Research Square

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Pumpkin Peel Valorization Using Green Extraction Technology to Obtain β-Carotene Fortified Mayonnaise

Keziban Kubra GUNGOR
Akdeniz University: Akdeniz Universitesi https://orcid.org/0000-0003-2430-4669
Mehmet Torun (torun@akdeniz.edu.tr)
Akdeniz University: Akdeniz Universitesi https://orcid.org/0000-0002-6287-2993

Research Article

Keywords: Pumpkin waste, green solvent, microemulsion solvent, ultrasound, β-carotene, mayonnaise

Posted Date: March 8th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1380190/v1

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Abstract

This study aimed to recover β-carotene from peels produced as a by-product during the industrial processing of pumpkins using a high-efficiency technology that produces no waste and is harmless to the environment. β-Carotene extraction from pumpkin peel was carried out by maceration and ultrasound-assisted technique, with sunflower oil instead of *n*-hexane as an environment-friendly solvent. Influence of the lecithin:PGPR (polyglycerol polyricinoleate) ratio was studied for microemulsion solvent method on β-carotene extraction. Response Surface Methodoloy was used to optimize the parameters of each performed treatment. The produced sunflower oil was utilized to prepare mayonnaise. Sensory flavor of the product, as well as the change in color and peroxide characteristics after rapid storage were also determined. Under optimal conditions, maceration with sunflower oil, maceration with *n*-hexane, ultrasound-assisted, and microemulsion solvent methods, extracted β-carotene levels were 99.83, 125.75, 127.93, and 149.71 mg/100 g DM, respectively. Most efficient β-carotene extraction was obtained utilizing a microemulsion system with 0.098% lecithin and 1.902% PGPR as the solvent. Mayonnaise made with β-carotene-rich sunflower oil was well received in terms of sensory quality, with no negative changes in the product's unique features. β-Carotene enhanced mayonnaise was more resistant to oxidation during storage than the control mayonnaise as shown by the results of color and peroxide values.

Highlights

- The extraction of β-carotene from pumpkin peel was investigated using green extraction solvents and techniques.
- RSM was used to optimize the β-carotene extraction conditions.
- Extraction efficiency was better in a microemulsion containing 0.098 % lecithin and 1.902 % PGPR as compared to sunflower oil.
- Using ultrasound, the maceration operation was made easier.
- Mayonnaise is made from sunflower oil that has been fortified with β-carotene.

Statement Of Novelty

The creation of strategies to manufacture value-added products from food processing wastes is currently one of the most important research field among various disciplines, particularly food and the environment. Waste evaluation can have a significant economic impact in addition to its environmental factors if a value-added product is developed. However, another point worth mentioning is that the technologies employed for waste evaluation in this study are harmless to human health and the environment. The goal of this research was to recover β-carotene from pumpkin peels, which are a process waste, and convert it to sunflower oil using maceration, ultrasound, and microemulsion solvent techniques. To the best of our knowledge, no comprehensive research has been done on the recovery of β-carotene from pumpkin peel using sunflower oil and microemulsion as green solvents.

Introduction

Waste management is one of the most significant problem faced by the agricultural and food industries in the 21st century [1]. The rise of the food business has resulted in an increase in the number of processing wastes and byproducts. In contrast to other food processing industries, the processing of fruits and vegetables into products such as juice, canned food, freezing, jam, and puree generates a significant amount of waste (peels, rinds, seeds, cores, rags, stones, pods, vine, shell, skin, pomace, and so on), which can amount to up to 25–30% [2, 3]. Despite the fact that these wastes are frequently redirected to other economically feasible non-food uses such as animal feed, compost, or a bio-energy source, their abundance of bioactive compounds, also known as phytochemicals, exposes their potential to be turned into additional value-added products [4]. As a result, valorizing fruit and vegetable waste for bioactive purposes is a waste

management alternative with a lot of promise in terms of sustainability, profitability, and overall human health enhancement [5]. Carotenoids (lutein, zeaxanthin, β-carotene), flavonoids (hesperetin, quercetin, genistein, and kaempferol), and phenolic acids are often found in higher concentrations in wastes than in edible components [6]. Although the bioactive molecules described are employed to improve the nutritional and functional aspects of many foods, phenolic compounds, particularly carotenoids, stand out due to their color and bioactive capabilities [7].

Carotenoids are natural pigments that serve a biological function in the protection of cardiovascular disease and cancer. Their usage as antioxidant agents has piqued attention in recent years [7, 8]. β-carotene, also known as E160a additive, is a key member of the carotenoids family with a wide range of applications in the food, pharmaceutical, and cosmetic industries [9]. It is a highly red orange-colored pigment and a vitamin A precursor with the ability to produce two retinol molecules when exposed to oxygen through the activity of β-carotene 15,15'-monooxygenase [10].

Apart from being used as a food color, β-carotene can also be used as a natural antioxidant since it protects lipids from free radical autoxidation by interacting with peroxyl radicals, limiting propagation and facilitating oxidation chain termination. By filtering light and lowering sensitizer excitation and subsequent energy transfer to generate singlet oxygen, it may also prevent photooxidation in vegetable oils [11]. Despite the fact that many fruits and vegetables, including pumpkin, carrot, apricot, grapefruit, squash, broccoli, and sweet potato, are high in β-carotene [12], pumpkin and carrot wastes are seen as cost-effective sources of waste processing [1].

Pumpkin belongs to the Cucurbitaceacee family, which includes around 800 species and 130 genera [13]. This fruit is one of the most widely produced agricultural products in the world, with a total production of 27.7 million tons per year in 2019 [14]. *Cucurbita pepo*, *C. maxima*, and *C. moschata* are the three most widely produced pumpkin species worldwide. The edible flesh (pulp) of the pumpkin can be eaten as a vegetable or used to make pies, bread, soup, desserts, or jams, and it can also be frozen or canned for industrial use [15, 16]. The industrial processing of pumpkin entails the separation of the edible portion of the fruit from the by-products (~ 25%), which are largely made up of peel (2.6–16%) and seeds (3.1–4.4%). Despite the fact that pumpkin seeds are frequently employed in the creation of snacks and edible oil, the peels, which contain significant levels of β-carotene, are seldom utilized to their full potential [17–19]. Kim et al. [20] studied the β-carotene content of three different pumpkin species' (*C. pepo*, *C. moschata* and *C. maxima*) components (meat, seed, and peel). The β-carotene content of the peels for all species was much higher than the other portions, while the β-carotene content of the flesh, seed, and peels of the *C. moschata* was 5.70, 7.15, and 68.30 mg/kg, respectively. For extraction of β-carotene and other important chemicals from plant food matrices, traditional extraction procedures (maceration, soxhelet, etc.) with common petrochemical solvents such as *n*-hexane, petroleum ether, or diethyl ether have been frequently used. These solvents, on the other hand, produce harmful volatile organic chemicals that harm oil, water, air, plants, animals, and human health. Petrochemical-based solvents are currently carefully regulated by European Directives and the Registration, Evaluation, Authorisation, and Restriction of Chemicals (REACH). As a result, new greener and more sustainable extraction strategies have become a top priority for academia and industry [21–25].

