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The Applications of Green Extraction: Production and Quality Characterization of Seed Oils Extracted From Red Pepper (*Capsicum Annuum* L.) Waste

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ABSTRACT

The study focused on the possibilities of evaluation of red pepper (*Capsicum Annuum* L.) seeds being a food industry waste. The moisture content (%), the total crude oil and ash content, color, the weight of 1000 seeds, the thickness and diameter of the seeds were characterized. The oils were extracted from the seeds using green techniques: cold-pressing, ethanol solvent, and ultrasound-assisted ethanol solvent extraction.Different techniques compared the production yield and quality characteristics of the oil samples. On average, linoleic acid (72.00%), oleic acid (11.76%), and palmitic acid (11.50%) were the predominant fatty acids in oils. The yield (16.80%) of the ultrasound-assisted technique was observed to be more effective than the others. The lowest content of acidity and the highest content of total carotenoids were found in the cold-press oil. The color, conjugated diene-triene values were higher with cold-pressing. The total phenolic contents and the antioxidant capacities were ranked in the following order: ethanol solvent (241.1 mg kg^{-1} and 79.84%), ultrasound-assisted (167.0 mg kg^{-1} and 67.18%), and cold press (131.8 mg kg^{-1} and 59.04%). The total tocopherols (1801.2 mg kg^{-1}) content was superior in the oil extracted with the ethanol solvent technique. The results were shown that the oil obtained by using the ethanol solvent extraction technique had better bioactive properties and so, antioxidant activity compared to other green extraction techniques.

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Yeşil Ekstraksiyon Uygulamaları: Kırmızı Biber (*Capsicum Annuum* L.) Atığından Ekstrakte Edilen Çekirdek Yağlarının Üretimi ve Kalite Karakterizasyonu

ÖZET

Çalışma, gıda endüstrisi yan ürünü/atığı olan kırmızı biber (*Capsicum Annuum* L.) çekirdeklerinin değerlendirilme olanaklarına odaklanmıştır. Nem içeriği (%), toplam ham yağ ve kül içeriği, renk, 1000-dane ağırlığı, çekirdeklerin kalınlığı ve çapı karakterize edilmiştir.Yağlar, yeşil teknikler uygulanarak çekirdeklerden ekstrakte edilmiştir: soğuk presleme, etanol solvent ve ultrason- destekli etanol solvent ekstraksiyonu. Yağ numunelerinin üretim verimleri ve kalite özellikleri farklı tekniklerle karşılaştırılmıştır. Ortalama olarak, linoleik asit (%72.00), oleik asit (%11.76) ve palmitik asit (%11.50) yağlarda baskın yağ asitleri olmuştur. Ultrason-destekli tekniğin, verim açısından (%16.80) diğerlerine göre daha etkili olduğu gözlenmiştir. En düşük asit içeriği ve en yüksek toplam karotenoid içeriği soğuk pres ile üretilen yağda tespit edilmiştir. Renk, konjuge dien-trien değerleri soğuk pres yöntemi ile daha yüksek elde edilmiştir. Toplam fenolik içerik ve antioksidan kapasite değerlerini şu şekilde sıralayabiliriz : etanol solvent (241.1 mg kg^{-1} ve %79.84), ultrason-destekli solvent (167.0 mg kg^{-1} ve %67.18) ve soğuk presleme (131.8 mg kg^{-1}) 1 ve %59.04). Etanol solvent tekniği ile ekstrakte edilen yağın toplam tokoferol (1801,2 mg kg^{-1}) içeriği daha üstün olmuştur. Sonuçlar, etanol solvent ekstraksiyon tekniği kullanılarak elde edilen yağın diğer yeşil ekstraksiyon tekniklerine kıyasla daha iyi biyoaktif özelliklere ve

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dolayısıyla antioksidan aktiviteye sahip olduğunu göstermiştir.

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INTRODUCTION

Pepper (*Capsicum Annuum* L.), a popular crop plant cultivated in various countries of the world, has great importance for the consumer, producer, and processing industries. The world's chili pepper and powder production are 4.255.050 tons (FAO, 2019). The seeds are discarded during the processing of red spice pepper. Seeds constitute 30% of the dried fruit's total weight, and these data show that a significant amount of food processing by-products is produced (Yaldız, 2008). However, these byproducts were usually consumed as animal and poultry feed materials, causing resource waste and environmental pollution. Recently, value-added utilization, including industrial byproducts, is gaining interest in the food processing industry.

