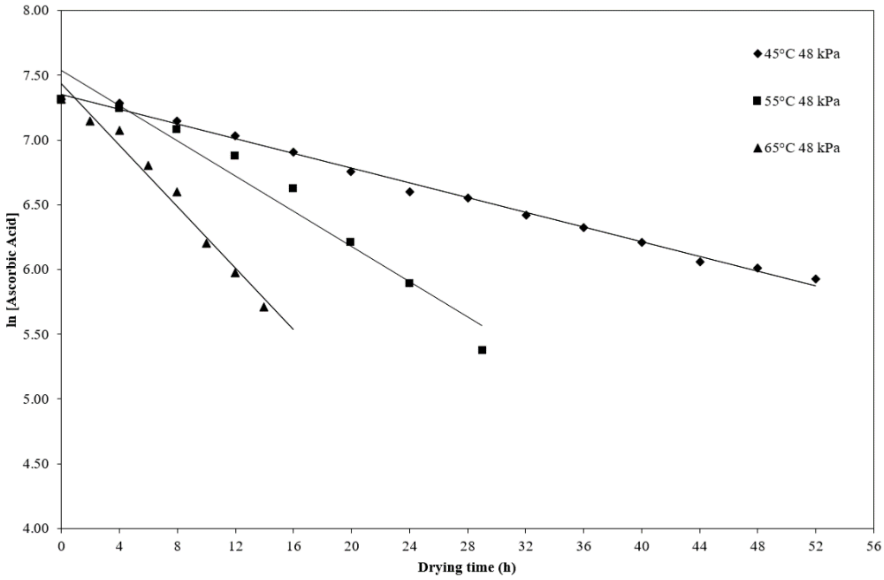


(A)

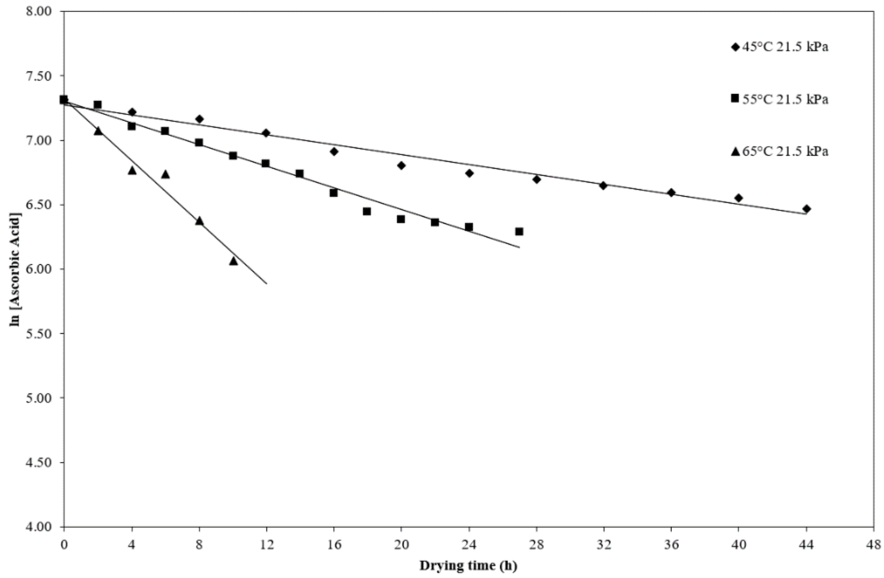


(B)

Figure 1. Effect of drying temperature at either 48.0 kPa (A) or 21.5 kPa (B) absolute pressure on the moisture contents of red pepper slices.



(A)



(B)

Figure 2. The degradation kinetics of ascorbic acid in red pepper slices dried at different temperatures at either 48.0 kPa (A) or 21.5 kPa (B) absolute pressure.