The discovery and design of the green extraction technology, according to [26], is centered on reducing energy usage, using ecologically friendly solvents, and generating a non-denatured extract free of pollutants. Vegetable oils are a promising alternative to standard solvents since they have a great potential for carotenoid extraction due to their oil solubility, do not emit volatile chemical compounds, are biodegradable, and can be employed directly in the formulation of food and cosmetic products [27–29, 25]. Furthermore, vegetable oils are thought to be an excellent barrier against oxygen and reducing oxidation processes. They can also serve as an energy source if the carotenoid-rich product is used in food compositions [30]. Even though vegetable oils can be used as a green solvent, one of the key disadvantages of utilizing extraction solvent is the high viscosity of oils, which results in low effective diffusivity and, as a result, low extraction yield even at high temperatures. Ultrasound-assisted extraction, which has advantages such as increased mass transfer, better solvent penetration, lower extraction temperatures, faster extraction rates, and higher extraction

yield, has been widely used to solve this problem in recent years for bioactive chemicals extraction. The propagation of ultrasound pressure waves and caviation forces have been linked to ultrasound extraction expansion, where bubles can collapse and generate localized pressure, impacting plant tissue rupture and enhancing target component transfer into solvent [31, 32, 23]. Surfactant-assisted extraction, also known as microemulsion extraction, is one of the ultrasonic approaches that may be suitable for increasing carotenoid extraction yield. Because it does not use any hazardous compounds during the extraction process, the microemulsion approach is considered a green and unique technique for extracting bioactives. Because of their lower viscosity than oil, lipophilic components may be extracted more easily, and they have a large solubilization capacity for both lipophilic and hydrophilic molecules [33–35]. Previous research has demonstrated that carotenoids (lycopene, lutein, and β-carotene) may be recovered successfully from a variety of sources, including tomato waste [36], marigold petal, carrot pomace [37], and sea buckthorn pomace [35]. Several studies have been reported on the recovery of carotenoids from different food and their by-products e.g. mango pulp [38], tomato [39], dry tomato waste [40] shrimp waste [41, 42, 27], pomegranate [31], carrot juice processing waste [43], citrus fruits waste [22], passion fruit peel [23], peach palm fruit [44] and bee pollen [45] by using various vegetable oils (sunflower, peanut, gingelly, mustard, sesame, palm, soybean, coconut, flaxseed, corn, canola, olive and rice bran oil). However, there are very few reports [25, 46, 47] on the potential of vegetable oil to extract carotenoid from pumpkin or pumpkin wastes. To the best of our knowledge, no comprehensive research has been done on the recovery of β-carotene from pumpkin peel using sunflower oil and microemulsion as green solvents. As a result, the goal of this study is to determine (1) the efficacy of sunflower oil and oil-in-water microemulsions as a potential alternative to *n*-hexane for β-carotene recovery from pumpkin peel, (2) the effect of ultrasound on increasing diffusion when sunflower oil is used as a solvent, (3) optimize the process conditions of each experiment using the Response Surface Method, and (4) the use of β-carotene loaded sunflower oil in mayonnaise production.

Material And Methods

Material

Pumpkin (*C. moschata*) peels were purchased from a pumpkin dessert producer in Antalya, and frozen at -80 °C without delay. The study was performed at the Food Engineering Laboratory of Akdeniz University. Frozen peels were dried in a freze dryer (OPERON FDU&FDB, Korea) at -70 °C and 40 mmHg absolute pressure till an equilibrium of moisture content (~4 %) was acquired. Freeze dried pumpkin peel powders were passed through 500 µm sieves to use in the experiments. Sunflower oil (Yudum, Balıkesir, Turkey) was purchased from the market. The lecithin, polyglycerol polyricinoleate (PGPR) and other chemicals used in the analysis were purchased from Sigma-Aldrich (St. Louis, MO, USA) and Merck (Darmstadt, Germany).

Ultrasound-assisted extraction using sunflower oil

The temperature (30-60 °C), time (0.5-30 min), peels/sunflower oil ratio (1-5/100 g/mL), and amplitude level (20-60 percent) were all studied in relation to total β-carotene extraction from peels to establish the ideal extraction parameters using an ultrasonic with sunflower oil as the solvent. An ultrasound generator (VC750, 750 W, Sonic and Materials, Inc., Mewtown, Conn., A.B.D.) fitted with a Ti-Al-V sonoprobe (13 mm) and an ultrasound device operating at a set frequency of 20 kHz was used to execute ultrasound-assisted extraction at a constant frequency of 20 kHz. Extraction was carried out at a constant temperature in a jacketed beaker (100 mL, 42 mm internal diameter, and 105 mm height). Water circulation (RW-3025 Lab Copanion, Korea) was delivered through a double-walled beaker with a water bath during the experiments to prevent overheating, and temperature was validated by monitoring with a thermocouple (CHY 500 K Thermometer, Tainan, Taiwan). Before analysis, the extracted extracts were filtered through glass microfibre paper (25 µm) to eliminate particle residues.

Conventional extraction of β-carotene from pumpkin peels

According to the response surface optimal custom design presented in Table 1, a maceration procedure using a shaking water bath (Daihan WSB-30, South Korea) was employed to extract β-carotene from pumpkin peels. For the extraction, a 1:100 ratio of pumpkin peel to sunflower oil was macerated under agitation (150 rpm) at various extraction temperatures (30-60 °C) and times (5-180 min). According to the results of the optimization research of ultrasound-assisted extraction conditions and early experiments, the peel/sunflower oil ratio (1:100) was chosen (data not shown). The experiment was also carried out under optimum conditions using n-hexane instead of sunflower oil to test the result of a commonly used extraction solvent. Before analysis, the extracted extracts were filtered through glass microfibre paper (25 µm) to eliminate particle residues.

Microemulsion of β-carotene extraction from pumpkin peels

The optimum temperature (60 °C) and time (180 min) determined in the conventional extraction experiment were used as process parameters in this section because the goal of the microemulsion solvent approach is to investigate the influence of yield enhancement for β-carotene extraction with respect to sunflower oil. Okoro et al. [48] preapered emulsion solvents, and mixture ratios of emulsifiers (lecithin and PGPR) in the emulsion were determined using mixture optimal custom design. The emulsifier was dissolved in sunflower oil using a magnetic stirrer at 42±2 °C for 15 minutes, and then the aqueous phase was added dropwise to the oil dispersion. At the same time, a rotor-stator system (Ultra Turrax T18, IKA, Germany) was used to homogenize the mixture at 14,000 rpm.

