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Kinetic Modelling of Polyphenol Oxidase Activity and Phenolic Compound Changes in Thermosonicated Strawberry Nectar During Storage

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ABSTRACT

In this study, some quality changes in the optimally thermosonicated (59°C-455 J g^{-1}) cloudy strawberry nectar during storage were evaluated and modelled. The changes of pH (3.40-3.78), residual polyphenol oxidase-(PPO) activity (24%-11%), total phenolic-(TP) content (688.7-543.2 mg L^{-1}), total monomeric anthocyanin-(TMA) content (142.5-84.4 mg L^{-1}), anthocyanin, and colorless phenolic compounds were analyzed during three months of storage at 4°C. The significant decrease (54%) which was observed in residual PPO activity can be related with the decrease in phenolic content of nectar. A high correlation was determined between the changes in pH and TP of nectar (R^2=0.983). While TMA content and anthocyanin compounds (pelargonidin-3-*O*-glucoside, pelargonidin-3-*O*-rutinoside, cyanidin-3-glucoside) were decreasing, chlorogenic acid, *p*-coumaric acid, ellagic acid, kaempferol, quercetin, (±)-catechin and (-)-epicatechin were increasing between the days 30 and 60. Pelargonidin-3-*O*-glucoside was decreased 36% at the end of storage (k=6.09x10^{-5} L (mg day)$^{-1}$). It was determined that the increase in PPO activity (R^2=0.986), degradations of TP (R^2=0.902), TMA (R^2=0.968), pelargonidin-3-glucoside (R^2=0.858), pelargonidin-3-rutinoside (R^2=0.965), and (-)-epicatechin gallate (R^2=0.871) were best fitted to second-order kinetic model. The half-time of TP content was 303 days, while the half of TMA content was degrading in 99 days.

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Termosonikasyon Uygulanan Çilek Nektarının Depolama Boyunca Polifenol Oksidaz Aktivitesi ve Fenolik Madde İçeriğindeki Değişimlerin Kinetik Modellenmesi

ÖZET

Bu çalışmada, optimum koşullarda (59°C-455 J g^{-1}) termosonikasyon uygulanan bulanık çilek nektarında depolama süresince meydana gelen bazı kalite değişimleri değerlendirilmiş ve modellenmiştir. pH (3.40-3.78), kalıntı polifenol oksidaz-(PFO) aktivitesi (24%-11%), toplam fenolik-(TF) (688.7-543.2 mg L^{-1}), toplam monomerik antosiyanin-(TMA) içeriği (142.5-84.4 mg L^{-1}), antosiyanin ve renksiz fenolik bileşik içeriklerindeki değişimler, 4°C'de üç ay depolama süresince belirlenmiştir. Depolama ile kalıntı PFO aktivitesinde gözlenen önemli düzeydeki azalma (%54), nektarın fenolik içeriğindeki azalma ile ilişkilendirilebilir. Nektarın pH ve TP değerlerindeki değişimler arasında yüksek korelasyon olduğu tespit edilmiştir (R^2=0.983). TMA içeriği ve antosiyanin bileşik içerikleri (pelargonidin-3-O-glukozit, pelargonidin-3-*O*-rutinosit, siyanidin-3-glukozit) azalırken, klorojenik asit, *p*-kumarik asit, elajik asit, kaempferol, kuersetin, (±)-kateşin, (-)-epikateşin içerikleri 30 ve 60. günler arasında artış göstermiştir. Pelargonidin-3-*O*-glucoside depolama sonunda %36 azalmıştır (k=6.09x10^{-5} L (mg gün)$^{-1}$). PFO aktivitesi (R^2=0.986), TP (R^2=0.902), TMA (R^2=0.968), pelargonidin-3-glukozit (R^2=0.858), pelargonidin-3-rutinozit (R^2=0.965) ve (-)-epikateşin gallat (R^2=0.871) parçalanmalarının ikinci dereceden

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kinetik model ile en yüksek uyum gösterdiği belirlenmiştir. TMA içeriğinin yarısı 99 günde parçalanıyorken, TF içeriğinin yarılanma süresi 303 gündür.

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INTRODUCTION

Strawberries (*Fragaria* x *ananassa*) contain significant amount of micronutrients related to human health like phenolic compounds. There is an increase in evidence of the positive effects of phenolic phytochemicals against cardiovascular diseases, some cancer types and neurodegenerative diseases (Giampieri, 2012). Not only colorful phenolic compounds of fruits, but also colorless ones, particularly phenolic acids and flavonoids are responsible for these health benefits. The antioxidant activity of strawberry is mainly derived from phenolic compounds, while ascorbic acid is responsible only about 10% of that activity in strawberry (Sun et al., 2002). Besides bioactive components, another reason for choosing the strawberry juice or nectar is their attractive and bright red color. Phenolic content and color of the cloudy strawberry nectar may be affected at the stages of processing and storage.

