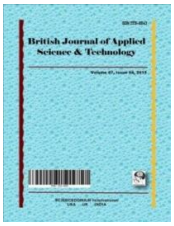

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Anthocyanin Degradation and Colour Kinetics of Cornelian Cherry Concentrate

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Authors' contributions

This work was carried out in collaboration between both authors ŞKY and EAE. Author EAE designed the study, coordinated and supervised the work. Author ŞKY performed literature searches and analyses. Writing the manuscript was done by both authors ŞKY and EAE, final structure supervised by author EAE. Both authors have read and approved the final manuscript.

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ABSTRACT

Aims: The purpose of present study is to analyze the physicochemical properties (pH, total acidity, total monomeric anthocyanin, total phenolics and, total antioxidant activity) and to investigate thermal degradation kinetics of anthocyanins and Hunter colour parameters of cornelian cherry (*Cornus mas* L.) concentrates at 60, 70 and 80°C.
Methods: Monomeric anthocyanin degradation fitted to a first order reaction kinetics. Hunter *L**, *a**, *b** values were measured to characterize colour; total colour difference (*TCD**), lightness (L^*), chroma (*C**), and hue angle (*h**°) were calculated from those values and, fitted to zero-order, first-order and combined kinetics model.
Results: The half-life values for anthocyanin degradation were 5.7, 4.3 and 2.1 h in cornelian cherry concentrate at 60, 70 and 80°C, respectively. Temperature dependence of anthocyanin degradation rate constants was expressed as activation energy, E_a, and E_a was calculated as 48.38 kj/mol between 60-80°C. *TCD**, *L**, *C**, and *h*°* gave best fits with combined kinetics model.
Conclusion: Cornelian cherry fruits are important source of phenolic compounds and anthocyanins, which are also good source of natural antioxidants. Anthocyanin degradation followed first order reaction kinetics, while changes in *L**, *C**, *h*°* and *TCD** followed combined kinetic model. The degradation rate increased as temperature increased.

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Keywords: Cornelian cherry; anthocyanin; colour; kinetics; thermal degradation.

1. INTRODUCTION

Cornelian cherry (*Cornus mas* L.) fruits are widely grown in different regions of Turkey, especially in eastern and northern Anatolia. Cornelian cherries are typically olive shaped, single-seeded fruits, 10–20 mm long. They are typically red. The fruits have a sweet-sour taste. They contain high amount of vitamin C and are rich in sugar, anthocyanins, organic acids and tannins [1]. In Turkey, approximately 12,800 tons of cornelian cherry fruit is produced per annum. The fruit is either consumed directly or processed into various products such as jam, marmalade, pestil (a dried form of marmalade produced in the eastern part of Turkey), paste, and sherbet or is dried. Cornelian cherry fruits have also been used for the medical treatment of gastrointestinal disorder and diarrhea in Turkey [2].

Fruits and vegetables are a good source of natural antioxidants, containing many different antioxidant components which provide protection against harmful-free radicals and have associated with lower incidence and mortality rates of cancer and heart diseases in addition to a number of other health benefits [3]. Anthocyanins are a group of naturally occurring phenolic compounds, which are responsible for the attractive colours of many flowers, fruits (particularly in berries), vegetables and related products derived from them [4]. Anthocyanins are becoming increasingly important as antioxidants and are related to a broad range of beneficial effects in human health and disease prevention. Recently, some studies have been published on the physical and chemical properties of cornelian cherry fruits and also their antioxidant capacity, total phenolics and anthocyanin content [5-7]. Thermal processing is one of the most widely used methods of preserving and extending the useful shelf life of foods [8]. It is the one of the most important factors that affects the stability of anthocyanins. Colour is an important organoleptic property in determining product quality, therefore minimizing the pigment losses during processing is of primary concern to the processor [9]. However, no information is available on the thermal degradation kinetics of cornelian cherry anthocyanins and colour values. Determination of the kinetic parameters is essential to predict the quality changes that occur during thermal processing. Therefore, the objectives of this study were (1) to determine the physicochemical properties of cornelian cherry fruit concentrate; (2) to investigate the thermal degradation kinetics of anthocyanins and Hunter colour parameters in prepared concentrates.

2. MATERIALS AND METHODS

2.1 Chemicals

Pectolytic enzyme, Panzym XXL, was kindly gifted by Sinerji A.Ş., Mersin, TURKEY. Folin-Ciocalteu reagent was purchased from Sigma Chemical Co. All the other reagents were of analytical grade and purchased from Sigma Chemical Co.

2.2 Plant Material

In this study, naturally grown cornelian cherry variety in Karıngit village of Elazığ, Eastern Anatolia, Turkey, was used. Fully ripe *Cornus mas* L. fruits were collected at optimum growth in September. No supplemental fertilizer was applied to the fruit supplied trees.