After the aqueous phase was fully mixed into the emulsion (after 50 minutes), the rotating speed was reduced to 11,000 rpm, and the emulsion was homogenized for another 4 minutes. Tsogtoo et al. [35] with certain changes exteacted pumpkin peel powder in produced emulsion solvent. Pumpkin peel powder (1 %) was added to the emulsion and blended for 1 minute at 11,000 rpm with ultraturrax. The homogenized mixture was then extracted in a shaking water bath (Daihan WSB-30, South Korea) by stirring at 150 rpm for 3 hours at 60 °C. To remove undissolved particles and the water-lipid phase, the suspension was centrifuged at 9,100 g for 20 minutes, then the lipophilic extract was filtered through glass microfibre paper (25 µm) before analysis.

Experimental design

RSM (response surface methodology) is a technique for analyzing experimental data and optimizing processes or goods. It's useful for obtaining desired answers by optimizing process variables (independent & dependent variables). For the extraction of β-carotene from pumpkin peel, β-carotene was the dependent value for all extraction optimizations, which were carried out using the Desing Expert 10.0 (Stat-Ease Co., USA) program and response surface approach. For conventional (16 experiment) and ultrasound-assisted (25 experiment) extraction, response surface ideal custom design was utilized, and for microemulsion (9 experiment) extraction, mixture optimal custom design was employed. These models were chosen because they allow the use of certain constant variable values. Independent variables for the conventional extraction were temperature (X_1) and time (X_2); temperature (Y_1), amplitude (Y_2), time (Y_3) and peel:solvent ratio (Y_3) for the ultrasound-assisted extraction; and lecithin (Z_1) and PGPR (Z_2) ratio for the microemulsion extraction (Table 1).

Experiments on conventional and ultrasound-assisted extraction were fitted to the quadratic model, whereas experiments on microemulsion extraction were suited to the cubic model. According to Eq. (1) and Eq. (2), the independent values could be written as second-order polynomial equations (2),

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{j=1+1}^{k} \beta_{ij} X_{ij} + e \quad (1)$$

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \sum_{j=1+1}^{k} \beta_{ij} X_i X_j + \beta_{i,j,k} X_i X_j X_k + e \quad (2)$$

where Y is the response variable , β_0 isintercept, β_i , β_{ii} , β_j andβ_k are the regression coefficients of the quadratic and cubic terms of the model, respectively, k is the number of the independent variables, X_i , X_j andX_k are the independent variables while e is error.

β-Carotene analysis

The amount of β-carotene in the extracts was evaluated using a spectrophotometer (Shimadzu UV-vis 160A) at an absorbance of 450 nm (absorbance maxima for β-carotene) against sunflower oil as a blank. The absorbance of different concentrations of β-carotene standards was used to plot the standard curve [49]. With the linear equation y=0.1054x+0.0147, the R^2 was 0.9998. The results were computed using the provided calibration curve and represented in milligrams of β-carotene per 100 grams of pumpkin skin (on dry basis).

Oil quality

The peroxide value of untreated sunflower oil and oil treated by extraction at the optimum conditions was examined to see how process variables affected oil quality. As indicated in the peroxide value determination section, the filtered oil was directly examined.

Mayonnaise production using β-carotene-loaded sunflower oil

To test oxidative stability and sensory acceptance, two distinct mayonnaises were made utilizing β-carotene loaded sunflower oil (under ideal maceration conditions) and untreated sunflower oil as a control. Mayonnaise was made using the methods described by Evanuarini, Hastuti [50] and Huang et al. [51]. Sugar, salt, mustard, and egg yolk were first combined in an ultraturax at 15,000 rpm for 1 minute, after which oil was added at a flow rate of 4-5 mL/min. The remaining vinegar, lemon juice, and water were added once the mixing procedure was completed, and the mixture was homogenized using an ultraturax. The mayonnaise was then transferred and preserved in glass jars.

Accelarated storage of mayonnaise

Mayonnaise samples (60 g) were placed in 100 mL glass bottles and incubated at 60 °C in the oven (Haniff et al. 2020). To conduct the accelerated oxidation test, each mayonnaise sample was tested at different time periods of 0, 24, and 72 hours. During storage, peroxide value and color assessments were performed, as well as a sensory study at the start of storage.

Peroxide value determination

Mayonnaise samples were frozen at -18 °C and thawed to separate oil for further examination. The mixture was centrifuged for 10 minutes at 10,000 g, and the separated oil was collected for peroxide analysis [52]. A total of 0.1 g of oil was extracted and diluted in a 10 mL glacial acetic acid:chloroform (3:2) combination. Iodine was produced when potassium iodide (0.25 mL) was introduced and reacted with the peroxide. The solution was titrated with standard solution 0.01 N sodium thiosulfate and starch as an indicator after adding 15 mL of distilled water. The value of peroxide was estimated using Eq (3).

Peroxide value (meq O_2/kg oil) = (S-B) x N x 1000 / W (3)

where S is the volume of sample expended thiosulfate, B is the volume of blank expended thiosulfate, N is the normality of NaOH while W is the weight of sample.

Color analysis

A colorimeter (Konica Minolta, CR-400, Japan) was used to determine the color of the mayonnaise, with L* denoting brightness, a* denoting redness, and b* denoting yellowness [53]. To get an average reading, measurements were made three times at different places. The tone angle (Hue angle, h°) was calculated using the a* and b* parameters according to Eq. (4):

$$h° = \tan^{-1}(b^*/a^*) \quad (4)$$

Sensory analysis

Panelists (total 15: 8 male, 7 female, from Akdeniz University's Department of Food Engineering) evaluated two mayonnaise samples (control and β-carotene loaded) in terms of brightness, color, thickness, smoothness, sour taste, salinity, sweetness, oiliness, rancid taste, odour, aroma, flavor, and overall acceptance. The hedonic test was used to assess consumer approval of the two types of mayonnaise, with scale scores ranging from 1 to 9, with 1 indicating extreme dislike and 9 indicating extreme liking (Wendin et al., 1999). The purpose of the study was to see how well mayonnaise made with β-carotene-rich sunflower oil would be received.

Statistical analysis

Optimum extraction conditions were determined using the Design Expert 10.0 programme (Stat-Ease Co., Mineapolis, USA). Statistical analysis of mayonnise samples were carried out using SAS system for Windows (SAS Institute, Cary, NC, USA). Analysis of Variance (ANOVA) was carried out to determine the presence of statistical significance. Duncan Multiple Ranges test was used to examine significant differences between samples and storage period. All data are presented as mean values ± standard deviation.

