Advances in Research
8(5): 1-9, 2016; Article no.AIR.31168
ISSN: 2348-0394, NLM ID: 101666096

SCIENCEDOMAIN *international*
www.sciencedomain.org

Color Stability of Freeze-dried Date Fruits (Barhi CV.) during Storage

Khaled A. M. Ahmed[1,2*] and Nasser M. El Ashmawy[1,2]

[1]Chair of Dates Technologies and Industry, College of Food and Agriculture Sciences, King Saud University, Saudi Arabia.
[2]Agricultural Engineering Research Institute (AEnRI), Giza, Egypt.

Authors' contributions

This work was carried out in collaboration equally between the two authors. Author KAMA wrote the final draft and approved the final manuscript.

Article Information

DOI: 10.9734/AIR/2016/31168
Editor(s):
(1) Marco Trevisan, Faculty of Agricultural Sciences, Institute of Agricultural and Environmental Chemistry, Catholic University of the Sacred Heart, Italy.
Reviewers:
(1) Celenk Molva, Izmir Instıtute of Technology,Turkey.
(2) Marco Iammarino, Istituto Zooprofilattico Sperimentale della Puglia e della Basilicata, Foggia, Italy.
(3) Kehinde Taiwo, Obafemi Awolowo University, Ile-Ife, Nigeria.
(4) Eliene Penha Rodrigues Pereira, Universidade Estadual de Campinas (UNICAMP), Brasil.
Complete Peer review History: http://www.sciencedomain.org/review-history/18215

Original Research Article

Received 24th December 2016
Accepted 6th March 2017
Published 15th March 2017

ABSTRACT

Fresh Date fruits "Barhi CV." were freeze dried as slices to characterize the dried fruit quality. CIELAB color parameters (L^*, a^*, and b^*) were measured as well as Chroma, the hue angle, the browning index and the total color difference parameters were derivative. The samples were stored for 12 months at three temperatures of 5, 15 and 25°C with an uncertainty of ±1℃ to assess the color change kinetics and quantify the degree of change during storage. The L^*, a^* and b^* values for fresh samples at room temperature were 93.16±0.15, 18.76±0.45 and 61.70±0.32, respectively, while they were 78.72±0.51, 29.52±0.07 and 62.75±0.14 after 12 months.
To explain the changing kinetics of the date slices, zero, first and second order models were attempted. Based on statistical analysis, the first-order model was found to be the best model for all CIELAB parameters. Analysis on the kinetic constants reveals that the temperature could affect the resulting color of the dried product, in turn, it contributes to the color changes of the freeze dried Barhi during storage. The values obtained for the activation energy for freeze-dried Barhi based on the selected models were between 4930 and 10850 kJ. mol^{-1} which were somewhat different from the reported values due to the variation in sample's type, treatment or process.

**Corresponding author: E-mail: kehmed@ksu.edu.sa, kamahmed2000@gmail.com;*

Keywords: Freeze-drying; color kinetics; Barhi; activation energy.

1. INTRODUCTION

Date palm (*Phoenix dactylifera L.*) plays significant roles in the economic, social and religious life of many countries of arid regions like Arabian Peninsula and Northern Africa. Among nearly 3000 cultivars around the world, about 450 of them are known in Saudi Arabia, which takes third place in the global production of date fruits [1,2].

Date fruits are berries and distinguished from others since they have three consumed maturation stages including Khalal, Rutab, and Tamar. At the Khalal stage, they are physiologically mature, sweet, hard and crisp with over 70% moisture content, bright yellow or red in color and very perishable [3]. Of all cultivars, the most popular and influential one suitable for marketing at Khalal stage is 'Barhi,' but due to the high moisture content, fruits have small storage life [2,3,4,5,6,7,8].

To date, traditional cooling stores are the most comprehensive way to preserve Barhi at Khalal maturity stage. This way does not preclude the existence of other ways less spread like controlled atmosphere cold stores (CA) extended to modified atmosphere packaging (MAP) [4,8,9].

The applications of freeze drying technique in food ranges from relatively simple preservable food, over food products like coffee, tea, crisp fruits and vegetables, some aromatic herbs to biotechnological or pharmaceutical products [10,11,12]. Many studies discuss the benefits of the freeze-drying technique. In preserving functional properties of hen egg yolk [13], improving the nutritional value of freeze dried Blueberries [14]. Its effect on the antioxidant properties of leaves and tea of ginger species [12]; color changes of freeze-dried strawberries [15] on quality parameters of freeze dried soursop fruit pulp [16].

Many studies discuss the physical, mechanical and nutritional properties of Barhi fruits at Khalal stage [17,18,19,20,21].

The color plays a significant role in food product quality attribute as it affects the visual interest of the product [16]. However, changes of color in food are a common phenomenon occurring during processing and storage [22,23,24,25]. In general, the rates of change often follow zero-order or first-order kinetics models, and the dependence of the changing rate constant on temperature can be described by Arrhenius-type equation [26,27].

Regardless of the nutritional value and economic importance of Barhi fruits on Khalal maturity stage, color change, and reaction kinetics during storage have not been described. The objective of the present study was to evaluate color changes in freeze dried Barhi during storage using basic and derived components of CIELAB color. In addition, water activity and moisture content were determined over the storage time. Finally, kinetics of color change in samples during storage were modelled.

2. MATERIALS AND METHODS

2.1 Sample Preparation

Date fruits (*Phoenix dactylifera L.* Barhi CV.) at Khalal maturity stage purchased from well-known commercial growers in Qasim region - Saudi Arabia in August 2014. Fruits were freshly harvested, quickly precooled and transported to the laboratory on the same day. Healthy fruits were graded for uniformity of color and size then washed with tap water, followed by pits removal with a small serrated. The samples were cut into rings with a thickness of 9±1 mm to avoid the effect of drying rate on structure [28].

