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Valorization of 'Rossa di Tropea' Onion Waste through Green Recovery Techniques of Antioxidant Compounds

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Abstract: The aim of this work was to maximize the recovery of the bioactive components from an important solid waste derivate from Tropea onion processing. To achieve this, three different extractive procedures (conventional for maceration, ultrasound, and microwave-assisted) were employed, using only food-grade extraction solvents such as water and ethanol:water (50:50). Solvent, temperature, microwave power, time, and their interaction were studied as the principal factors that might affect the extractability rates. The obtained data suggest that the hydroalcoholic mixture proved to be the best for each of the techniques developed and at each time and temperature considered. In particular, the best results were achieved by conventional extraction for 60 min at 40 °C (total flavonoids content: 25.64 ± 1.40 mg QE g^{-1} d.w.; total anthocyanins content: 0.78 ± 0.01 mg C-3-GLUC g^{-1} d.w.). The UHPLC analysis of the optimally obtained extract revealed that the principal phytochemicals recovered were quercetin (5322.61 ± 0.32 mg kg^{-1}) and quercetin 3-4′-diglucoside (1023.80 ± 0.34 mg kg^{-1}) after conventional and ultrasound-assisted extraction, respectively. In this perspective, the implementation of sustainable, food-grade extraction processes to recover value-added substances from solid onion waste could play a crucial role both in reducing the waste load and in formulating natural food additives with functional properties, with a potential direct industrial impact.

Keywords: antioxidant compounds; green extractions; microwave-assisted extraction; Tropea onion wastes; ultra-high-performance liquid chromatography; ultrasound-assisted extraction

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1. Introduction

Red onion skins are a rich source of natural bioactive compounds with marked antioxidant properties, such as flavonoids and anthocyanins [1,2]. Notable differences relating to total flavonoid content have been shown among the different onion varieties (red and white). The concentration of flavonoids is substantially higher in red onions, which are praised for their remarkable beneficial effects on health. Flavonoid compounds are mainly concentrated in onion skin rather than in the edible part [3,4]. A high content of quercetin was found in dry red onion skin, approximately 32-fold higher than the flesh layers [5]. Moreover, Albishi et al. [1] reported that the HPLC analysis revealed that onion skin is rich in quercetin and kaempferol, compounds with great antioxidant activity. Dry onion skin also has a distinct concentration of quercetin derivatives compared to the edible part [6]. In fact, as reported by Perez-Gregorio et al. [7], flavonol content tends to decrease from the outer to the inner scales and from the top to the base of the onion. On the contrary, anthocyanin concentration did not show variation from the outer to inner scales. Total anthocyanin levels also showed a non-significant decrease from the top to the bottom of the bulb [7]. About 10% of total flavonoid content is represented by anthocyanins, and these compounds are mainly present in the skin and in the outer layers, compared to the

edible inner part [8]. Gennaro et al. [9] also reported that dried onion skin features a lot of anthocyanins and flavonols, particularly glycone forms that correspond to 2% of the total weight in the non-edible part. Therefore, 63% of total red onion anthocyanins are contained in the outer layers, that is, in the OSW.

Because onions are especially rich in these phytochemicals [10], the recovery of these compounds from onion solid waste represents an important issue in relation to both lowering the environmental impact from food waste disposal and utilizing high added-value substances with beneficial aspects [11].

In this context, biomass management represents a crucial issue in relation to the correct reuse of by-products over time. For instance, the application of macroscopic pre-treatment, such as the drying procedure to reduce water content, leads to greater matrix stability and ensures better bioactive compounds [12,13] in the by-products with major stability and extractability. The extraction process represents the earliest critical phase to obtain high added-value components from a food matrix; for this reason, different enhanced techniques could be applied. In Table 1, some scientific research that has been used by other authors to extract antioxidant compounds from onion skin is reported. In this regard, conventional techniques (solid-liquid extractions) have been widely applied for the recovery of bioactive compounds [14]. On the other hand, the use of alternative techniques, such as ultrasound- or microwave-assisted extraction, could reduce the extraction time and increase the yield and quality of extraction. In this regard, developing sustainable and green extraction techniques is a crucial point in the process of valorizing onion processing waste in order to extract secondary metabolites from the plant and to intensify the extraction yield [15].

Table 1. Extraction methods used by other authors to extract anthocyanins from onions.

Publication Year	Extraction Mehod	Principal Antioxidant Compounds	Reference
2010	Maceration with acetone, water, and acetic acid (70:29.5:0.5, *v*/*v*/*v*).	Total phenolic content in red onion: 2.2 mg GAE/g d.w. TEAC value: 15.4 mmol TE/g d.w.	[16]
2011	Maceration with a mixture of methanol: water:HCl (70:29.5:0.5, *v*/*v*/*v*)	TPC: 52.7 mg g^{-1}; TF: 43.1 mg g^{-1}; DPPH: 60.5% Inhibition; ABTS: 85.3% Inhibition	[17]
2013	Ultrasounds for 20 min at 30 °C. Mixture of methanol, acetone, and water (7:7:6, *v*/*v*/*v*)	TPC: 23.67 mg g^{-1}; TF:20.22 mg g^{-1}; DPPH: 0.152 mmol TE g^{-1}; ABTS: 15.37 mmol TE g^{-1}	[1]
2014	Extraction with ethanol, hot water, and subcritical water	The ethanol extraction increased the total phenolic content (327.5 mg GAE/g extract) and flavonoid content (183.95 mg QE/g extract); DPPH (72.25% inhibition) in the onion peel extract.	[18]
2018	Maceration with 80% aqueous ethanol	TPC: 6.12 mg g^{-1}; TF: 4.82 mg g^{-1}; DPPH: 60.5% inhibition; ABTS: 85.30% inhibition	[19]
2019	Extraction with a deep eutectic solvent system consisting of choline chloride:urea (ChCl:urea)	Under optimum conditions, the highest TPC value was 222.97 mg gallic acid equivalent (GAE) g^{-1} d.w.	[20]
2021	Ultrasound-assisted extraction (UAE); ethanol/water	Maximum flavonoid content was 23.9 ± 0.2 mg QE/g DOSW	[21]
2022	Microwave extraction	The total flavonoid extraction yields reached 47.83 ± 0.21 mg/g	[22]

In this context, solvents such as methanol or ethanol, with a significantly lower polarity than water, encourage the solubilization of polyphenols [23], most of which are poorly soluble in water. Thus, ethanol could reasonably be expected to lower the polarity of water, allowing the solubilization of higher amounts of polyphenols. This agrees with results supporting the fact that polyphenols can be easily solubilized in polar protic media, such as a hydroalcoholic mixture [24].

