

CURVE FITTING PARAMETERS OF COLOR VARIABLES OF PISTACHIO NUT CREAM DURING STORAGE PERIOD

Ö. Faruk Gamlı^{1*}, İbrahim Hayoğlu²

¹Korkut Ata University, Vocational High School, Bahçe - Osmaniye, Turkey

²Harran University, Agricultural Engineering, Food Engineering Department, Şanlıurfa - Turkey

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Abstract

Pistachio nut cream was produced by using pistachio nut, powdered sugar, defatted milk powder, margarine, lecithin and vanilla. Spreadable pistachio nut creams were stored at 4 and 20 °C up to 240 days. Curve fittings of color variables (L , a , b) and moisture content (%), 2-tiobarbutric acid, browning indices, total chlorophyll, chlorophyll a and b values of spreadable pistachio nut cream were investigated during the storage period. Different mathematical expressions investigated for the curve fittings as exponential, logarithmic, rational, polynomial, Peleg, Weibull, Gaussian, power, Fourier and sin functions. Exponential and cubic polynomial equations gave the best fitting results due to the high regression coefficient (r^2), and lower RMSE (%) and SSE (%) values.

Keywords: Pistachio nut cream, color variables, curve fittings, exponential and polynomial equations

ANTEPFISTIĞI KREMASININ RENK DEĞİŞKENLERİNİN DEPOLAMA ESNASINDAKİ EĞRİ UYDURMA PARAMETRELERİ

Özet

Antepfıstığı kreması, pudra şekeri, yağsız süt tozu, margarin, lesitin ve antepfıstığı kullanılarak üretilmiştir. Sürülebilir antepfıstığı kreması, 4 ve 20 °C'de 240 gün süreyle muhafaza edilmiştir. L , a , b renk değişkenleri ve nem miktarı (%), 2.tiobarbütrik asid, esmerleşme indisi, toplam klorofil, klorofil a ve b değerleri arasındaki matematiksel ilişkilerin belirlenmesine çalışılmıştır. Matematiksel ilişkilerin araştırılmasında eksponensiyel, logaritmik, oransal, polinom, Peleg, Weibull, Gauss, üslü model, Fourier ve sinüs eşitlikleri kullanılmıştır. Eksponensiyel ve polinom eşitliklerinin yüksek regresyon sabiti (r^2), düşük RMSE (%) ve SSE (%) değerlerine göre en uygun eşitlikler olduğu belirlenmiştir.

Anahtar Kelimeler: Antepfıstığı kreması, renk değişkenleri, eğri uydurma, eksponensiyel ve polinom eşitlikleri

* Corresponding author / Yazışmalardan sorumlu yazar;

✉ farukg69@gmail.com,

☎ (+90) 328 861 2282,

☎ (+90) 328 861 2658

INTRODUCTION

Pistachio nut is mainly grown in many regions of the world, such as Iran, USA, Turkey, Greece, and Italy. It is consumed as salted, roasted and also used in dessert production such as baklava and nut cream production in Turkey, especially within Gaziantep and Şanlıurfa region, as a main ingredient. Pistachio nut contains K and P and also various amounts of Ca, Mg, and Fe. Annually 35000 tons of pistachio nut are produced in Turkey. The different cultivars of pistachios are grown in the cities within the southeast region in our country such as Siirt, Ohadi, Halebi, Kirmizi, and Uzun. Pistachio nut contains 22 % protein, 55 % fat, 18 % carbohydrate and 5 % moisture (1). Fatty acid content of pistachio nut is 7-10 % of palmitic, 0.9-2.5 % of stearic, 54-71 % of oleic, 16-35 % of linoleic acid (2). Pistachio nut is being used in the production of baklava (a special type of dessert in Turkey) and nut paste. Dried pistachios are highly susceptible to lipid oxidation because of high content of lipids, and the lipid oxidation causes off-flavor development that concerns for the shelf life stability of many confections containing pistachios (3). The nuts are rich in chemical composition and nutrients. The beneficial effects of nuts are attributed to such characteristics as polyunsaturated/ saturated fat ratio, high percentage of monounsaturated fat and high-fiber content (4). The dessert manufacturers prefer Kirmizi and Uzun cultivars in baklava and nut paste production, due to their special green color, flavor and texture. The pistachio nut paste is a sweet product having a semi-hard texture, which is produced by mixing the ground pistachio with glucose-sucrose solution. The mixture is kneaded up to a desired texture obtained (5). Different products can be produced by using nut having different texture such as peanut paste (6), walnut paste (7), pistachio nut paste (5), hazelnut paste (8), and chocolate peanut spread (9). During the production of nut containing foods, they are subjected to heat treatment, and the most common application is roasting of nuts. During the heat treatment, especially roasting, the desirable flavor and aroma development occur. Chemical and biological changes of nut lipids are detected as a result of the heat treatment such as free fatty acidity, iodine, peroxide and acid values of oils (4). The proteins of acid-soluble fraction are sensitive to the heat treatment and may have