Results And Discussion

RSM modeling

Depending on the method used to extract bioactive components from any product, there are a variety of process variables to consider. For β-carotene recovery from pumpkin peel, the effects of extraction time and temperature in maceration; extraction time, temperature, amplitude level, peel:sunflower oil ratio in ultrasound assisted extraction; and PGPR and lecithin ratio in microemulsion solvent extraction were investigated in this study. The model's adequacy and fitness, as well as the link between variables, were investigated using regression analysis and lack of fit variables, as shown in Table 2. The “lack of fit” values of the models varied between 0.0726 and 0.7245, those were non-significant ($p>0.05$). The R^2 (0.9650, 0.9258, 0.9405) and $Adj\text{-}R^2$ values (0.9475, 0.8219, 0.9047) shows a notable correlation between experimental and predicted values of the response variable. To obtain β-carotene in sunflower oil, the maceration temperature and time were 59 °C and 162 minutes, respectively. The projected β-carotene value under these conditions was 103.74 mg/100 g DM, with a desirability level of 1.00 on a 0-1 scale. The experimental value obtained under ideal conditions was very close to the RSM-based model's anticipated value, indicating that the created model can accurately predict β-carotene extraction from pumpkin peel utilizing sunflower oil as a solvent (Table 3). The extract was extracted with hexane under the same conditions as the maceration process. The extract contained 125.75 mg/100g DM of β-carotene. The extraction of β-carotene using sunflower oil has a 79.39 % efficiency when compared to hexane. The ultrasound assisted extraction and microemulsion solvent extraction had a desirability level of 1.00 and 0.947, respectively. While the ultrasound aided extraction best circumstances were as follows: extraction period of 21 minutes, 42 °C temperature, 1 % peel:sunflower oil ratio, and amplitute level of 52 %, the optimum ratio was 0.098 % lecithin and 1.902 % PGPR. For ultrasound aided and microemulsion solvent extraction, the estimated recovery values of β-carotene were 125.94 mg/100 g DM and 155.97 mg/100 g DM, respectively. The experimental value obtained under ideal conditions was in good agreement with the RSM-based model's estimated value as shown in Table 3.

Effect of maceration process variables on β-carotene extraction

The experimental findings for the maceration procedure using sunflower oil ranged from 76.93 to 103.01 g/100 g DM, depending on the selected points (Table 4). Figure 1 shows that the β-carotene content of sunflower oil increased as the extraction temperature and duration increased. This discovery could be explained by the fact that as the viscosity of the oil employed as a solvent decreases with temperature, the diffusion coefficient and mass transfer rate increases. Long-term interaction between the solvent and the solid phase was linked to an increase in β-carotene yield when the extraction period was elongated. Razi Parjikolaei et al. [27] found that as the extraction temperature increased from 25 to 70 °C, the amount of astaxanthin increased from 8.6 mg/kg to 14.7 mg/kg.

Chutia and Mahanta (2021) found that when the extraction temperature was increased to 60 °C, 54 % of the carotenoids recovered from passion fruit peels using vegetable oil were removed during the first 30 minutes. The authors also claimed that prolonging the time to 3 hours boosted extraction efficiency by almost 80 %. The largest amount of carotenoids could be obtained at 70 °C and 150 minutes, according to a study on the optimization of carotenoid extraction conditions utilizing different vegetable oils from shrimp waste. The number of carotenoids in the extract grows until the extraction temperature reaches 70 °C. Sachindra, Mahendrakar [41] claimed that above this temperature, the amount of carotenoids reduced due to degradation.

Effect of ultrasound process variables on β-carotene extraction

According to Table 4, the average β-carotene values of the samples recovered by ultrasound using sunflower oil ranged from 44.37.72 to 118.44 mg/100 g DM. The recovery of β-carotene was impacted ($p<0.01$) by amplitude level, extraction time, and peel:solvent ratio. With reducing extraction temperature and ultrasound amplitude level at the same time, the amount of β-carotene decreased (Figure 2). With extraction temperatures below 45 °C, the amount of β-carotene increases the most as the amplitude increases. At a moderate extraction temperature (about 45 °C), the amount of β-carotene obtained increased with increasing duration. Furthermore, at this temperature, the extraction efficiency improves when the amount of pumpkin peel is reduced while maintaining a constant solvent amount. The β-carotene value increased with the rise of these two independent variables in the interaction of extraction time and ultrasound amplitude. Similar results were also found by Chutia, Mahanta [23]. The highest carotenoid amount was obtained at 50 °C and 50 minutes of extraction time. They discovered that as the temperature rose up to 50 degrees Celsius, it began to fall. The solubility of cell contaminants and the disintegration of some other components have been proposed as explanations for the decrease in high temperatures. With the help of ultrasonography, Goula et al. [31] were able to recover caarotenoids from pomegranate waste. Temperature of 51.5 °C, amplitude of 58.8 %, and time of 30 minutes were found to be ideal. Up to 40 % efficiency, there was a positive benefit, but after that, there was a negative effect. The increase in solid-liquid contact as a result of rising cavitation with increasing amplitude has a favorable effect. As a result, it makes it easier for the solvent to penetrate the matrix. The unfavorable effect was attributed to deterioration at even greater amplitude levels. In carotenoid extraction with ultrasonic assistance, [21] found that the extraction time was significantly shortened compared to the tarditional approach, and that 40 °C temperature and 20 min time produced the best results in terms of β-carotene efficiency.

Microemulsion solvent extraction: influence of lecithin and PGPR ratio

The goal was to see how microemulsion solvent systems affected β-carotene extraction in order to improve sunflower oil extraction efficiency. The best maceration conditions (59 °C, 162 minutes, 1 % pumpkin peel:sunflower oil ratio) were used as extraction variables, and the best soy lecithin:polyglycerol polyricinoleate (PGPR) ratio was chosen based on the maximum β-carotene recovery. The samples' average β-carotene levels ranged from 67.82 to 160.93 mg/100 g DM (Table 4). The results revealed that the mixture with the lowest lecithin content and the highest PGPR content recovers the most β-carotene (Figure 3). As a matter of fact, a blend of 0.098 percent lecithin and 1.902 percent PGPR was established as

the best ratio. Soy lecithin and PGPR have relatively similar HBL (hydrophilic-lipophilic balance value) values (between 4 and 7). When utilized at a concentration of 0.1 to 0.3 %, lecithin has little effect on shear stress. It raises shear stress by 0.3 to 0.5 %; however, unlike lecithin, PGPR has been shown to lower shear stress [54]. Indeed, based on the findings of this investigation, it is plausible to conclude that mass transfer rises as the PGPR ratio in the microemulsion increases. Tween 80 was utilized as an emulsifier in the microemulsion method of extracting β-carotene from carrot pulp by Roohinejad et al. [37]. When compared to the usage of hexane, the extraction efficiency was found to be higher. They discovered that tiny microemulsion particles with hydrophilic-lipophilic characteristics enhanced the passage of carotenoids through the cell membrane. Another investigation on the extraction of carotenoids from sea buckthorn pomace discovered that carotenoid extraction efficiency was higher in oil/water emulsion than in organic solvent and oil. The presence of a large amount of water in the pomace promotes the swelling of plant cells, diffusion of oil droplets through the cell membrane, and dissolution/solubilization of the bioactive chemicals in the oil, all of which increase carotenoid delivery [35].