In addition, heat treatments contribute to cause the thermal destruction of cell walls and sub cells during the extraction process, which promotes the release of internal components [25]. The utilization of waste from pigmented onions, and the importance of factors such as temperature, could make onion waste a great source of anthocyanins as water-

soluble pigments and other precious molecules, useful for the elaboration of value-added products [26].

Particularly, this work chose Tropea onion waste. The 'Rossa di Tropea' onion is a typical variety cultivated in Calabria, in the South of Italy, and it is distinguished by the pink/red colored bulbs, sweet flavor, and characteristic organoleptic properties, thanks to their high content in flavonols [27]. Furthermore, this onion cultivar was granted with Protected Designation of Origin (PDO) and Protected Geographical Indication (PGI) trademarks [28].

For these reasons, this study was focused on the extraction of valuable compounds from onion solid waste, through sustainable extraction techniques (conventional, ultrasound-, and microwave-assisted extraction) and food grade extraction solvent, such as water and a hydroalcoholic mixture. In addition, the effects of extraction solvents, time, and temperature were studied to valorize a production waste by developing techniques to reduce environmental pollution and to use food grade solvents with a good extraction efficiency.

2. Materials and Methods

2.1. Sampling

Red onions (*Allium cepa* L., *cv. Tropea*) were supplied by a local producer in the province of Reggio Calabria (Italy). The bulbs were transported to the laboratory, and the outer dry and semi-dry layers were separated, as well as the apical and basal trimmings, which were considered as onion solid waste (OSW), and used in the extraction processes. Firstly, the OSW was dehydrated (50 °C) until a humidity of 17%, then pulverized in a domestic blender, and then stored in vacuum bags

2.2. Extraction Procedures

In this work, several extraction procedures: conventional solid-liquid (maceration), ultrasound (UAE), and microwave-assisted (MAE) were carried out, with the aim to maximize the recovery of antioxidant compounds, applying the same method reported in another work [14]. Figure 1 shows the experimental scheme that was followed. For the extraction of dried onion solid wastes (OSW), different procedures were applied, as shown in Figure 1. Different extraction variables were studied, such as type of solvent: water (H_2O) and ethanol:water (EtOH: H_2O, 50:50); temperatures: 25, 40, and 70 °C; times: conventional and UAE were 30, 60, and 120 min, while for MAE they were 5 and 15 min.

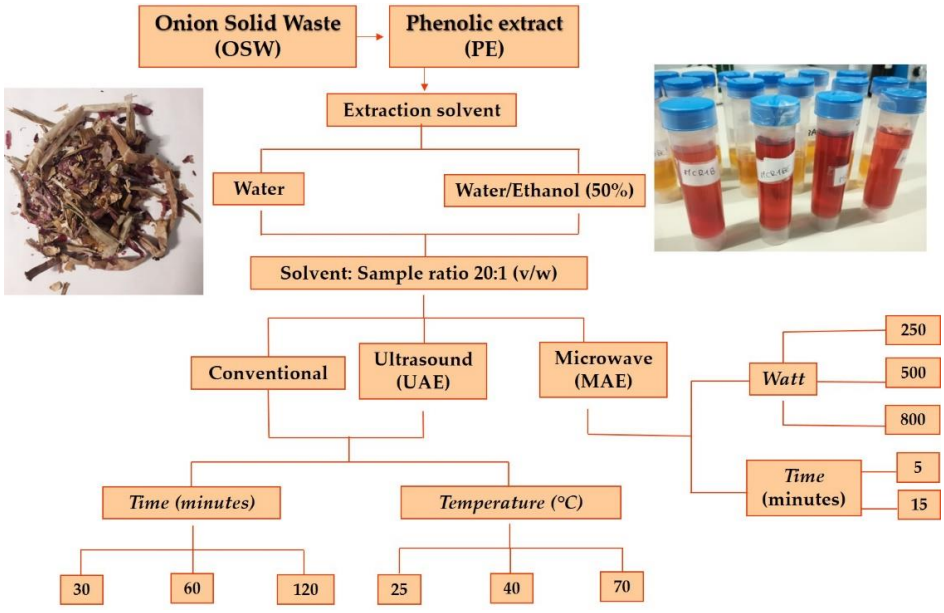

Figure 1. Experimental scheme.

- Conventional solid-liquid extraction

Conventional extraction for maceration was carried out following the method reported by Jang et al. [29], appropriately modified. An amount of 2.5 g of OSW and 50 mL of solvent (H_2O or EtOH:H_2O) were added and stirred in for fixed times and temperatures. Then, the solutions were centrifuged (5000 rpm, 5 min, 4 °C, in a NF 1200R, Nüve, Ankara, Turkey) and filtered (Büchner apparatus with 0.45 µm filter paper); the supernatant was recovered and made up to a volume of 50 mL with extraction solvent (H_2O or EtOH:H_2O). Before analysis, the extracts were filtered (syringe filter, nylon, 0.45 µm).

- Ultrasound-assisted extraction

Ultrasound-assisted extraction (UAE) was executed following the methodology reported by Imeneo et al. [14]. An amount of 5 g of OSW and 100 mL of solvents (H_2O or EtOH:H_2O) were mixed and subjected to an extraction condition in a Sonoplus Ultrasonic homogenizer (Series 2000.2, HD 2200.2, BANDELIN, Ultraschall seit 1955). In the ultrasonic homogenizers used for the extraction, the ideal temperature conditions were reached by controlling and regulating in terms of radiation amplitude (%) and radiation rate per second. After the extraction time, samples were centrifuged (5000 rpm, 5 min, 4 °C) and filtered with 0.45 µm filter paper, the supernatant was recovered and made up to a volume of 100 mL with extraction solvent (H_2O or EtOH:H_2O). Before analysis, the extracts were filtered (syringe filter, nylon, 0.45 µm).