2.2 Freeze Drying (FD)

Freeze drying was achieved in a laboratory-scale FreeZone 6 benchtop freeze dry system (Labconco Kansas, USA). The slices were spread uniformly in a single layer on a stainless-steel tray. The samples were frozen for 24h at -22℃ in a freezing/heating chamber and freeze dried at an absolute pressure of 85–90 Pa.

2.3 Storage of Samples

A batch of six hundred grams of FD samples was put on exposed Petri plates. Each batch was stored at three different temperatures (5, 15 and 25℃ with 1℃ uncertainty) for 12 months. Each month average of 50 g was taken out as a destructive sample to perform the measurements.

2.4 Water Activity and Moisture Content Determination

The water activity (*aw*) of the FD samples as fresh once was determined using an Aqua Lab (Model CX2, Decagon Devices, Pullman, WA) water activity meter. The moisture content of the fresh samples was determined based on the standard procedure (AOAC, 2005). For the analysis, the samples were dried for 48 h at 70℃ under a vacuum of 0.27 bar (Vacutherm model VT 6025, Heraeus Instrument, D-63450.Hanauer, Germany).

2.5 Color Measurements

According to the CIELAB color system, the color parameters (*L*, a*, b**) were measured using the LabScan XE (Hunter Associates Laboratory. Inc., VA, USA) spectrophotometer that has 0°/45° optical geometry. Beside the CIELAB color parameters, additionally delivered parameters were calculated [29,30] as follows:

- The total color difference (ΔE),

$$\Delta E = \sqrt{(a_0^* - a^*)^2 + (b_0^* - b^*)^2 + (L_0^* - L^*)^2} \quad (1)$$

- Chroma,

$$chroma = \sqrt{a^{*2} + b^{*2}} \quad (2)$$

- Hue angle,

$$hue\ angle = tan^{-1}\left(\frac{b^*}{a^*}\right) \quad (3)$$

- Browning index (BI),

$$BI = \frac{[100(x - 0.31)]}{0.17}$$

$$where\ x = \frac{(a^* + 1.75L^*)}{(5.645L^* + a^* - 3.012b^*)} \quad (4)$$

Where (a_0^*) , (a^*) represents the greenness components; (b_0^*) , (b^*) are the yellowness component and (L_0^*) , (L^*) are the lightening component of CIELAB color space for fresh and FD samples, respectively.

2.6 Kinetics of Color Change

All CIELAB color parameters including the derivative ones were used to determine the reaction order and reaction rate constant of the color degradation of FD samples [31,32,33] using the following formula:

$$\frac{dC}{d\theta} = kC^n \quad (5)$$

Where $\frac{dC}{d\theta}$ is the rate of phenomena *C*, *k* is reaction rate constant, *n* is the reaction order, and θ is the time (month). Solving eq. 5 in zero, first and second order (i.e. n=0, 1 and 2) result in the following derived formulas:

$$C = C_0 + k_0\theta \quad (6)$$

$$C = C_0 e^{k_1\theta} \quad (7)$$

$$\frac{1}{C} = \frac{1}{C_0} + k_2\theta \quad (8)$$

Where k_0, k_1, and k_2 are the reaction rate constants for zero, first and second order, respectively.

These constants can be estimated from the slope of linear plot left-hand term of Eqs. 6, and 8 vs. θ while from Eq. 7 can be determined from the slope of the logarithmic plot left-hand term of the equation vs. θ, otherwise, kinetic rate constants can be calculated from a non-linear regression.

The dependency of temperature on reaction rate constant value (k_0, k_1, and k_2) can be determined using the Arrhenius equation as follows:

$$k = A_0 e^{-\left[\frac{E_a}{RT}\right]}$$

Where *k* is the pre-exponential factor (min^{-1}), E_a is activation energy (kJ/mol), R is the general gas constant (8.314 $J.mol^{-1}$ K^{-1}), and T is the absolute temperature (K).

2.7 Data Analysis

Data was analyzed for multiple comparisons by analysis of variance with least significant differences (LSD) between means at 5% significance level using SAS 9.2 software (SAS Institute, Cary, NC). Experimental data were fitted to the three kinetic models and processed by using MATLAB 2015a (MathWorks Inc., Natick, MA) to estimate the kinetic rate constants. Statistical parameters such as the coefficient of determination (R^2), relative percent errors (PE), the sum of squared errors (SSE) and root mean square error (RMSE) were used as criteria to determine the goodness of fit. A fit was considered safe when high values of R^2 and lowest value of SSE and RMSE in addition to the value of PE below 10%, [33].

3. RESULTS AND DISCUSSION

3.1 Water Activity and Moisture Content

The fresh Barhi fruits at Khalal stage have been found to have high values of MC_w ranging from 85% to 93% [8,9,17,20]. In this study, the measured value was 89.88%±2.43 for fresh samples, while it was 3.09 %±0.44 for FD ones. On the other hand, the water activity of fresh samples was 0.855±0.001 while it was 0.236±0.001 for freeze-dried samples.

Table 1 summarizes the values of MC_w, and *aw* for FD samples over the storage time. The results showed a significant effect of temperature on both moisture content and water activity of freeze-dried samples. Although *aw* is a temperature dependent phenomena in general, the effect of temperature on the *aw* is product-specific. This means that some products are direct proportion and other are reverse proportion since temperature affects the factors that control water activity in the food [24,34,35,36]. For freeze dried Barhi, a direct proportion was detected between temperature and water activity. On the other hand, storage time indicated a significant effect on both of moisture content and water activity most probably due to some moisture intake from the environment over the time; even there were significance differences in moisture content and water activity, they still small (highest values were 16.6%, 0.365 respectively).