2.3 Preparation of Cornelian Cherry Juice and Concentrate

All the foreign materials such as pieces of branches and leaves and also unripe and damaged fruits were removed from fruit samples by hand. The cleaned fruits were washed under cold tap water, stalks and seeds were removed. Fruits were ground by using a laboratory blender. Juice was immediately filtered through muslin to remove pulp from the juice. Then the juice was depectinized with 1.0% (v/w) Panzym XXL at 50°C for 2 h. The depectinized juice was allowed to rest at 4°C for 24 h. The juice was again filtered through five layer muslin and finally double layer filter paper to obtain a clear juice. Clear juice was concentrated from 18.46 to 43.52° Brix by BÜCHİ Rotary Evaporator (Rotavapor R-3 model, BÜCHI Loborthechnik AG, Flawil, Switzerland) at 40°C.

2.4 pH and Soluble Solids (TSS) Content

The pH and soluble solids content of the juice were measured immediately after concentration process using a pH meter (Nel-890 Model, Ankara, Turkey) and a digital refractometer (PTR 46X, England) at 20°C, respectively. The refractometer was calibrated using distilled water. The soluble solids content was expressed

as °Brix. All measurements were done in triplicate and the average results reported.

2.5 Titratable Acidity

The titratable acidity of the concentrates was measured using a pH meter, where the juice was titrated against 0.1 N NaOH until the pH reached 8.2. The acidity was expressed as percentage of citric acid [10].

2.6 Determination of Total Phenolics

The total phenolic content was determined by the Folin-Ciocalteu method [11]. 100 µL of sample (diluted 1:5 (v:v) with methanol) was mixed with 6 ml of twice distilled water and 500 µL of Folin-Ciocalteu reagent was added. After waiting 5 minutes at room temperature, 1.5 mL of sodium carbonate (20% w/v) was added to adjust optimum pH for the reaction. The mixture was vortexed and incubated at room temperature (~23°C) for 2 h and absorbance was measured at 765 nm using a UV-VIS Lambda 25 spectrophotometer (Perkin Elmer, Shelton, USA). Gallic acid was used as a standard and, the content of total phenolics was expressed in mg gallic acid equivalents (GAE) per liter of concentrate. A mixture of water and reagents was used as a blank. All analyses were done in triplicate (n = 3).

2.7 Determination of Total Monomeric Anthocyanins

Total monomeric anthocyanin content was determined by pH-differential method described by Giusti and Wrolstad [12], using two buffer systems: potassium chloride buffer, pH 1.0 (0.025 M), and sodium acetate buffer, pH 4.5 (0.4 M). The concentrate samples were diluted in a ratio of 1:10 with twice distilled water. A 0.4 ml of diluted sample was mixed with 3.6 ml of corresponding buffers and allowed to equilibrate for 15 minutes at room temperature. The absorbance of each solution was measured at 510 nm (λ_{max}) and 700 nm, using UV-VIS Lambda 25 spectrophotometer (Perkin Elmer, Shelton, USA). Total monomeric anthocyanins were calculated as mg cyanidin-3-glucoside per liter concentrate according to the following equation:

$$\text{Total monomeric anthocyanins (mg/L)} = A \times MW \times DF \times 1000 / (\varepsilon \times l) \quad (1)$$

where $A = (A_{510} - A_{700})_{pH\ 1.0} - (A_{510} - A_{700})_{pH\ 4.5}$; MW (molecular weight) = 449.2 g/mol for cyanidin-3-glucoside; DF = dilution factor (10) as final volume per initial volume; 1 = path length in cm; ε = 26,900 molar extinction coefficient in L/mol/cm for cyanidin-3-glucoside; 1000 = conversion factor from g to mg. Absorbance readings were made against twice distilled water as blank.

2.8 Determination of Antioxidant Activity

DPPH assay was done according to the method of Brand-Williams et al. [13] with some modifications. The stock solution was prepared daily by dissolving 1.2 mg DPPH with 50 mL methanol. 100 µL of diluted sample in the ratio of 1:10 (v:v) with methanol was mixed with 3900 µl of $6x10^{-5}$ mol L^{-1} DPPH in methanol. The mixture was vortexed and left to stand for 30 min in dark place at room temperature. Then the absorbance was measured at 515 nm using UV-VIS Lambda 25 spectrophotometer (Perkin Elmer, Shelton, USA). The percent of reduction of DPPH was calculated by the formula reported by Tural and Koca [2]:

$$\%\ \text{DPPH reduction} = [(A_C - A_S)/A_C] \times 100 \quad (2)$$

where A_C = absorbance of a control (t = 0 min), A_S = absorbance of a tested sample at the end of the reaction (t = 30 min). Methanol was used as blank and control sample was prepared with the same volume of methanol mixed with DPPH stock solution. All assays were done in triplicate (n = 3).

2.9 Colour Measurements

Colour measurements were done using a HunterLab Colourflex (A-60-1010-615 Model Colourimeter, Hunter Associates Lab. Inc. Reston VA, USA). The instrument was standardized each time with a black and a white (L = 91.10, a = 1.12, b = 1.26) tile. The colour values were expressed as *L** (lightness), *a** (redness/greenness) and *b** (yellowness/ blueness). Total colour difference (*TCD**), chroma (*C**), and hue angle ($h^{*\circ}$) parameters were calculated and modeled. Colour values were the means of triplicate measurements.