Sunflower oil quality depending on extraction conditions

Thermal processes and ultrasound cavitation during the extraction have the potential to produce radical compounds in the oils utilized in the extraction. Peroxide analysis of the sunflower oil utilized in the extraction and the enhanced sunflower oil obtained under the optimum circumstances of each extraction process was performed for this purpose. The oils' initial peroxide value was found to be 3.30 meq O_2/kg oil. For maceration and ultrasonic assisted extraction procedures used under optimum circumstances, this value climbed to 3.44 meq O_2/kg oil and 4.01 meq O_2/kg oil, respectively. In terms of food safety, the maximum peroxide value of oils is regulated to 15.0 meq O_2/kg oil, according to the Codex Alimentarius Standard [55]. The peroxide value of the treated oil was found to be within the limit, but there was an increase in peroxide value after the ultrasound-assisted extraction. Caviation may be produced by lipid oxidation and deterrence as a result of structural and functional component changes. The effect of ultrasound caviation on oxyradical specied was also mixed with metals found naturally in food oils [31].

Properties of β-carotene-loaded mayonnaise

Aside from the fact that using sunflower oil for β-carotene recovery eliminates petroleum-based solvents and results in a safer and higher-quality extract or product, one of the most significant benefits of this method is that the enriched oil can be used directly without the need for solvent removal. In fact, β-carotene-loaded sunflower oil was employed in the preparation of mayonnaise, and the sensory approval of the final product was assessed. During the accelerated storage period, the color, peroxide, *p*-anisidine, and totox values were also evaluated. Figure 4 shows the sensory evaluation scores for sunflower oil generated with control (directly sunflower oil) and sunflower oil supplemented with β-carotones. All of the scores of the β-carotene loaded mayonnaise samples were higher than the control mayonnaise samples, despite the fact that the difference was statistically insignificant. There was a significant difference ($P<0.05$) in overall acceptance, with the panelists preferring the β-carotene loaded mayonnaise over the control sample. These findings revealed that mayonnaise made with β-carotene-rich sunflower oil was well received in terms of sensory quality, with no negative changes in the product's unique features.

Because color is one of the most important sensory elements that influences the willingness to purchase or taste a product, it has a significant impact on consumer preference [56]. Color measurements were taken for this purpose (Figure 5). It is obvious that β-carotene-rich sunflower oil created various color properties in mayonnaise, as expected (Figure 6). While the control samples' lightness (L*) value (84.94) was similar to mayonnaise data reported in the literature [57, 56], β-carotene loaded mayonnaise color indicated a lower lightness value (78.25). According to Santipanichwong, Suphantharika [58], adding β-carotene to mayonnaise decreased the L* value because the carotenoid molecules absorbed some of the light, resulting in less light being reflected back from the mayonnaise samples. The yellowness (b* value) of

control mayonnaise was discovered to be 15.39, and as expected, adding β-carotene to the oil enhanced the yellowness value to 29.87. The lipophilic β-carotene pigment, which has a distinctive orange-yellow tint, is responsible for this rise [38]. The hue angle values of the β-carotene-loaded mayonnaise were near to 90 degrees, confirming the yellow color, with no significant changes ($P>0.05$) amongst the samples. At the end of the accelerated storage period, the brightness and yellowness values in both mayonnaise samples fell significantly ($P<0.05$). According to [59], the lightness of mayonnaise samples can be attributed to non-enzymatic browning processes with carbonyl compounds generated during lipid oxidation as a substrate, as well as brown-colored oxypolymers produced by polymerization from the lipid oxidation derivatives. [60] similarly concluded that oxidation caused a decrease in the lightness and yellowness of mayonnaise during storage. When compared to the control sample, the lightness and yellowness of the samples produced with β-carotene loaded oil decreased at a very low rate towards the conclusion of the storage period, according to this study. These findings were linked to the antioxidant activity of β-carotene, which has been shown to inhibit oxidation to some extent.

Mayonnaise, like other fatty foods, is subject to spoiling owing to lipid oxidation [61]. Peroxide value determination is a method for evaluating peroxides and hydroperoxides concentrations during the first stage of lipid oxidation [52]. The peroxide value of the β-carotene loaded mayonnaise was studied during accelerated storage conditions to see how well it performed as an antioxidant in mayonnaise. The results are shown in Figure 7. At the beginning, 24 hours, and 48 hours, the peroxide value of β-carotene loaded mayonnaise (0.91 meq O_2/kg oil) was lower than the control sample (9.59 meq O_2/kg oil). At the end of the accelerated storage time, there was no significant difference ($P>0.05$) between mayonnaise samples. The findings corroborated prior findings that the peroxide value in mayonniase samples rose over time [62, 63, 59]. Peroxide values of several mayonnaise samples with added rosemary, oregano, and ginger extracts revealed lower initial peroxide values and a reduced range of rise during storage, according to Kwon et al. [64]. Mayonnaises made with carotene-rich oils have lower peroxide values during both manufacture and storage, indicating that oxidation happens more slowly in beta-carotene-rich oil. Salami et al. [65] found that canola oil containing pumpkin peel extract had the maximum oxidative stability, indicating that it performed better than *tert*-butylhydroquinone in preventing oil oxidation during the frying process.

Conclusion

The effectiveness of sunflower oil as a green solvent for extracting β-carotene from pumpkin peel and the potential use of the resulting β-carotene-loaded oil in mayonnaise is investigated in this study. Additionally, an ultrasound-assisted and microemulsion solvent strategy has been investigated to improve the efficiency of this greener technology. The results showed that hexane, a popular solvent, extracted 20.61% more β-carotene than sunflower oil under the same maceration circumstances. However, β-carotene extraction became more efficient with hexane when sunflower oil was employed as a solvent, and 19.38% more efficient when a microemulsion solvent was utilized in a mixture of 0.098% lecithin and 1.902% PGPR. The ideal situation of 59°C and 162 minutes showed best results for β-carotene extraction. The results indicated that not only did ultrasonic aided extraction enhance the amount of β-carotene extracted, but it also reduced the extraction temperature and time. The most promising result was found using microemulsion solvent in this study. Further research into the components that transfer from the pumpkin peel to the water phase will make the approach even more relevant in future studies. Although one of the most significant benefits of the method utilized in this study is that the resulting oil can be used right away, β-carotene-rich oil has been tested in the preparation of mayonnaise. Mayonnaise made with β-carotene-rich sunflower oil was well reviewed by consumers, with no negative changes in the product's unique features. During the accelerated storage test, the color and peroxide value analysis findings were judged as being more resistant to oxidation of mayonnaise made with β-carotene-rich oil, as well as sensory acceptance.

Declarations

Data Availability

Data will be available on request.

Acknowledgement

The authors would like to thank the Research Administration Unit of Akdeniz University (Antalya, Turkey) for financial support (Project no: FYL-2020-5456).

Contributions

Methodology, formal analysis, investigation, writing-original draft: Keziban Kubra Gungor; Methodology, writing-review & editing, supervision, funding acquisition: Mehmet Torun.

Conflict of Interest

The authors report no declarations of interest.