a role in flavor volatile production during the roasting process (10).

The color is an important factor that affects the acceptability of the product and plays an important role in appearance and processing of the food materials. The colors of the food materials are affected by a variety of reactions such as pigment degradation, browning reaction such as Maillard reaction, enzymatic browning and ascorbic acid oxidation due to thermal processing (11). Hunter color parameters such as *L*, *a**, *b** are widely used to describe the color change during the thermal processing for the fruits and vegetables such as strawberry juice and tomato puree (12), spinach (13), kiwifruits (14), pomegranate juice concentrate (15), grape juice and leather (pestil) (16). Hunter parameters are also widely used to describe visual colors (*L*, whiteness/ darkness; *a*, redness/ greenness; *b*, yellowness/ blueness) and to provide useful information for the quality controls of fruits, vegetables and its products (13). In addition to *L*, *a** and *b** values, 2-tiobarbutric acid values, browning indices and chlorophyll contents are used to reveal color in food products. The browning index refers to pureness of brown color and is important factor for drying process due to enzymatic and non-enzymatic browning reactions (14, 17). 2-tiobarbutric acid test is a good method for determining the degradation of fat containing food materials, it reacts with malondialdehyde (oxidation products of linoleate) producing a pink color chromogen that can be measured spectrophotometrically at different wavelengths (450, 530 and 538 nm) (18).

It is reported that the color variables have been recommended to predict chemical and quality changes in many food products. *L* values of paprika raisin, pineapple concentrates, grape fruits, apple slices, concentrated apple, peach and plump related with brown pigment concentrations (19). It is reported that the tristimulus reflectance color variables changed with moisture content of dried apricots. *L* and *b* values of dried apricot samples increased but the values decreased during the rehydration of dried apricots and changes in color variables with moisture content at 15.49-30.20 % were linear. It is said that the change in reflectance color values of samples after rehydration may be attributed to the change in the spectral characteristics of light reflected from dried apricots (19). It is

reported that the water activity of paprika varies with industrial processing methods and has an effect on color parameters during storage period. It is said that as the water activity of paprika increased, the rate constant of color degradation at the reference temperature linearly increased and the changes in L , a , b and total color difference values were affected significantly by processing time, temperature and water activity so a linear relationship was found between the water activity and the rate constant of the color parameters of paprika (20). It is reported that there is a close relationship between color values of L , a , b and heating process during the preparation of food products and long terms of storage conditions of food materials (21). There was a close relationship between color variables of L , a , b of tomato purees and moisture content (%) during convectional drying (22); the effect of moisture content on the color variables of walnut cultivars is significant (23) and color variables of soybean and soy-bulgur varied according to the moisture content (24).

There are several references based on the color kinetics of food materials in the literatures. The kinetic models are widely used for describing the reaction rate as a function of experimental variables during the processing and storage period (14, 15, 25).