2.10 Degradation Studies

Thermal degradation of cornelian cherry concentrate was studied in 43.52 °Brix

concentrate at 60, 70 and 80°C. Aliquots of 10 mL of samples were put into screw-cap test tubes to prevent evaporation and test tubes were placed into oven preheated to a given temperature. At regular time intervals (0, 2, 4, 6, 8, and 10 h), samples were removed from the oven (NÜVE EN500, Ankara, Turkey) and rapidly cooled by plunging into an ice bath to stop further degradation. Contents of total anthocyanins and colour values of the samples were measured immediately.

2.11 Degradation Kinetics of Anthocyanins

Previous studies showed that thermal degradation of anthocyanins followed a first-order reaction [4,14-16]. This kinetic type was expressed by the following equation:

$$C = C_o * \exp\ (\pm k_1 * t) \quad (3)$$

where C_o is the initial anthocyanin contents and C is the anthocyanin contents after time t (min) of heating at the given temperature while k_1 is the first order rate constant. The parameters of first order kinetic model (Eq. (3)) were estimated (Sigma Plot 10.0 Windows version, SPSS Inc.).

Half-lifes ($t_{1/2}$) which is the time needed for 50% degradation was calculated by the following equation:

$$t_{1/2} = -ln0.5/k_1 \quad (4)$$

where $t_{1/2}$ is the half-lifes and, k_1 is the first order degradation rate constant (h^{-1}).

The effect of temperature on the degradation rate constants was expressed by the linearized Arrhenius equation by plotting ln k against 1/T in which the temperature dependence of k was quantified by the activation energy E_a according to Eq. (5).

$$\ln k = lnA_o - \frac{E_a}{RT} \quad (5)$$

where k is the rate constant (min^{-1}), A_o is the frequency factor (min^{-1}), E_a is the activation energy (kJ/mol), R is the universal gas constant (8.314 J/mol/ K), T is the absolute temperature (Kelvin, K). The E_a value was calculated from the slope of the straight lines given by Eq. (5), using Sigma Plot (Sigma Plot 10.0 Windows version, SPSS Inc.).

2.12 Kinetics Model of Visual Colour

The complexity of fruit juices and derivatives implies a wide range of enzymatic and non-enzymatic browning reactions caused by thermal treatments. Consequently it is difficult to establish a reaction mechanism and to obtain a kinetic model describing the global process adequately [17]. There are numerous references on the kinetics of colour of food materials in the literature. The majority of these works report zero-order (Eq. (6)) or first-order (Eq. (3)) degradation reaction kinetics.

$$C = C_0 \pm k_o * t \quad (6)$$

Sometimes the relatively simple models described do not adequately represent colour change mechanism. That is why a combined kinetics has been developed, in which the non-enzymatic colour change reactions are considered to consist of two stages. A first stage of coloured polymeric compound formation following zero order kinetics, second stage supposes decomposition of coloured polymers into non-coloured compounds following a first order kinetics. According to this combined kinetics, the colour change mechanism can be expressed by [17,18]:

$$C = \frac{k_0}{k_1} - \left[\frac{k_o}{k_1} - C_0\right] exp(\pm k_1 * t) \quad (7)$$

The terms C and C_0 are the concentrations of colour parameters at any time t and initial concentration, respectively; k_0 is the zero-order kinetics constant, k_1 is the first-order kinetics constant in Eqs. (3), (6), (7).

Total colour difference (TCD^*), chroma (C^*), and hue angle ($h^{*\circ}$) parameters were calculated by using L^*, a^*, b^* values (Eqs. (8)- (10)) [19]:

$$TCD^* = \sqrt{(L_0^* - L^*)^2 + (a_0^* - a^*)^2 + (b_0^* - b^*)^2} \quad (8)$$

$$C^* = \sqrt{a^{*2} + b^{*2}} \quad (9)$$

$$h * ^\circ = \arctan\ (b^*/a^*) \quad (10)$$

where, L_0^* (0.98), a_0^* (4.17) and b_0^* (0.78) refer to initial values, and L^*, a^* and b^* refer to colour values at various times during heat treatment.

2.13 Statistical Analysis

Experimental data were subjected to two way ANOVA and the means were compared by Duncan's multiple range test at $P < 0.05$ significance level using SPSS version 17 (SPSS Inc., Chicago, IL, USA). The parameters of kinetic models and Arrhenius equation were estimated by either linear regression procedure or non-linear regression iterative procedure (Sigma Plot 10.0 Windows version, SPSS Inc.).

3. RESULTS AND DISCUSSION

3.1 Physical and Chemical Characteristics of Concentrate

Table 1 shows some properties of concentrate. Titratable acidity as percent citric acid and pH of cornelian cherry concentrate was determined as 1.49% and 2.90, respectively and, these results were relevant with previous findings [2,20,21].

Total monomeric anthocyanin, total phenolic matter and total antioxidant activity of cornelian cherry concentrate determined as 207 mg/L, 0.0218 GAE/L and, 96% inhibition, respectively. As compared to the studies of Tural and Koca [2] on physico-chemical and antioxidant properties of cornelian cherry fruits grown in Turkey, content of total phenolics was relevant with their studies but, total monomeric anthocyanin content and total antioxidant activity values were higher than their findings.

