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Obtaining valuable components from various citrus product wastes by different extraction methods

D. Uygunöz, G. Çifçi, Ö. Ozan Demirci, E. Möröydor Derun*

Department of Chemical Engineering, Yildiz Technical University, 34210, Istanbul, Türkiye,

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This study aimed to obtain valuable components from various citrus product wastes using conventional and ultrasonic-assisted extractions. Wastes obtained from orange, mandarin, and lemon fruits, the three most commonly grown citrus fruits in Türkiye and around the world, were used as raw material sources [1]. Green extraction techniques stand out with features such as higher efficiency, shorter time requirement, and lower cost when compared to traditional extraction techniques [2]. By comparing extraction techniques, multifaceted comparisons were made between the citrus types used as raw materials and the properties of the valuable components to be obtained. The valuable components targeted to be extracted from citrus fruits were determined as pectin and hesperidin, considering their industrial usage areas [3]. Citrus fruit wastes were dried, and the moisture content of each citrus species was determined, then the citrus species were extracted by using conventional and ultrasonic-assisted extraction methods. Extracts were characterized by using Fourier transform infrared spectrometry (FTIR), ultraviolet-visible spectrometry (UV-VIS) and liquid chromatography-mass spectrometry (LC-MS) analyses. According to UV-Vis analysis, the band covering the range of 240–280 nm (max absorbance around 255–265 nm) was attributed to the A–C benzoyl system, confirming the flavonoid structure. All extracts showed similar peaks in FTIR analysis [4]. Hesperidin content of the optimized mandarin extract determined by LC-MS analysis was 430.2 $mg.L^{-1}$. It is envisaged that the extracted valuable components will be used in various industrial areas. In the future, it is aimed to add the bioactive component data obtained as extracts to the literature.

Keywords: Citrus waste; extraction; bioactive component; quantitative analysis

INTRODUCTION

Citrus fruits, known as the *Rutaceae* family, are a fruit family with an annual production exceeding 130 million tons as of 2015. Citrus fruits are crucial for Turkish agriculture, particularly in the Mediterranean region. Around 2168,000 tons of citrus fruits are produced annually, with oranges, tangerines, and lemons being the main varieties. Around 20% of the citrus plants are used for industrial purposes, generating significant waste. The most cultivated citrus species are orange, tangerine, lime, lemon, grapefruit, citrus and bergamot [5].

The peel parts of citrus products, which are produced because of their consumption and use in industrial processes and are called waste, have a high content of valuable components. The by-products can be utilized for livestock feed, biofuel production, and for the extraction of pectin, phenolic compounds, and essential oils. With the extraction applied on citrus waste, it is aimed to prevent the loss of high amounts of valuable components. Examples of components found in citrus fruits include ascorbic acid compounds, carotenoids, essential oils, antioxidants, sugars, flavonoids, dietary fibers, polyphenols, and minor elements. Waste and by-products obtained from citrus fruits contain significant amounts of valuable compounds and offer various opportunities in technological and health-promoting areas. Citrus by-products contain several biologically active compounds (BACs), including polyphenols, carotenoids, and essential oils. Among these, polyphenols and carotenoids are known for numerous health benefits, mostly due to their antioxidant properties. These utilizations of citrus wastes not only help reduce waste but also create value-added products, contributing to the sustainability and economic viability of the citrus processing industry [6, 7]. The economic loss and environmental damage factors that will occur because of the disposal of raw materials that are not subject to extraction, have been reduced.

Citrus waste has become quite useful in various industries, especially in medicine, cosmetics, and food, due to the abundant supply of valuable components [8]. Pectin and hesperidin are important components found in citrus fruits. Pectin is widely used as a gelling agent, emulsifier, stabilizer, thickener and heavy metal adsorbent in food, medicine, cosmetics and other industries. Hesperidin is a flavanone glycoside found abundantly in citrus fruits. It has antioxidant activity and plays an important role in the pharmaceutical

* To whom all correspondence should be sent: moroydor@yildiz.edu.tr

industry, which is one of the factors of significance in obtaining these bioactive components [9, 10].

