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The Conversion of Pistachio and Walnut Shell Waste into Valuable Components with Subcritical Water

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Abstract: Pistachio and walnut shells accumulate in large quantities as waste during food processing and represent a promising lignocellulosic biomass for the extraction of valuable components. Subcritical water technology was used as an environmentally friendly technique to study the extraction of active ingredients and other valuable degradation products from walnut and pistachio waste. Subcritical water extraction (SWE) was carried out under different process conditions (temperature (150–300 °C) and short reaction times (15–60 min)) and compared with conventional extraction using different organic solvents (acetone, 50% acetone and ethanol). The extracts obtained from pistachio and walnut shell waste are rich in various bioactive and valuable components. The highest contents of total phenols (127.08 mg GA/g extract at 300 °C for 15 min, from walnut shells), total flavonoids (10.18 mg QU/g extract at 200 °C for 60 min, from pistachio shells), total carbohydrates (602.14 mg TCH/g extract at 200 °C for 60 min, from walnut shells) and antioxidant activity (91% at 300 °C, for 60 min, from pistachio shells) were determined when the extracts were obtained via subcritical water. High contents of total phenols (up to 86.17 mg GA/g extract) were also determined in the conventional extracts obtained with ethanol. Using the HPLC method, sugars and their valuable derivatives were determined in the extracts, with glucose, fructose, furfurals (5-hydroxymethylfurfural (5-HMF) and furfural) and levulinic acid being the most abundant in the extracts obtained by subcritical water. The results show that subcritical water technology enables better exploitation of biowaste materials than conventional extraction methods with organic solvents, as it provides a higher yields of bioactive components such as phenolic compounds and thus extracts with high antioxidant activity, while at the same time producing degradation products that are valuable secondary raw materials.

Keywords: pistachio shells; walnut shells; subcritical water extraction; conventional extraction; waste biomass; valuable compounds; sugars; furfurals

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1. Introduction

Recently, due to the depletion of natural resources, increasing greenhouse gas emissions and ever-growing amounts of waste, there is a growing interest in finding the best way to convert waste biomass into valuable components and energy. The potential of discarded food and agricultural biomass in terms of the variety of natural compounds that can be obtained from it is very broad and includes many markets (including pharmaceuticals, food industry, cosmetics, etc.). Obtaining various chemical compounds from sustainable sources is an interesting research goal from both an environmental and economic point of view. This contributes to the development of a circular economy that focuses on minimizing waste and tends to replace raw materials from non-renewable synthetic sources with raw materials from natural renewable sources [1].

The fruits of the pistachio (*Pistacia vera* L.) and the walnut (*Juglans regia* L.) contain many nutrients, but only the kernel is edible, the outer shell, which represents more than 50% of the entire fruit, is considered waste and discarded. The total global production of

pistachios and walnuts (in-shell) in 2022/2023 is estimated to be 747.31 thousand tons [2] and 2.6 million tons [3], respectively. The shell of walnuts consists of 22.2–30.2% hemicellulose, 25.5–27.9% cellulose and 39.1–52.3% lignin [4,5], while the shell of pistachios consists of 20–32% hemicellulose, 30–55% cellulose and 12–38% lignin [6,7]. Usually agricultural biomass waste (walnut and pistachio shells) is incinerated to generate heat. This method of disposing of biomass waste is energy inefficient and pollutes the air. Walnut and pistachio shells, which are among the most important wastes in the nut processing industry, have become very interesting for various researches. The shells of various nuts are often used to produce activated carbon [8,9], to isolate cellulose nanocrystals [7,10], as fillers in polymer composites [11,12] and as adsorbents for the removal of dyes [13,14] and heavy metals from water [15,16]. As the demand for natural antioxidants in the food industry is dynamically increasing, agricultural and food wastes are becoming an ideal material for obtaining phenolic compounds as natural antioxidants [4,17,18].