- Microwave-assisted extraction

The microwave-assisted extraction was conducted according to Li et al. [30], and it was appropriately modified.

A Microwave Digestion System (ETHOS EASY, Millestone) was employed for the extraction, equipped with an easyTEMP thermal sensor-ATC-CE, which made it possible to evaluate the thermal conditions and regulation of the microwave power (watt). Particularly, it was found that 250 W corresponds to 25 °C; 500 W corresponds to 40 °C; 800 W corresponds to 70 °C.

An amount of 2.5 g of OSW and 50 mL of solvent extraction were mixed and homogenized with ultraturrax (IKA T 25, Staufen, Germany). After, the solutions were relocated into PTFE-TFM vessels of 100 mL (SK-15 easyTEMP, high-pressure rotor). The vessels were put in the middle of the microwave apparatus, heated (brought at the chosen temperature in 3 min), and maintained at temperature for 5 or 15 min according to the experimental project. Then, the mixtures were cool to room temperature for 10 min. After the extraction time, samples were centrifuged (5000 rpm, 5 min, 4 °C) and filtered with 0.45 µm filter paper. Before analysis, the extracts were filtered (syringe filter, nylon, 0.45 µm).

2.3. Analytical Methods

2.3.1. Total Flavonoid Content

Total flavonoid content (TF) was determined applying the method reported by Munir et al. [31], appropriately modified. An aliquot of extract (0.5 mL), 2 mL of deionized water, and 0.15 mL of $NaNO_2$ (5%, *w*/*v*) were placed in a 5-mL flask and incubated at room temperature (5 min). Then, 0.15 mL of $AlCl_3$ (10%, *w*/*v*) were added and incubated for 6 min); after that, 2 mL of NaOH (4%, *w*/*v*) was mixed, and deionized water was used to make it up to volume. Simultaneously a blank solution was prepared. The reaction mix was left to settle for 15 min in the dark; after this time, the absorbance was read (510 nm) using a double-beam ultraviolet-visible spectrophotometer (Perkin-Elmer UV-Vis λ2, Waltham, Massachusetts, U.S.) and comparing values to a calibration line (quercetin concentration between 20 and 50 mg L^{-1}). The results were expressed as mg of quercetin g^{-1} of OSW dry weight (mg QE g^{-1} d.w.).

2.3.2. Determination of Anthocyanin Content

Total anthocyanin content (TAC) was determined following the pH differential method [32] on the OSW extracts (appropriately diluted = 1:5, *v*:*v*). This method evaluates the chromatic

changes depending on the pH (between 1.0, potassium chloride, 0.025 M and 4.5, sodium acetate, 0.4 M). The absorbance was recorded using a spectrophotometer at wavelengths of 520 and 700 nm, for solutions at pH 1.0 and pH 4.5, respectively. Anthocyanin pigment concentration was expressed as mg of cyanidine 3-glucoside g^{-1} of OSW dry weight (mg c-3-gluc g^{-1} d.w.), by the following calculation:

$$\frac{A * MW * DF * 10^3}{\varepsilon * 1}$$

where:

A = ($A_{520nm} - A_{700nm}$) pH 1.0 − ($A_{520nm} - A_{700nm}$) pH 4.5;
MW (molecular weight) = 449.2 g mol^{-1} for cyanidine 3-glucoside (cyd-3-glu);
DF = dilution factor established in D;
10^3 = factor for conversion from g to mg.
1 = pathlength in cm;
ε = 26,900 molar extinction coefficient, in L*mol^{-1}*cm^{-1}, for cyd-3-glu.

2.3.3. Antioxidant Activity Determination

- DPPH assay

The antioxidant activity of OSW extracts was determined by DPPH assay, following the method reported by Brand-Williams et al. [33]. This assay represents a spectrophotometric discoloration method, where a free radical DPPH (2,2-diphenyl-1-picrylidrazyl) and the antioxidants present in the extract to be tested are reacted. An aliquot of antioxidant extract (50 µL of wavery extract or 25 µL of hydroalcoholic extract) was added to DPPH (6×10^{-5} M methanol solution), up to a maximum volume of 3 mL, and left under darkness for 15 min at room temperature. The absorbance was recorded using a spectrophotometer at wavelengths of 515 nm, and the results were expressed as µM Trolox equivalents g^{-1} of OSW dry weight (µM TE g^{-1} d.w.), compared with a Trolox calibration curve (from 6 to 21 µM).

- ABTS assay

The antioxidant activity of OSW extracts was determined by the ABTS (2,2′-azino-bis acid (3-ethylbenzothiazolin-6-sulfonic acid) assay, following the method reported by De Bruno et al. [34]. This antioxidant assay (as DPPH) also acts with the same reaction mechanism between radical and antioxidant, leading to a discoloration of the solution. The reaction mixture was prepared by mixing 25 µL of wavery extract or 10 µL of hydroalcoholic extract with the ethanol solution of $ABTS^+$ (up to a maximum volume of 3 mL). The absorbance was recorded using a spectrophotometer at wavelengths of 734 nm after 6 min at 734 nm. The results were expressed as µM Trolox equivalents g^{-1} of OSW dry weight (µM TE g^{-1} d.w.), compared with a Trolox calibration curve (from 3 to 18 µM).

2.3.4. UHPLC Determination of Individual Antioxidant Compounds

The ultra-high-performance liquid chromatography (UHPLC) determination of individual antioxidant components was carried out following Romeo et al. [35], with appropriate modifications. A chromatographic system (UHPLC PLATINblue, Knauer, Berlin, Germany) was used, equipped with a PDA-1 (photo diode array detector) PLATINblue (Knauer, Berlin, Germany) and a C18 column (Knauer blue orchid, 1.8 µm, 100 mm × 2 mm). For the chromatographic analysis, 5 µL of each extract (filtered with nylon syringe filters, 0.22 µm, diameter 13 mm) was injected in the system, where the column was maintained at 30 °C. Two different mobile phases used were: (A) water (pH 3.10 with acetic acid) and (B) acetonitrile; the gradient elution program consisted of: 0–3 min, 95% A; 3–15 min, 95–60% A; 15–15.5 min, 60–0% A. After that, the initial conditions were restored. Ultimately, the restoration of was reached. External standards at different concentrations (between 1 and 100 mg kg^{-1}) were used for the quantification of each individual component. The

results were expressed as mg kg^{-1} of OSW dry weight (mg kg^{-1} d.w.). The UHPLC-PDA method was validated for the limit of quantification (LOQ) and limit of detection (LOD), defined as the lowest concentration in the standard solution with the percentage of the relative standard deviation (% RSD) $\leq$ 10%, and they were calculated following the equations: LOD = SD $\times$ 3.3 and LOQ = SD $\times$ 10.