In a study conducted by Du *et al*. (2024), it is aimed to provide a non-thermal approach to obtain pectin from citrus plants with high-intensity pulsed electric field (HIPEF) which features remarkable efficiency and low energy usage. The process analysis performed with ion chromatography, high-performance liquid chromatography, Fourier-transform infrared spectroscopy, proton nuclear magnetic resonance spectroscopy, and rheology. Comparisons were made on two processes for producing pectins; a high-intensity pulsed electric field (HIPEF) pretreatment of citrus peel powder followed by a milder acidic extraction (pH 2, heating at 70 °C for 1 h; pectin termed HIPEF-CP), and a conventional direct hot-acid extraction (pH 2, heating at 90 °C for 2 h; pectin termed CP). The HPIEF with assisted acidic extraction was compared with the acidic extraction method. As a result, it is stated that the amount of antioxidant, emulsifying and emulsion-stabilizing abilities of HIPEF-CP are better than those of CP [11]. In another study by Panwar *et al.* (2023), it is aimed to extract pectin from the peels derived from *citrus limetta* by adopting a process known as ultrasonic-aided extraction (UAE). The utilization of the design of Box-Behnken improved the process, resulting in a maximum pectin yield of 28.82%. The UAEP exhibited superior antioxidant activity and demonstrated comparable water/oil retention capabilities and emulsifying qualities when compared to commercially available pectin. Under ideal conditions, the Box-Behnken design yielded a maximum extraction of 28.73 ± 0.12%. The pectin that was obtained had a high degree of esterification, and it exhibited superior antioxidant and thermal characteristics compared to commercially available pectin. The morphological analysis identified variations on the surface, which enhanced the extraction process [12]. Zhang *et al.,* (2023) conducted a study to examine the characteristics of *citrus maxima* (also known as pomelo fruit) flowers (FCM) and explore potential applications for FCM due to its high concentration of valuable elements such as phenolic compounds, flavonoids, naringin, and hesperidin. The study focused on investigating the qualities of FCM tea by utilizing ultrasonic-assisted extraction and hot water to extract bioactive components. In addition, ethanol extraction was performed to assess the fat-soluble and volatile compounds. The determination process is held by GC-MS technique. In addition, especially for valuable compounds of hesperidin and naringin, solutions are prepared using methanol as a solvent. The results prove that there are 88 compounds obtained in FCM. It is stated that by the help of ultrasonic-aided extraction technique, *citrus maxima* by-products are significant sources for obtaining beneficial elements due to plants' rich components [13].

In this study, it is aimed to compare the extraction processes of different citrus species (orange, mandarin, lemon) waste grown in the Mediterranean region with ultrasound-assisted extraction and traditional extraction methods and to obtain pectin and hesperidin components considering their usage areas in the chemical industry. Within the scope of the study, wastes of orange, mandarin and lemon fruits were extracted by ultrasound-assisted extraction, sequential extraction and conventional extraction methods. The chemical properties of the bioactive components in the extracts were characterized by Fourier transform infrared spectrometry (FTIR) and ultraviolet-visible spectrometry (UV-VIS) analyses.

EXPERIMENTAL

Materials

The raw materials used in the study, citrus fruits (lemon, mandarin, orange), were supplied from the Mediterranean region of Türkiye. Acetone, citric acid and ethanol were used as solvents in the experimental study. Acetone was supplied as 99.5% extra pure acetone from Tekkim Company (product number TK.010050.02501). Citric acid and ethanol were both supplied from Merck Company as citric acid monohydrate (CAS Number: 5949-29-1) and ethanol (CAS Number: 64-17-5). Magnetic stirrer (Wisestir) was used for mixing and shaking processes and an oven (Ecocell 111, Germany) was used for drying processes. Weighing processes were carried out with an analytical balance (Weightlab Instruments). Ultrasonic-assisted extraction was carried out with ultrasonic bath (Isolab, Germany).