During processing stage, it was indicated that conventional thermal processing has adverse effect on bioactive properties of juices including strawberry juice (Patras et al., 2010). Ultrasound is one of the non-thermal techniques which are preferred to eliminate or reduce the negative effects of thermal treatment. It consists of sound waves with high frequency (>16 kHz). Thermosonication, the combination of thermal treatment and ultrasound, is reported as a good alternative to thermal pasteurization of strawberry juice, and can improve the polyphenol retention of juice compared to the thermal pasteurization (Lafarga et al., 2019). Thermosonication is applicable treatment in order to obtain polyphenol oxidase (PPO) inactivation in cloudy strawberry juice, while important quality parameters of nectar can be remaining similar to the non-processed one. It was shown that optimized conditions of thermosonication by response surface methodology could improve the retention of some bioactive compounds of juice (Dündar et al., 2019; Lafarga et al., 2019). Regarding the PPO inactivation and changes in color and some bioactive components (ascorbic acid, total phenolic, monomeric anthocyanin), Dündar et al. (2019) were determined the optimum thermosonication parameters as 59°C and 455 J g^{-1}, earlier. Thereby, the negative effect of processing period was minimized with the aid of the optimization study. However, there is not a wide knowledge about the degradation of colorless phenolic compounds. The need to reveal the degradation kinetics of bioactive components is important.

In this research, the cloudy nectar produced from strawberry puree (to obtain higher bioactive content) and optimally thermosonicated (to minimize the negative effect of processing) was stored at 4°C which is a better condition to ensure higher stability of polyphenols during three months. The changes in pH, PPO activity, total phenolic content, total monomeric anthocyanin content, anthocyanin and colorless phenolic compounds were revealed during storage. Also, the degradation kinetic outputs of TP, TMA, pelargonidin-3-glucoside-(plg-3-glc), pelargonidin-3-*O*-rutinoside (plg-3-*O*-rut), (-)-epicatechin gallate in strawberry nectar were determined.

MATERIAL and METHOD

Strawberries (*Fragaria* x *ananassa* Duch.) cv. Rubygem which are farmed by Cukurova University Agricultural Faculty (Adana, Turkey) were harvested at the same stage of maturity to produce nectar. Strawberry nectar (50% fruit puree, 0.5 g L^{-1} titrable acidity and 10°Brix at 25°C) processed with the same method which was used earlier in optimization study to eliminate the differences based on material. The thermosonication parameters combination of 59°C and 455 J g^{-1} was used. The thermosonication treatment was carried out with laboratory-scale ultrasonic device (S14-sonotrode-UP200S-Hielscher/Germany), a temperature controller, a digital power-meter and digital timer at a constant temperature&time to apply optimum processing. The nectar was placed in double-walled glass beaker with a cooling/heating system during thermosonication. The average ultrasound power was measured as 150 W during processing. Temperature was controlled by a water-circulator, and the treated nectar was cooled to room temperature immediately. In total, 5 L nectar was mixed to eliminate the difference from the material, before filling the glass bottles.

Ultrasound energy density parameter (UED, J g^{-1}) and its relationship with ultrasonic power (P, W), treatment time (t, s) and sample amount (m, g) were explained with following equation (Eq. 1);

$$UED = \frac{P.t}{m} \quad (1)$$

Analyses

All the chemical analyses were performed at the 0, 10, 20, 30, 60 and 90th day of storage (4°C) and repeated at least three times.

pH

The pH measurements of strawberries were carried out using Mettler Toledo pH-meter at 25°C.

PPO activity

The strawberry nectar (10 g) mixed with 20 mL sodium phosphate buffer (pH 7.0), 4%PVPP, 1%triton X-100 and 50 µL 1 M NaCl to determine residual PPO activity. The mixture was centrifuged (30 min-6000 rpm-4°C) and supernatant (100 µL) was added to catechol solution (with 0.07 M phosphate buffer (pH 5.8)) while blank was catechol solution with 100 µL diluted water. The absorbance values recorded per minute during 15 min at 420 nm (Sulaiman et al., 2015). The plot of time-absorbance graph which was calculated from linear portion of curve was used for determining the activity. Following Eq. 2 was used to determine the percent residual activity of PPO:

$$Residual\ PPO\ activity\ (\%) = \frac{A_t}{A_0}\ x\ 100 \quad (2)$$

where A_t and A_0 symbolize the slope values of the thermosonicated and non-thermosonicated nectars, respectively.