Due to their high lignin content, walnut and pistachio shells are rich in polyphenols, which have numerous health-promoting effects [19,20]. Some studies confirm that pistachio and walnut shells contain many valuable bio-compounds (polyphenols), which can be obtained from pistachio and walnut shells using various techniques (ultrasonic extraction, standard shaking method [4], microwave [21], conventional extraction and Soxhlet extraction) and various organic solvents (methanol, acetone, ethanol, chloroform, n-butanol and water). Han et al. [4] extracted polyphenolic compounds from walnut shells with ethanol/water as a solvent using an ultrasonic bath, an ultrasonic probe and a standard shaking method. The highest content of total phenolic compounds (52.8 mg gallic acid equivalents (GAE)/g dry weight (DW)) was obtained with the ultrasonic extraction when the particle size of the shells was between 45 and 100 mesh [4]. In the following, autohydrolysis assisted by microwave processes was used to depolymerize hemicellulose and amorphous cellulose in walnut shells to xylose, glucose, acetic acid, levulinic acid, 5-HMF and furfural [22]. Cardullo et al. [23] prepared extracts from pistachio shells with various alcohols and water. The extracts with very low yields (0.37–2.21% w/w) contained phenolic acids and their derivatives, flavonoids and hydrolysable tannins [23].

Subcritical water extraction (SWE) is an environmentally friendly method that uses subcritical water as a solvent and represents an alternative to conventional extraction using organic solvents [24]. Water is non-toxic, non-flammable and produces less greenhouse gases and waste that would need to be disposed of separately, which is a major advantage over organic solvents, which are toxic (harmful) [25]. SWE is most commonly used for the extraction of bioactive compounds from environmental, food and plant sources. The most important parameter of SWE is temperature, as it strongly influences the chemical and physical properties of water. By reducing polarity at elevated temperatures, high extraction yields can be achieved with subcritical water extraction technology. The reduction in surface tension enables better wetting of the extraction material with water and faster dissolution of the compounds. The reduced viscosity of the water increases its penetration into the extraction material, which also accelerates extraction [26,27]. The ionic product of subcritical water increases with temperature, reaches a maximum at approx. 300 °C and by further increase of the temperature it decreases again [17]. Subcritical water is therefore a highly reactive medium. In general, when biomass is processed in subcritical or supercritical water, numerous reactions (hydrolysis, dehydration, decarboxylation, aromatization, condensation, polymerization/depolymerization, hydrogenation/dehydrogenation, isomeric reactions, gasification) [28,29] can take place, degrading normally insoluble biomass and its compounds to degradation products such as carbohydrates, furfurals, organic acids [30], gasses and bio-oil [31]. Extractives such as phenolic compounds (phenolic glycosides, high molecular weight polyphenols) can be hydrolyzed to aglycones or further degraded. The course of the reactions is highly dependent on the reaction temperature and time, which can be manipulated to increase the selectivity of the reaction to desired products. SWE is used to extract components such as antioxidants, essential oils and especially phenolic compounds, which are in principle poorly soluble in water at atmospheric pressure, but soluble

in subcritical water [32,33]. By changing the temperature and pressure of the subcritical water, the extraction of the components can be regulated depending on whether they are polar, semi-polar, low-polar or non-polar components. In addition, SWE enables effective extraction in a short time, in contrast to some conventional methods which often take longer. Natural materials already contain water, so primary drying of the material before SWE is generally not necessary, as water acts as a solvent in this case, which is a major advantage over conventional extractions [34]. In addition to grinding the material, many extraction techniques that use organic solvents often require drying as a pre-treatment step. This is because the water present in the material prevents the organic solvent from penetrating the material effectively, so additional energy must be invested in the process to achieve a satisfactory extraction yield. Furthermore, in some cases, the drying process reduces the content of bioactive compounds in the material [35].

In previous studies, various valuable components (methylxanthines, antioxidants, phenols) were separated from cocoa [36], chestnut [37], horse chestnut [38], peanut [39] and pecan [40] shells using subcritical water. However, there is a lack of studies using subcritical water for the extraction and/or decomposition of pistachio and walnut shells into valuable components. Erşan et al. [20] investigated the extraction of pistachio shells in a semi-continuous reactor in the temperature range of 110 to 190 °C at a flow rate of 4 mL/min through the column. It was found that pistachio shell extract contains various phenols (gallic acid and its derivatives), flavonoids (quercetin hexosides) and other components (5-HMF). Through hydrothermal process catalyzed by two bases (KOH and Na_2CO_3) and an acid (HCl) the walnut shells were converted into liquefied organic compounds. The main compounds from the hydrothermal process catalyzed by bases were phenol derivatives. Small amounts of cyclopentene derivatives and C_{12}-C_{18} fatty acids were also detected. HCl as a catalyst promoted the formation of levulinic acid, but the conversion rates were very low [41]. In another few studies, the shells of pistachios, walnuts and other nuts were used to generate hydrogen-rich gas with supercritical water as a medium [42–44].