Red pepper seeds are the most important sources of essential nutrients such as protein, oil, nutritional fiber, and fat-soluble vitamins. They draw attention to their bioactive and functional components having antimicrobial, anti-cancerogenic, and antioxidant activities (Fıratlıgil-Durmuş, 2008). The tocopherol is responsible for reducing the levels of free radicals and preventing peroxidation reactions (Elisia et al., 2013; Baenas et al., 2019). And increasing the total tocopherol content of the oils helps to the enhancement of human health and oil quality. Chouaibi et al., (2019) also reported that red pepper seed oils are excellent sources of tocopherols such as α, β, γ, and δ. Yang et al., (2010) reported that it has a robust antioxidant mechanism with alpha-tocopherol and capsaicin contents. Also, polyphenols, phytosterols, and aromatic compounds are included in pepper seed oils as important bioactive compounds (Chouaibi et al., 2019). Polyphenols are natural antioxidants because they remove free radicals and play an essential role in the oxidative stability of unsaturated fatty acids (Harborne et al., 1999; Kamal-Eldin 2005). Red pepper seed oil is also rich in carotenoids, especially capsanthin, lutein, and beta-carotene (Konçsek et al., 2018). Carotenoids play an important role in reducing cancer and coronary heart diseases (Reische et al., 2002). It was stated that unsaturated fatty acids are abundant in red pepper seed oil and saturated fatty acids; mainly palmitic, stearic, and myristic acid are present in it (Perez-Galvez et al., 1999; El-Adawy & Taha 2001; Nehir-Demir, 2011; Konçsek et al., 2018). It is suitable for consumption as a food owing to its high oleic and linoleic acid content. This ingredient enables it to be used in the production of margarine, salad, and cooking oil due to its nutritional quality and health benefits (Jarret et al., 2013).

The conventional solvent extraction technique is one of the most widely used methods to extract oil from food. "Soxhlet" extraction is a conventional solvent extraction method that is time-consuming and requires excessive amounts of solvents. Also, these solvents used are toxic to environment and human health. Consumers have been choosing reliable, economical, and environmentally friendly products regarding food safety. Because of that, products are tried to be produced with a green approach (Farr & Proctor, 2014; Siger et al., 2015). The development of new alternative methods has become compulsory (Wang & Weller, 2006). Several new alternatives to conventional methods have been preferred for their advantages, such as high extraction efficiency, ease, short extraction time, reliability, and high-quality products, including cold pressing extraction, ultrasound-assisted extraction, microwave-assisted extraction, and supercritical extraction as the green extraction methods (Tiwari, 2015). These green extraction techniques offer some potential to minimize or eliminate the utilization of toxic solvents and to extract bioactive lipid-soluble compounds while developing a better-quality final product (Ramadan, 2020). Cold press oils are noteworthy in terms of health since it is possible to obtain edible quality oil without the need for refining processes (Moreau & Kamal-Erdin, 2009). Recently, cold-pressed oils have received attention due to their minor bioactive compounds as natural antioxidants and characteristic natural flavor (Bozdoğan-Konuşkan, 2020). In addition, using ultrasonics for oil extraction is preferred to new modern extraction methods due to the high capital investment and high energy consumption disadvantages of these new alternatives (Tiwari, 2015). Ultrasound-assisted extraction is one of the modern, non-thermally effective techniques to obtain bioactive components and oil from different sources. The ultrasonic application enables the transfer of the material by mechanically breaking the cell walls. The extraction process is faster than other extraction methods since the cell wall disappears in this way. Today, the application of ultrasound offers a choice for a solvent that may replace toxic solvents such as hexane, chloroform, diethyl ether, and petroleum ether with alternative solvents such as ethanol and ethyl acetate, which are a GRAS solvent with a green approach.

The study aimed to produce the oils from red pepper seeds by three green extraction techniques to examine the effect of the methods on the oil extraction yield and on the physical, chemical, and bioactive properties.

MATERIAL and METHOD

Materials

Red pepper (*Capsicum annum* L.) seeds as an industrial food waste were provided by MÜSAN Food Co. Ltd. (Kahramanmaraş, Turkey). The seeds were the post-production seeds of red pepper fruits harvested in the August-October harvest season for spicy red pepper products. The seeds were dried under the sun (moisture content ≤ 6%) within that season. The seeds were ground into a powder with an average particle size of 500 µm by an electrical grinder (model Scm 2934; Sinbo, İstanbul, Turkey). All reagents were provided by Merck (Darmstadt, Germany) and Sigma-Aldrich (St. Louis, ABD) and were of the analytical grade.

Method

First of all, the conditions for selecting the best solvent, temperature and time for the oil yield of the ultrasound assisted solvent extraction technique were determined. Then, the oil samples from the seed were obtained by using Ultrasound-assisted solvent extraction (UAE), solvent extraction (SE), and cold pressing techniques (CP).