Total Phenolic Content

The phenolic contents were determined by using the Folin-Ciocalteu with some modifications (Abdullakasim et al., 2009). Strawberry nectar (5 mL) and 80% methanol were mixed and centrifuged in a tube at 6000 rpm for 10 min at 4°C (Heraeus Bofuge Primo R, Germany). The 100 µL Folin-Ciocalteu reagent and 3000 µL deionized water were added to appropriately diluted 100 µL sample/standard solution. Then, 20% Na_2CO_3 solution (100 µL) was added to mixture and incubated at room temperature for 2 h in the dark. Finally, absorbance measurements were conducted using Perkin Elmer Lambda 25-UV/VIS (Massachusetts/USA) spectrophotometer at 765 nm. Gallic acid was used as standard and TP contents were expressed in milligrams per L as gallic acid equivalents (mg GAE L^{-1}).

Total Monomeric Anthocyanin

TMA of strawberry nectar was determined by the pH differential method (Giusti and Wrolstad, 2001). 0.025 M potassium chloride (KCI, pH=1 (adjusted with HCI)) and 0.4 M sodium acetate ($CH_3COONa.3H_2O$, pH=4.5 (adjusted with HCl)) buffers were used in this analysis. Potassium chloride (4.5 mL) and sodium acetate buffer were added to two different tube separately. The supernatant (0.5 mL) which was collected for total phenolic content analysis was used. Measurements were performed with spectrophotometer at 520 nm and 700 nm.

TMA was expressed as cyanidin-3-glucoside in terms of mg L^{-1} by using following equations (Eqs.3-4).

$$A = ((A_{520} - A_{700})_{pH=1} - (A_{520} - A_{700})_{pH=4.5}) \quad (3)$$

$$Monomeric\ anthocyanin\ content\ \left({}^{mg}/_{kg}\right) = \frac{(A \cdot MW \cdot DF) * 1000}{(\varepsilon \cdot L)} \quad (4)$$

where A; difference between absorbances, MW; anthocyanin molecule weight (449.2), DF; Dilution factor, ε; Molar absorption coefficient (26900) and L; Light path of spectrophotometer cuvette (1 cm-length).

Phenolic Compounds

To determine phenolic compounds, strawberry nectar was mixed with 5 mL of 80% methanol in teflon tube and then the tubes were centrifuged at 6000 rpm for 10 min at 4 °C. The supernatant was filtered (PTFE, 0.25 µm filter) and then injected to the HPLC (Shimadzu LC-20AT, Japan) C18 XTerra column (Waters, 4.6×250 mm). Injection (20 µL) to column was conducted at 25°C and absorbance detected with Photo Diode Array detector at 280, 320 and 520 nm while mobile phase flow rate was 1 mL min^{-1} (gradient flow) (Ağçam et al., 2014).

Kinetic Modelling

The changing kinetics of PPO activity, total phenolic, total monomeric anthocyanin, pelargonidin-3-glucoside, pelargonidin-3-rutinoside contents of nectar were investigated. The obtained data during the 90 days of storage were used to determine the best fitted mathematical model (zero, first, half or second-order models) to the degradation kinetics by using Curve Fitting Toolbox, Matlab ver. 7.10 (MathWorks Inc./USA/2010). The intagrated forms of zero, first, half and second-order models were given in Eqs. (5)-(8), respectively.

$$X_t = X_0 + k_x t \quad (5)$$

$$2\sqrt{X_t} - \sqrt{X_0} = k_x t \quad (6)$$

$$ln\,{}^{X_t}/_{X_0} = -k_x t \quad (7)$$

$$\frac{1}{X_t} - \frac{1}{X_0} = k_x t \quad (8)$$

where k_X is the reaction rate constant, X_0 *and* X_t are the initial and after time of storage concentrations of phenolic compounds (mg L^{-1}), respectively, and t is the reaction time (days).

The goodness of model fitting to the experimental data was determined with the aid of correlation

coefficient-(R^2), adjusted coefficients of determination-(R^2_{adj}), confidence-intervals-(ConfI) and root-mean-square-error-(*RMSE*) values (Remini et al., 2015).

Statistical Analysis

The variance and Duncan's multiple tests of obtained values during storage were conducted with SPSS (PASW Statistic 18 for Windows, USA) packet program to determine significant differences ($P<0.05$) between mean values.