3.2 Degradation Kinetics of Total Monomeric Anthocyanins

Degradation of anthocyanins during heating was plotted as a function of time (Fig. 1). Decrease in anthocyanin content was 63.77%, 71.50% and 89.37% for heating at 60, 70, 80°C, respectively, at the end of 600 min. It is clear from Fig. 1 that the thermal degradation of cornelian cherry anthocyanins followed first order reaction kinetics with respect to temperature. The extent of anthocyanin degradation was significantly higher ($P < 0.05$) (Table 2) at higher temperatures [22] and, degradation showed faster decreasing trend for the first two hours and rather slower decreasing trend during the course of treatment time (Fig. 1). That is, as anthocyanin concentration decreased the degradation rate also decreased. These results show that the rate of the degradation is directly proportional to the concentration of pigment, agree with those of previous studies [4,14-16,23,24].

Table 1. Characteristics of cornelian cherry concentrate

	Concentrate
pH	2.90
Total soluble solids (°Brix)	43.52
Titratable acidity (% citric acid)	1.49
Total monomeric anthocyanins (mg/L)	207
Total phenolics (GAE)	0.0218
Total antioxidant activity (% inhibition)	96
Colour	
*L**	0.98
*a**	4.17
*b**	0.78

The kinetic parameters of anthocyanin degradation during heating were given in Table 3. The k_1 values for anthocyanin degradation were 0.002, 0.027 and 0.054 min^{-1} in cornelian

Table 2. Results of analysis of variance

	Source	Sum of squares	df	Mean square	F	Sig.
Anthocyanin content	Time	15859.722	2	7929.861	117.190	0.000
	Temperature	116603.889	5	23320.778	344.642	0.000
*a**	Time	3.112	2	1.556	48.756	0.000
	Temperature	36.343	7	5.192	162.668	0.000
*b**	Time	0.024	2	0.012	2.933	0.072
	Temperature	0.950	7	0.136	33.141	0.000
*L**	Time	0.099	2	0.050	5.572	0.010
	Temperature	1.175	7	0.168	18.899	0.000
*C**	Time	2.822	2	1.411	39.970	0.000
	Temperature	36.132	7	5.162	146.197	0.000
h°	Time	0.131	7	0.019	23.128	0.000
	Temperature	0.073	2	0.037	45.419	0.000
*TCD**	Time	3.184	2	1.592	52.226	0.000
	Temperature	38.321	7	5.474	179.598	0.000

cherry concentrate at 60, 70 and 80°C, respectively. As temperature increased k_1 values increased (Table 3) and the degradation rate was dependent on temperature, being faster at high temperatures. It can be concluded that anthocyanin degradation was greatly dependent on temperature as indicated by higher k_1 values at higher temperatures [22].

Since no kinetic data have been found in the literature on the thermal degradation of cornelian cherry anthocyanins, we compared the thermal stability of cornelian cherry anthocyanins with other anthocyanin sources. Table 3 also shows that the $t_{1/2}$ values for anthocyanin degradation were 5.7, 4.3 and 2.1 h in cornelian cherry concentrate at 60, 70 and 80°C, respectively. As temperature increased $t_{1/2}$ values decreased in consistent with faster reaction rates accompanied by higher k_1 values. Wang and Xu [4] reported that the $t_{1/2}$ values for anthocyanin degradation were 16.7, 8.8 and 4.7 h in blackberry juice (8.90° Brix) at 60, 70 and 80°C, respectively. Cemeroğlu et al. [23] reported that the $t_{1/2}$ values for anthocyanin degradation were 24.0, 10.9 and 4.4 h in sour cherry concentrate (45° Brix) at 60, 70 and 80°C, respectively. Compared to both the blackberry juice anthocyanins and sour cherry concentrate anthocyanins, cornelian cherry concentrate (43.52 °Brix) anthocyanins were more susceptible to high temperatures. These results clearly indicate that anthocyanins from cornelian cherry concentrate are the least heat-stable, followed by those from blackberry juice and sour cherry concentrate. In literature different anthocyanin composition was also reported for *Cornus mas* [1,3]. Cornelian cherry has different anthocyanin composition than blackberry [4], sour cherry [4], and blood carrot [15] anthocyanin. In this respect as reported by Wang and Xu [4] and Yang et al. [25] different susceptibilities of fruit juice anthocyanins to heat might be due to their varying anthocyanidin composition.

To determine the effect of temperature on the parameters studied, the constants obtained from Eq. (3) were fitted to Arrhenius equation Eq. (5) at 60, 70 and 80°C (Fig. 2). The calculated activation energy E_a was 48.38 kj/mol (Table 3). This value is lower when compared the results of other studies [4,22,23]. A low activation energy signified a higher rate of reaction for anthocyanins whereas a higher activation energy indicated a retarded rate of degradation [26]. These results were consistent with $t_{1/2}$ values since cornelian cherry had the least $t_{1/2}$ values at each case. The difference in activation energy values could be due to different soluble solid contents [23] and compositional change in samples being treated [16].