The objective of this study was to determine the best mathematical equation for the curve fittings of color variables (L , a , b) and moisture content (%), 2-tiobarbutric acid, browning indices, total chlorophyll, chlorophyll a and b values of spreadable pistachio nut cream during the storage period.

MATERIALS AND METHODS

Materials

Pistachio nuts were roasted between 160 and 165 °C for 8-10 min. Roasted pistachio nuts were grounded, and powdered sugar and defatted powdered milk were added. Margarine, lecithin and also powdered vanilla were added to the mixture. The mixing procedure was carried out until the desired spreadable texture obtained. In the production of spreadable nut cream; sugar, margarine, defatted milk, lecithin and vanilla were

used at a constant proportion of pistachio nut (10 %). Two different storage temperatures were applied in the experimental procedures. The spreadable nut creams were filled in to the glass jars around 250-260 g within polypropylene covers and samples were stored at 4 and 20 °C for 240 days.

METHODS

Analytical Procedures

Protein, ash, carbohydrate, fat, cellulose and moisture contents (%) (26), 2-tiobarbutric acid values (18), browning indices (A_{420}) (27), total chlorophyll, chlorophyll a and b (28), L , a , and b (29) values of spreadable pistachio nut cream were determined during storage period at 4 and 20 °C.

Curve Fitting Procedures

The curve fitting procedures were applied due to the mathematical expressions such as power, exponential, logarithmic, polynomial, rational, Fourier, Weibull, Gaussian, sin functions, and Peleg's equations between L , a , b values and color variables, moisture content (%), 2-tiobarbutric acid, browning indices, total chlorophyll, chlorophyll a , b components of spreadable pistachio nut cream for curve fitting procedures.

Statistical Analysis

The software package program of Matlab (R200b) was used for the numerical calculations. The regression constant (r^2) changes between 0 and 1, and it is used for determining of the success of data deviations for the curve fitting procedures. r^2 values approaches to 1 if the curve fittings are successful (30,31).

$$r^2 = \frac{\sum (M_{Rcalc,i} - M_{Rav.exp,i})^2}{\sum (M_{Rexp,i} - M_{Rav.exp,i})^2}$$

The sum of square error (SSE) refers to the amount of deviation for the matched values. SSE values approaches to zero if the fitting procedures are successful (13,30).

$$SSE = 1/N \sum (M_{Rexp,i} - M_{Rcalc,i})^2$$

The root of mean square error (RMSE %) is another parameter that used for the curve fitting procedure. RMSE values approaches to zero if the curve fitting procedures are successful (32-34).

$$RMSE \% = \left[\frac{\sum (M_{Rcalc,i} - M_{Rexp,i})^2}{N} \right]^{0.5} \cdot 100$$

RESULTS AND DISCUSSIONS

Spreadable pistachio nut cream contain 0.792 % cellulose, 7.274 % of protein, 1.245 % ash, 29.926 % fat, 9.777 % of moisture and 51.990 % of carbohydrates (26). The moisture contents of spreadable pistachio nut cream are presented in Fig.1. The moisture contents changed from 9.777 % to 9.375 % at 4 and 20 °C during the storage period respectively.

The color values of L, a, and b values of the pistachio nut cream were affected during the storage period at 4 and 20 °C. The lightness L value decreased with drying time indicating that samples become darker. L values changed between 44.76 and 33.89 at 4 °C; 44.76 and 31.51 at 20 °C respectively. The ‘a’ values of the samples changed between -1.77 and 1.19 at 4 °C; -1.77 and 2.94 at 20 °C respectively. The changes from negative to positive a value indicates that the samples are green at first and the pistachio nut creams lost their greenness and become dirty green color. The changes in a values can be

explained the decomposition of the pigments and formation of brown pigments during storage period (14, 34).

The b values of spreadable pistachio nut creams increased from 15.99 to the 19.24 at 4 °C; from 15.99 to the 18.91 at 20 °C respectively.