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Tables

Table 1. Levels of independent variables

Maceration	**Level**		
Independent variables	**-1**	**0**	**1**
X_1, Extraction temperature (°C)	30	45	60
X_2, Extraction time (min.)	5	92.5	180
Ultrasound-assisted extraction	**Level**		
Independent variables	**-1**	**0**	**1**
Y_1, Extraction temperature (°C)	30	45	60
Y_2, Amplitude level (%)	20	40	60
Y_3, Extraction time (min.)	0.5	15.25	30
Y_4, Solid:liquid ratio (%)	1	3	5

Microemulsion extraction			**Level**				
Independent variables	**-3**	**-2**	**-1**	**0**	**1**	**2**	**3**
Z_1, Lecithin ratio (%)	0	0.5	0.675	1	1.325	1.5	2
Z_2, PGPR ratio (%)	0	0.5	0.675	1	1.325	1.5	2

Table 2. Analysis of variance (ANOVA) results for the fitted models.

Parameters		Maceration extraction	Ultrasound assisted extraction	Microemulsion extraction
p value	Model	<0.0001	0.0007	0.0017
	Lack of fit	0.7245	0.0726	0.1584
R^2		0.9650	0.9258	0.9405
Adjusted R^2		0.9475	0.8219	0.9047

Table 3. Observed and predicted values of β-carotene at the optimum conditions (mg/100g DM)

	Maceration	Ultrasound assisted exraction	Microemulsion solvent extraction
Predicted value	103.74	125.94	155.97
Experimental value	99.83	127.93	149.71
Difference (%)	3.77	1.58	4.01

Table 4. Experimental design and response values for β-carotene

Maceration				Ultrasound-assisted extraction						Microemulsion solvent extraction			
Number	X_1	X_2	β-carotene (mg/100g DM)	Number	Y_1	Y_2	Y_3	Y_4	β-carotene (mg/100g DM)	Number	Z_1	Z_2	β-carotene (mg/100g DM)
1	0	0	99.00	1	0	0	0	-1	118.44	1	-1	1	137.26
2	-1	1	93.35	2	-1	-1	0	1	51.96	2	3	-3	79.33
3	1	0	102.25	3	-1	1	1	1	94.93	3	-3	3	147.99
4	0	0	99.07	4	-1	1	-1	1	61.39	4	0	0	86.94
5	1	0	102.18	5	0	0	0	-1	111.30	5	-3	3	160.93
6	0	-1	88.07	6	1	0	0	0	86.70	6	3	-3	77.72
7	1	-1	89.66	7	0	-1	-1	-1	77.03	7	1	-1	67.82
8	0	-1	86.37	8	1	1	-1	-1	97.35	8	0	0	72.50
9	-1	0	87.38	9	1	1	0	1	79.93	9	-2	3	131.49
10	-1	0	91.91	10	-1	-1	1	-1	103.14				
11	1	1	103.01	11	0	-1	-1	0	84.38				
12	0	0	97.35	12	1	1	1	-1	105.61				
13	-1	-1	76.93	13	0	-1	1	0	99.52				
14	0	1	101.15	14	1	0	0	0	73.97				
15	0	0	94.73	15	1	-1	1	1	69.39				
16	0	1	100.85	16	-1	-1	-1	-1	76.10				
				17	0	0	0	1	103.21				
				18	0	1	-1	0	95.79				
				19	0	-1	1	0	104.57				
				20	-1	-1	-1	1	32.72				
				21	-1	1	0	-1	109.89				
				22	0	0	0	1	101.71				
				23	1	-1	0	-1	93.62				
				24	1	-1	-1	1	44.37				
				25	1	0	0	0	88.41				

Figures

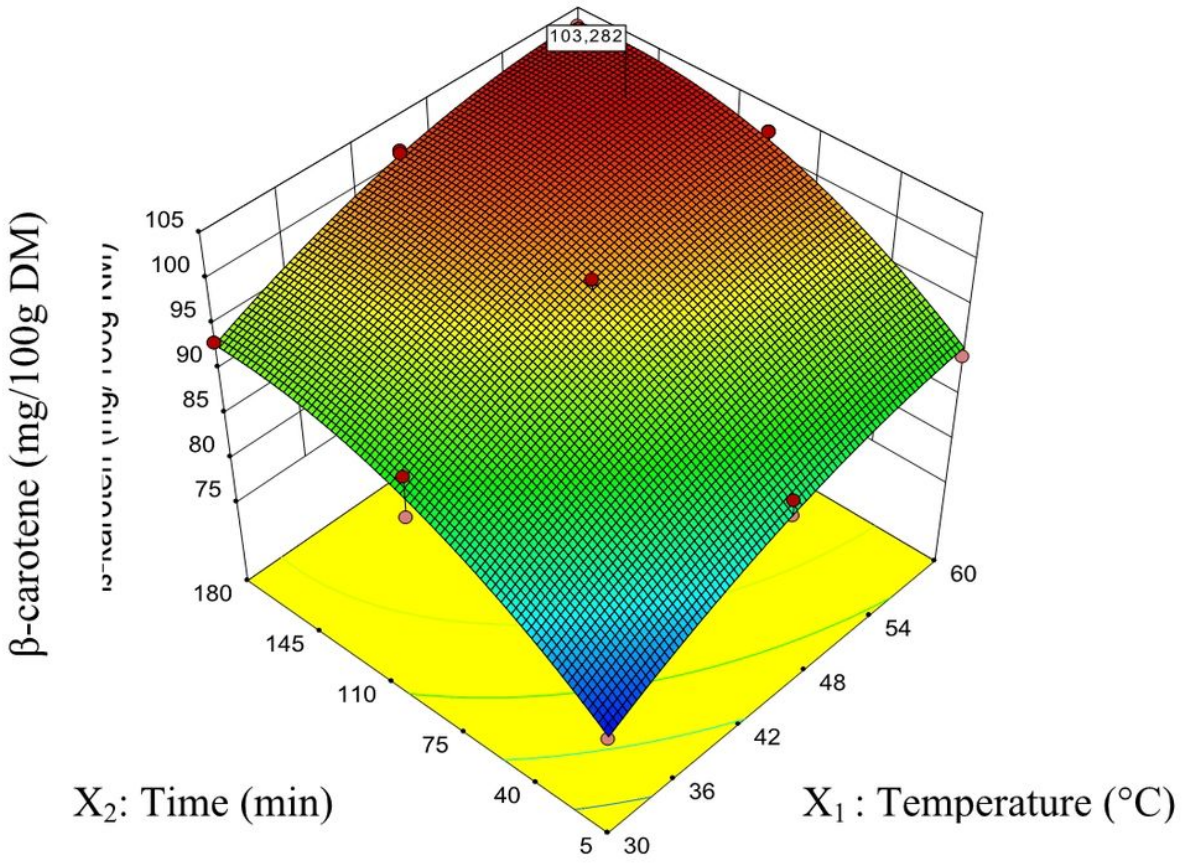


Figure 1

Effect of extraction temperature and time on β-carotene recovery during maceration