Table 1 gives the calculated kinetic parameters for first order kinetic model for ascorbic acid loss. It is seen from Table 1 that the reaction rate constant of ascorbic acid degradation increases with increasing drying temperature. For example, the reaction rate constants for the ascorbic acid degradation of red pepper samples dried at 45, 55 and 65°C under an absolute pressure of 21.5 kPa were calculated as 0.0193, 0.0422 and 0.1960 h^{-1}, respectively. When the Q_{10} values given in Table 1 are examined, it was determined that the degradation rate of ascorbic acid was increased 2.4 times by increasing the temperature from 45°C to 55°C in drying processes under 48.0 kPa absolute pressure. It was found that the reaction rate increased 2.2 times in the case of drying under the pressure of 21.5 kPa at the same drying temperatures.

In the study, it was determined that ascorbic acid was effected not only by the drying temperatures but also by the absolute pressure of the drying chamber. As a matter of fact, when the half-life values given in Table 1 are examined, it has been determined that loss of ascorbic acid occurs faster by increasing the absolute pressure of the drying chamber. For example, the half-life time values obtained as a result of drying processes at 45°C under both absolute pressure of 48.0 kPa and 21.5 kPa were calculated as 24.40 hours and 35.91 hours, respectively. This result shows that the level of vacuum value has a significant effect on the half-life time value of ascorbic acid.

Table 1. The kinetic parameters[a] for ascorbic acid losses in red pepper slices during drying at three different temperatures and two different absolute pressure

Drying Pressure (kPa)	Drying Temperature (ºC)	Q_{10} value	k (h^{-1})	$t_{1/2}$ (h)	E_a (kJ/mol)
	45	2.394	0.0284	24.40	
48.0	55		0.0680	10.19	70.85
	65	2.034	0.1383	5.01	
	45	2.187	0.0193	35.91	
21.5	55		0.0422	16.42	81.43
	65	2.834	0.1196	5.79	

[a]Q_{10}, k, $t_{1/2}$ and E_a: temperature coefficient, reaction rate constant, reaction half life time and activation energy, respectively.

Degradation Kinetics of Color Values

The *L*, *a* and *b* values for fresh red peppers were 27.54 ± 0.12, 28.58 ± 0.34 and 9.76 ± 0.25, respectively. The Hunter *L*, *a* and *b* values of the red pepper samples dried at two different absolute pressures and at three different temperatures with the vacuum dryer were measured at certain intervals in the drying process. For the kinetic modeling of color degradation of red pepper samples, zero-order and first-order kinetic models were used. Calculated kinetic parameters of color values in red peppers during various drying conditions are given in Tables 2 and 3. The results revealed that, regardless of the drying conditions, both zero- and first-order reaction kinetic models can be used adequately and equally for all values (*L*, *a* and *b*) with R^2 values from 0.8995 to 0.9968. The R^2 values of both models were not significantly different, that is why it was impossible to affirm that one model was superior to the other. The results obtained were in agreement with reported literature kiwifruits [20] and carrots [21]. As in the other color parameters, kinetic modeling of the changes in *ΔE* values was done. When the Tables 2 and 3 are examined, it can be seen that the changes in *ΔE* is better suited to the zero-order reaction model. Since the R^2 values of the zero-order reaction model are closer to 1 than the R^2 values calculated for the first-order reaction model, it is concluded that the zero-order kinetic model represents the change better. Dadalı et al. [22] dried the okra samples with different microwave powers by microwave drying method and measured Hunter *L*, *a* and *b* color values of the samples during drying. They also calculated the *ΔE* values of the samples using the measured color values. As a result, when the microwave power increases the *ΔE* values increases and the change in the *ΔE* values corresponds to the zero-order reaction model.

The Q_{10} and the activation energy values of the color values for the red pepper samples dried at different temperatures under 48.0 kPa and 21.5 kPa absolute pressure are given in Tables 2 and 3. When the activation energy values of Hunter *L*, *a* and *b* color values given in Table 2 are examined, it is seen that the activation energy calculated for the *a* value change is larger than the *L* and *b* values. This is an indication that *a* value is more influenced by temperature changes in vacuum drying processes at 45, 55 and 65°C under 48.0 kPa absolute pressure. When the Q_{10} values for the *a* and *b* values in the same table are examined, it is seen that the effect of increasing the temperature from 45°C to 55°C is higher than the temperature from 55°C to 65°C. In Table 3, it is seen that the activation energy values calculated to express the effect of the temperature changes on the *b* value are larger than the activation energy values of the other color parameters.