The browning indices of spreadable pistachio nut cream were affected during the storage period at 4 and 20 °C. The indices of cream increased with storage period, changed between 0.359 and 0.484 at 4 °C; 0.359 and 0.547 at 20 °C respectively (Fig. 2).

Total chlorophyll contents of spreadable pistachio nut decreased during the storage period at 4 and 20 °C. Total chlorophyll values of nut creams changed between 12.374 and 8.994 at 4 °C; 12.374 and 5.894 at 20 °C respectively (Fig. 3).

Chlorophyll a contents of spreadable pistachio nut decreased during the storage period at 4 and 20 °C. Chlorophyll a values of spreadable nut creams changed between 5.347 and 2.954 at 4 °C; 5.347 and 3.319 at 20 °C respectively (Fig. 4).

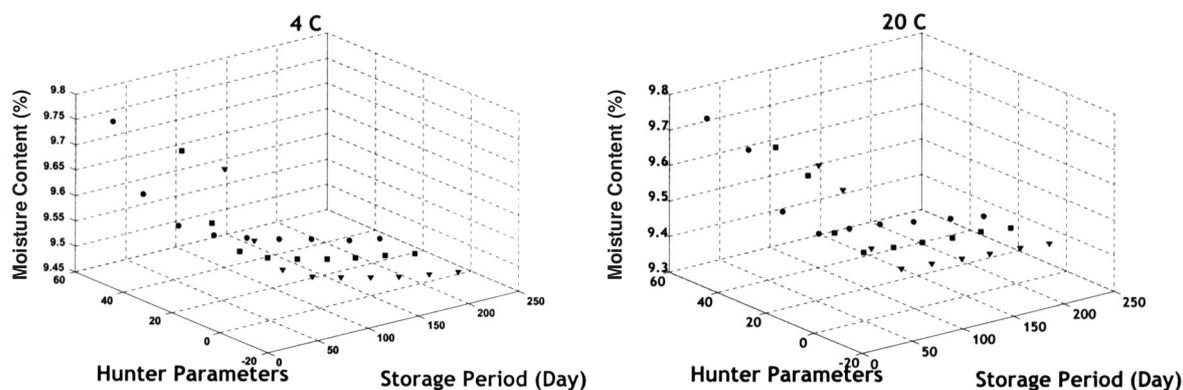


Fig.1 Moisture contents (%) of spreadable nut cream during the storage period at 4 and 20 °C (L:●, a:▼, b:■)

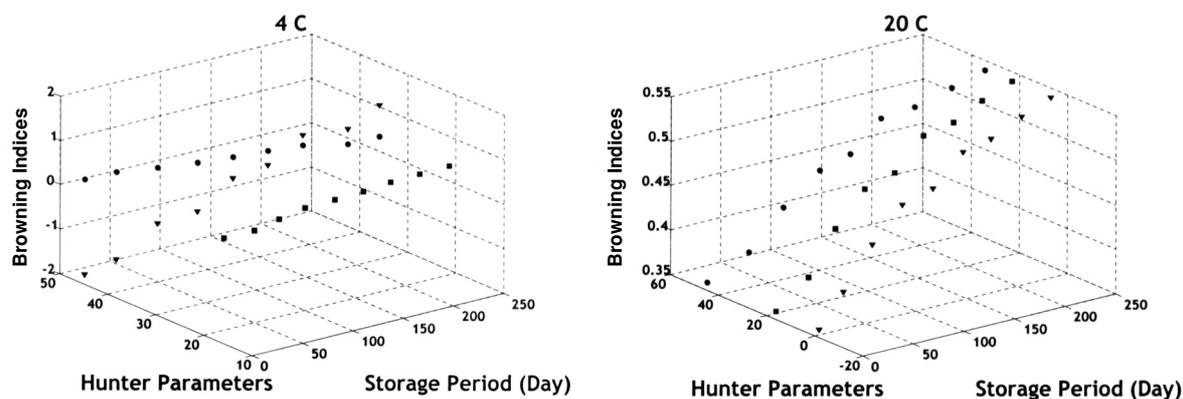


Fig. 2 Browning indices of spreadable nut cream during the storage period at 4 and 20 °C (L:●, a:▼, b:■)