2.4. Statistical Data Elaboration

The results of the analyses were elaborated as mean (n = 4) $\pm$ standard deviations.

Significant differences ($p < 0.05$) were obtained by one-way analysis of variance (ANOVA) and multivariate analysis (MAVOVA) with Tukey's post hoc test at $p < 0.05$. Pearson's coefficient was used to study the correlation among TF, TAC, and antioxidant assays. SPSS Software (Version 15.0, SPSS Inc., Chicago, IL, USA) was used for statistical elaboration.

3. Results

3.1. Conventional Solid-Liquid Extraction

In this research, different extraction parameters were studied, with the aim to maximize the recovery of antioxidant compounds from OSW; among these, as can be seen in Table 2, the type of used solvent significantly influenced the extraction process ($p < 0.01$). In fact, the MANOVA confirmed that the application of different extraction solvents (W or W/EtOH) and the interconnection with other process variables, such as the extraction temperature and time, significantly influenced the recovery of TF and TAC and the antioxidant activity. The other studied variables, such as extraction temperature and time, also showed a statistical influence on the dependent variables considered, with the only exception of TF and DPPH. Therefore, a separate ANOVA was performed for each dependent variable, with each ANOVA valued at an alpha level of 0.05.

Table 2. Multivariate statistical analysis of conventional OSW extracts.

	TF	TAC	ABTS	DPPH
Solvent	**	**	**	**
Temperature	ns	**	**	**
Time	**	**	**	ns
Solvent × Temperature	**	**	ns	*
Solvent × Time	**	ns	ns	**
Temperature × Time	**	**	**	**
Solvent × Temperature × Time	**	**	**	*

The relevance of the symbols is given by the statistical analysis (ANOVA), by the Tukey's test. ** Significance at $p < 0.01$; * Significance at $p < 0.05$; ns, not significant. TF, total flavonoid content; TAC, total anthocyanin content; DPPH and ABTS, antioxidant activity assays.

The watery extracts (W) showed a lower recovery of TF and antioxidant activity compared to the hydroalcoholic extracts (W/EtOH, Table 3), confirming the extraction trend already reported in other works in literature [31,36]. In fact, as described by Makris [26] and Nile et al. [19], solvent composition strongly influenced its properties. For example, density and dynamic viscosity, which influence the extraction amount, determine the phenolic content and thus antioxidant activity of the final extracts.

Among the watery extracts, the best regarding the TF content appeared to be the extract obtained at 70 °C for 30 min, with 14.32 $\pm$ 0.71 mg QE g^{-1} d.w. of OSW. At the same time, these extraction conditions were not the best in terms of TAC, ABTS, and DPPH activity, for which the best parameters were 40 °C and 60 min, supported by the lower correlation coefficient between TF and ABTS (r = 0.49) and DPPH (r = 0.66) than TAC (r = 0.87 and r = 0.89 for ABTS and DPPH, respectively). The fact that a higher flavonoid content does not always correspond to a higher antioxidant activity of the extracts could be explained by the circumstance that only one method or assay is not adequate to establish in a meticulous and complete way the antioxidant activities of several phytochemicals. Thus,

it is necessary to make use of various approaches to quantify the antioxidant activities of flavanols recovered from OSW [37].

Table 3. Total flavonoid content (TF), total anthocyanin content (TAC), DPPH, and ABTS assay values of conventional solid-liquid extraction.

		TF			TAC		
		(mg QE g^{-1} d.w.)			(mg C-3-GLU C g^{-1} d.w.)		
Minutes	**°C**	**W**	**W/EtOH**	**Sign.**	**W**	**W/EtOH**	**Sign.**
30	**25**	9.85 ± 0.93 ^{b}	21.30 ± 0.49 ^{a}	**	0.18 ± 0.01 ^{a}	0.65 ± 0.03 ^{a}	**
	40	4.84 ± 0.19 ^{c}	16.66 ± 1.32 ^{b}	**	0.15 ± 0.04 ^{a}	0.32 ± 0.07 ^{b}	**
	70	14.32 ± 0.71 ^{a}	19.47 ± 2.16 ^{ab}	**	0.08 ± 0.01 ^{b}	0.37 ± 0.08 ^{b}	**
	Sign.	**	**		**	**	
60	**25**	3.88 ± 0.13 ^{c}	18.09 ± 0.83 ^{b}	**	0.08 ± 0.03 ^{b}	0.39 ± 0.05 ^{b}	**
	40	10.33 ± 0.91 ^{a}	25.64 ± 1.40 ^{a}	**	0.32 ± 0.05 ^{a}	0.78 ± 0.01 ^{a}	**
	70	6.74 ± 0.40 ^{b}	19.59 ± 2.29 ^{b}	**	0.15 ± 0.03 ^{b}	0.28 ± 0.06 ^{c}	**
	Sign.	**	**		**	**	
120	**25**	5.22 ± 0.46 ^{a}	20.61 ± 2.03 ^{a}	**	0.14 ± 0.05 ^{a}	0.47 ± 0.01 ^{a}	**
	40	3.98 ± 0.25 ^{b}	17.17 ± 0.65 ^{b}	**	0.12 ± 0.03 ^{a}	0.34 ± 0.02 ^{b}	**
	70	3.81 ± 0.59 ^{b}	18.47 ± 1.55 ^{ab}	**	0.03 ± 0.00 ^{b}	0.31 ± 0.05 ^{b}	**
	Sign.	**	*		**	**	
		ABTS			**DPPH**		
		(μM TE g^{-1} d.w.)			(μM TE g^{-1} d.w.)		
Minutes	**°C**	**W**	**W/EtOH**	**Sign.**	**W**	**W/EtOH**	**Sign.**
30	**25**	26.55 ± 2.67 ^{a}	76.27 ± 5.92 ^{a}	**	8.50 ± 0.45 ^{a}	29.42 ± 1.31 ^{a}	**
	40	20.01 ± 0.99 ^{b}	60.49 ± 9.79 ^{b}	**	6.44 ± 0.75 ^{b}	25.93 ± 2.04 ^{b}	**
	70	16.34 ± 1.06 ^{c}	66.97 ± 7.34 ^{ab}	**	7.25 ± 0.39 ^{b}	30.44 ± 1.50 ^{a}	**
	Sign.	**	*		**	**	
60	**25**	16.88 ± 2.44 ^{b}	62.42 ± 3.59 ^{b}	**	5.26 ± 0.53 ^{b}	27.06 ± 2.14 ^{a}	**
	40	31.03 ± 1.48 ^{a}	94.11 ± 3.31 ^{a}	**	10.63 ± 1.10 ^{a}	30.68 ± 0.85 ^{a}	**
	70	19.98 ± 0.26 ^{b}	56.78 ± 9.80 ^{b}	**	6.45 ± 0.57 ^{b}	21.88 ± 3.18 ^{b}	**
	Sign.	**	**		**	**	
120	**25**	18.08 ± 0.90 ^{a}	69.13 ± 3.61 ^{a}	**	6.57 ± 0.38 ^{a}	37.95 ± 5.27 ^{a}	**
	40	10.72 ± 0.30 ^{b}	57.47 ± 6.36 ^{b}	**	5.68 ± 0.77 ^{a}	26.13 ± 4.72 ^{b}	**
	70	12.46 ± 1.45 ^{b}	64.56 ± 3.98 ^{ab}	**	2.39 ± 0.17 ^{b}	30.02 ± 3.33 ^{ab}	**
	Sign.	**	*		**	*	