3.2 CIELAB Primary and Derivative Components

The *L**, *a**, and *b** values were presented in Table 2, while the derivative ones (Chroma, Hue angle, BI and ΔE) were shown in Table 3. The color of fresh fruit sample was similar to freeze-dried samples at zero storage time. The average *L**, *a**, and *b** values were 93.16±0.15, -18.76±0.45 and 61.70±0.32, respectively.

A lightning component in CIELAB color space (*L**) represents how dark is the sample. The sample significantly darkened in respect of the temperature and the storage time as seen in Table 2. On the other hand, the yellowness component (positive b* values) increased considerably with temperature while it decreased over time. In contrast, the greenness component (negative a* values) decreased considerably with both temperature and storage time.

To better understand, the derivative color components (Chroma, Hue angle, BI, and ΔE) were analyzed (Fig. 1). The results revealed that the hue angle (Fig. 1b) and ΔE (Fig. 1d) increased as temperature and time increased. While Chroma (Fig. 1a) and BI (Fig. 1c) decreased as storage time increased.

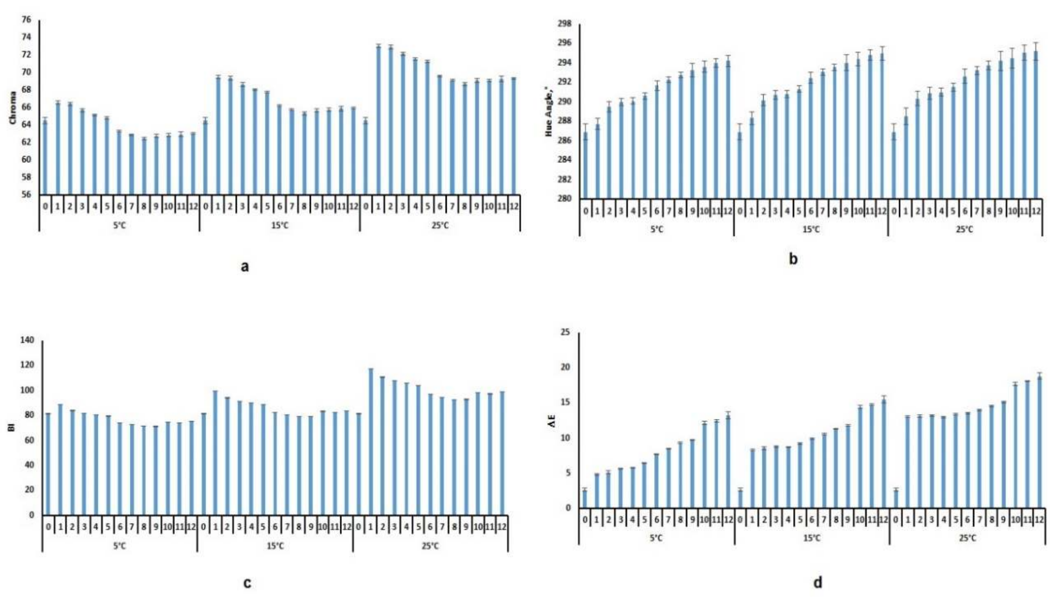

Fig. 1. The derivative color components vs. temperature and storage time [Chroma (a), Hue angle (b), *BI (c)*, and Δ*E* (d)]

Table 1. Moisture content and water activity of freeze dried Barhi over the storage time

Storage time (month)	MC$_w$%			aw		
	25℃	15℃	5℃	25℃	15℃	5℃
0		**7.500^{A,m}±0.800**			**0.236^{A,l}±0.001**	
1	9.850^{A,l}±0.420	9.220^{B,l}±0.390	8.380^{C,l}±0.360	0.274^{A,k}±0.001	0.262^{B,k}±0.001	0.238^{C,k}±0.001
2	11.13^{A,k}±0.103	10.420^{B,k}±0.120	9.470^{C,k}±0.110	0.275^{A,kj}±0.001	0.263^{B,kj}±0.001	0.239^{C,kj}±0.001
3	11.430^{A,j}±0.100	10.700^{B,j}±0.090	9.730^{C,j}±0.080	0.277^{A,j}±0.001	0.265^{B,j}±0.001	0.241^{C,j}±0.001
4	11.740^{A,i}±0.100	10.990^{B,i}±0.090	10.000^{C,i}±0.090	0.281^{A,i}±0.002	0.268^{B,i}±0.002	0.244^{C,i} ±0.001
5	12.070^{A,h}±0.130	11.300^{B,h}±0.130	10.270^{C,h}±0.110	0.284^{A,h}±0.001	0.272^{B,h}±0.001	0.247^{C,h}±0.001
6	12.370^{A,g}±0.100	11.570^{B,g}±0.090	10.520^{C,g}±0.080	0.287^{A,g}±0.001	0.274^{B,g}±0.001	0.249^{C,g}±0.001
7	13.130^{A,f}±0.080	12.300^{B,f}±0.070	11.180^{C,f}±0.070	0.299^{A,f}±0.002	0.286^{B,f}±0.002	0.260^{C,f}±0.002
8	13.460^{A,e}±0.060	12.610^{B,e}±0.060	11.460^{C,e}±0.060	0.305^{A,e}±0.002	0.291^{B,e}±0.002	0.265^{C,e}±0.001
9	14.430^{A,d}±0.100	13.360^{B,d}±0.400	12.28^{C,d}±0.080	0.314^{A,d}±0.001	0.299^{B,d}±0.004	0.273^{C,d}±0.001
10	14.710^{A,c}±0.090	13.770^{B,c}±0.090	12.520^{C,c}±0.080	0.326^{A,c}±0.002	0.312^{B,c}±0.001	0.284^{C,c}±0.001
11	15.240^{A,b}±0.550	14.270^{B,b}±0.510	12.970^{C,b}±0.470	0.337^{A,b}±0.005	0.323^{B,b}±0.006	0.293^{C,b}±0.005
12	15.990^{A,a}±0.560	14.970^{B,a}±0.520	13.610^{C,a}±0.480	0.364^{A,a}±0.009	0.349^{B,a}±0.009	0.317^{C,a}±0.008