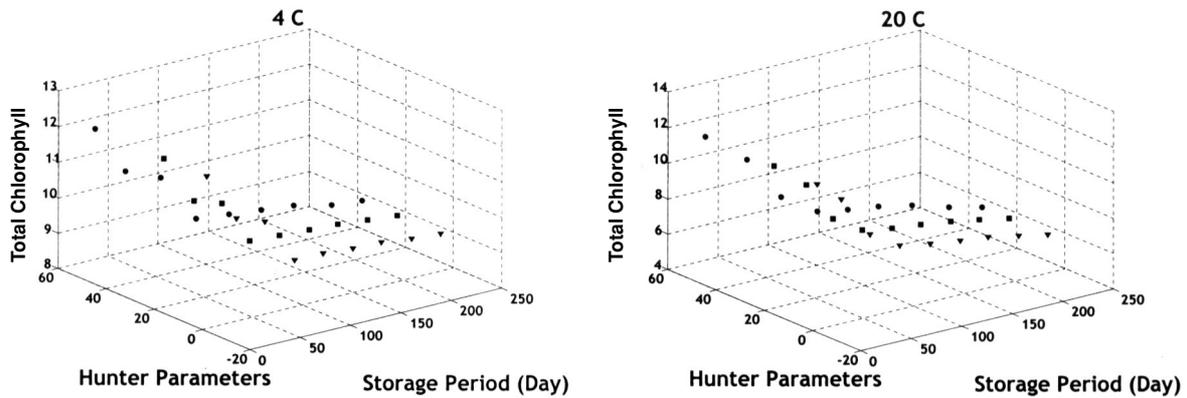


Fig. 3 Total chlorophyll values of spreadable nut cream during the storage period at 4 and 20 °C (L:●, a:▼, b:■)

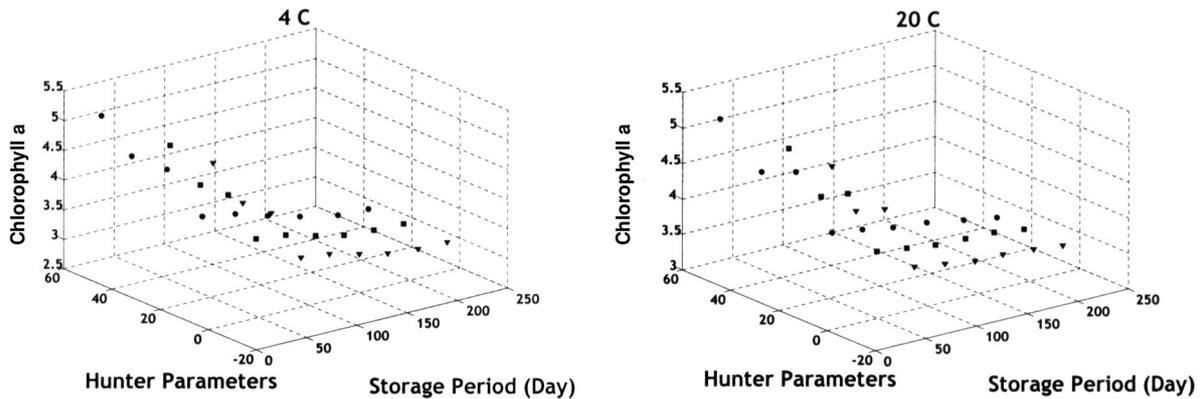


Fig. 4 Chlorophyll a contents of spreadable nut cream during the storage period at 4 and 20 °C (L:●, a:▼, b:■)

Chlorophyll b contents of spreadable pistachio nut decreased during the storage period at 4 and 20 °C. Chlorophyll b values of spreadable nut creams changed between 6.217 and 3.443 at 4 °C; 6.217 and 4.886 at 20 °C respectively (Fig. 5).