The aim of this work was to investigate the conversion of waste walnut and pistachio shells to bioactive and valuable compounds with subcritical water as a green solvent. The influence of the process conditions (temperature, reaction time) on the extraction yield and their influence on the content of the analyzed compounds in the extracts was investigated. The content of total phenols, total flavonoids and total carbohydrates was determined in the extracts, and the antioxidant activity was determined using the DPPH method. The content of various sugars and their valuable derivatives (levulinic acid, furfurals), which were generated at higher temperatures, was determined using the HPLC method. The electricity consumption for the conversion of waste biomass via SWE into valuable products on a laboratory scale was also estimated. Moreover, in the present study, the extraction efficiency of phenolic compounds and antioxidant activity of extracts obtained with subcritical water under different process conditions were compared with that of conventional extraction using acetone, ethanol and 50% aqueous acetone solution as solvent.

2. Materials and Methods

2.1. Materials

The biowaste (pistachio and walnut shells) was provided by a local grocery store (Maribor, Slovenia). D-(+)-glucose (99.5%), lactose, 1,6-anhydroglucose (99%), levulinic acid (98%), D-(-)-fructose (≥98%), furfural (99%), 5-hydrohymethylfurfural (≥99%), 5-methylfurfural (99%), (phenol (≥96%), trifluoroacetic acid, Folin-Ciocalteu's phenol reagent, sodium carbonate (Na_2CO_3), 2,2-diphenyl1-picrylhydrazyl (DPPH), gallic acid, quercetin and sodium acetate (CH_3COONa) were purchased from Sigma Aldrich (Steinheim, Germany). Cellobiose (99%) and aluminum chloride hexahydrate 98% ($AlCl_3 \cdot 6H_2O$) were obtained from Merck (Darmstadt, Germany). Absolute ethanol (EtOH, ≥99.9%), n-hexane (≥98.5%), 96% sulfuric acid (H_2SO_4) and methanol (MeOH, ≥99.9%) were purchased from Carlo Erba Reagents (Val de Reuil, France) and LabExpert Kefo (Ljubljana, Slovenia). Nitrogen (99.5%) as inert gas was supplied by Messer (Ruše, Slovenia). Methanol (≥99.9%)

and trifluoroacetic acid were used for HPLC analysis and purchased from J.T. Baker and Sigma-Aldrich. All standards and solvents were of analytical grade and were used without further purification.

2.2. Methods

2.2.1. The Characterization of Pistachio and Walnut Shells with TGA/DSC and Elemental Analysis

Thermal gravimetric analysis (TGA) with Differential Scanning Calorimetry (DSC) analysis (TGA/DSC1 STAR, Mettler Toledo, Columbus, OH, USA) were performed to identify the thermal behavior of pistachio and walnut shells. The samples (about 40 mg) were analyzed in a temperature range from 30 to 600 °C under air atmosphere using a heating rate of 10 °C/min [45].

The elemental analyses of pistachio and walnut shells before SWE were performed using a Perkin Elmer 2400 Series II System Analyzer (Waltham, MA, USA) and the content of carbon, hydrogen, nitrogen and sulphur was determined [46].