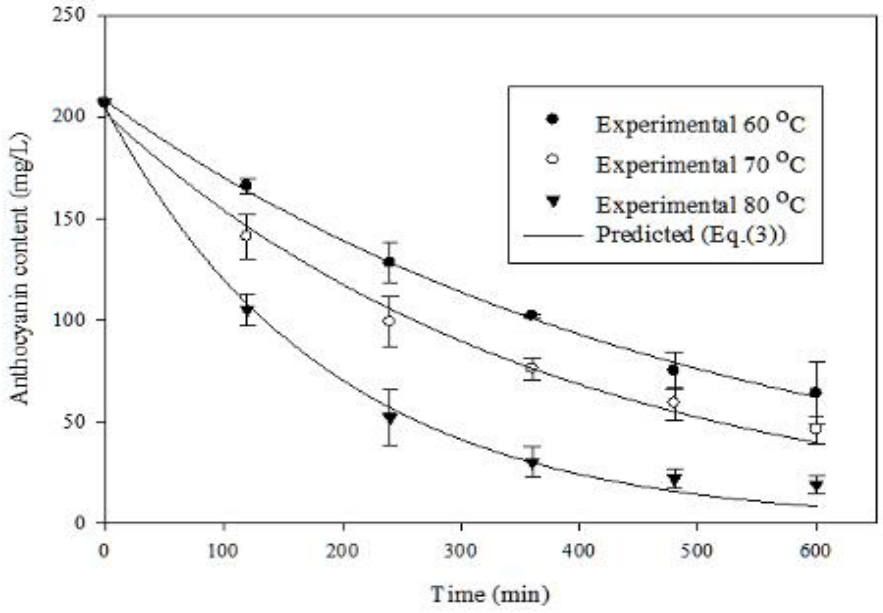

Fig. 1. Degradation of anthocyanins in cornelian cherry concentrates during heating at 60, 70 and 80°C

Table 3. Effect of temperature on k, $t_{1/2}$ and E_a values of anthocyanins degradation in cornelian cherry concentrate (43.52° Brix)

Concentrate type	Temperature (°C)	k_1[a] x 10^3 (min^{-1})	$t_{1/2}$ (h[b])	E_a (kJ/mol)[c]
Cornelian cherry	60	2.0 (0,9980)[d]	5.7	48.38 (0,9428)[d]
	70	2.7 (0,9920)	4.3	
	80	5.4 (0,9929)	2.1	

[a]*Rate constant,* [b]*Half-life,* [c]*Activation energy,* [d]*Numbers in parentheses are the determination coefficients*

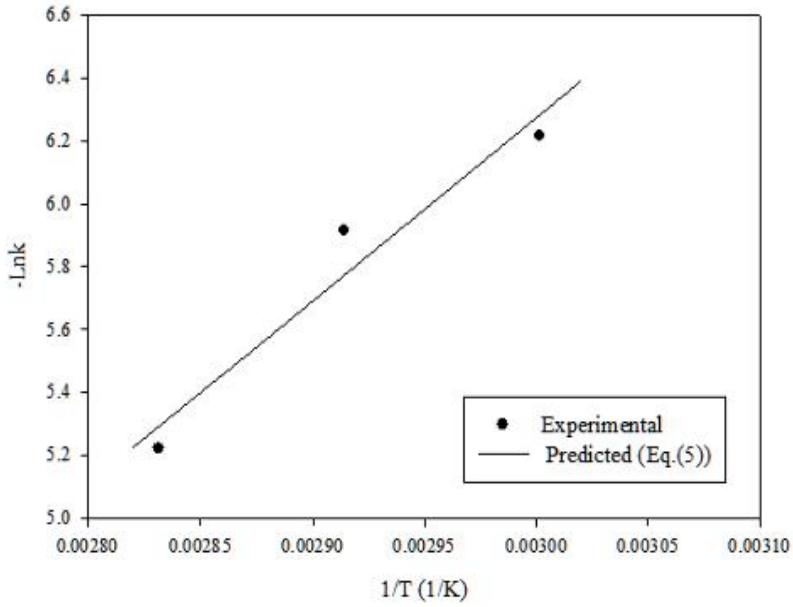

Fig. 2. The Arrhenius plot for degradation of anthocyanins in cornelian cherry concentrate during heating

3.3 Change in Visual Colour

Colour of cornelian cherry concentrate during the thermal treatment was characterized in terms of L^*, a^* and b^* values. It was observed that a^*, b^* and L^* values decreased during heating processes at 60, 70, 80°C (Fig. 3). Decrease in a^* value was 57.5%, 61.6% and 71.0% for heating at 60, 70, 80°C, respectively. Decrease in b^* value was 29.4%, 39.4% and 45.4% for heating at 60, 70, 80°C, respectively. Decrease in b^* value during heating process was reported by other authors in pineapple puree [27] and, double concentrated tomato paste [28]. Decrease in L^* value was 26.5%, 30.6% and 35.3% for heating at 60, 70, 80°C, respectively. The L^* value decreased significantly ($P < 0.05$) with time and treatment temperature. Reduction in b^* and L^* were not very severe as compared to a^* value. Decrease in L^* during heating process was found by other authors [27,28]. Decrease of Hunter L^* and a^* values was expressed due to fading of the red colour as heat destroyed anthocyanin pigments which are unstable in fruit juices and polymerization of anthocyanins with other phenolics [29].