The 2-tiobarbitric acid values of pistachio nut cream changed during the storage period at 4 and 20 °C. TBA values of nut creams changed between 0.124 and 0.264 at 4 °C; 0.124 and 0.278 at 20 °C respectively (Fig. 6).

There is a close relationship between L values and increase in browning of food materials and pigment degradations (15, 25). Decrease in L values of Hunter parameter was due to loss of color (become darker) due to the pigment destruction (25). Browning measurement can be used for the samples due to the variation in lightness either calculated from the Hunter parameters or measured due to absorbance value of the samples (25).

Regression analysis procedures were applied to the color parameters of spreadable pistachio nut creams for curve fitting procedures. Table 1

presents the relationship among color parameters (L, a, b) with moisture content (%) and browning indices. In order to obtain best fitting results, different mathematical expressions were analyzed and fitting parameters were determined by non-linear regression analysis (Mathlab 2009b).

Exponential expression gave better fittings for color variables (L, a, and b) and moisture contents (%) of spreadable pistachio nut cream and regression coefficients (r^2) changed between 0.8195 and 0.9968 at 4 °C. Cubic polynomial expression was found the color variables and moisture contents of nut cream at 20 °C and r^2 changed between 0.8635 and 0.9532. Cubic polynomial expression gave better fittings for the color variables (L, a, b) and 2-tiobarbitric acid of nut cream due to the statistical results at 4 and 20 °C. Regression coefficients changed between 0.9231 and 0.9902 for L, a, b and TBA values of nut cream samples. Regression coefficients changed between 0.9429 and 0.9802 for L, a, b and browning indices of spreadable nut cream at 4 and 20 °C.

Exponential and cubic polynomial equations found for curve fitting between color variables of

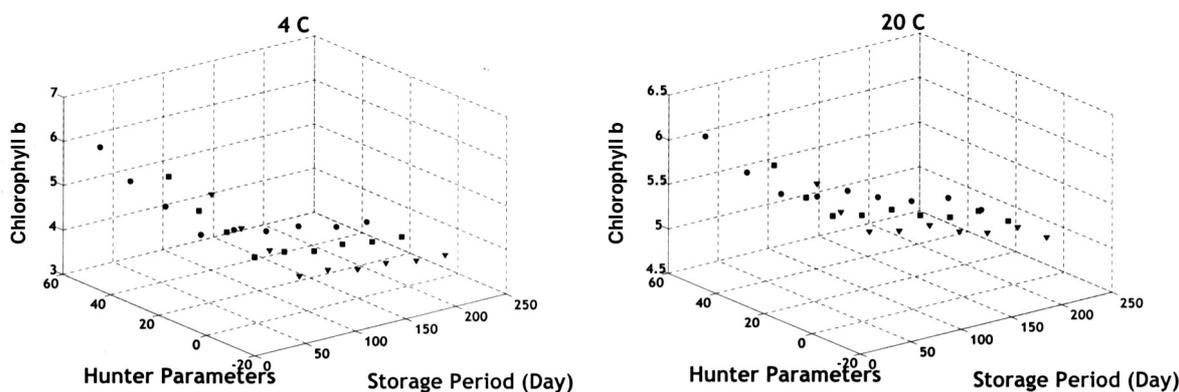


Fig. 5 Chlorophyll b values of spreadable nut cream during the storage period at 4 and 20 °C (L:●, a:▼, b:■)