2.2.2. Biomass Waste Treatment with Subcritical Water

The extraction of pistachio and walnut shells in subcritical water was carried out in a 75 mL high-pressure, high-temperature batch reactor (Parr Instruments, Moline, IL, USA) (Figure 1), which can operate up to 538 °C and 545 bar, respectively. The shells were selected, washed with deionized water to remove impurities, dried at 105 °C for 24 h to remove water, and then ground to obtain a product with a particle size of 2–3 mm. For SWE, 2 g of the shells were weighed, and 20 mL of distilled water was added to obtain a material to solvent ratio of 1:10 (g/mL). The reaction mixture (shells and distilled water) and the magnetic stirrer were placed in the reactor and sealed. The reactor was then placed on a stand and connected to a pressure gauge and a digital thermocouple for temperature measurement. The heating wire was wrapped around the reactor and a magnetic stirrer was placed underneath. Before starting the experiment, the reaction mixture was flushed three times with inert gas (nitrogen) to prevent the oxidation of the products. The initial pressure in the reactor was set to 40 bar. The reaction mixture was then heated to the desired temperature (31 °C/min to 150 °C, 30 °C/min to 200 °C, 24 °C/min to 250 °C, 21 °C/min to 300 °C) and the pressure in the reactor was simultaneously increased (53 bar at 150 min, 60 bar at 200 °C, 74 bar at 250 °C and 89 bar at 300 °C). As soon as the desired temperature was reached, the reaction time was measured (15 min, 30 min and 60 min). After the completion of the hydrothermal reaction, the reactor was immediately immersed in cold water and cooled to room temperature. The gas was then released from the gas valve and the reactor was opened. The contents of the reactor were filtered. The experiments were carried out three times under the same conditions and the data given are the average values of three repetitions.

2.2.3. Conventional Extraction

5 g of ground material (particle size ≅ 0.5 mm) was extracted with 100 mL of different solvents (acetone, ethanol, and 50% aqueous acetone solution) at 40 °C and atmospheric pressure for 2 h. The extraction solution was then cooled and filtered. The solvent was evaporated using rotavapor, and the extraction yield was calculated and expressed in wt.%. The extracts were stored for further analysis.

2.2.4. The Determination of Antioxidant Activity of Dry Extract

The antioxidant activity of the extracts was determined with the radical method using the radical 2,2 diphenyl-1-picrylhydrazyl (DPPH), as explained in a previous work [36]. An aliquot of the extract (77 µL, concentration 1 mg/mL) was mixed with 3 mL of DPPH solution and incubated in the dark for 15 min. The absorbance of the samples was measured at 515 nm using a UV-VIS spectrophotometer (Cary 50, Varian, Palo Alto, CA, USA). All measurements were done in triplicate. The antioxidant activities were expressed in %.

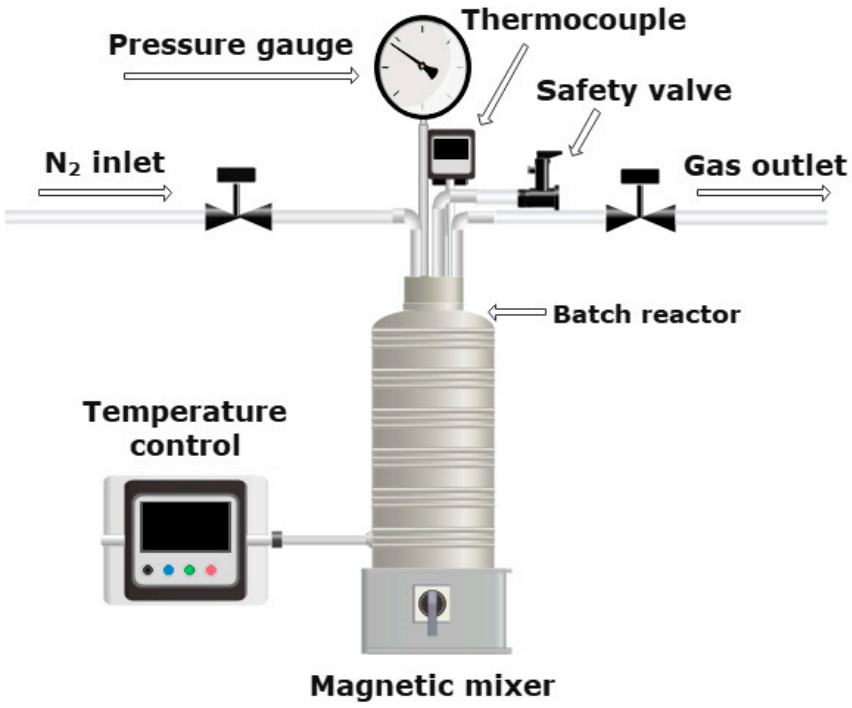


Figure 1. Scheme of apparatus for batch SWE.