Pretreatment and humidity analysis of citrus waste

The peels of orange, mandarin and lemon fruits, supplied from the Mediterranean region, were separated, washed with tap water, then with distilled water. Peels were cut to 1×1 cm size and dried at 60°C, 24 h. After the drying process, peels were weighed, then grinded and sieved to a particle size of 180 µm. Sieved samples were weighed and the amount of moisture in the peels for the dry weights of citrus fruits were calculated using equation (1). Then, the samples were kept in a desiccator for later use.

$$Humidity\ ratio = \frac{Wet\ Weight - Dry\ Weight}{Wet\ Weight} \times 100 \quad (1)$$

Extraction of citrus waste

The conventional extraction process was carried out with the ratios of citrus peel to solvent as 0.05 g/mL, 0.1 g/mL, 2 g/mL and 0.4 g/mL for each species. The determined ratios of citrus peel and acetone:water solution were mixed in a magnetic stirrer at 40 °C for 30 min. The extracts obtained after the mixing process were filtered using filter paper. The filtered extracts were stored at +4 °C to analyze the bioactive components [14].

The ultrasound-assisted extraction process was carried out using an ultrasonic water bath operating at 60 kHz frequency and 40 °C temperature. 50 vol% acetone-water solution was used as the solvent. For sample preparation, proportions of 0.05 g, 0.1 g, 0.25 g and 0.5 g of ground citrus peel samples per 10 mL of solvent were combined in glass vials. Then, the samples were left in the ultrasonic water bath for 30 min [14]. The extracts were filtered and then stored at 4°C for the analysis of bioactive components.

For the sequential extraction process that is studied and reported previously by Zhou *et al.*, (2022), 5% citric acid-water solution was used as the solvent. The samples to be used in this process were combined at a 1:15 (g/mL) sample-solvent ratio. Then, the prepared samples were mixed in a magnetic stirrer at 90°C for 100 min. The liquid (filtrate) and solid (extract) phases of the extracts obtained from the mixing process were filtered. The separated liquid phase (filtrate) was centrifuged at 4000 rpm for 4 min. The supernatant was mixed with an equal volume of 99.5% ethanol and left to coagulate for 2 h. Then, the supernatant-ethanol mixtures were centrifuged at 4000 rpm for 4 min. The produced pectin samples were rinsed three times with 99.5% ethanol to form wet pectin. The remaining solid component (extract) was combined with 3% (aq.) NaOH solution at a ratio of 1:8 (g/mL) and subjected to extraction at 60°C for 90 min. After this process, the mixture was brought to ambient temperature and vacuum filtered. The pH of the filtrate was adjusted to 4.0 using 50% HCl solution and allowed to settle for 2 h. Hesperidin was isolated by centrifugation at 4000 rpm for 4 min followed by three consecutive water washings. Wet hesperidin was obtained at the end of this procedure. As a final step, wet hesperidin and pectin were dried until constant weight. Pectin and hesperidin yields were determined using equations (2) and (3), respectively.

$$PEV(\%) = \frac{P}{m} \times 100 \quad (2)$$

$$HEV(\%) = \frac{H}{m} \times 100 \quad (3)$$

where PEV and HEV are the pectin and hesperidin yield, respectively, P is the weight of dried pectin in g, H is the weight of dried hesperidin in g, and m is the amount of dried citrus powder [15].

Characterization

For the analysis of valuable bioactive components, UV-Vis spectrophotometry, FTIR spectroscopy and LC-MS analyses were used.

The phenolic compound content of the extracted samples after the conventional and ultrasonic-assisted extraction processes was qualitatively analyzed by UV-Vis spectrophotometry. This was performed as a first step before further analysis to see if phenolic compounds were extracted from the samples. Samples containing 0.05 g/mL of grinded citrus peel sample-solvent from all 3 species were used for the extract analysis obtained by the conventional method, while samples containing 0.5 g/mL of grinded citrus peel sample-solvent from all 3 species were used for the extract analysis obtained by the ultrasonic-assisted extraction method. 0.1 mL of extracts were mixed with the extraction solvent to make a 5 mL solution. The absorbance of this solution was measured in the wavelength range of 190-1100 nm [16].