RESULTS and DISCUSSION

Change of pH

The pH value of nectar was between 3.40 and 3.78 during storage (Fig. 1.a.). It was determined that there was a significant decrease in pH values of nectar beginning from the 20th day ($P<0.05$). The decrease in pH can be related with the biochemical reactions, lactic and acetic acid bacteria activities. Moreover, condensation between amino acids and carbonyl groups of glucose may be the cause of the pH decrease (Carabasa-Giribet et al., 2000; Wang et al., 2006). The stability of pH during the first 20 days of storage can be the result of ultrasound inactivation effect on microorganisms (Muzaffar et al., 2016) or the lag-phase of microbial growth. pH value can affect the colorless phenolic compounds of strawberries (Oliveira et al., 2015), and lower pH (~2.5) may induce the higher ellagic acid content in the strawberry. So, the decreasing of pH can be considered as a desirable change to preserve polyphenols.

Change of Residual PPO Activity

The residual PPO activities of nectars stored at 4°C for 90 days were given in Fig. (1). The obtained results showed that the maximum PPO activity (24%) was observed at the beginning of the storage, while the minimum PPO activity (11%) was at the end of storage (decreased by 54%). Therefore, it can be seen that the optimum thermosonication ensured the PPO inactivation irreversibly. The residual PPO level can be affected by decreasing pH and polyphenol content (Fig. 1). Although the pH decrease was not too much in this study, the pH level of the medium may have a great impact on the PPO activity (Jiang, 1999).

The PPO activity in fruit juices results in the enzymatic browning, anthocyanin degradation and formation of unstable o-quinones. Further interactions between *o*-quinones and amino acids, protein or other compounds result in black-brownish color pigments, called as melanin (Ağçam et al., 2017). PPO is the most resistant one to heat among the enzymes which are found in strawberry puree mixed with sugar (Chakraborty et al., 2015). The decrease in the anthocyanin content is not only because of oxidative reactions, but also condensation reactions of monomeric anthocyanin with other phenolic compounds (Pacheco-palencia et al., 2007).

Change of TP Content

The obtained TP levels were changed between 688.7 mg L^{-1} and 543.2 mg L^{-1}. There was no significant difference in the first month of storage, but TP content of nectar decreased by 22% at the end ($P<0.05$) (Fig. 1.c.). Phenolic components can be found in a soluble form in the vacuole of cell or a bounded form with pectin, cellulose, hemicellulose, lignin traces (Bhat et al., 2011). It was known that ultrasound processing can help to destroy plant cell wall and membrane leading to enhance mass transfer of intracellular materials to the medium. Some earlier researches showed that ultrasonication can cause an increasing in TP content of juices (Bhat & Goh, 2017; Dündar et al., 2019). Besides, PPO which had higher activity at the beginning of storage might have destructive effect on polyphenols. These reverse effects on TP content may be tolerated each other, and it can be the reason of that the changes were not significant during first month. Ultrasonication may induce the hydroxyl radical formation in juice. The non-significant phenolic content increase in the earlier part of storage also can be related to the interaction between hydroxyl radical, and aromatic rings (Bhat et al., 2011). It is possible that after the 30th day, the releasing stopped, and PPO kept continue to degrade the phenolic compounds. Also, the occurring change in pH of nectar after the 30th day of storage may have affected the TP content indirectly, in relation with the level of PPO activity. Because, the changings of these two properties of nectar, pH and TP, with time were similar and the R^2 is 0.9833.

Change of TMA Content

The monomeric anthocyanin contents of nectars which were thermosonicated in optimum conditions, and stored at 4°C during three months were shown in Fig. 1.d.. TMA content of nectar was the highest (142.53 mg L^{-1}) at the beginning of storage, while it was the lowest (74.70 mg L^{-1}) at the end. There is no conflict between the TMA content of nectars and the total concentration of individual anthocyanin compounds. The storage time has a significant effect on the TMA content of cloudy strawberry nectar. Approximately half of the TMA degradation has occurred in the first 20 days, and the rest was lost at the end of the storage. The rate of decrease in TMA content was higher at the beginning of the storage period, and highly decreased after the 60th day of this period.