2.2.5. The Determination of Total Phenolic Content in Dry Extract

The content of total phenols in the obtained extracts was determined spectrophotometrically using the Folin-Ciocalteu method, which is based on the oxidation reaction of the phenolic compounds with a reagent [36]. A total of 0.5 mL of the extract was mixed with 2.5 mL of the Folin-Ciocalteu reagent (diluted 1:10 in water) and 2 mL of Na_2CO_3 solution (75 mg/mL). The samples were incubated for 5 min at 50 °C in a water bath. They were then cooled at room temperature for 30 min. The absorbance was measured using a UV-VIS spectrophotometer (Cary 50, Varian, Palo Alto, CA, USA) at a wavelength of 760 nm. All measurements were performed in triplicate. The total amount of phenolic compounds was calculated using a standard curve for gallic acid (y = 9.8636x + 0.0396; R^2 = 0.9990) and expressed as mg gallic acid (GA) per g extract.

2.2.6. The Determination of Total Flavonoids in Dry Extract

The total flavonoids content in the extracts was determined using the aluminium chloride colorimetric method [47]. A total of 1.5 mL of a 96% alcohol solution, 0.5 mL of a 10% $AlCl_3 \cdot 6H_2O$ solution, 0.1 mL of 1M CH_3COONa and 2.8 mL of distilled water were added to 0.5 mL of the extract solution. The samples were then mixed and incubated at room temperature for 40 min. The absorbance of the samples was measured at a wavelength of 415 nm. All measurements were done in triplicate. The total amount of flavonoids was calculated using a standard curve of quercetin (QU) (y = 6.2872x + 0.0112; R^2 = 0.9986) and expressed as mg QU/g extract.

2.2.7. The Determination of Total Carbohydrates in Dry Extract

The content of total carbohydrates (TCH) in the extracts was determined using the phenol-sulfur colorimetric method, which is described in more detail in study [36]. A total of 1 mL of the extract was mixed with 0.5 mL of a 5% aqueous phenol solution and 2.5 mL of concentrated H_2SO_4. The samples were then placed in an ultrasonic bath for 10 min and then left to stand at room temperature for 20 min to develop color. In hot acidic medium, glucose is dehydrated to hydroxymethylfurfural, which forms a green color product with phenol and has an absorption maximum at 490 nm [30]. All measurements

were done in triplicate. Total carbohydrates were calculated using a standard curve of glucose (y = 11.392x + 0.0458; R^2 = 0.9986) and expressed as mg TOH/g extract.

2.2.8. HPLC Analysis

The determination of 5-HMF, furfural and 5-MF in the extract solution was carried out using an Agilent HPLC, 1200 series system (Waldbronn, Germany), equipped with a binary pump, an autosampler, a column heater, a variable wavelength detector and an Agilent ZORBAX Eclipse XBD C18 column (4.6 × 150 mm; 3.5 µm) at a temperature of 25 °C. The mobile phase consisted of solvent A and solvent B. Solvent A was methanol and solvent B was a mixture of water and 0.1% trifluoroacetic acid. The gradients of the method were as follows: 0 min 90% B, 18 min 65% B and 20 min 90% B. The flow rate through the column was set to 1 mL/min. The volume of the injected extract sample was 10 µL. The detection of 5-HMF, furfural and 5-MF was carried out at a wavelength of 280 nm.

The aqueous extract solutions were also analyzed using a Shimadzu Nexera HPLC system (Shimadzu, Kyoto, Japan) equipped with a DGU-20A SR degasser, an LC-20AD XR pump, a SIL-20AC XR autosampler and a CTO-20AC column heater. The sugars and sugar derivatives were detected with the RI detector. The separation was performed isocratically on the chromatography column Rezex RHM Monosaccharide H+ (300 × 7.8 mm) at 80 °C with a flow rate of 0.55 mL/min and 5 mM H_2SO_4 in water as the mobile phase. The products obtained were quantified using the calibration curves of standards. The results were expressed in mg compound/g extract [48].