Determination of UAE Conditions

The solvent extraction conditions were determined using an ultrasound-assisted solvent extraction technique in the ratio of 1:10 (solid: solvent; w/v). Ethanol, ethyl acetate, and hexane were used as the solvent, and an ultrasound bath (Jeiotech UC-10 brand with 40 kHz ultrasound frequency and max.300 W ultrasound power) was used for UAE. Distinct experiments were executed at 20, 40, and 60 °C of the temperatures for 20 and 40 minutes.

Ultrasound-Assisted Solvent Extraction (UAE)

The ground seeds were exposed to the ultrasound effect at high density by using the optimum conditions determined in the previous section. The supernatants were filtered, and the solvent in the extract phase was volatilized by a rotary evaporator (Hei-VAP Value model, Heidolph, Germany) under vacuum at 40 °C.

Solvent Extraction (SE)

The solvent extraction was the non-ultrasound-assisted conventional solvent extraction. It was performed using the same ultrasound bath Jeiotech UC-10 brand without ultrasonic vibrations. The extraction conditions were carried out using the same UAE procedure method.

Cold Press (CP)

The cold-pressed oil was obtained using a cold-pressing machine (model:6YL-68, Henan Double Elephants Machinery I/E Co., Ltd., China) at the range of 25-60 °C the machine operating temperatures. After the cold-pressing process, the extracted oil was passed through a cloth filter, and then the lipid fraction was centrifugated to purify from solid particles.

Analyses

Seed Analyses

The seed's moisture content (%) was determined gravimetrically according to the AOAC method (AOAC, 2000). The total crude oil and ash content were detected according to AOAC 935.47 method (AOAC, 1998) and the AOCS Ba 5a-49 method (AOCS, 1997a), respectively. Minolta Colorimeter (CR-400) was used to analyze the seeds' a*, b*, and L values. The thickness and diameter of the seeds were investigated by a digital caliper (Asimeto). The weight of 1000 seeds was determined by measuring the weight of 100 seeds (Yılmaz et al., 2015).

Seed Oil Analyses

Oil extraction yields were calculated according to Equation (1).

$$\text{oil yield } \% = [(\text{weight of oil (g)})/(\text{weight of seed (g)})] \times 100 \quad (1)$$

Free fatty acidity (as % oleic acid), peroxide value, and conjugated diene-triene values of the oil samples were measured by AOCS Ca 5a-40 method (AOCS, 1997b), AOCS Cd 8-53 method (AOCS, 1984), and AOCS Ch 5-91 method (AOCS, 1989), respectively. Instrumental color values of the oils were obtained using a Minolta CR-400 colorimeter with CIE Hunter color measurement systems. The refractive index was analyzed with a desktop Abbe refractometer (Atago Refractometer, Tokyo, Japan) at 20°C.

Fatty acid composition

Methyl esters of the fatty acids were prepared using AOCS Ce 1j-07 (AOCS, 2007) and AOAC 996.06 (AOAC, 2005) methods. The fatty acid composition of the oil samples was determined with a Gas Chromatograph (Shimadzu GC-2025) equipped with an Rt-2560 capillary column (100m 0.25mm ID with 0.2 µm film thickness).

Total phenolic content

Determination of the total phenol contents (TPC) of seed oils was spectrophotometrically carried out by measuring the absorbance at 760 nm with the Folin-Ciocalteu reagent. TPC was expressed as mg of gallic acid (GAE) per kg seed oil (Kozlowska et al., 2016).

Antioxidant activity

The percent of inhibition was calculated by the DPPH (2, 2-diphenyl-1-picrylhydrazyl) radical scavenging procedure with some modifications based on the method of Brand-Williams et al., (1995). The antioxidant activity was determined as the percent of inhibition by using Equation (2);

$$\% \text{ Inhibition}=\left[1-\left(\frac{A_{sample}}{A_{control}}\right)\right]x100 \qquad (2)$$

Total carotenoid content

UV-1800 model-vis spectrophotometer (Shimadzu, Kyoto, Japan) was used to measure total carotenoid content according to the method described by Guizhen et al., (2007). Total carotenoid content was calculated according to Equation (3).

$$\text{Total carotenoid content (mg kg}^{-1}\text{)}=\frac{Ay\text{ (ml)}\times 10^6}{A^{\%}\text{(cm)}\times 1000\text{ g}} \qquad (3)$$

where A is the absorbance (at 445 nm), y is the extracting solution quantity (ml), g is the sample weight, $A^{\%}$ cm is the carotenoid molecule's average absorption coefficient 2500.