Means within a column with different letters are significantly different by Tukey's post hoc test. Abbreviation: sign., significance; ** significance at $p < 0.01$; * significance at $p < 0.05$; W: water; W/EtOH: hydroalcoholic mixture.

The values investigated in this study were comparable to those stated by Benítez et al. [38] for TF in onion outer scales and brown skin, who found that a decline of total phenolics and flavonoids was detected from the outer to the inner layers of the bulb.

Concerning the extracts obtained with the W/EtOH mixture, the best extraction conditions were found to be similar to the previous ones, 40 °C and 60 min, with a TF of 25.64 ± 1.40 mg QE g^{-1} d.w. of OSW. The only exception was noticed for the DPPH values, among which the highest one was detected at 25 °C and 120 min. This aspect could be clarified by the lower correlation coefficient between TF and DPPH (r = 0.39) rather than

between TF and ABTS (r = 0.93), as well as for the TAC. Antioxidant activity in foodstuffs depends on numerous factors, such as polarity, solubility, metal-chelating capacity, and the method applied for its valuation [1]. Commonly, it is considered that onion varieties rich in polyphenols (yellow, red, purple) show higher antioxidant activity [17], but the connection has been shown to be stronger with the flavonoid portion rather than total phenols [39]. In agreement with the literature [40], it is obvious that the amounts of anthocyanins in OSW samples considered in this study are much lower than those of flavonoids [41].

The data obtained in this study were comparable to those stated by Makris and Kefalas [42], who stated that the greatest extraction amount was obtained at 40 °C, while either at 20 °C, 60 °C, or beyond, its values were lower, demonstrating the influence of temperature on the extraction process. Indeed, temperature of the extraction process influenced the molecule stability due to the chemical and enzymic degradation and/or losses by thermal decomposition; these have been indicated to be the leading aspect producing the drop in polyphenol content [43]. In addition to thermal decomposition, extraction time became crucial since larger extraction periods might provoke more evident polyphenol losses. The severe influence that extraction time may exert could indicate that extraction might be protracted until the maximum yield is achieved [11].

Even if the best extraction conditions of both kinds of extracts considered in this study are similar, the greatest extractability rate of bioactive compounds and the antioxidant activity in the hydroalcoholic ones confirm the highly significant influence of the extraction solvent on the process, as observed previously by multivariate analysis (Table 2).

3.2. Ultrasound-Assisted Extraction

The analytical results detected from the extracts obtained by ultrasound-assisted extraction was subjected to multivariate analysis to evidence statistical differences (Table 4). All variables taken into consideration in our study and the different interaction of them, influenced in a highly significant way ($p < 0.01$), were the total flavonoids (TF) and anthocyanins content (TAC) and the expression of the antioxidant activity.

Table 4. Multivariate statistical analysis of ultrasound-assisted extraction (UAE) of OSW extracts.

	TF	TAC	ABTS	DPPH
Solvent	**	**	**	**
Temperature	**	**	**	**
Time	**	**	**	**
Solvent × Temperature	**	**	**	**
Solvent × Time	**	**	**	**
Temperature × Time	**	**	**	**
Solvent × Temperature × Time	**	**	**	**

The relevance of the symbols is given by the statistical analysis (ANOVA) by the Tukey's test. ** Significance at $p < 0.01$; TF, total flavonoid content; TAC, total anthocyanin content; DPPH and ABTS, antioxidant activity assays.

Looking at the W extracts (Table 5), the extraction performed at 70 °C for 30 min was the best one in terms of all dependent variables considered. There seemed to be an increasing trend in the extraction rate as the temperature increases for 30-min extractions, until the TF and TAC values of 6.52 ± 0.03 mg QE g^{-1} d.w. and 0.07 ± 0.00 mg C-3-GLUC g^{-1} d.w. of onion solid waste, respectively.

Table 5. Total flavonoid content (TF), total anthocyanin content (TAC), DPPH, and ABTS assay values of ultrasound-assisted extraction.