2.2.9. The Assessment of the Energy Costs of the Laboratory Process

The costs for the conversion of pistachio and walnut shells into active ingredients and other valuable products in subcritical water at a temperature of 200 °C and 300 °C and a reaction time of 15 and 60 min (maximum extraction yield, high content of valuable compounds) were roughly estimated for the experimental batch reactor on a laboratory scale. In addition, the energy consumption for a pilot process with a reactor capacity of 200 L and for an industrial-scale process with a capacity of 10,000 L was also calculated. The energy required to heat the material in the laboratory reactor was calculated based on the heat transfer power (0.15–0.30 kW for the laboratory reactor, 54–108 kW for the pilot reactor and 1800–3600 kW for the industrial reactor) and the heating time. Heat losses during heating were neglected.

3. Results and Discussion

3.1. The Elemental Analysis of Raw Material

The results of the elemental analysis of pistachio and walnut shells are presented in Table 1, where the content of oxygen was calculated by the mass balance.

Table 1. Ultimate analysis of pistachio and walnut shells.

	Elemental Composition (wt.%)				
Biomass Waste	**C**	**H**	**N**	**S**	**O** [1]
Pistachio shells	44.98	6.34	0.20	0.45	48.03
Walnut shells	47.72	6.41	0.56	0.30	45.01

[1] Obtained by mass balance.

As expected, the elemental composition of both shells consisted mainly of carbon and oxygen, since lignocellulosic biomass is composed of three basic macromolecular components, namely cellulose, hemicellulose and lignin. It was found that walnut shells contain slightly more carbon than pistachio shells. The reason for this could be the high content of lignin (up to 52%) [4] in walnut shells.

3.2. The TGA/DSC Properties of Raw Material

The thermal behavior of pistachio and walnut shells waste was monitored with TGA and DSC analysis (Figure 2). In both materials, the main constituents are cellulose, hemicellulose, and lignin. The first mass loss (5–6%) of pistachio and walnut shell materials starts at 40 °C and ends at 230 °C and corresponds to the loss of physically bound water [49]. This mass loss appears as an endothermic peak on the DSC curve and the enthalpy is 189.8 J/g in the case of walnut shells and 175 J/g in the case of pistachio shells. In the following, the second mass loss started at 230 °C and ended at 380 °C, with weight losses between 52 and 59%. In this range, two exothermic peaks can be seen on the DSC curve, which probably correspond to the complete degradation of hemicellulose and cellulose. As known from the literature, the decomposition range of hemicellulose is between 210 and 325 °C, of cellulose between 310 and 400 °C and of lignin between 160 °C and 900 °C [50]. In this study, the first peak is in the range between 240 and 325 °C (ΔH = 56 J/g) in the case of walnut shells and between 240 and 335 (ΔH = 119 J/g) in the case of pistachio shells and corresponds to the degradation of hemicellulose. The second exothermic peak appears in the range between 330 °C and 355 °C for walnut shells (ΔH = 30.13 J/g) and between 335 °C and 390 °C for pistachio shells (ΔH = 33.18 J/g) and corresponds to cellulose/lignin degradation [51]. The results of this study are consistent with the results from the literature [51,52]. The maximum weight loss (48% for walnut shells, 56% for pistachio shells) was observed in a temperature range between 240 °C and 360 °C. Minor weight losses were observed at higher temperatures up to 600 °C (about 13% in both cases).