***Means with the same lower case letter were not significantly in column (storage time) while those in uppercase letters were not significantly in rows (temperature) ($p \leq 0.05$)*

Table 2. Basic color components of freeze-dried Barhi over the storage time

ST	L*			a*			b*		
	5℃	15℃	25℃	5℃	15℃	25℃	5℃	15℃	25℃
0		**93.16A$^{.a}$±0.15**			**-18.76^{A,a}±0.45**			**61.70^{A,f}±0.32**	
1	90.18^{A,b}±0.12	87.48^{B,b}±0.12	83.98^{C,b}±0.11	-20.24^{A,b}±0.15	-21.86^{B,b}±0.16	-23.17^{C,b}±0.17	63.40^{C,b}±0.18	65.93^{B,b}±0.19	69.23^{A,b}±0.20
2	90.44^{A,c}±0.18	87.72^{B,c}±0.17	84.21^{C,c}±0.17	-22.14^{A,c}±0.20	-23.91^{B,c}±0.22	-25.34^{C,c}±0.23	62.58^{C,c}±0.21	65.08^{B,c}±0.22	68.34^{A,c}±0.23
3	90.14^{A,c}±0.05	87.43^{B,c}±0.04	83.93^{C,c}±0.04	-22.46^{A,d}±0.18	-24.25^{B,d}±0.20	-25.70^{C,d}±0.21	61.70^{C,d}±0.15	64.16^{B,d}±0.16	67.37^{A,d}±0.17
4	90.12^{A,c}±0.09	87.42^{B,c}±0.09	83.92^{C,c}±0.09	-22.38^{A,d}±0.08	-24.16^{B,d}±0.09	-25.62^{C,d}±0.10	61.16^{C,e}±0.08	63.60^{B,e}±0.09	66.78^{A,e}±0.09
5	89.70^{A,d}±0.07	87.01^{B,d}±0.07	83.53^{C,d}±0.07	-22.80^{A,e}±0.10	-24.62^{B,e}±0.10	-26.10^{C,e}±0.11	60.68^{C,f}±0.13	63.10B,f±0.13	66.26^{A,f}±0.14
6	89.50^{A,e}±0.15	86.81^{B,e}±0.15	83.34^{C,e}±0.14	-23.38^{A,f}±0.11	-25.25^{B,f}±0.11	-26.76^{C,f}±0.12	58.80^{C,g}±0.10	61.15^{B,g}±0.10	64.21^{A,g}±0.11
7	89.16^{A,f}±0.08	86.48^{B,f}±0.08	83.02^{C,f}±0.08	-23.79^{A,g}±0.11	-25.73^{B,g}±0.08	-27.23^{C,g}±0.12	58.16^{C,h}±0.08	60.48^{B,h}±0.09	63.50^{A,h}±0.10
8	88.70^{A,g}±0.07	86.04^{B,g}±0.07	82.59^{C,g}±0.06	-24.16^{A,h}±0.08	-26.09^{B,h}±0.09	-27.65^{C,h}±0.10	57.56^{C,i}±0.15	59.86^{B,i}±0.15	62.85^{A,i}±0.16
9	88.46^{A,h}±0.16	85.80^{B,h}±0.16	82.37^{C,h}±0.15	-24.74^{A,i}±0.11	-26.72^{B,i}±0.12	-28.32^{C,i}±0.12	57.66$^{C.ij}$±0.19	59.96^{B,ij}±0.20	62.96^{A,ij}±0.21
10	85.46^{A,i}±0.29	82.89^{B,i}±0.28	79.58^{C,i}±0.27	-18.76^{A,j}±0.45	-27.15^{B,j}±0.07	-28.66^{C,j}±0.19	57.56^{C,ij}±0.16	59.86^{B,ij}±0.17	62.86^{A,ij}±0.17
11	85.36^{A,i}±0.11	82.80^{B,i}±0.11	79.48^{C,i}±0.11	-20.24^{A,k}±0.15	-27.65^{B,k}±0.13	-29.31^{C,k}±0.14	57.46^{C,jk}±0.24	59.76^{B,jk}±0.25	62.76^{A,jk}±0.28
12	84.54^{A,j}±0.55	82.01^{B,j}±0.53	78.72^{C,j}±0.51	-22.14^{A,l}±0.20	-27.83^{B,l}±0.09	-29.52^{C,l}±0.07	57.46^{C,k}±0.13	59.75^{B,k}±0.13	62.75^{A,k}±0.14

**Means with the same lower case letter were not significantly in column (storage time) while those in uppercase letters were not significantly in rows (temperature), at $p \leq 0.05$. ST represents storage time in months*