3.4 Degradation Kinetics of Visual Colour

Total colour difference (TCD^*), lightness (L^*), chroma (C^*), and hue angle ($h^{*\circ}$) parameters were used and modeled since the most common L^* a^* b^* coordinates do not express hue and chroma directly and difficult to interpret independently [19,30]. Therefore, TCD^*, C^* and $h^{*\circ}$ parameters were calculated by using L^*, a^*, b^* values (Eqs. (8)-(10)) and experimental data for change in parameters L^*, C^*, $h^{*\circ}$ and TCD^* were fitted to zero-order (Eq. (6)), first-order (Eq. (3)) and combined kinetic model (Eq. (7)) and the best fit was selected as model due to the highest determination coefficients.

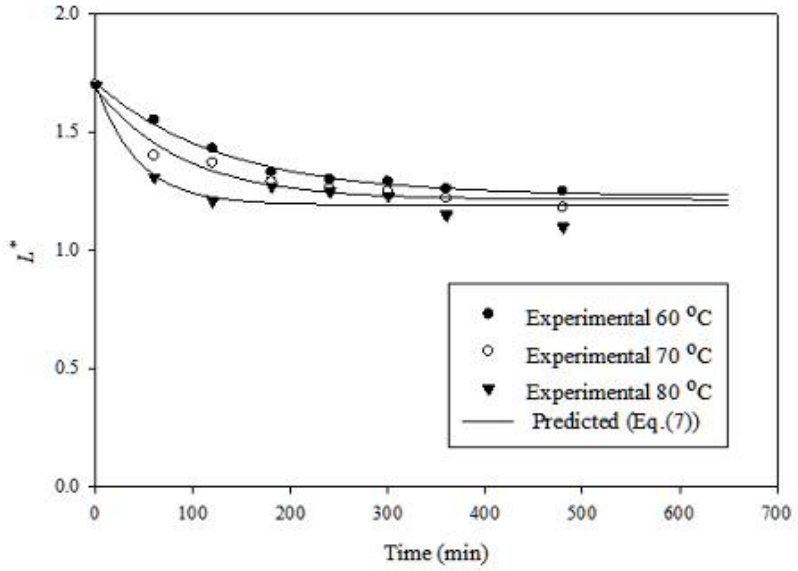

Fig. 3. Variation of lightness (L^*) value of cornelian cherry concentrate during heating at 60, 70 and 80°C

Since L^* is a measure of colour on the light-dark axis, decrease in L^* value indicates that the samples were turning darker. In this study, the combined kinetic described the experimental data of L^* better than zero and first order kinetics models due to having highest determination coefficients (R^2) (Table 4). Variation of L^* value of cornelian cherry concentrate fitted to combined model during heating at 60, 70 and 80°C is given in Fig. 3. In each temperature, k_o values was found higher than k_1, that is the rate of colour formation based upon Maillard reactions is higher than the rate of colour destruction based upon pigment destruction for L^* value (Table 4). It was reported that when the ratio of kinetic constants k_o (colour appearance) and k_1 (pigment destruction) is greater than unity, Maillard reaction predominates over pigment destruction [31]. In this respect, decrease in L^* due to heat treatment at 60, 70, 80°C gave the best fit with combined kinetic model and, predominantly caused by Maillard reaction resulting in darkening of colour and this darkening will fasten as temperature increased. In literature, change in lightness has been fitted first order kinetics for pineapple puree [27]; apple pulp, peach pulp and plum pulp [32]; pear puree [17] and peach puree [18]. However, Barreiro et al. [28] have been reported that most of the quality-related reaction rates are either zero or first order reactions and the statistical difference between the two types may be small. Similar result was reported by Lozano and Ibarz [32].

The chroma (C^*) is a measure of chromaticity, which denotes the purity or saturation of the colour [33]. C^* was calculated from Eq (9). Fig. 4 represents the variation of C^* value of cornelian cherry concentrate during heating at 60, 70 and 80°C. Decrease in C^* value was 55.4%, 59.9% and 68.1% for heating at 60, 70, 80°C, respectively. The C^* value decreased significantly ($P < 0.05$) (Table 2) with time and treatment temperature. That is, stability of red colour of cornelian cherry concentrate decreased as increasing treatment time and temperature. Experimental data of C^* was described by combined model better than zero and first order kinetics models due to having highest determination coefficients (R^2) (Table 4). The kinetic parameters of combined model were given in Table 4. The highest values were observed at 60°C. In each temperature, k_o values found nearly two times higher than k_1, that is Maillard reaction predominates over pigment destruction [31] even though, model fits were revealed that change in C^* can not be explained as simple as one step zero or first order kinetics due to poor determination coefficients, 0.4272-0.7301; 0.5081-0.7965, respectively. Reyes and Cisneros-Zevallos [34] have been reported that the decrease in chroma values would be related to the degradation of anthocyanins. Wrolstad et al. [30] reported that a confoulding phenomena regarding chroma is that it will increase with pigment concentration to a maximum, and then decrease as the colour darkens. At course of