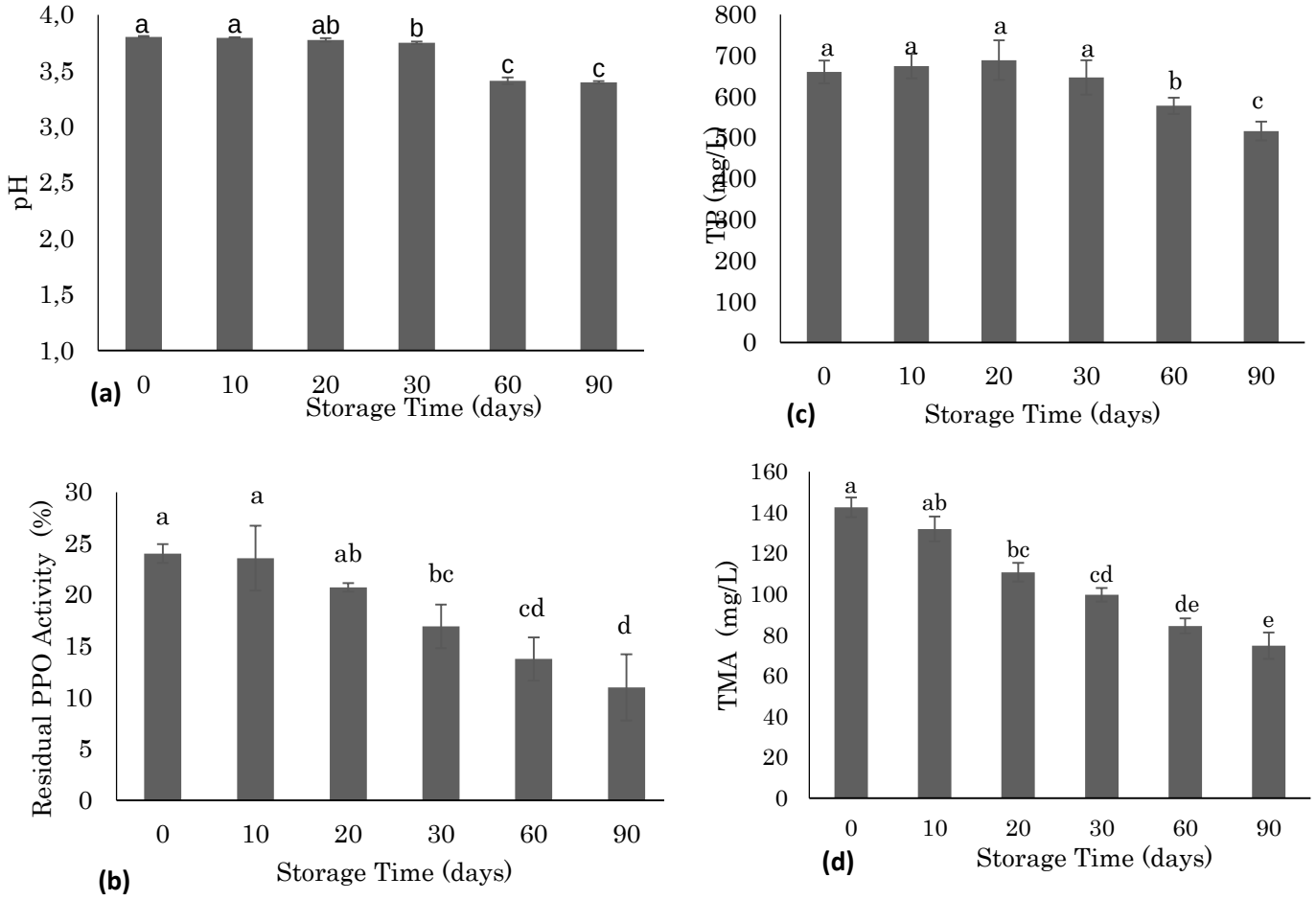

Figure 1. The pH (a), residual polyphenol oxidase (PPO) activity (b), total phenolic (TP) (c), and total monomeric anthocyanin (TMA) (d) contents of strawberry nectar during storage.

Şekil 1. Depolama boyunca çilek nektarlarının pH değeri (a), kalıntı polifenol oksidaz (PPO) aktivitesi (b), toplam fenolik (TP) (c) ve toplam monomerik antosiyanin (TMA) (d) içerikleri

[a-e] The difference between the groups with the different letter in the same line is significantly important ($P<0.05$).

Similar TMA results obtained at the pasteurized strawberry juice stored during 32 weeks at different temperatures (Buvé et al., 2018). The possible reasons of significant decrease in TMA can be enzymatic oxidation, non-enzymatic reactions or condensation reaction.