Table 2 The kinetic parameters of color values of red pepper slices dried at 48 kPa absolute pressure

Color values	Temperature (°C)	Zero-Order Model				First-Order Model			
		k_0	R^2	Q_{10} value	E_a (kJ mol^{-1})	k_1 (h^{-1})	R^2	Q_{10} value	E_a (kJ mol^{-1})
	45	0.0501	0.9864	1.19		0.0017	0.9845	1.29	
L	55	0.0598	0.9385		47.13	0.0022	0.9410		47.98
	65	0.1448	0.8995	2.42		0.0050	0.9032	2.27	
	45	0.1180	0.9046	2.41		0.0044	0.9181	2.55	
a	55	0.2848	0.9818		51.41	0.0112	0.9845		54.53
	65	0.3703	0.9578	1.30		0.0148	0.9720	1.32	
	45	0.0757	0.9910	1.57		0.0083	0.9861	1.80	
b	55	0.1186	0.9777		32.04	0.0149	0.9862		37.18
	65	0.1547	0.9549	1.30		0.0190	0.9724	1.28	
	45	0.1382	0,9533	2.27		0.0253	0.9314	2.94	
ΔE	55	0.3132	0,9834		50.47	0.0745	0.8801		54.97
	65	0.4251	0,9591	1.36		0.0857	0.8317	1.15	

Table 3 The kinetic parameters of color values of red pepper slices dried at 21.5 kPa absolute pressure

Color Values	Temperature (°C)	Zero-Order Model				First-Order Model			
		k_0	R^2	Q_{10} value	E_a (kJ mol^{-1})	k_1 (h^{-1})	R^2	Q_{10} value	E_a (kJ mol^{-1})
L	45	0.1239	0.9852	1.49		0.0050	0.9860	1.44	
	55	0.1841	0.9932		34.83	0.0072	0.9955		30.11
	65	0.2700	0.9968	1.47		0.0098	0.9959	1.36	
a	45	0.1402	0.9887	2.08		0.0056	0.9830	2.04	
	55	0.2913	0.9937		43.32	0.0114	0.9946		43.95
	65	0.3676	0.9704	1.26		0.0149	0.9732	1.31	
b	45	0.0273	0.9633	2.74		0.0031	0.9606	2.90	
	55	0.0749	0.9780		62.27	0.0090	0.9865		64.07
	65	0.1092	0.9853	1.46		0.0129	0.9875	1.43	
ΔE	45	0.1922	0.9906	1.79		0.0511	0.9531	1.55	
	55	0.3439	0.9959		39.75	0.0794	0.8691		37.85
	65	0.4663	0.9865	1.36		0.1191	0.8172	1.50	

When the Tables 2 and 3 are compared with each other, it can be seen that the *a* and *L* values, which are important in terms of color during vacuum drying of red pepper, were less influenced by temperature changes with low pressures. Drying of red pepper samples under absolute pressure of 21.5 kPa resulted in less loss of redness than drying at 48.0 kPa.

CONCLUSION

In this study, it was observed that drying time increases with an increase in absolute pressure. Degradation kinetics of ascorbic acid in red pepper slices during vacuum drying followed a first-order reaction. Zero-order and first-order reaction models were used to explain the color change kinetics, and it was observed that the R^2 values of both models were not significantly different. That is why it is impossible to affirm that one model was superior to the other. On the other hand, total color change (ΔE) followed a zero-order reaction model during vacuum drying. The reaction rate constants for these constituents of red peppers were highly dependent on the drying conditions, and activation energy values for ascorbic acid under both absolute pressure of 48.0 kPa and 21.5 kPa were calculated as 70.85 and 81.43 kJ/mol, respectively. Current study on the loss kinetics of ascorbic acid and color parameters in red pepper slices dried in vacuum dryer. Further work should be carried out to explore the changes in the physicochemical properties of the dried red pepper during storage.

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