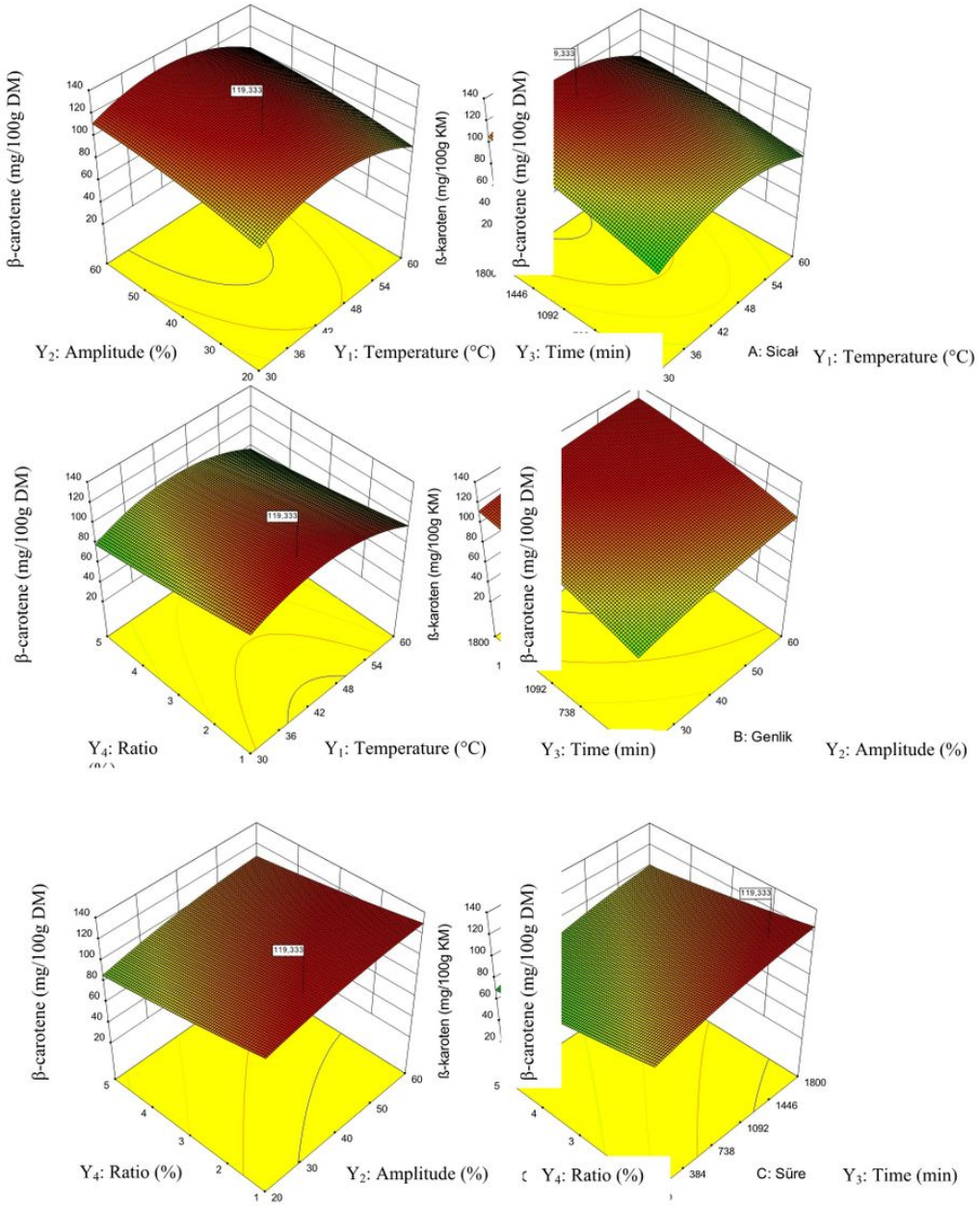


Figure 2

Effects of extraction temperature, amplitude, solid:liquid ratio and extraction time on β-carotene recovery during ultrasound-assisted extraction

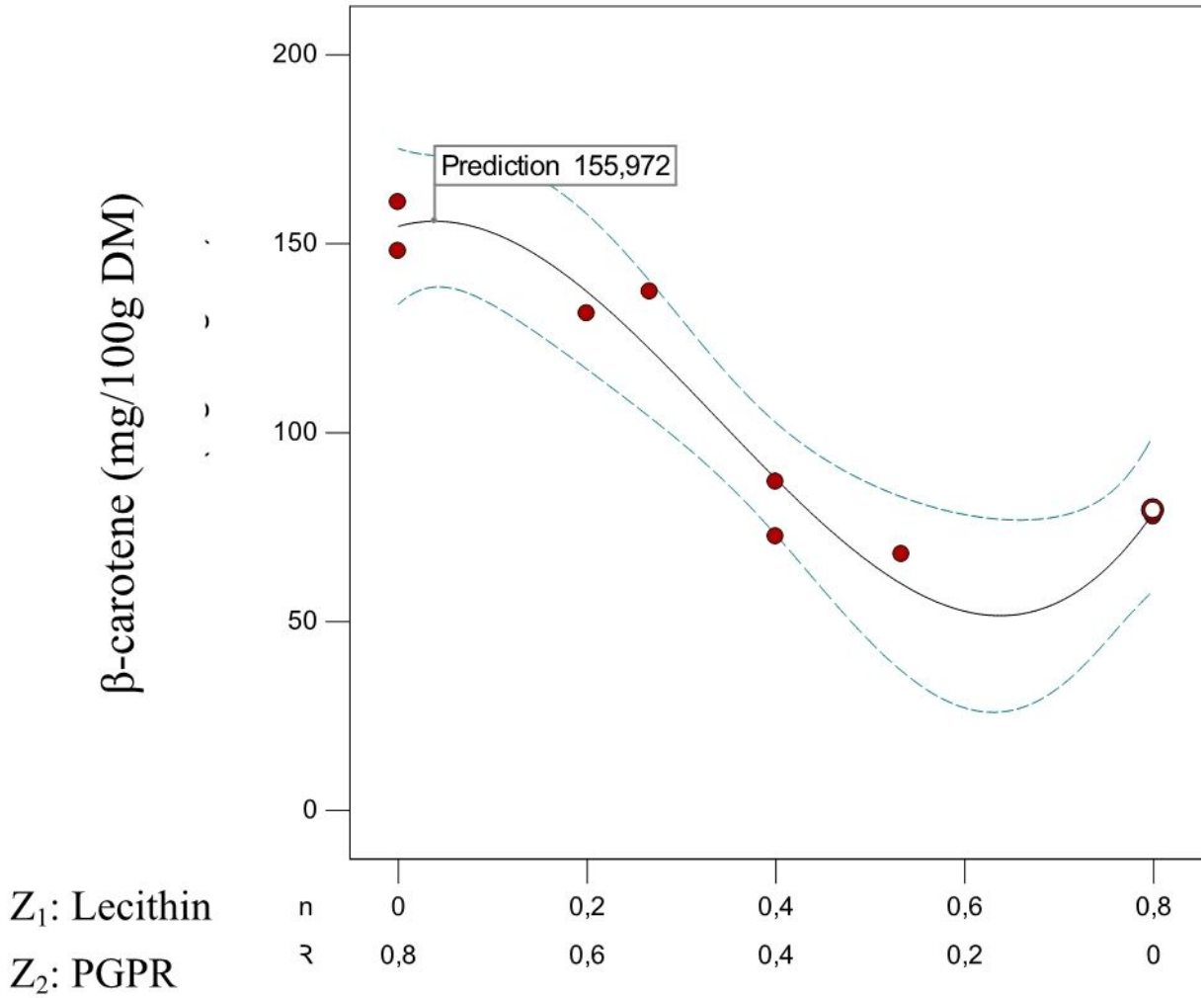


Figure 3

Effect of lecithin and PGPR ratios on β-carotene recovery for microemulsion solvent