Change of Anthocyanin Compounds

The change in anthocyanin compounds of nectar was given in Table 1. Pelargonidin-3-O-glucoside, pelargonidin-3-*O*-rutinoside, cyanidin-3,5-diglucoside and cyanidin-3-glucoside were determined in strawberry nectars. The most predominant anthocyanin was pelargonidin-3-*O*-glucoside with the concentration of 92.37±4.88 mg L^{-1} at the 0^{th} day, while it decreased during storage till 59.14±1.48 mg L^{-1} at the end. The levels of other detected anthocyanin also decreased with the storage time. Four relatively major anthocyanin in the obtained chromatogram could not been identified due to lack of commercial standards, and their concentrations were calculated in terms of pelargonidin-3-glucoside as unknown. The unidentified phenolic compounds (U1-4) may be cyanidin-3-malonil, pelargonidin-3-malonilglucoside or pelargonidin-3-acetylglucoside. The results showed that the sum of anthocyanin compounds (~125 mg L^{-1}, day 0) and total monomeric anthocyanin content (~142 mg L^{-1}, day 0) are coherent. The difference between them could be resulted from the other non-identified minor anthocyanins. The stability of anthocyanins is affected by other components in the medium. However, there is not much details about the degradation steps of anthocyanins. Some different compounds can be formed during anthocyanin degradation like protocatechoic acid and its aldehyde form derived from the pelargonidin-3-glucoside (Abid et al., 2014). Enzymatic and non-enzymatic reactions can be the reasons of color changes with the pigment polymerization and browning (Wrolstad et al., 1990).

Change of Colorless Phenolic Compounds

Besides anthocyanins, some colorless phenolic compounds of strawberry nectar were determined (Suplementary files 2-3), in this study. Caffeic acid, chlorogenic acid, *p*-coumaric acid, kaempferol, (±)-catechin, protocatechuic acid ethyl ester (PAEE), ellagic acid, ferrulic acid, quercetin, (-)-epicatechin and (-)-epicatechin gallate contents of nectar were given in Table 1. The most predominant colorless phenolic, (-)-epicatechin gallate, concentration decreased approximately 60% during storage at 4°C from 136.93 mg L^{-1} to 81.89 mg L^{-1}. (±)-catechin and (-)-epicatechin contents followed that, respectively. Some colorless phenolics such as epicatechin gallate and caffeic acid decreased consistently, while the others did not show the same tendency during the three months of storage. Chlorogenic acid, *p*-coumaric acid, kaempferol, (±)-catechin, PAEE, ellagic acid, quercetin and (-)-epicatechin concentrations of nectar showed fluctuation during storage. There are no significant differences between the levels of ellagic acid and quercetin at the first day and last day of storage ($P>0.05$). The reason of the irregular changes in the levels of U1, U2 anthocyanins and some colorless phenolic can be the interactions between different phenolic compounds during storage. It was determined that changes in these anthocyanins and colorless phenolics were opposite. Thereby, it can be assumed that an interaction between them like pigmentation might be occurred. Generally, the addition of copigment to juice increases the color stability. On the other hand, it was reported that ferrulic and caffeic acids decreased color stability of the acylated anthocyanins during 200 days of storage (Eiro & Heinonen, 2002). These phenolic acids which are also found in strawberry might interfere with the acylated anthocyanins.

Kinetic Parameters

The changing kinetics of PPO activity, TP, TMA, plg-3-glc, plg-3-O-rut and (-)-epicatechin gallate contents were evaluated to determine the best fitted mathematical model (zero, first, half or second-order models). The kinetic parameters, rate constant (*k*) and half-time ($t_{1/2}$) as well as the R^2, adjusted-R^2 and *RMSE* of the models through a least square fitting procedure were given in Table 2. The content of each compound that was investigated, and the kinetic model with highest correlation coefficient is accepted to explain the order of changing. The half-lives of TP, TMA, plg-3-glc, plg-3-rut and (-)-epicatechin gallate were 303, 99, 164, 183 and 132 days, respectively. The half-lives showed that the most abundant anthocyanins can be more stable than the other anthocyanins found in strawberry ($t_{1/2}$ of TMA less than $t_{1/2}$ of Plg-3-glc and Plg-3-rt). When the half-lives of TP (303 days) and TMA (99 days) are considered, TF content was more stable than TMA. This can be caused from the stability of some colorless phenolic compounds. The degradation kinetics of phenolic compounds individually or in total were followed the second ordered-kinetic model with R^2 values between 0.8577 and 0.9677. Among the investigated kinetic properties of strawberry nectar, PPO activity changing with storage time showed the highest R^2 (0.9857, second-order) and reaction rate constant (5.693×10^{-4} L $(mg\ day)^{-1}$) with the half-life of 73 days. Although some researchers agreed that degradation kinetic of anthocyanin fit the first order kinetic model in different juices or fruits (Del Pozo-Insfran et al., 2004; Patras et al., 2010; Zheng et al., 2007), others stated that the degradation were best described with pseudo-first order (Oliveira et al., 2014) or second order kinetics (Özkan, 2002). The degradation during roasting Cocoa was best fitted to first-order kinetic model by Fernandez-Romero et al. (2020) and Loncaric et al. (2018) stated that catechin and epicatechin degradations were best fitted to the first order kinetic model in some different mediums during thermal treatments. Also, Wang and Xu (2007) stated that the degradation kinetic of anthocyanin content in blackberry juice followed first order reaction kinetic and the half-life was calculated as 330 days at 5°C. This differences between the results of this study and other studies in literature can be related with the differences between food matrices like pH, chemical structure, anthocyanin, enzyme, protein and metal ion concentration (Rein, 2005).