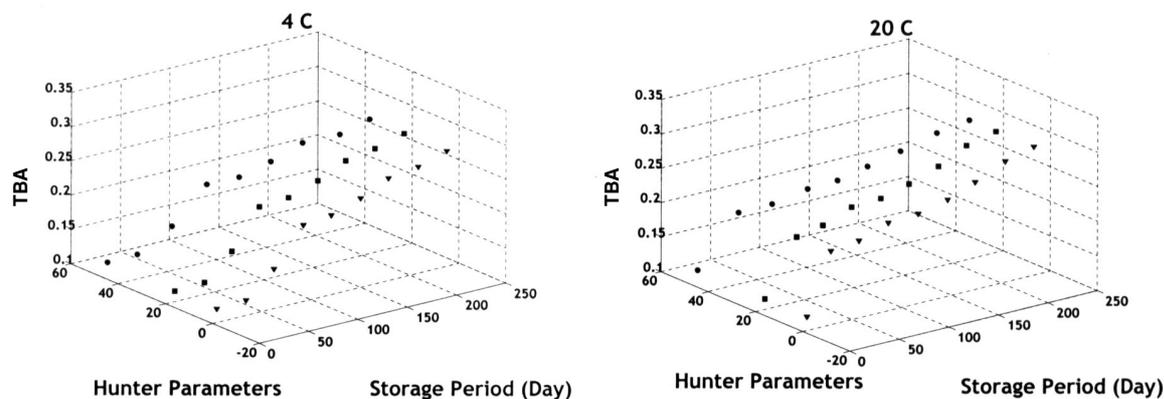


Fig. 6 2-tiobarbutric acid values of spreadable nut cream during the storage period at 4 and 20 °C (L:●, a:▼, b:■)

Table 1. Mathematical relationships among *L*, *a*, *b*, moisture content, 2-tiobarbutric and browning indices

Storage Temp. °C	Parameters	Express.	Constants				r ²	RMSE (%)	SSE (%)
			a	b	c	d			
4	L-MC	a*	9.585	-0.0006	0.0102	0.1278	0.9832	0.06653	0.0221
	a-MC	a*	3.87e ⁻⁷	-7.438	9.499	-0.0045	0.9968	0.00741	0.000274
	b-MC	a*	20.2	-0.144	5.514	0.0205	0.8195	0.00557	0.01554
20	L-MC	b*	995	-2.86e ⁴	2.74e ⁵	-8.76e ⁵	0.9532	1.197	7.168
	a-MC	b*	0.0436	-0.1013	-0.2448	9.904	0.9544	0.396	0.0786
	b-MC	b*	0.034	-1.722	28.77	-149.6	0.8635	0.06859	0.2352
4	L-TBA	b*	9.92e ⁻⁵	-0.0125	0.5116	-6.524	0.9880	0.0742	0.000275
	a-TBA	b*	1790	-978.7	190.1	-13.63	0.9719	0.2241	0.2512
	b-TBA	b*	1035	-589.9	131.9	6.676	0.9902	0.1609	0.1295
20	L-TBA	b*	-6.66e ⁻⁵	0.00782	-0.2679	3.62	0.9863	0.00668	0.000223
	a-TBA	b*	0.00143	-0.0017	0.0251	0.182	0.9845	0.00709	0.000252
	b-TBA	b*	-7036	4536	-910.4	72.54	0.9231	0.4421	0.9771
4	L-BI	b*	-1.17e ⁴	1.41e ⁴	-5695	811.9	0.9705	0.8713	3.796
	a-BI	b*	3493	-4267	1747	-240.7	0.9672	0.2419	0.2926
	b-BI	b*	1360	-1612	657.5	-75.3	0.9631	0.3122	0.4874
20	L-BI	b*	-6144	8416	-3866	632.3	0.9802	0.7794	3.037
	a-BI	b*	2766	-3858	1793	-276.1	0.9647	0.333	0.5545
	b-BI	b*	-734.7	1075	-498.6	90.23	0.9429	0.3808	0.7252

(MC: moisture content, TBA: 2-tiobarbutric acid, BI: browning indices)

a*: $y = ae^{bx} + ce^{dx}$, b*: $y = ax^3 + bx^2 + cx + d$

Table 2. Mathematical relationships among L, a, b, total chlorophyll, chlorophyll a and b values