FTIR analysis was performed to analyze the functional structures of bioactive components (hesperidin and pectin) found in citrus extracts. The analysis was carried out in the wavelength range of 4000–450 cm^{-1} with ATR technique [17].

LC-MS was used to determine the hesperidin content in the liquid extract. The mandarin extract obtained by ultrasound-assisted extraction was analyzed using an Agilent 6530 LC MS-QTOF system. A standard hesperidin sample was employed, and single mass spectrometry operating in negative mode was used to achieve the quantitative determination.

RESULTS AND DISCUSSION

Humidity ratio results

Humidity ratios of grinded citrus samples were calculated based on equation (1) and are given in Table 1. Humidity ratios of each citrus species were similar and around 74-75%. Mandarin has the highest humidity ratio of 75.5% which may due to its thin peel structure that retains more moisture.

Table 1. Humidity calculations of grinded citrus samples

Sample	Wet weight (g)	Dry weight (g)	Humidity ratio (%)
Lemon	97.4470	25.3360	74.00
Mandarin	114.7380	30.1140	75.50
Orange	266.0710	69.4380	74.00

Humidity ratio results of the produced pectin samples from each citrus species after sequential extraction are presented in Table 2. Humidity ratios of pectin from orange (65.29%) and from mandarin (62.17%) were much higher than that of lemon (26.80%). This difference may be caused by the difference between the chemical compositions of citrus species and peel structures that effect the pectin content.

Table 2. Humidity ratios of pectin samples according to citrus fruits

Sample	Wet weight (g)	Dry weight (g)	Humidity ratio (%)
Lemon	0.7515	0.5517	26.80
Mandarin	3.0500	1.1539	62.17
Orange	5.4422	1.8885	65.29

Humidity ratio results of produced hesperidin samples from each citrus species after sequential extraction are presented in Table 3. Hesperidin products revealed similar humidity ratio varying between 93-98%.

Table 3. Humidity ratios of hesperidin samples according to citrus fruits

Sample	Wet weight (g)	Dry weight (g)	Humidity ratio (%)
Lemon	1.7305	0.0660	96.19
Mandarin	0.8579	0.0600	93.01
Orange	1.1582	0.0250	97.84

Pectin and hesperidin yields of products obtained from sequential extraction are presented in Table 4. Lemon yielded the highest hesperidin as 3.30% while mandarin yielded the highest pectin as 94.625%. Panwar *et al.* (2023) reported a yield of pectin 28.82% using UAE from *citrus limetta* peels [12]. Gu *et al.* (2016) reported a yield of 0.48 ± 0.02 mg/g hesperidin using ionic liquid vacuum microwave-assisted method from *Sorbus tianschanica* leaves [18]. Karbuz &Tugrul (2021) found pectin yield for lemon between 5.97-10.11% and for mandarin between 5.72-11.29% which were obtained *via* ultrasonic-assisted extraction [19].

Table 4. Yields for pectin and hesperidin according to citrus fruits

Sample	Pectin yield (%)	Hesperidin yield (%)
Lemon	27.585	3.30
Orange	57.695	1.25
Mandarin	94.625	3.00

UV-Vis spectrophotometric results

Wavelength/absorbance graphs were plotted as a result of UV/Vis spectrophotometric analyses of citrus extracts obtained from conventional and ultrasonic-assisted extraction processes. UV/Vis graphs of extracted samples of orange (C-O), mandarin (C-M) and lemon (C-L) from conventional extraction are presented in Figure 1. UV/Vis graphs of extracted samples of orange (US-O), mandarin (US-M) and lemon (US-L) from ultrasonic-assisted extraction are presented in Figure 2.