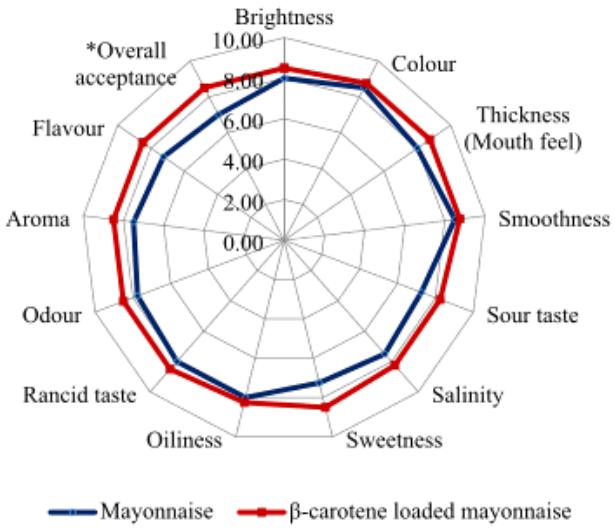


Figure 4

Sensory analysis results of the mayonnaise samples. * indicates significant at P<0.05.



Figure 5

Images of control mayonnaise (a); β-carotene loaded mayonnaise (b).

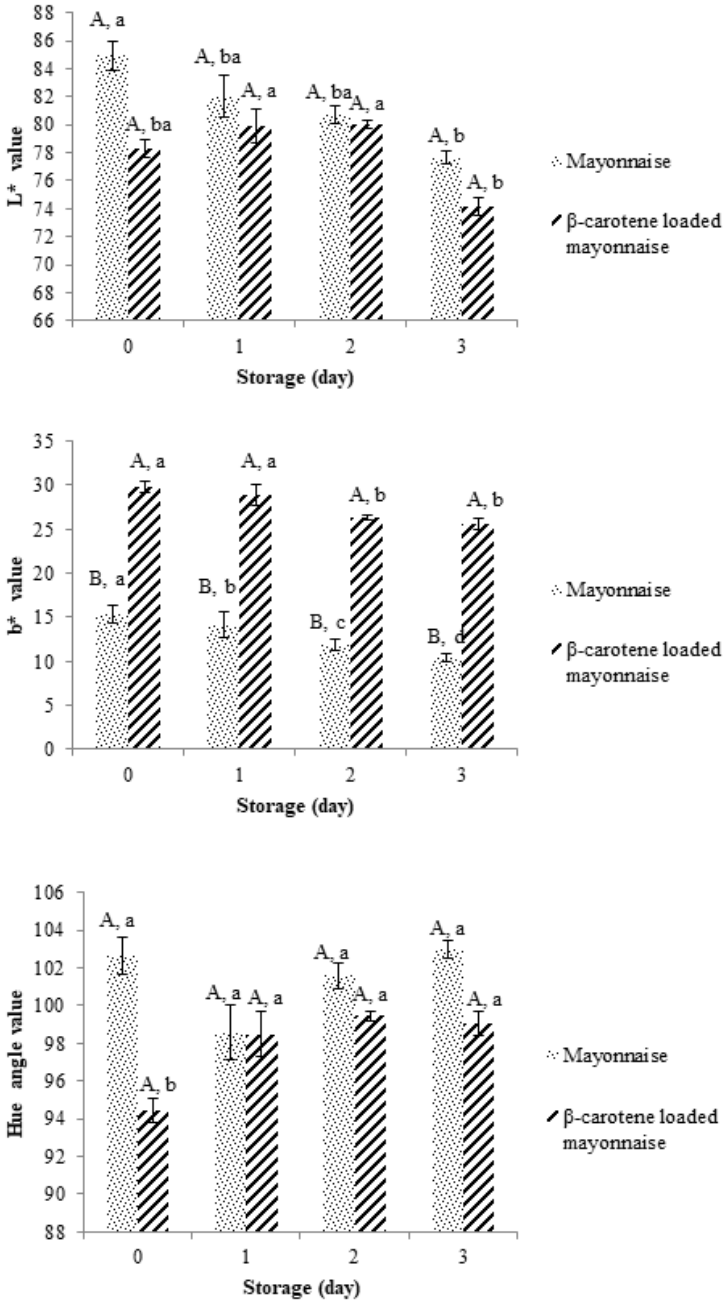


Figure 6

Color values of mayonnaise depending on accelerated storage period. Uppercase superscript letters in the same line and superscript lowercase letters in the same storage time indicate a significant difference of $P<0.05$.

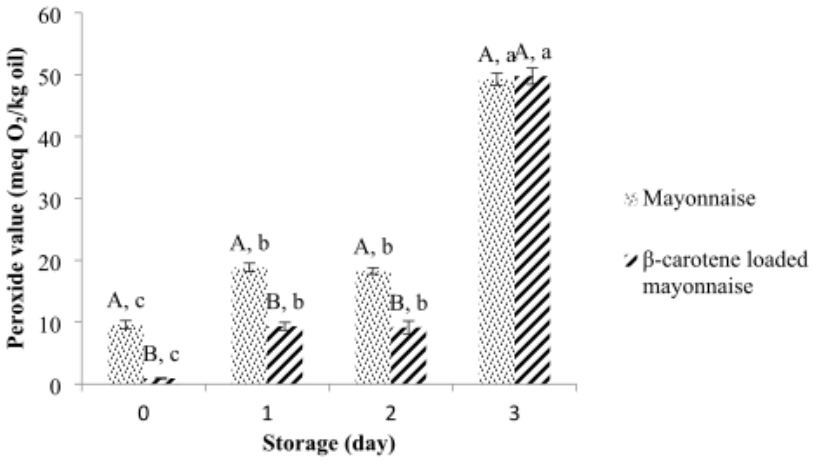


Figure 7

Peroxide values of mayonnaise samples depending on accelerated storage period. Uppercase superscript letters in the same line and superscript lowercase letters in the same storage time indicate a significant difference of $P<0.05$.

Supplementary Files

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- Graphicalabstract.docx