heat treatment, degradation of anthocyanins was 63.77%, 71.50% and 89.37% for heating at 60, 70, 80°C, respectively. However, no statistically significant ($P > 0.05$) correlation between C^* and anthocyanin degradation at 60°C can be caused by the defined phenomena due to the highest residual pigment concentration as compared to those at 70 and 80°C. In the same manner, undefinite trend of kinetic constants can also be caused by the same phenomena.

Hue angle ($h^{*\circ}$) describes what the average person thinks of in speaking of colour (i.e., green, red, yellow, etc.) [32]. $h^{*\circ}$ is expressed in degrees, with 0^o corresponding +a* axis (red), then continuing to 90^o for the +b* axis (yellow), 180° for –a* (green) and finally 270° for –b* (blue) [19]. $h^{*\circ}$ was calculated from Eq. (10) and The variation of $h^{*\circ}$ value of cornelian cherry concentrate during heating at 60, 70 and 80°C (Fig. 5). Increase in $h^{*\circ}$ value was 64.0%, 60.0% and 76.0% for heating at 60, 70, 80°C, respectively. Ignoring the poor fit of 70°C, it was seen that $h^{*\circ}$ value increased significantly ($P < 0.05$) (Table 2) with increasing time and treatment temperature (shifting towards 90°). Parameters of combined kinetic model for lightness*, chroma*, hue* and *TCD** values were given in Table 4. In each temperature, the rate of colour formation is lower than the rate of colour destruction based upon pigment destruction with lower k_o values than k_1. Increase in $h^{*\circ}$ value can be associated to the formation of yellow chalcone species [34]. Yang et al. [25] reported that change in a^* and $h^{*\circ}$ values would be related to the degradation of redness and anthocyanins. They reported that in most degradation studies, increase in $h^{*\circ}$ is used as an indicator for the degradation of anthocyanins. However, in this study there was no statistically significant correlation between anthocyanin degradation and $h^{*\circ}$ value for temperatures of 60, 70 and 80°C ($P > 0.05$).

*TCD** is a colorimetric parameter used to characterize the variation of colour in foods calculated by Eq. (8). [18]. Fig. 6 shows the variation of *TCD** value of cornelian cherry concentrate during heating at 60, 70 and 80°C. *TCD** value at the end of heat treatment was 2.68, 2.90 and 3.31 for heating at 60, 70, 80°C, respectively. The *TCD** value increased significantly ($P < 0.05$) (Table 2) with time and treatment temperature. Combined kinetic described the data of *TCD** better than zero and first order kinetics models (Table 4). In each temperature, since the ratio of kinetic constants k_o and k_1 is greater than unity, Maillard reaction predominates over pigment destruction [31]. The same order of reaction was found by other researchers [17,18,31].

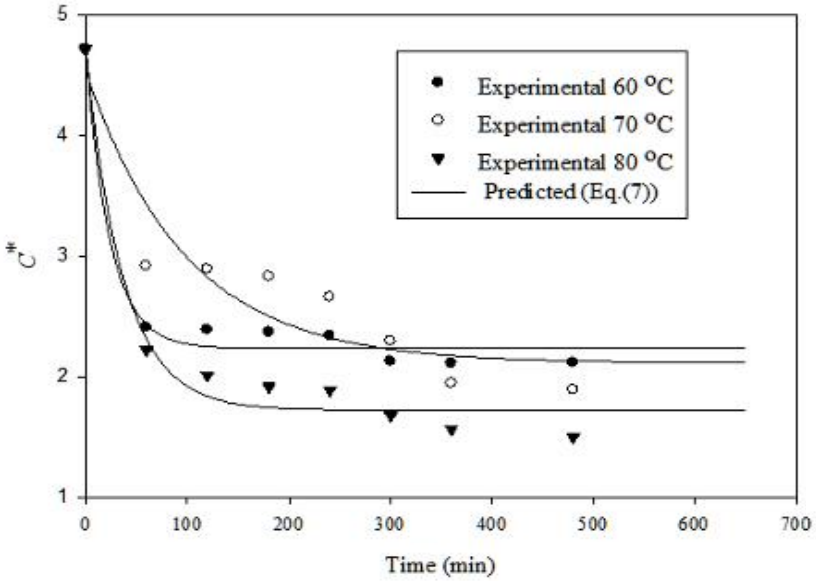

Fig. 4. Variation of chroma (C^*) value of cornelian cherry concentrate during heating at 60, 70 and 80°C