Total tocopherol content

Total tocopherol analysis was performed by determining the absorbance at 520 nm in UV–vis spectrophotometer of the reaction of iron (II), which is formed because of oxidation of ethanol with iron (III) chloride, with 2-2 dipyridyl (Wong et al., 1988). The outcomes were given as mg tocopherol kg^{-1} oil.

Statistical Analysis

The results were given as the mean ± standard error. Statistical significance was admitted at a level of P<0.05. The data were statistically analyzed by a three-way analysis of variance (ANOVA). Duncan tests for solvent-temperature interactions and independent student-T tests for the times were used to compare means (SPSS v.23, IBM, USA).

DISCUSSION

The results of the physical and compositional properties of red pepper seeds are shown in Table 1. The main characteristics of seeds are by the data for the capia pepper seeds reported by Arsunar (2014), except for crude oil content. The crude oil, moisture, and total ash values of the seeds were close to those observed by Chouaibi et al., (2019) and Zou et al., (2015). Especially the oil content in the seed was 20.58%, which was higher than in a *Capsicum frutescens* variety red pepper seed (19.32%) (Fıratlıgil-Durmuş, 2008) and *Capsicum annum* red pepper seed (11.04%) (Azabou et al., 2017), but lower than that in paprika variety seed (25.61%) (El-Adawy & Taha, 2001). Variations in properties may be due to the differences in origin, variety, harvesting time, and growing conditions of the seeds.

Table 1 The physicochemical properties of red pepper seeds

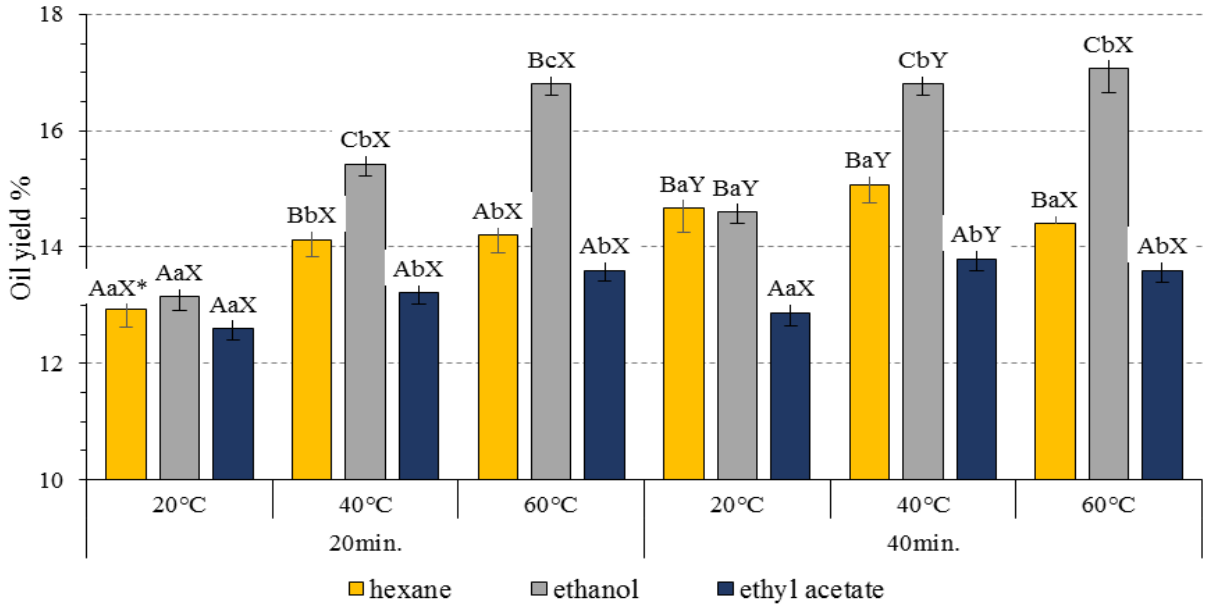
Tablo 1. Kırmızı biber çekirdeklerinin fizikokimyasal özellikleri

Properties	Seed
Moisture (%)	5.57±0.03
Total ash (%)	3.06±0.02
Crude oil (%)	20.58±0.13
1000-Seed weight (g)	5.69±0.08
Color	
L	53.71±1.20
a*	10.09±0.27
b*	26.52±0.26
Particle size (mm)	
Diameter	3.26±0.16
Thickness	0.74±0.03