		TF			TAC		
		(mg QE g^{-1} d.w.)			(mg C-3-GLUC g^{-1} d.w.)		
Minutes	**°C**	**W**	**W/EtOH**	**Sign.**	**W**	**W/EtOH**	**Sign.**
30	**25**	1.55 ± 0.07^{c}	10.94 ± 0.22^{c}	**	0.05 ± 0.00^{b}	0.19 ± 0.01^{b}	**
	40	3.58 ± 0.17^{b}	13.58 ± 1.13^{b}	**	0.04 ± 0.00^{c}	0.26 ± 0.02^{a}	**
	70	6.52 ± 0.03^{a}	16.22 ± 0.33^{a}	**	0.07 ± 0.00^{a}	0.29 ± 0.02^{a}	**
	Sign.	**	**		**	**	
60	**25**	2.59 ± 0.13^{b}	13.28 ± 0.49^{b}	**	0.02 ± 0.00^{b}	0.29 ± 0.02^{b}	**
	40	1.18 ± 0.06^{c}	20.79 ± 0.56^{a}	**	0.03 ± 0.00^{a}	0.50 ± 0.01^{a}	**
	70	4.15 ± 0.11^{a}	13.54 ± 0.38^{b}	**	0.04 ± 0.00^{a}	0.25 ± 0.02^{c}	**
	Sign.	**	**		**	**	
120	**25**	2.37 ± 0.10^{c}	22.71 ± 0.63^{a}	**	0.03 ± 0.00^{b}	0.59 ± 0.02^{a}	**
	40	3.50 ± 0.11^{a}	23.12 ± 0.52^{a}	**	0.05 ± 0.00^{a}	0.48 ± 0.02^{b}	**
	70	2.67 ± 0.16^{b}	15.92 ± 0.17^{b}	**	0.03 ± 0.00^{b}	0.29 ± 0.01^{c}	**
	Sign.	**	**		**	**	
		ABTS			**DPPH**		
		(μM TE g^{-1} d.w.)			(μM TE g^{-1} d.w.)		
Minutes	**°C**	**W**	**W/EtOH**	**Sign.**	**W**	**W/EtOH**	**Sign.**
30	**25**	16.00 ± 1.21^{ab}	36.16 ± 0.43^{b}	**	0.38 ± 0.13^{b}	11.84 ± 1.43^{c}	**
	40	14.74 ± 1.90^{b}	47.61 ± 0.67^{a}	**	1.45 ± 0.46^{a}	14.52 ± 0.39^{b}	**
	70	19.03 ± 2.79^{a}	46.53 ± 2.69^{a}	**	1.34 ± 0.38^{a}	17.27 ± 0.50^{a}	**
	Sign.	*	**		**	**	
60	**25**	15.77 ± 1.28	47.36 ± 1.97^{b}	**	0.14 ± 0.04^{b}	15.75 ± 1.34^{b}	**
	40	15.62 ± 0.68	57.18 ± 0.61^{a}	**	0.18 ± 0.08^{b}	23.43 ± 1.29^{a}	**
	70	16.09 ± 2.03	47.04 ± 3.73^{b}	**	0.52 ± 0.19^{a}	14.69 ± 1.00^{b}	**
	Sign.	ns	**		**	**	
120	**25**	21.44 ± 2.08^{a}	66.30 ± 1.95^{a}	**	0.15 ± 0.03^{b}	23.06 ± 0.33^{b}	**
	40	16.77 ± 1.27^{b}	59.18 ± 1.97^{b}	**	0.79 ± 0.29^{a}	25.17 ± 0.40^{a}	**
	70	15.03 ± 2.76^{b}	45.80 ± 4.01^{c}	**	0.12 ± 0.06^{b}	15.59 ± 0.69^{c}	**
	Sign.	**	**		**	**	

Means within a column with different letters are significantly different by Tukey's post hoc test. Abbreviation: sign., significance; ** significance at $p < 0.01$; * significance at $p < 0.05$; W: water; W/EtOH: hydroalcoholic mixture.

As previously discussed for the conventional extraction, also in UAE, an obvious influence by the extraction solvent can be seen, with W/EtOH being the best one. As reported by Vojvodić et al. [36], for onion peel, ethanol has been demonstrated to be better than water. Considering the 30-min extractions in both W and W/EtOH, a significant upward trend was noted with increasing temperature both in terms of extraction yield of TF and TAC and antioxidant activity, with the maximum value at 70 °C. A similar trend was noticeable with the W/EtOH extractions performed at 25 °C and 40 °C for all times considered, with an increasingly better performance as the extraction time increases, and an optimum at 120 min. Total flavonoid and anthocyanin extraction content from onion solid waste showed to decrease at temperatures higher than 40 °C, in agreement with

previous studies [27,44]. Indeed, temperature cannot be risen above specific levels, as this has been proven damaging to anthocyanins, provoking their thermal degradation [45,46]. These aspects confirm the high significant influence of time and temperature on the studied extraction process.

Although the influence of high temperature on the extraction yield of phenolic compounds has been proven to be positive in numerous situations [47–49] because of the promoted polyphenol diffusion and their improved solubility [50,51]; in this research, TF and TAC of onion solid waste decreased at temperatures higher than 40 °C for 60- and 120-min extractions. Indeed, contrary to previous reports, temperature cannot be increased beyond certain limits, as this has been proven detrimental to anthocyanins [45,46,52]. In this regard, the highest TF was detected for the extraction at 25 °C and 40 °C for 120 min, showing a high correlation ($r > 0.90$) to the other variables considered. The results stated by Albishi et al. [1] are comparable to those of the present research for total flavonoid and anthocyanin content in the red onion peel. Moreover, results obtained from the current work confirmed what was reported by Lee et al. [18], that the DPPH radical scavenging activity of the onion peel extract was higher in ethanol compared to hot water. Velioglu et al. [53] and Shahidi and Naczk [54] reported that the antioxidant activity of food products depends on the chemical nature of its components and not always on their quantities, because their efficiencies vary significantly.

3.3. Microwave-Assisted Extraction

The multivariate analysis of data was carried out also for the extracts obtained by microwave-assisted extraction, and the results are reported in Table 6. Among the independent variables examined in this research, the extraction solvent and power revealed a highly significant influence on the extraction process. In fact, the MANOVA pointed out that a different solvent (W or W/EtOH) significantly affected ($p < 0.01$) the extraction yield of TF and TAC and the ABTS and DPPH results. The extraction power and its interaction with time also showed a significant influence, with the only exception of TF.