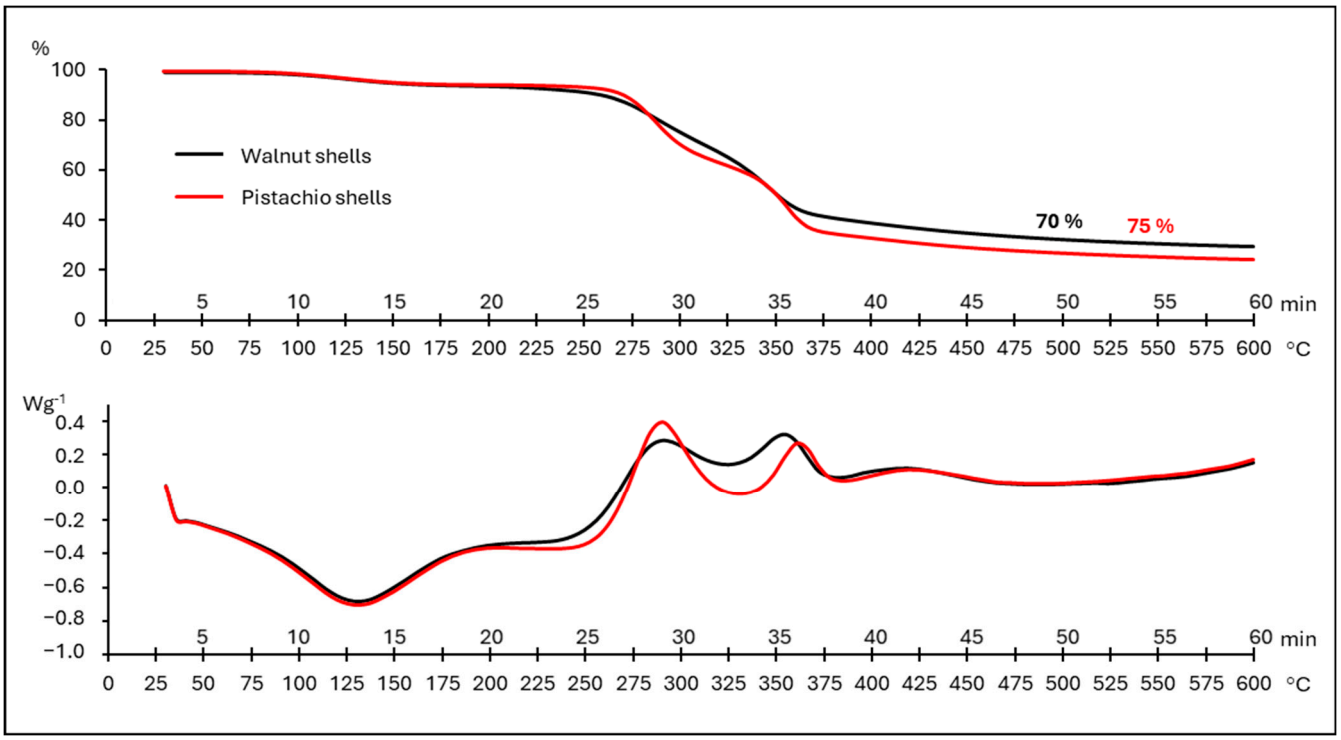


Figure 2. TGA/DSC thermogram of pistachio and walnut shells.

3.3. Extraction Yield

Figure 3 shows the maximum yields obtained in the extraction with subcritical water under different conditions and in the conventional extraction with acetone, ethanol and 50% acetone. At the lowest temperature (150 °C) and a reaction time of 60 min, the extraction yield was 8.17% for walnut shells and 26.18% for pistachio shells. Under these conditions, a lot of undegraded material remained in the reaction mixture (91% for walnut shells and 73% for pistachio shells). In order to achieve better conversion of the waste material, the temperature was increased to 200 °C. At this temperature, the maximum extraction yield

was obtained in both cases, namely after 15 min (41.05%) for pistachio shells and after 60 min (31.61%) for walnut shells. The yield of the SWE (Figure 3a) decreased with increasing temperature from 200 °C to 300 °C in almost all cases, indicating that further decomposition of the products most likely occurred during the extraction of the material. However, when walnut shells were extracted at 200 °C, an increase in yield was observed with an increasing reaction time of up to 60 min. When comparing the results for both raw materials, it can be seen that processing with subcritical water led to a slightly earlier decomposition of the pistachio shells. This finding can also be confirmed with the TGA analysis, where a slightly earlier mass loss is observed in the case of pistachio shells, which is probably due to the degradation of a possibly higher content of hemicellulose (which decomposes faster with temperature) in the pistachio shells. In addition, walnut shells contain more lignin, which is reflected in the higher hardness of the material [53], and as a result they tend to decompose later than pistachio shells. Erşan et al. [20] extracted pistachio hulls with subcritical water in a semi-continuous reactor and achieved the highest yield of extraction at 150 °C and 30 min; the yield was quite high (70.9 g extract/100 g pistachio shells) and decreased with increasing temperature [20]. The difference in extraction yield is most likely due to the different size of the shell particles extracted, which was smaller in the case of Erşan et al. [20] (0.5–1 mm) than in our case (2–3 mm), resulting in earlier decomposition of the material. In our case, the lowest extraction yield was obtained at 300 °C and 60 min (8% for pistachio shells, 15% for walnut shells). The results indicate that high temperatures and longer reaction times promote the formation of volatile decomposition products [20] or char formation via the condensation and re-polymerization of liquid products [54].