Ethanol and ethyl acetate as green alternatives to hexane were used in ultrasound-assisted solvent extractions (UAE) to determinate solvent extraction conditions. The oil yields are presented in Fig. 1. The oil yields were 12.6-16.8% for 20 min of extraction time and 12.9-17.1% for 40 min. The triplet interaction among the time-solvent temperature was statistically not significant (P>0.05), but the double interactions were very significant (P<0.05). There is no difference between the oil yields of solvents at 20 °C for 20 minutes in the time-temperature relationship. The best yield in this period was observed in ethanol solution at 40 °C. Likewise, the ethanol solution at 40 °C for 40 minutes gave the best yield. There was no difference between the times at temperatures at 60 °C as comparing the times in the solvent-temperature relationship. Differences were found between all the oil yields at 40 °C and the others except the ethyl acetate solvent at 20 °C. It was determined no difference in the yields of 40th minutes of hexane and ethyl acetate solvents as the temperatures in the solvent-time relationship were evaluated. Thus, ethanol was selected as solvent at the extraction conditions of a ratio of 1:10 (w/v), the temperature of 40 °C, and times of 40 minutes.

The previous studies related to solvent extraction support the present data. Ethanol can be used as an alternative solvent for red pepper seeds instead of hexane, commonly used to obtain oil from seeds. It was reported that using green solvents such as ethanol may compete favorably with usual organic solvents and maximize the oil yield from *Echium* seeds. The cavitation effects occur due to different temperatures and pressures during UAE, depending on the used solvent. This situation results in different fat contents being released into the medium because of varying cell wall disruption levels and mass transfer rates. Also, it was stated that a low temperature, like 40 °C and a short time like, 40 minutes, optimum extraction conditions to obtain high oil yield by avoiding oxidation of fatty acids (Tian et al., 2013; Samaram et al., 2015; Sicaire et al., 2016; Xu et al., 2016; Castejón, 2018).

The physicochemical properties of the red pepper seed oils extracted by CP, UAE, and SE methods are presented in Table 2.



*The same letters on the bars include statistically the similarity at the level of 5% (the series 'A-C' for the differences among the solvents at the similiar time and the same temperatures, series 'a-c' for the differences among the temperatures for each solvent at the same time, and series 'X-Y' for the differences

Figure 1. Oil yield from ultrasound-assisted extraction at different times, temperatures, and solvents
Şekil 1. Farklı çözücü, sıcaklık ve sürelerde uygulanan ultrason-destekli ekstraksiyonu yağ verimleri

Table 2. Physicochemical properties of red pepper seed oils
Tablo 2. Kırmızı biber çekirdek yağlarının fizikokimyasal özellikleri

Property	CP	UAE	SE
Oil Yield (%)	11.32±0.07^{c}	16.80±0.12^{a}	14.50±0.17^{b}
Refractive Index (20°C)	1.4765±0.0001^{a}	1.4747±0.0001^{c}	1.4757±0.000^{b}
Free Fatty Acidity (% oleic acid)	3.97±0.05^{c}	6.25±0.21^{b}	8.59±0.12^{a}
Peroxide Value (meq O_2 kg^{-1} oil)	8.33±0.33^{b}	9.83±0.33^{a}	6.67±0.33^{c}
Color			
L	23.96±0.00^{b}	24.39±0.01^{a}	22.56±0.00^{c}
a*	9.00±0.03^{b}	10.66±0.01^{a}	8.76±0.03^{c}
b*	7.52±0.01^{b}	8.79±0.02^{a}	6.42±0.03^{c}
Conjugated Diene Value (K_{232})	7.69±0.03^{b}	8.63±0.02^{a}	7.07±0.03^{c}
Conjugated Triene Value (K_{270})	1.92±0.04^{c}	3.36±0.04^{a}	2.41±0.03^{b}

^{a,b,c} Values within a row with different superscripts differ significantly at P<0.05.

There are not enough similar studies to compare the data about UAE oil extraction for all the mentioned analyses. The ultrasonic procedure provides easy transfer of the oil out of the cell by mechanically breaking the cell walls, which is the leading oil extraction hurdle by pressing from oilseeds and increasing efficiency. Thus, oil extraction was faster than other methods with ultrasound applications. Higher oil yield was obtained with ultrasound application from chia seeds compared to the extraction procedure without ultrasound in a study by De Mello et al., (2015). Additionally, the results obtained in the present study based on the effect of extraction methods on oil yield agree with the results by Li et al., (2015), Sicaire et al., (2016), and Moradi et al., (2018).

The free fatty acidity values of the oil samples varied between 3.97% and 8.59%, and the free fatty acid content of the cold press extracted seed oil was lower than the values reported by other methods ($P<0.05$). This is thought to be due to the polarity of the solvent used in solvent extractions. According to the determined results, the free fatty acidity value of cold extracted seed oil was like the one found by Yılmaz et al., (2015) but higher than those reported by Chouaibi et al., (2019) and Domokos et al., (1993). The results for solvent extractions were higher than those obtained by El-Adawy and Taha (2001) and show like results obtained by Jarret et al., (2013).