Table 6. Multivariate statistical analysis of microwave-assisted extraction (MAE) of OSW extracts.

	TF	TAC	ABTS	DPPH
Solvent	**	**	**	**
Power	**	*	**	**
Time	**	ns	**	ns
Solvent × Power	**	ns	*	**
Solvent × Time	ns	ns	**	ns
Power × Time	**	**	**	**
Solvent × Power × Time	**	ns	**	**

The relevance of the symbols is given by the statistical analysis (ANOVA) by the Tukey's test. ** Significance at $p < 0.01$; * significance at $p < 0.05$; ns, not significant. TF, total flavonoid content; TAC, total anthocyanin content; DPPH and ABTS, antioxidant activity assays.

Looking at the 5-min watery extracts (Table 7), there was no significant difference among the values of all the dependent variables considered, which suggests that in this case there was no influence at all by the power on the extraction process. Contrary to this, the 15-min extractions showed a highly significant difference among them, with the 250- and 500-watt extractions being the best ones. Indeed, it seems that over this power there was a drop in both the extraction yield of valuable compounds and the expression of antioxidant activity. As determined by multivariate analysis, there was no influence of extraction time on the TAC and DPPH variables, contrary to what can be found for TF and ABTS. In fact, for extractions at 250 and 500 watts, there is a significant increase in total flavonoid content and antioxidant activity values, passing from 5 to 15 min of extraction, whereas a drop of values can be seen for extractions carried out at 800 °C, which indicated that a higher TF could be linked to a proportional antioxidant activity, in accordance with what was reported by Juàniz et al. [13]. However, the proportionality between the polyphenolic

content and the antioxidant activity was not a general trend, as suggested by previous studies [44,55,56]. Although higher polyphenol levels are frequently associated with a higher reducing power, increased extraction temperatures might negatively affect radical scavenging activity [49].

Table 7. Total flavonoid content (TF), total anthocyanin content (TAC), DPPH, and ABTS assay values of microwave-assisted extraction.

		TF			TAC		
		(mg QE g^{-1} d.w.)			(mg C-3-GLUC g^{-1} d.w.)		
Minutes	**Watt**	**W**	**W/EtOH**	**Sign.**	**W**	**W/EtOH**	**Sign.**
5	**250**	5.83 ± 1.41	13.49 ± 0.94 ^{b}	**	0.22 ± 0.04	0.43 ± 0.02 ^{b}	**
	500	4.58 ± 1.09	13.99 ± 0.06 ^{b}	**	0.30 ± 0.01	0.50 ± 0.02 ^{a}	**
	800	6.26 ± 0.99	18.04 ± 0.83 ^{a}	**	0.27 ± 0.06	0.52 ± 0.01 ^{a}	**
	Sign.	ns	**		ns	**	
15	**250**	9.58 ± 1.36 ^{a}	19.09 ± 0.45 ^{a}	**	0.31 ± 0.01 ^{a}	0.55 ± 0.05 ^{a}	**
	500	9.19 ± 2.84 ^{a}	15.23 ± 0.50 ^{b}	**	0.26 ± 0.05 ^{a}	0.47 ± 0.02 ^{b}	**
	800	3.89 ± 0.58 ^{b}	13.27 ± 0.74 ^{c}	**	0.17 ± 0.01 ^{b}	0.44 ± 0.03 ^{b}	**
	Sign.	**	**		**	**	
		ABTS			**DPPH**		
		(μM TE g^{-1} d.w.)			(μM TE g^{-1} d.w.)		
Minutes	**Watt**	**W**	**W/EtOH**	**Sign.**	**W**	**W/EtOH**	**Sign.**
5	**250**	21.20 ± 3.31	41.24 ± 3.70 ^{b}	**	8.81 ± 1.40	9.21 ± 0.37 ^{b}	ns
	500	20.75 ± 2.20	50.08 ± 2.66 ^{a}	**	7.94 ± 1.28	12.68 ± 0.52 ^{a}	**
	800	21.17 ± 2.41	55.18 ± 6.16 ^{a}	**	7.25 ± 1.04	12.36 ± 0.82 ^{a}	**
	Sign.	ns	**		ns	**	
15	**250**	24.99 ± 0.94 ^{a}	59.29 ± 3.49 ^{a}	**	10.38 ± 0.51 ^{a}	13.00 ± 0.25 ^{a}	**
	500	27.22 ± 3.26 ^{a}	60.29 ± 1.66 ^{a}	**	7.54 ± 0.32 ^{b}	9.50 ± 0.38 ^{c}	**
	800	16.59 ± 1.22 ^{b}	48.34 ± 1.39 ^{b}	**	5.31 ± 0.99 ^{c}	11.60 ± 0.46 ^{b}	**
	Sign.	**	**		**	**	

Means within a column with different letters are significantly different by Tukey's post hoc test. Abbreviation: sign., significance; ** significance at $p < 0.01$; ns, not significant; W: water; W/EtOH: hydroalcoholic mixture.

On the other hand, the W/EtOH extracts showed a different trend, as both 5- and 15-min extracts presented significant differences (Table 7). Specifically, they showed an inverse extraction trend depending on whether the extraction was conducted for a short or longer time; in the first case, the 800 watt was the best power when combined with a 5-min extraction time, with a maximum TF value of 18.04 ± 0.83 mg QE g^{-1} d.w. of onion solid waste, in contrast to 15-min extractions, where the best power was 250 watts (19.09 ± 0.45 mg QE g^{-1} d.w. of OSW). Thus, the time requirement in MAE was greatly reduced compared to the conventional techniques and UAE [20].

In accordance with other literature studies [1,57], red onion skins are the richest in terms of total anthocyanin content when compared with other onion varieties. The TAC values obtained in this study were higher than those reported by Gorinstein et al. [57], in which the highest content of anthocyanins in red onion skin was 10.04 ± 0.90 mg C-3-gluc 100 g^{-1} skin, and by Lauro and Francis [58], who reported that the total anthocyanins in red onions was 7–21 mg 100 g^{-1} sample.