CONCLUSION

Thermosonication is reported as an alternative way to conventional thermal treatment. In this study, the effect of storage (three months-4°C) on pH, residual PPO activity, TP, TMA, anthocyanin / colorless phenolic compounds and the degradation kinetics of some compounds of optimally thermosonicated strawberry nectar were determined. PPO activity and TP content (after first month) decreased during storage ($P<0.05$). The TMA content and anthocyanin compounds were decreasing, while colorless phenolic compounds did not show regular changing tendencies. The degradation kinetics of TP, TMA, pelargonidin-3-glucoside and pelargonidin-3-*O*-rutinoside followed a second order model, while ascorbic acid degradation fit the first order model. The TP content was the most stable among the investigated quality parameters with the longest half-life of 303 days. At the beginning of storage, the changing of anthocyanin can be less effective on the TP content than the changing of colorless phenolic content. Besides, concentration of some colorless phenolic compounds were shown fluctuation during storage.

Table 1. Changes in phenolic compound content (mg L^{-1}) of strawberry nectar during storage (4°C)
Çizelge 1. Çilek nektarının depolama (4°C) boyunca fenolik bileşen içeriğindeki (mg L^{-1}) değişimler

		Days					
		0	10	20	30	60	90
Anthocyanins	Pelargonidin-3-*O*-glucoside	92.37±4.88^{a}	85.87±1.72^{b}	70.97±2.21^{c}	69.53±1.13^{c}	66.90±1.71^{c}	59.14±1.48^{d}
	Pelargonidin-3-*O*-rutinoside	20.53±0.48^{a}	19.68±0.38^{b}	17.22±0.13^{c}	17.13±0.08^{c}	15.33±0.54^{d}	13.75±0.50^{e}
	Cyanidin-3,5-diglucoside	1.39±0.07^{a}	1.15±0.02^{b}	0.89±0.04^{c}	0.95±0.01^{c}	1.18±0.03^{b}	1.13±0.07^{b}
	Cyanidin-3-glucoside	0.68±0.07^{a}	0.60±0.03^{b}	0.51±0.04^{c}	0.52±0.01^{c}	0.49±0.02^{c}	0.41±0.05^{d}
	U1	8.38±0.23^{c}	8.00±0.42^{c}	13.35±0.54^{a}	12.01±0.24^{b}	7.02±0.24^{d}	5.70±0.05^{e}
	U2	1.21±0.05^{b}	1.19±0.08^{b}	1.91±0.14^{a}	1.79±0.02^{a}	1.05±0.02^{c}	0.81±0.02^{d}
	U3	0.41±0.03^{a}	0.38±0.05^{a}	0.23±0.02^{b}	0.24±0.01^{b}	0.22±0.01^{b}	0.17±0.02^{c}
	U4	0.38±0.02^{a}	0.38±0.02^{a}	0.27±0.03^{b}	0.20±0.03^{c}	0.18±0.03^{c}	0.17±0.02^{c}
Phenolic acids	Caffeic acid	16.72±0.79^{a}	16.30±0.79^{a}	12.97±0.23^{b}	12.67±0.39^{b}	12.52±0.37^{b}	12.07±0.34^{b}
	Chlorogenic acid	15.67±0.4^{b}	15.89±1.26^{b}	13.23±0.34^{c}	13.76±0.35^{c}	17.55±0.70^{a}	17.58±0.63^{a}
	p-Coumaric acid	4.77±0.4^{a}	4.52±0.12^{b}	0,65±0.15^{e}	0.59±0.02^{e}	2.45±0.06^{c}	2.26±1.13^{d}
	Ellagic acid	6.46±0.08^{a}	4.04±0.54^{c}	1,05±0.07^{d}	1.45±0.36^{d}	5.12±0.51^{b}	6.43±0.17^{a}
	Ferrulic acid	0.87±0.16^{a}	0.77±0.02^{ab}	0.64±0.05^{c}	0.69±0.02^{b}	0.74±0.12^{ab}	0.52±0.04^{c}
	PAEE*	5.80±1.97^{b}	2.94±0.72^{c}	2.04±0.24^{c}	2.07±0.17^{c}	2.63±0.16^{c}	10.34±0.9^{a}
Flavonols	Kaempferol	4.80±0.77^{b}	4.50±0.39^{b}	1.15±0.28^{c}	1.36±0.13^{c}	8.80±0.20^{a}	8.56±0.94^{a}
	Quercetin	9.78±3.03^{a}	5.65±0.22^{b}	1.10±0.48^{c}	1.28±0.2^{c}	11.33±1.56^{a}	9.80±1.02^{a}
Flavanols	(±)-Catechin**	79.04±3.62^{a}	69.74±3.62^{b}	27.54±1.85^{d}	31.33±1.81^{d}	46.84±1.12^{c}	42.51±3.08^{c}
	(-)-Epicatechin	28.53±6.47^{ab}	10.34±0.67^{c}	5.68±0.44^{c}	6.26±0.41^{c}	24.49±3.42^{b}	31.65±4.10^{a}
	(-)-Epicatechin gallate	136.93±3.96^{a}	139.60±3.91^{a}	109.64±1.60^{b}	96.42±4.77^{c}	92.37±1.67^{c}	81.89±2.73^{d}