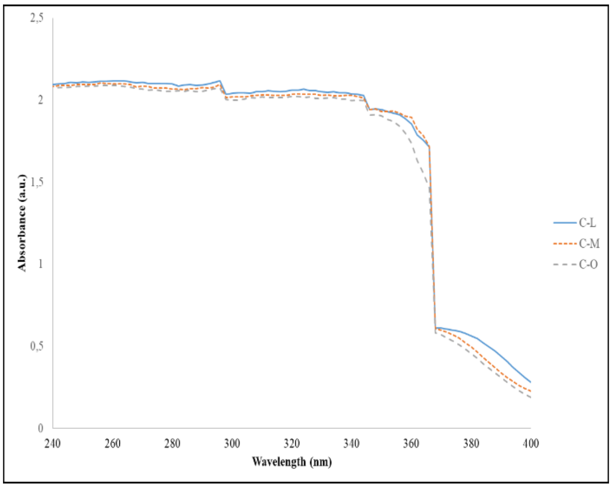

Figure 1. UV-Vis analysis of extracted samples from conventional extraction; C-L for lemon, C-M for mandarin, C-O for orange extract.

As a result of the UV-Vis analyses, the peak wavelength range giving the highest absorbance for all 3 citrus types in extracts obtained by conventional extraction method was observed as 280-290 nm. This range was determined as 290-300 nm wavelength for ultrasonic assisted extraction. Band, covering the range of 240–280 nm (max absorbance around 255–265 nm) attributed to the A–C benzoyl system confirming the flavonoid structure [4].

There is a direct proportion between this absorbance amount and the molecular bonds that the components have. In other words, as the weak bonds between molecules get stronger, the absorbance amount increases.

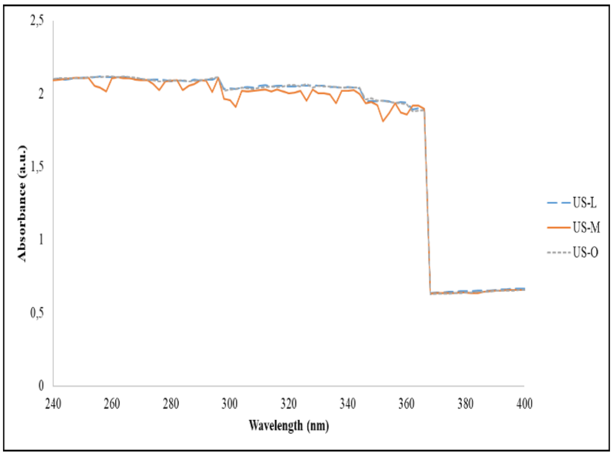

Figure 2. UV-Vis analysis of extracted samples from ultrasonic-assisted extraction; US-L for lemon, US-M for mandarin, US-O for orange extract

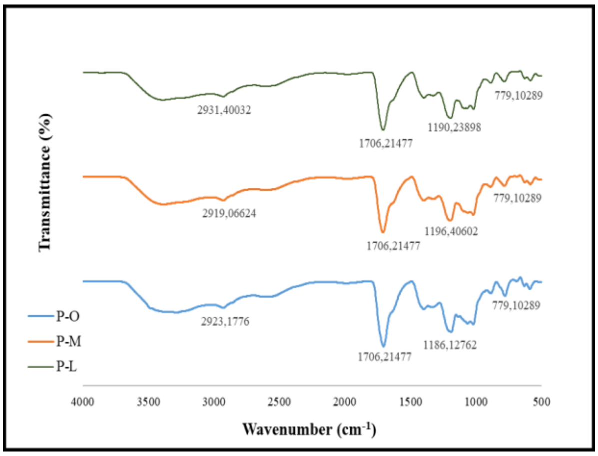

Figure 3. FTIR analysis of pectin samples obtained by sequential extraction; P-O for orange, P-M for mandarin, P-L for lemon peel extracted samples.