3.4. Comparison among the Diffent Extraction Procedures (Conventional, UAE, and MAE)

After analyzing all the extracts obtained, for each extraction procedure, the best extracts were selected. The chosen extracts were selected not only for their total content of bioactive compounds and antioxidant activity, but also for their cost-effectiveness and time savings. For all methods considered, the hydroalcoholic mixture (W/EtOH, 50%) was the best extraction solvent. For each type of extraction, the optimal extraction conditions that were selected were: 60 min at 40 °C for conventional, 120 min at 25 °C for UAE. and 5 min at 800 watts for MAE. All major flavonoids of the selected extracts were identified and quantified by the UHPLC system. Coefficient of correlation (R^2), regression equations, and limits of detection (LOD) and quantification (LOQ) for each antioxidant compound are reported in Table 8.

Table 8. Regression equation, correlation coefficient (R^2), limit of detection (LOD), and limit of quantification (LOQ) in standard solutions (UHPLC).

Compounds	Regression equation	R^2	LOD mg kg^{-1}	LOQ mg kg^{-1}
Rutin	y = 46.07x − 14.44	0.9994	0.0968	0.35
Isorhamnetin	y = 86.25x − 222.23	0.9995	0.07678	0.57
Quercetin	y = 59.097x + 119.01	0.9999	0.4565	2.35
Kaempferol	y = 76.663x − 124.87	0.9994	0.0324	1.68
Quercetin-3-O-glucoside	y = 101.59x − 328.28	0.9997	0.0247	1.54
Quercetin-3-4-diglucoside	y = 51.525x + 22.18	0.9997	0.07876	1.98
Apigenin-7-O-glucoside	y = 136.17x + 176.33	0.9998	0.02346	0.25

Isorhamnetin-3-O-glucoside, quercetin, and quercetin 3,4′-diglucoside were among the main flavonols determined, and among the minor ones, there was isorhamnetin and quercetin 3-glucoside (Table 9). According to the literature, one of the main flavonols in outer onion scales was the quercetin 3,4′-diglucoside [38,59]. The OSW includes a specific range of polyphenols, many of them derived from quercetin and quercetin glucosides by peroxidase action [60,61].

Table 9. Phenolic characterization of selected hydroalcoholic (W/EtOH) of OSW extracts (mg kg^{-1} d.w.).

Compounds	Conventional	UAE	MAE	Sign.
Rutin	44.79 ± 0.30 ^{c}	125.03 ± 0.05 ^{a}	98.43 ± 0.13 ^{b}	**
Isorhamnetin	114.01 ± 0.02 ^{a}	62.37 ± 0.02 ^{b}	60.04 ± 0.03 ^{c}	**
Quercetin	5322.61 ± 0.32 ^{a}	179.21 ± 0.17 ^{b}	148.95 ± 0.05 ^{c}	**
Kaempferol	256.27 ± 0.13 ^{a}	29.03 ± 0.01 ^{b}	27.20 ± 0.07 ^{c}	**
Quercetin-3-O-glucoside	69.54 ± 0.01 ^{c}	85.02 ± 0.10 ^{a}	84.09 ± 0.12 ^{b}	**
Quercetin-3-4-diglucoside	454.55 ± 0.18 ^{c}	1023.80 ± 0.34 ^{a}	916.08 ± 0.04 ^{b}	**
Apigenina-7-O-glucoside	9.82 ± 0.03	ND	ND	**

Means within a row with different letters are significantly different by Tukey's post hoc test. Abbreviation: ND, not detected; ** significance at $p < 0.01$. Conventional: solid-liquid extraction at 40 °C for 60 min; UAE: ultrasound-assisted extraction at 120 °C for 25 min; MAE: microwave-assisted extraction at 800 W for 5 min.

The obtained results confirmed what was stated in the literature, as quercetin 3,4-diglucoside was identified among the predominant class of flavonoids present in the onion, and quercetin 3-glucoside was reported to be one of the minors [40]. In accordance with Albishi et al. [1], quercetin 3,4-diglucoside and quercetin were among the main phenolics in the selected onion solid waste extracts, thanks to their higher thermal stability than other flavonoids, such as kaempferol [25]. In addition, both losses and gains

in quercetin derivate content in onions was reported, depending on the heat treatment circumstances [4,40,59,62,63]. Indeed, the softening effect due to heat-induced wall and cell fractures could also impact phenolic extractability [64,65]. The greatest amount of quercetin (5322.61 ± 0.32 mg kg^{-1} d.w.) was recovered from onion solid waste by conventional method. This result confirms the highest radical scavenging activity detected by a DPPH assay previously reported (Table 3). Indeed, as reported by Nuutila et al. [5], among the onion flavonoids, quercetin showed the most efficient DPPH radical scavenging activity, and it also reacted more quickly than the other flavonoids, such as rutin and kaempferol, and is one of the major flavonoids detected [66]. Some minor flavonoids, such as luteolin and myricetin derivates, quantified in onions by other authors, were not identified in the studied extracts, probably due to differences in onion cultivar or agricultural practices adopted [38,39,67,68]. The influence of field treatment on flavonoid levels was already described by Rodrigues et al. [40], as well as the effect of post-harvest practices [41].

However, the results obtained in this study are comparable with what was described by Albishi et al. [1], who reported that quercetin, quercetin 3,4-diglucoside, and kaempferol were prevalent in all onion samples considered. In addition, Sellappan and Akoh [39] observed that the kaempferol in onions was observed to be in minor amounts in comparison to quercetin.

4. Conclusions

In conclusion, it was observed that the solvent system composed of W/EtOH 50% can efficiently extract flavonoids and anthocyanins from onion solid waste through conventional, ultrasound, and microwave extraction processes. Looking at the comparative data discussed previously (Table 8), it can be stated that the W/EtOH 50% and conventional extraction (for 60 min at 40 °C) could be applied successfully as a food grade alternative technique for recovering valuable phenolic compounds from onion solid waste, representing a crucial point in the valorization of food waste as functional ingredients. In fact, the implementation of similar extraction techniques by food industries would build the basis for the growth and expansion of green processes to enhance the value of food waste and the sustainable production of new value-added products in the food, pharmaceutical, and cosmetic sectors.

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