Table 3. Derivative color components of freeze dried Barhi over the storage time

ST	Chroma			Hue angle			BI			ΔE		
	5℃	15℃	25℃	5℃	15℃	25℃	5℃	15℃	25℃	5℃	15℃	25℃
0		**$64.49^{A,k}\pm0.36$**			**$-73.09^{A,l}\pm0.37$**			**$81.10^{A,j}\pm0.85$**			**$2.61^{A,l}\pm0.28$**	
1	$66.55^{C,a}\pm0.18$	$69.46^{B,a}\pm0.19$	$73.01^{A,a}\pm0.19$	$-72.29^{C,k}\pm0.14$	$-71.66^{B,k}\pm0.13$	$-71.49^{A,k}\pm0.14$	$88.58^{C,a}\pm0.56$	$99.22^{B,a}\pm0.66$	$117.17^{A,a}\pm0.81$	$4.84^{C,k}\pm0.11$	$8.28^{B,k}\pm0.10$	$13.05^{A,k}\pm0.10$
2	$66.38^{C,b}\pm0.19$	$69.33^{B,b}\pm0.19$	$72.88^{A,b}\pm0.21$	$-70.51^{C,j}\pm0.20$	$-69.82^{B,j}\pm0.20$	$-69.65^{A,j}\pm0.20$	$83.93^{C,b}\pm0.52$	$93.82^{B,b}\pm0.60$	$110.67^{A,b}\pm0.74$	$5.06^{C,j}\pm0.23$	$8.52^{B,j}\pm0.19$	$13.16^{A,j}\pm0.16$
3	$65.66^{C,c}\pm0.18$	$68.59^{B,c}\pm0.20$	$72.11^{A,c}\pm0.21$	$-69.99^{C,i}\pm0.13$	$-69.29^{B,i}\pm0.13$	$-69.11^{A,i}\pm0.13$	$81.72^{C,c}\pm0.38$	$91.24^{B,c}\pm0.46$	$107.49^{A,c}\pm0.58$	$5.60^{C,i}\pm0.08$	$8.76^{B,i}\pm0.12$	$13.19^{A,i}\pm0.14$
4	$65.12^{C,d}\pm0.10$	$68.04^{B,d}\pm0.11$	$71.53^{A,d}\pm0.11$	$-69.90^{C,i}\pm0.06$	$-69.19^{B,i}\pm0.06$	$-69.01^{A,i}\pm0.06$	$80.41^{C,d}\pm0.30$	$89.69^{B,d}\pm0.35$	$105.55^{A,d}\pm0.40$	$5.73^{C,i}\pm0.07$	$8.67^{B,i}\pm0.08$	$12.98^{A,i}\pm0.10$
5	$64.82^{C,e}\pm0.13$	$67.74^{B,e}\pm0.13$	$71.22^{A,e}\pm0.14$	$-69.40^{C,h}\pm0.08$	$-68.68^{B,h}\pm0.08$	$-68.50^{A,h}\pm0.08$	$79.34^{C,e}\pm0.31$	$88.45^{B,e}\pm0.30$	$104.08^{A,e}\pm0.44$	$6.42^{C,h}\pm0.10$	$9.23^{B,h}\pm0.09$	$13.39^{A,h}\pm0.09$
6	$63.27^{C,f}\pm0.09$	$66.16^{B,f}\pm0.09$	$69.56^{A,f}\pm0.10$	$-68.31^{C,g}\pm0.10$	$-67.56^{B,g}\pm0.10$	$-67.37^{A,g}\pm0.11$	$74.17^{C,h}\pm0.49$	$82.44^{B,h}\pm0.57$	$96.67^{A,h}\pm0.71$	$7.70^{C,g}\pm0.06$	$9.89^{B,g}\pm0.10$	$13.53^{A,g}\pm0.12$
7	$62.84^{C,hgi}\pm0.10$	$65.73^{B,hgi}\pm0.11$	$69.10^{A,hgi}\pm0.11$	$-67.74^{C,f}\pm0.08$	$-66.95^{B,f}\pm0.06$	$-66.78^{A,f}\pm0.09$	$72.56^{C,i}\pm0.27$	$80.53^{B,i}\pm0.29$	$94.43^{A,i}\pm0.39$	$8.48^{C,f}\pm0.08$	$10.56^{B,f}\pm0.08$	$14.00^{A,f}\pm0.11$
8	$62.42^{C,j}\pm0.16$	$65.30^{B,j}\pm0.17$	$68.67^{A,j}\pm0.18$	$-67.23^{C,e}\pm0.04$	$-66.44^{B,e}\pm0.04$	$-66.25^{A,e}\pm0.05$	$71.27^{C,j}\pm0.28$	$79.08^{B,j}\pm0.33$	$92.65^{A,j}\pm0.42$	$9.30^{C,e}\pm0.09$	$11.28^{B,e}\pm0.08$	$14.57^{A,e}\pm0.09$
9	$62.74^{C,i}\pm0.19$	65.65B,i±0.20	$69.04^{A,i}\pm0.21$	$-66.77^{C,d}\pm0.10$	$-65.98^{B,d}\pm0.11$	$-65.78^{A,d}\pm0.11$	$71.20^{C,j}\pm0.68$	$79.02^{B,j}\pm0.79$	$92.66^{A,j}\pm0.97$	$9.68^{C,d}\pm0.06$	$11.78^{B,d}\pm0.09$	$15.12^{A,d}\pm0.13$
10	$62.82^{C,hi}\pm0.18$	$65.73^{B,hi}\pm0.17$	$69.08^{A,hi}\pm0.16$	$-66.38^{C,c}\pm0.03$	$-65.60^{B,c}\pm0.04$	$-65.49^{A,c}\pm0.17$	$74.70^{C,g}\pm0.54$	$83.16^{B,g}\pm0.66$	$98.10^{A,g}\pm1.02$	$12.13^{C,c}\pm0.23$	$14.40^{B,c}\pm0.23$	$17.68^{A,c}\pm0.21$
11	$62.91^{C,gh}\pm0.26$	$65.84^{B,gh}\pm0.27$	$69.26^{A,gh}\pm0.31$	$-65.98^{C,b}\pm0.05$	$-65.17^{B,b}\pm0.05$	$-64.96^{A,b}\pm0.05$	$74.06^{C,h}\pm0.45$	$82.40^{B,h}\pm0.52$	$97.13^{A,h}\pm0.75$	$12.45^{C,b}\pm0.13$	$14.76^{B,b}\pm0.10$	$18.09^{A,b}\pm0.08$
12	$62.99^{C,g}\pm0.09$	$65.92^{B,g}\pm0.13$	$69.3^{A,g}\pm0.12$	$-65.80^{C,a}\pm0.11$	$-65.02^{B,a}\pm0.0$	$-64.80^{A,a}\pm0.09$	$75.04^{C,f}\pm0.57$	$83.62^{B,f}\pm0.71$	$98.66^{A,f}\pm0.89$	$13.19^{C,a}\pm0.50$	$15.51^{B,a}\pm0.48$	$18.85^{A,a}\pm0.46$