FTIR analysis results

FTIR spectra of pectin obtained from the sequential extraction of orange (P-O), mandarin (P-M) and lemon (P-L) was indicated in Figure 3. The wavelength with the lowest transmittance for all three citrus species was determined to be approximately 1706.215 cm^{-1}. In this analysis, it is observed that the transmittance decreases as the substance concentration increases. From this relationship, the existence of an inverse proportion between the substance concentration and transmittance was determined. It can be observed that the spectroscopic profiles of the pectin compound are parallel despite being obtained from different citrus species. Absorption in the 800–1200 cm^{-1} wave range is specified as the fingerprint zone for carbohydrates [19]. The lowest transmittance value determined falls in the FTIR spectrum peak of carbonyl C=O stretch. The bands at 2923.1776 cm^{-1} -2931.40032 cm^{-1} can be determined as alkane C–H stretching vibration. The bands at 1186.12762- 1196.40602 cm^{-1} are attributed to aromatic C=C stretch [20]. The band at 1706.21477 cm^{-1} can determine the bioactive component as pectin due to its stretching vibrations of the carbonyl group (υC=O) which is directly related to its gelling mechanism [21-23].

LC-MS analysis results

The chromatogram of the lowest concentration of hesperidin 0.035 ppm is given in Figure 4. It was concluded that the mandarin extract was rich in hesperidin components observed at an m/z = 609 which is in agreement with the literature [24]. The hesperidin was found as 430.2 mg/L in mandarin extract (Table 1).

Table 1. Determination of hesperidin in mandarin extract

Extract	Extraction method	Hesperidin amount ($mg.L^{-1}$)
Mandarin	Ultrasound-assisted extraction	430.2 ± 3.27*

* n = 3, mean ± SD.

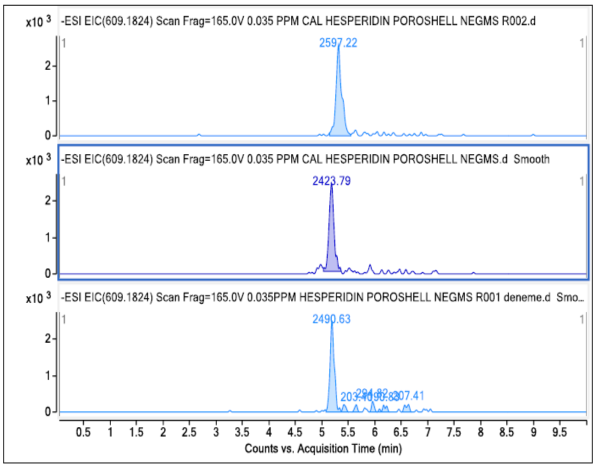

Figure 4. LC-MS spectra of hesperidin observed in the mandarin extract.

Hesperidin, which is known to exhibit strong antioxidant, anti-inflammatory and neuroprotective qualifications, has been reported in the literature to be generally found in citrus fruits [24].

CONCLUSION

In the present study, lemon, mandarin and orange waste peels supplied from the Mediterranean region of Türkiye were evaluated in terms of valuable compound composition. To create a new approach to reduce waste, provide environmental sustainability and prove the importance of environmental waste recycling, lemon, orange and mandarin wastes were subjected to extraction processes. The pectin and hesperidin contents of these wastes were successfully evaluated using ultrasonic-assisted extraction, conventional extraction and sequential extraction. It was proven that citrus wastes obtained from the Mediterranean region can be used to obtain hesperidin and pectin. In addition, the advantages of different extraction methods were demonstrated. The UV-Vis spectrophotometry and FTIR analyses were successfully applied and the chemical structures of the extracted citrus compounds were characterized. The efficiency of the three extraction methods in obtaining hesperidin and pectin was compared. In addition, the study revealed the level of efficiency of environmentally friendly extraction techniques using the example of the ultrasonic-assisted extraction method. The conditions, efficiency and environmental effects of the whole process were observed. Phenolic compounds in citrus extracts may have potential uses in many areas such as health, food, cosmetics and agriculture, if further analyses are completed.

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