The refractive index (20 °C) value for CP (1.4765) was significantly higher than those obtained by UAE (1.4747) and SE (1.4757) ($P<0.05$). A study by Shahidi (2005) suggested that the refractive index values of oils are varied depending on the degree of unsaturation, molecular weight, chain length of the fatty acids, and degree of conjugation. The refractive index value of CP oil in the present study was higher than that obtained by Chouaibi et al., (2019) and Arsunar (2014). It was observed that the refractive index values were slightly lower than the values obtained in the present study comparing the study with pepper seed oil by Ma et al., (2019).

Peroxide value (PV) is one of the main quality criteria of oils (Codex Alimentarius Commission, 1982). It is due to the concentration of peroxides and hydroperoxides that occurred in the initial phase of lipid oxidation (Zhang et al., 2010). PV of the oil samples ranged from 6.67 to 9.83 meq O_2 kg^{-1} oil. The peroxide values of CP and SE oils were significantly lower than that of UAE-extracted oil ($P<0.05$). The formations of primary oxidation products (conjugated diene, peroxide) increase in oils as the intensity of ultrasound increases (Hosseini et al., 2015). The results were within the average values defined by the Food Standards Commission for vegetable oils; that is, peroxide values of the oil samples did not exceed 15 meq O_2 kg^{-1} oil limitation (Turkish Food Codex 2012).

The UAE oil had higher L*, a*, and b* values. A significant difference in luminosity was determined in the samples ($P<0.05$). L*, a*, and b* values of the SE oil were lower than that of the oils extracted by other methods. The results showed that the UAE was darker-colored and had more redness-yellowness than the other oils. That darker color may be related to Maillard's reactions. This result was in agreement with the report of Hosseini et al., (2015).

The oxidative degradation level in oils can be determined more effectively by measuring the conjugated diene (K_{232}) and triene (K_{270}) formation together with the peroxide value (Kıralan & Kıralan 2017). The conjugated diene (CD) values of the oil samples ranged from 7.07 to 8.63, and also the conjugated triene (CT) values ranged from 1.92 to 3.36. Other oils extracted were significantly lower than UAE oil's CD and CT values ($P<0.05$). There are no studies about CD and CT values of CP and UAE oil. The results obtained from SE were higher than that of solvent extraction with hexane by Azabou et al., (2017). These high values indicate that *C. annum* seed oil contains high amounts of primary and secondary oxidation products, such as hydroperoxides and aldehydic carbonyl components (Azabou et al., 2017). There was a good correspondence between these results and the findings of Hosseini et al., (2015), who studied the effect of ultrasound on the physicochemical properties of some edible oils. Similarly, Hosseini et al., (2015) found that the UAE increased CD and CT values compared to the control methods. These results demonstrated that as the intensity of ultrasound, the formation of primary oxidation products (peroxides and conjugated dienes) increases, and the ultrasound (cavitation phenomenon) causes the rapid increase of primary oxidation of edible oils.

The fatty acid compositions of the oils extracted by CP, UAE, and SE techniques are presented in Table 3.