**Means with the same lower case letter were not significantly in column (storage time) while those in uppercase letters were not significantly in rows (temperature), at p ≤ 0.05. ST represent storage time in months*

Table 4. The reaction rate kinetic constants for CIELAB parameters

		Zero -order				First-order				Second-order			
		K_0	R^2	RMSE	PE%	K_1	R^2	RMSE	PE%	K_2	R^2	RMSE	PE%
L*	5℃	-0.006058	0.908	0.9925	6.44	0.0703	0.915	0.0 00130	2.15	-0.5238	0.814	0.9482	29.84
	15℃	0.01887	0.910	0.388	4.49	0.08228	0.924	0.00089 1	3.56	-0.5238	0.813	0.9482	1.39
	25℃	-0.000998	0.903	0.7321	6.54	0.091641	0.921	0.0 00206	2.01	-0.5029	0.813	0.9093	1.31
a*	5℃	0.01887	0.950	0.388	1.49	0.045	0.954	0.3704	1.08	0.0008228	0.924	0.000891	3.56
	15℃	-0.00999	0.903	0.7321	0.54	0.048	0.953	0.4034	1.29	0.0001641	0.900	0.000206	2.01
	25℃	-0.01667	0.893	3.193	12.98	0.051	0.953	0.4249	3.82	0.0001996	0.658	0.000543	12.63
b*	5℃	0.000164	0.901	0.000206	2.01	0.051002	0.903	0.7321	1.54	-0.5894	0.895	0.7603	6.12
	15℃	0.000199	0.659	0.000543	12.63	0.0667	0.893	3.1 93	1.98	-0.6128	0.695	0.7929	7.79
	25℃	-0.01291	0.977	0.007519	2.79	0.09988	0.984	0.4 059	1.31	-0.6434	0.895	0.8313	11.24
BI	5℃	-1.249	0.872	3.301	14.51	0.0100	0.886	0.0005 43	5.63	-0.01667	0.692	3.193	12.98
	15℃	-1.442	0.664	3.88	17.09	0.01291	0.977	0.007519	2.79	0.1002	0.983	0.4059	14.31
	25℃	-1.713	0.640	4.86	15.92	0.017242	0.844	0.00013 5	1.84	-0.00606	0.807	0.9642	1.25
ΔE	5℃	0.8229	0.961	0.627	4.89	0.01291	0.977	0.007519	2.79	0.1002	0.983	0.4059	14.31
	15℃	0.698	0.805	0.8548	26.19	0.015613	0.964	0.0041 29	8.65	-0.00606	0.807	0.9642	11.25
	`	0.5461	0.805	1.018	30.84	0.017585	0.953	0.000831	1.52	0.01877	0.928	0.4233	4.09

3.3 Kinetics of Color Change

Experimental data for the change in *L*, b** and *a** of freeze dried Barhi were fitted to the three kinetic models (Eq. 6, Eq. 7 and Eq. 8) as well as *BI* and *ΔE*. Table 4 shows the reaction rate kinetic constants. The results revealed that, regardless of the storage temperature, for *L** both zero- and first-order reaction kinetic models can be used adequately with R^2 values from 0.903 to 0.924. The first-order model was found to have higher R^2 and lowers RMSE and PE values. Thus, the first-order model kinetic was superior. The rate reaction constant values (k_1) were lower at all temperature levels than those of the zero-order model (k_0). Furthermore, *b** and *a** values followed the first-order model kinetic (Table 3).

In contrast with the rate reaction constant (k_1) for *L**, the k_1 values were higher at all tested temperatures than those of the zero-order model k_0 for *b** and *a** kinetics.

However, the results of *L** kinetic agreed with other studied [22,23,26,27,37,38,39,40,41,42, 43,44,45,46,47,48,49,50] and were different from other studies [25,45]. Moreover, Similar results for *a** kinetic were found in other studies [22,23,27,37,38,39,40,41,44,46,48,50] while it differed from some of the results obtained by other authors [26,42,45,47,49]. On other hand, the *b** kinetic was in good agreement with the related literature [22,23,26,27,37,38,39,40,41, 42,45,46,48,50] but differed from some of the studies [28,47].