$^{a-e}$ The difference between the groups with the different letter in the same line is significantly important (P<0.05).
*PAEE: protocatechuic acid ethyl ester. **The sum of (-) and (+)-catechin was presented as (±)-Catechin level in the table. ±standard deviation
U1, U2, U3 and U4 are unknown 1, 2, 3 and 4, respectively.

Table 2. The correlation coefficients of different degradation orders and kinetic performance outputs
Çizelge 2. Farklı parçalanma derecelerinin korelasyon katsayıları ve kinetik performans çıktıları

Compounds	R^2				R^2_{adj}				*RMSE*				Reaction Rate constant* (L (mg day)$^{-1}$)	ConfInt	$t_{1/2}$ (days)
	Zero	*Half*	*First*	*Second*	*Zero*	*Half*	*First*	*Second*	*Zero*	*Half*	*First*	*Second*			
PPO	0.9388	0.9576	0.9722	**0.9857**	0.9235	0.947	0.9652	**0.9821**	1.473	0.1476	0.05838	**2.598x10^{-3}**	5.693 x10^{-4}	1.90 x10^{-4}	73
TP	0.8935	0.8967	0.8991	**0.9018**	0.8669	0.8708	0.8739	**0.8773**	24.37	0.4903	0.03965	**6.584x10^{-5}**	0.54x10^{-5}	4.82 x10^{-6}	303
TMA	0.8868	0.9123	0.9351	**0.9677**	0.8585	0.8903	0.9188	**0.9596**	9.958	0.4248	0.07148	**4.956x10^{-4}**	3.98x10^{-5}	4.65 x10^{-5}	99
Plg-3-glc	0.7783	0.7993	0.8198	**0.8577**	0.7229	0.7492	0.7747	**0.8221**	6.569	0.359	0.0785	**9.412x10^{-4}**	6.09x10^{-5}	6.89 x10^{-5}	164
Plg-3-O-rut	0.9184	0.9326	0.9452	**0.9652**	0.8981	0.9158	0.9315	**0.9566**	0.815	0.08969	0.03928	**1.868x10^{-3}**	2.60x10^{-4}	1.37 x10^{-4}	183
(-)-Epicatechin gallate	0.7795	0.8036	0.8273	**0.8714**	0.7243	0.7545	0.7841	**0.8392**	12.61	0.5643	0.101	**8.079x10^{-4}**	5.55 x10^{-5}	5.92 x10^{-5}	132

PPO: polyphenoloxidase residual activity, TP: Total phenolic content, TMA: Total monomeric anthocyanin, plg-3-gl: Pelargonidin-3-glucoside, plg-3-O-rut: Pelargonidin-3-*O*-rutinoside, R^2: correlation coefficient, R^2_{adj} adjusted coefficients of determination, *RMSE*: root-mean-square-error
$t_{1/2}$: half-life; ConfInt: confidence interval was calculated with 95% of probability.
*The reaction rate constants and half-lives were determined according to best fitted kinetic model for each compound/quality parameter.

Therefore, changing.behaviors of colorless phenolic compounds during storage in different foods can investigated by analyzing quality parameters in shorter time intervals with further studies. The knowledge gained from this study could be useful for further shelf-life studies of strawberry nectar after thermosonication, evaluating the effect storage on quality parameters, and revealing the relations between them

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Author contributions

The authors declare that they have contributed equally.

Conflict of interest statement

The authors declare no conflict of interest.

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