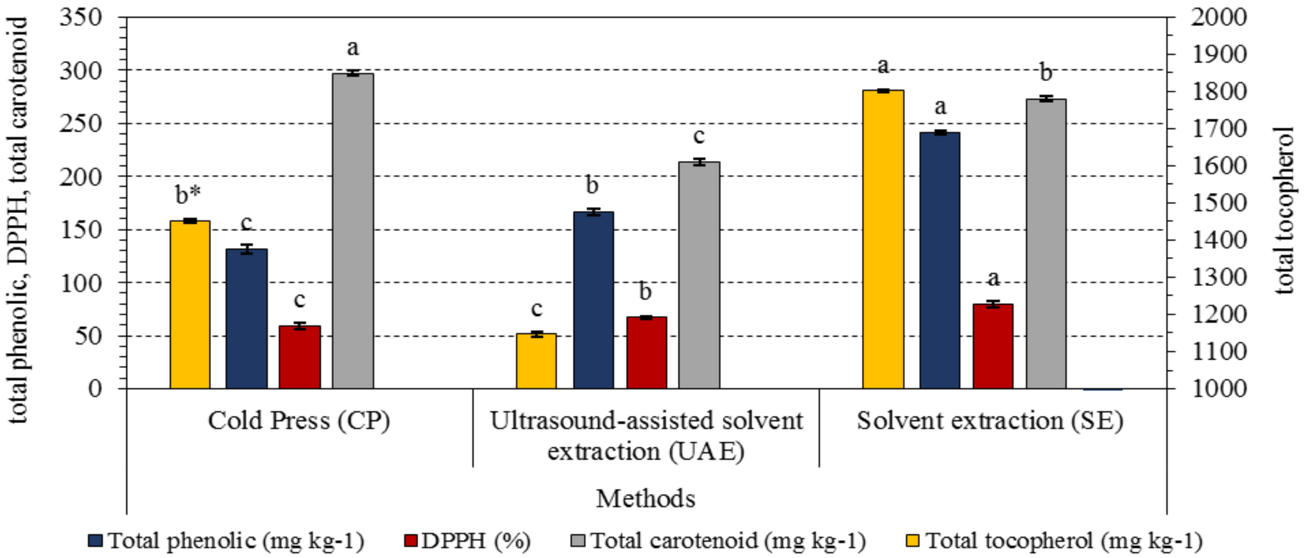
While the predominant unsaturated fatty acids of all samples were oleic and linoleic acid, the predominant saturated fatty acids were stearic and palmitic acid. The linoleic acid contents were determined to be 72.194, 72.052, and 71.826% for SE, CP, and UAE oils, respectively. The oleic acid contents were found to be 11.840, 11.808, and 11.670% for SE, UAE, and CP oils, respectively. Alfa-linolenic acid ($C_{18:3\ n\text{-}3}$), palmitoleic acid ($C_{16:1}$), arachidic acid ($C_{20:0}$), myristic acid ($C_{14:0}$), cis-11-eicosenoic ($C_{20:2}$), lignoceric ($C_{24:0}$), and behenic ($C_{22:0}$) acids were present in minor amounts. Nevertheless, there are no significant differences between extraction techniques applied to the oils in terms of prominent fatty acids (linoleic and palmitic acid) and also cis-11-eicosenoic acid content ($P>0.05$). The differences in the composition and ratio of fatty acids may be related to the affinity of the fatty acids to the solvent and the solubility. Solubility may depend on different concentration ranges, extraction temperature, and pressure. When compared with these studies reported for the samples, it was observed that the palmitic, linoleic acid, linolenic, stearic, and oleic acid content was in the range of 11.08-13.84%, 67.77-80%, 0.278-0.380%, 2.71-3.40% and 7.90-14.56%, respectively. The results obtained from the present study are in agreement with those reported by Domokos et al., (1993), Pérez-Gálvez et al., (1999), El-Adawy and Taha (2001), Fıratlıgil-

Durmuş (2008), Matthaus and Özcan (2009), Li et al., (2011), Embaby and Mokhtar (2011), Arsunar (2014), Konçsek et al., (2018), Azabou et al., (2017), Chouaibi et al., (2019), Ma et al., (2019).

Table 3. The fatty acid compositions of red pepper seed oils (%)
Tablo 3. Kırmızı biber çekirdek yağlarının yağ asit kompozisyonları (%)

Fatty acid	CP	UAE	SE
Myristic acid ($C_{14:0}$)	0.238±0.002^{a}	0.223±0.005^{b}	0.196±0.000^{c}
Palmitic acid ($C_{16:0}$)	11.290±0.040	11.702±0.211	11.290±0.004
Palmitoleic acid ($C_{16:1}$)	0.203±0.002^{b}	0.273±0.031^{a}	0.213±0.001^{ab}
Stearic acid ($C_{18:0}$)	3.211±0.029^{a}	3.026±0.009^{c}	3.115±0.020^{b}
Oleic acid ($C_{18:1n9c}$)	11.670±0.045^{b}	11.808±0.021^{a}	11.840±0.044^{a}
Linoleic acid ($C_{18:2n6c}$)	72.052±0.037	71.826±0.200	72.194±0.075
Arachidic acid ($C_{20:0}$)	0.324±0.003^{a}	0.281±0.002^{c}	0.291±0.001^{b}
cis-11-eicosenoic ($C_{20:2}$)	0.132±0.001	0.137±0.007	0.133±0.002
α-Linolenic acid ($C_{18:3n3}$)	0.344±0.003^{a}	0.297±0.000^{b}	0.285±0.000^{c}
Behenic acid ($C_{22:0}$)	0.232±0.002^{a}	0.189±0.003^{c}	0.199±0.001^{b}
Lignoceric acid ($C_{24:0}$)	0.304±0.003^{a}	0.238±0.006^{b}	0.244±0.010^{b}

^{a,b,c} Values within a row with different superscripts differ significantly at P<0.05.