ΔE, which is used to characterize the variation of total colors followed the first order kinetic [22,27,37,38,39,46,48,50]. Also, *BI* values were similar to the results obtained in the literature [39,40,42].

Based on the models, the calculated activation energy values for FD Barhi were 4930, 18500, 17890, 13100, 10850 kJ. mol $^{-1}$ for a*, b*, BI, ΔE, and L* values, respectively. Those values were different from the values given in color change obtained other studies. This may be due to the variation in sample's type, treatment or process.

4. CONCLUSION

In the present study, Barhi fruit slices were freeze-dried (FD) and examined. The effect of the FD process on the color change, water activity, and moisture content was determined over 12-month storage time. Based on the experimental data, all CIELAB color parameters were significantly affected by temperature and storage time. Based on the statistical analysis, the first-order model could be used to fit the data for of color change in freeze-dried Barhi fruit slices.

ACKNOWLEDGEMENTS

This research work was financially supported by King Saud University, Vice Deanship of Research Chairs, Saudi Arabia.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Bashah MA. Date varieties in the Kingdom of Saudi Arabia. In: Guidance booklet, palm and dates. King Abdulaziz Univ. Press. Riyadh; 1996.
2. Zaid A, De Wet PF. Botanical and systematic description of the date palm. In: Zaid, A. (Ed.). Date palm cultivation. FAO, Rome. 1999;1-28.
3. Barreveld WH. Date palm products. Agricultural Services Bulletin No. 101, Food and Agriculture Organization of the United Nations (FAO), Rome, Italy; 1993.
4. Al-Redhaiman KN. Modified atmosphere improves storage ability, controls decay, and maintains quality and antioxidant contents of Barhi date fruits. Food, Agriculture & Environment. 2004;2(2):25-32.
5. Hassan BH, Alhamdan AM, Elansari AM. Stress relaxation of dates at Khalal and Rutab stages of maturity. Journal of Food Engineering. 2005;66:439–445.
6. Loutfy I El-Juhany. Degradation of date palm trees and date production in Arab countries: Causes and potential rehabilitation. Australian Journal of Basic and Applied Sciences. 2010;4(8):3998-4010.
7. Alsaed AK, Mehyar GF, Arar A. Effect of harvesting time and storage temperature on the duration of Balah stage of 'Barhi' dates. Ital. J. Food Sci. 2013;25:345-353.
8. Alhamdan AM, Diaeldin O Elkhair, Khaled AM Ahmed. Modeling of respiration rate of fresh date fruits (Barhi cultivar) under aerobic conditions. Journal of Advanced Agricultural Technologies. 2015;2(2):120-124.
9. Alhamdan AM, Bakri H, Alkahtani H, Diaeldin Abdelkarim, Mahmoud Y.

Freezing of fresh Barhi dates for quality preservation during frozen storage. Saudi Journal of Biological Sciences; 2016. Available:http://dx.doi.org/10.1016/j.sjbs.2016.02.003

10. Tsinontides SC, Rajniak P, Pham D, Hunke WA, Placek J, Reynolds SD. Freeze drying-principles and practice for successful scale-up to manufacturing. Int. J. Pharm. 2004;280:1–16.
11. Pan Z, Shih C, McHugh TH, Hirschberg E. Study of banana dehydration using sequential infrared radiation heating and freeze-drying. LWT-Food Sci. Technol. 2008;41:1944–1951.
12. Chan EW, Lim YY, Wong SK, Lim KK, Tan SP, Lianto FS, Yong MY. Effect of different drying methods on the antioxidant properties of leaves and tea of ginger species. Food Chem. 2009;113:166–172.
13. Jaekel T, Dautel K, Ternes W. Preserving functional properties of hen's egg yolk during freeze-drying. J. Food Eng. 2008;87:522–526.
14. Mejıa-Meza EI, Jaime AY, Connie MR, Neal MD, Barbara R, Frank Y, Carter C. Improving nutritional value of dried blueberries (*Vaccinium corymbosum L.*) combining microwave-vacuum, hot-air drying, and freeze drying technologies. International Journal of Food Engineering. 2008;4(6):10.
15. Hammami C, René F. Determination of freeze-drying process variables for strawberries. Journal of Food Engineering. 1997;32:133-154.
16. Adela M Ceballos, Gloria I Giraldo, Carlos E Orrego. Effect of freezing rate on quality parameters of freeze dried soursop fruit pulp. Journal of Food Engineering. 2012;111:360–365.
17. Ahmed AI, Ahmed AWK, Robinson RK. Chemical composition of date varieties as influenced by the stage of ripening. Food Chemistry. 1995;54:305−309.
18. Ali Mohamed AY, Khamis AS. Mineral ion content of the seeds of six cultivars of Bahraini date palm (*Phoenix dactylifera L.*). Journal of Agricultural and Food Chemistry. 2004;52:6522−6525.
19. Abdul A Allaith. Antioxidant activity of Bahraini date palm (*Phoenix dactylifera* L.) fruit of various cultivars. International Journal of Food Science and Technology. 2008;43:1033−1040.
20. Al Farsi MA, Lee CY. Nutritional and functional properties of dates: A review. Critical Reviews in Food Science and Nutrition. 2008;48:877−887.
21. Manjeshwar SB, Bantwal RV, Shaun MK, Harshith PB, Praveen KV. A review of the chemistry and pharmacology of the date fruits (*Phoenix dactylifera L.*). Food Research International. 2011;44:1812–1822.
22. Ayhan Topuz. A novel approach for color degradation kinetics of paprika as a function of water activity. LWT - Food Science and Technology. 2008;41:1672-1677.
23. Franco P, Pedro M, Karl K, Kit G. Color changes and acrylamide formation in fried potato slices. Food Research International. 2005;38:1–9.
24. Sze P Ong, Chung L Law, Ching L Hii. Effect of pre-treatment and drying method on color degradation kinetics of dried salak fruit during storage. Food Bioprocess Technol. 2012;5:2331–2341.
25. Soleiman H, Shahin R, Seyed SM, Mortaza A. Application of computer vision technique for on-line monitoring of shrimp color changes during drying. Journal of Food Engineering. 2013;115:99–114.
26. Benjar C, Athapol N. Color degradation kinetics of pineapple puree during thermal processing. LWT. 2007;40:300–306.
27. Franco P, Oscar B, Domingo M, Pedro M, Karl K, Kit G. Color kinetics and acrylamide formation in NaCl soaked potato chips. Journal of Food Engineering. 2007;79:989–997.
28. Kumar HSP, Radhakrishna K, Nagaraju PK, Rao DV. Effect of combination drying on the physicochemical characteristics of carrot and pumpkin. Journal of Food Processing and Preservation. 2001;25(6): 447–460.
29. Maskan A, Sevim K, Medeni M. Effect of concentration and drying processes on color change of grape juice and leather (pestil). Journal of Food Engineering. 2002;54:75–80.
30. Antal T. Comparative study of three drying methods: Freeze, hot air-assisted freeze and infrared-assisted freeze modes. Agronomy Research. 2015;13(4):863–878.
31. Lau MH, Tang J, Swanson BG. Kinetics of textural and color changes in green asparagus during thermal treatments. Journal of Food Engineering. 2000;45(4): 231–236.
32. Jaya S, Das H. Accelerated storage, shelf life, and color of mango powder. Journal of