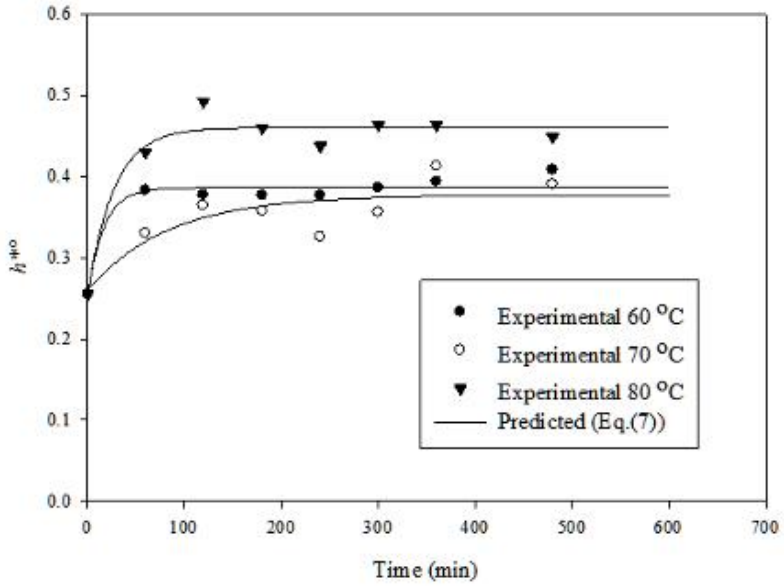

Fig. 5. Variation of hue angle (h^*°) value of cornelian cherry concentrate during heating at 60, 70 and 80°C

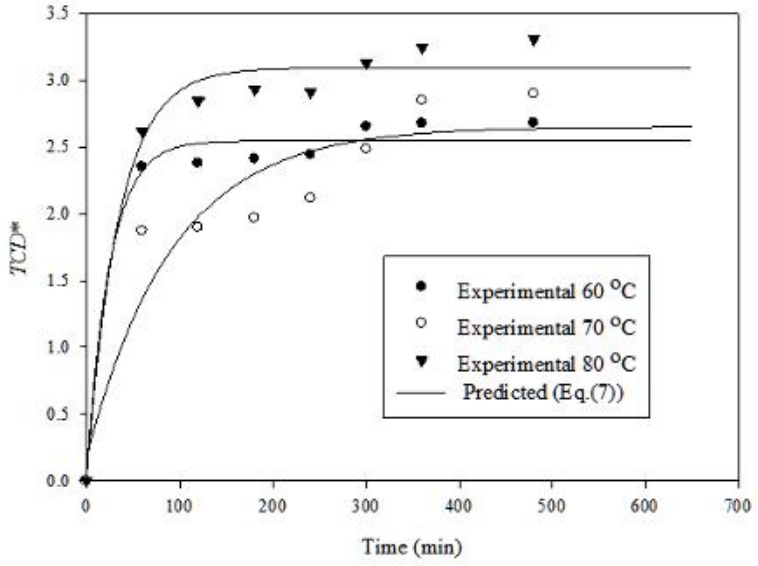

Fig. 6. Change in total colour difference (*TCD) value of cornelian cherry concentrate during heating at 60, 70 and 80°C**

Table 4. Kinetics parameters of combined model (Eq. (7)) for lightness (*L), chroma (*C**), hue angle (h^*°) and total color difference (*TCD**) values**

Colour parameter	Temperature (°C)	$C_o \pm SE$	$k_o \pm SE$	$k_1 \pm SE$	R^2
*L**	60	1.7078±0.0142	0.0094±0.0010	0.0076±0.0007	0.9939
	70	1.6841±0.0348	0.0136±0030	0.0112±0023	0.9666
	80	1.6980±0.0631	0.0276±0.0109	0.0231±0.0088	0.9151

Colour parameter	Temperature (°C)	$C_o \pm SE$	$k_o \pm SE$	$k_1 \pm SE$	R^2
C^*	60	4.7141±0.1328	0.0941±0.0282	0.0421±0.0122	0.9836
	70	4.5349±0.3445	0.0215±0.0109	0.0102±0.0042	0.8857
	80	4.7050±0.1843	0.0465±0.0108	0.0270±0.0056	0.9779
$h^{*\check{}}$	60	0.2551±0.0126	0.0228±0.0230	0.0589±0.0598	0.9493
	70	0.2602±0.0287	0.0045±0.0029	0.0120±0.0081	0.7290
	80	0.2547±0.0197	0.0169±0.0071	0.0367±0.0157	0.9490
TCD^*	60	0.0014±0.1397	0.1027±0.0275	0.0403±0.0111	0.9828
	70	0.1738±0.3564	0.0288±0.0098	0.0109±0.0044	0.8849
	80	0.0068±0.1744	0.0893±0.0168	0.0289±0.0057	0.9815

SE: Standard error of estimation, R^2: determination coefficient

4. CONCLUSION

Cornelian cherry fruits are important source of phenolic compounds such as anthocyanins and, are also good source of natural antioxidants. Anthocyanin degradation followed first order reaction kinetics, while changes in L^*, C^*, $h^{*\circ}$ and TCD^* followed combined kinetic model. The degradation rate increased as temperature increased. Determination of the thermal degradation kinetics of anthocyanins and colour values is essential to predict the quality changes that occur during thermal processing.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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