*The same letters on the bars include statistically the similarity among the extraction methods at the level of

Figure 2. The total phenolic content, DPPH%, total carotenoid content, and total tocopherol content of the oils
Şekil 2. Yağların toplam fenollik içeriği, %DPPH, toplam karotenoid ve toplam tokoferol içerikleri

It was shown that the total phenolic content (TPC), antioxidant activities (DPPH%), total carotenoid content (TCC), and total tocopherol content (TTC) of the oil samples are in Figure 2. TPC ranged from 131.8 to 241.1 mg kg^{-1} of oil (P<0.05). SE oil included excellent amounts of total phenolics, followed in decreased order by UAE and CP oils. The results show that the CP technique is unsuitable for producing an oil rich in total phenol. The reason is the inability of polyphenols to leak from the cell wall, as the pressure can sometimes be applied irregularly in cold pressing. However, it was observed that the application of ultrasound caused a statistically significant decrease in the phenolic content of the seed oil (P<0.05). Polyphenol content positively affects oxidative stability, nutrition, and health. The amount and types of phenolic substances contained in edible oils may alter depending on many factors, such as seed type, growing conditions, climate, processing, or extraction techniques. The TPC of the samples was higher than those reported by Chouaibi et al., (2019) but agree with those obtained by Jimenez et al., (2007). Already, Jimenez et al., (2007) reported that ultrasound assessment had a significant effect on polyphenols, which can lead to a decrease in TPC.

The samples's equivalent radical scavenging activities

(DPPH%) ranged from 59.04 to 79.84%. The antioxidant capacity was observed at the highest level in SE oil and the lowest level in CP oil ($P<0.05$). Red pepper seed oil has a high antioxidant capacity due to its high content of vitamin E, polyphenols, and unsaturated fatty acids; mainly phenolic and tocopherol components are the most effective antioxidants (Fazel et al., 2008). There is a positive correlation between the samples' DPPH % and TPC values. Ma et al., (2019), Zhong et al., (2018), and Delfan-Hosseini et al., (2017) also reported similar results.

TCC of the CP, SE, and UAE oils were 296.80, 272.67, and 213.73 mg kg^{-1} oil, respectively. The techniques have statistically significant effects on the carotenoid content of the extracted oils ($P<0.05$). The variety of seeds, cultivation conditions, seasonal factors, extraction techniques, and these factors' interactions significantly affect the carotenoid content of oil. Further, it is thought that thermal-sonication applications decrease carotenoid content due to causing for destroying some carotenoid compounds (Konçsek et al., 2018). While there is not any study related to the carotenoid content of SE and UAE oils, the findings for CP oil are lower than that obtained by Domokos et al., (1993) and Konçsek et al., (2018) and higher than the results of Chouaibi et al., (2019).

The extraction techniques significantly affected the tocopherol contents ($P<0.05$). TTC of the oils were 1450.2, 1146.8, and 1801.2 mg kg^{-1} oil for CP, UAE, and SE, respectively. These results showed that tocopherols are more extractable by chemical techniques using organic solvents. In general, it has been observed that ultrasound application affects and causes statistically a decrease in the total tocopherol content ($P<0.05$). This situation may come from the increased temperature during the ultrasound application. TTC of CP oil sample was significantly higher than that reported by Domokos et al., (1993), Konçsek et al., (2018), Chouaibi et al., (2019), but was lower than that found by Arsunar (2014).

CONCLUSION

This study examined oil extraction efficiency from red pepper seed assisted by ultrasound, ethanol solvent, and cold-pressing as green techniques. The results revealed that red pepper seeds might be an excellent potential food source thanks to their valuable content and chemical, biological and ecological importance. So, there more studies are needed for their functional properties. It has been observed that the applied techniques provide different advantages in terms of oil yield and quality parameters. By ultrasound-assisted solvent extraction, a modern non-thermal procedure, it was possible to obtain maximum yield oil. It was concluded that the solvent extraction method is more effective producing oils by preserving their bioactive components and that it is preferable to obtain red pepper seed oil. The use of toxic solvents was eliminated by these green extraction techniques applied in this study, and better-quality seed oils were produced with a green approach regarding food safety. Although one of the most widely used methods for obtaining edible quality vegetable oils is the cold pressing method, this method yields oil with low efficiency. Research on the discovery of new resources needed by the food industry and efficient use of available resources should be increased. At this point, industrial waste products have been evaluated with this study, and necessary steps have been taken.

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Contribution of the Authors as Summary

The consultancy of this study was carried out by ALI, and the planning was carried out by ALI and ABA. Laboratory analyzes of the study were done by ABA. The authors contributed to the article writing and ALI reviewed and approved the final version.

Statement of Conflict of Interest

Authors have declared no conflict of interest.

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