Food Processing and Preservation. 2005;29:45–62.
33. Al-Awaadh Alhussein M, Bakri H Hassan, Khaled AM Ahmed. Hot air drying characteristics of sukkari date (*Phoenix dactylifera* L.) and effects of drying condition on fruit color and texture. International Journal of Food Engineering. 2015;11(3):421-434.
34. Labuza, Theodore P, Bilge Altunakar. Water activity prediction and moisture sorption isotherms. CH 5 Water Activity in Foods: Fundamentals and Applications. IFT Press. Blackwell Publishing Professional USA. 2007;109-154.
35. Parra R, Magan N. Modelling the effect of temperature and water activity on growth of *Aspergillus niger* strains and applications for food spoilage molds. Journal of Applied Microbiology. 2004;97: 429–438.
36. Louise Slade, Harry Levine. Beyond water activity: Recent advances based on an alternative approach to the assessment of food quality and safety. Critical Reviews in Food Science and Nutrition. 1991;30(2-3): 115-360.
37. Lien DT Phuong. Kinetic of chlorophyll degradation and color change in bitter gourd during heat treatment. International Journal of Engineering Sciences & Research Technology. 2016;5(4):616-622.
38. Reza AC, Behnam A. New model for colour kinetics of plum under infrared vacuum condition and microwave drying. Acta Sci. Pol. Technol. Aliment. 2016;15(2):131–144.
39. Charanjiv Singh, Sharma HK. Kinetics of color change and quality parameters of uncoated and sodium alginate coated dehydrated pineapple samples during storage. International Journal of Food and Nutritional Sciences. 2015;4(3):41-49.
40. Saini CS, Sharma HK. Effect of pectin coating on colour and quality of dehydrated pineapple during storage. Asian J. Dairy & Food Res. 2016;35(2): 120-129.
41. Sara A, Neda M Azad, Ebrahim H, Asgar F, Gholam HA. Kinetic of color and texture changes in rehydrated figs. Tarım Bilimleri Dergisi – Journal of Agricultural Sciences. 2015;21:108-122.
42. Kalika Gupta, Alam MS. Mass and color kinetics of foamed and non-foamed grape concentrate during convective drying process: A comparative study. Journal of Engineering and Technology Research. 2014;6(4):48-67.
43. Chunthaworn S, Achariyaviriya S, Achariyaviriya A, Namsanguan K. Color kinetics of longan flesh drying at high temperature. Procedia Engineering. 2012;32:104–111.
44. Shao-Qian CAO, Liang LIU, Siyi PAN. Thermal degradation kinetics of anthocyanins and visual color of blood orange juice. Agricultural Sciences in China. 2011;10(12):1992-1997.
45. Mohapatra D, Bira ZM, Kerry J, Frías JM, Oliveira FAR. Postharvest hardness and color evolution of white button mushrooms (*Agaricus bisporus*). Journal of Food Science. 2010;75(3):146-152.
46. Nuray K, Hande SB, Feryal K. Kinetics of colour changes in dehydrated carrots. Journal of Food Engineering. 2007;78: 449–455.
47. Aysun Maskan, Sevim Kaya, Medeni Maskan. Effect of concentration and drying processes on color change of grape juice and leather (pestil). Journal of Food Engineering. 2002;54:75–80.
48. Pedro C Moyano, Vanessa K Rjııoseco, Paola A Gonzaalez. Kinetics of crust color changes during deep-fat frying of impregnated French fries. Journal of Food Engineering. 2002;54:249–255.
49. Maskan M. Kinetics of color change of kiwifruits during hot air and microwave drying. J. Food Eng. 2001;48(2):169–175.
50. Barreiro JA, Milan M, Sandoval AJ. Kinetics of color change of double concentrated tomato paste during thermal treatment. Journal of Food Engineering. 1997;33:359-371.

Peer-review history:
The peer review history for this paper can be accessed here:
http://sciencedomain.org/review-history/18215