Storage Temp. °C	Parameters	Express.	Constants				r ²	RMSE (%)	SSE (%)
			a	b	c	d			
4	L-TChl	a*	35.75	0.0182	-6.04e ¹²	-3.028	0.962	0.9884	4.885
	a-T Chl	b*	-0.6932	9.212	-40.81	59.03	0.9511	0.2955	0.4367
	b-T Chl	a*	7.16e ⁷	-1.806	19.62	-0.0168	0.9399	0.3983	0.7933
20	L-T Chl	b*	0.1681	-4.691	44.12	-101.4	0.9897	0.5626	1.583
	a-T Chl	b*	-0.0725	1.917	-16.86	50.76	0.9822	0.2369	0.2806
	b-T Chl	b*	0.0143	-0.2467	0.287	22.91	0.9609	0.3152	0.4966
4	L-Chl a	a*	32.73	0.0613	-3.75e ¹¹	-8.457	0.9708	0.866	3.75
	a-Chl a	b*	-0.6932	9.212	-40.81	59.03	0.9511	0.2955	0.4367
	b-Chl a	a*	1582	-2.257	19.06	-0.0342	0.9679	0.2913	0.4243
20	L-Chl a	b*	9.97	-131.4	573.4	-789.7	0.9481	1.261	7.954
	a-Chl a	b*	-3.354	43.26	-184.9	262.7	0.9707	0.3033	0.460
	b-Chl a	a*	15.95	-0.00010	2.94e ⁶	-4.141	0.8779	0.557	1.551
4	L-Chl b	a*	37.72	0.02846	-4.54e ⁵	-3.177	0.9839	0.643	2.067
	a-Chl b	b*	-0.3993	6.277	-32.96	56.41	0.944	0.6163	0.5001
	b-Chl b	a*	117	-0.9633	14.33	0.01403	0.9705	0.2794	0.3902
20	L-Chl b	a*	10.43	0.234	-2.75e ⁷	-3.311	0.964	1.05	5.514
	a-Chl b	a*	1135	-1.21	-9.3e ⁻¹³	4.593	0.9837	0.2261	0.2555
	b-Chl b	b*	6.814	-110.7	594.4	-1036.6	0.9854	0.1926	0.1855

(T Chl: total chlorophyll, Chl a: chlorophyll a, Chl b: chlorophyll b)
a*: $y = ae^{bx} + ce^{dx}$, b*: $y = ax^3 + bx^2 + c^2 + d$

L, a, b and total chlorophyll, chlorophyll a and b values of nut cream samples due to the statistical results of r², RMSE (%) and SSE (%) (Table 2). Polynomial expression gave better fitting for color values of L, a, b and total chlorophyll values of nut cream samples at 20 °C. Exponential expression was found for L, a, but cubic polynomial expression was found for b values at 4 °C.

Higher regression coefficient (r²) and lower RMSE (%) and SSE (%) values were found for L, a, b and chlorophyll a values of spreadable pistachio nut cream. r² changed between 0.8779 and 0.9708 for the color variables of L, a, b and chlorophyll a values at 4 and 20 °C respectively. Cubic polynomial and exponential expression were found for the fittings of L, a, b and chlorophyll b values of nut cream samples. Regression coefficients (r²) changed between 0.944 and 0.9854 at 4 and 20 °C.

CONCLUSION

Mathematical relationship between color variables of spreadable pistachio nut cream (L, a, b) and moisture contents (%), browning indices, 2-tiobarbutric acid and chlorophyll values were investigated by different expressions. Exponential and polynomial expressions were found for fitting results due to statistical results (regression

coefficient, RMSE and SSE) at 4 and 20 °C. The statistical results showed that moisture content (%) affected color values of spreadable pistachio nut cream. There were close relationships among the moisture content (%) and color variables (L, a, b), 2-tiobarbutric acid, browning indices, total chlorophyll, chlorophyll a and b values of pistachio nut creams according to the statistical results and this relationships can be mentioned by cubic polynomial and exponential equations.

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