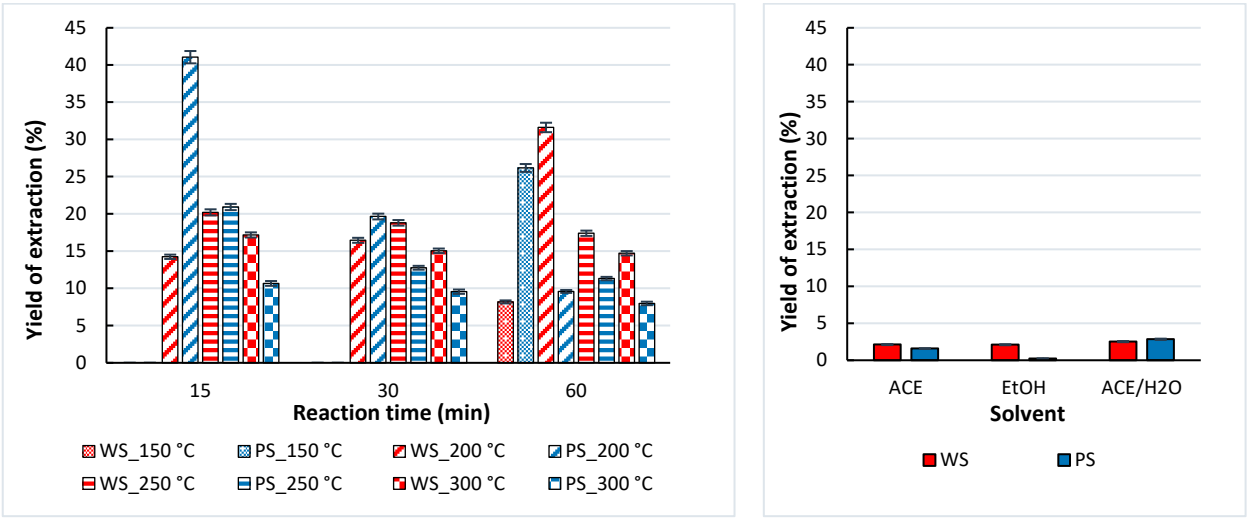


Figure 3. The yield of extraction of pistachio and walnut shells (PS-pistachio shells; WS-walnut shells) obtained via (**a**) subcritical water at different conditions and (**b**) conventional extraction with different solvents (ACE-acetone, EtOH-ethanol, ACE/H_2O-50% acetone).

The yields of the conventional extractions (Figure 3b) are significantly lower compared to the results of the extraction with subcritical water. The low yield after the conventional extraction of pistachio shells with different solvents was also reported by Cardullo et al. [23], where the highest yield of extraction (2.21%) was obtained with water and the lowest with ethanol (0.94%). In our case, the highest extraction yield was obtained using a 50% aqueous acetone solution as the solvent, 2.85% in the case of pistachio shells and 2.52% in the case of walnut shells. The lowest yield of conventional extraction was obtained for pistachio shells when ethanol (0.23%) was also used as a solvent. Thus, compared to SWE, the yield of conventional extraction was much lower and it required a longer extraction time. This

could be a consequence of hydrolysis during processing in subcritical water, whereby more water-soluble compounds (carbohydrates, various sugars) were extracted from the shells.

3.4. The Antioxidant Activity of Extracts

Pistachio and walnut shells contain a high proportion of lignin. Lignin is a natural phenolic macromolecule [53]. The antioxidant activity of lignin is directly related to the ability of its phenolic group to scavenge and neutralize free radicals. In addition, the antioxidant capacity of lignin is determined by its structure and total phenolic content, especially by its molecular weight and polydispersity, methoxide content and aliphatic content [55,56]. In our study, high antioxidant activities of the dry extracts were observed, which increased with temperature and reaction time (Figure 4a). The highest antioxidant activity of the pistachio shell extract (90%) was determined at a temperature of 300 °C and 60 min, while the activity of the walnut shell extract (72%) was slightly lower and was determined at 300 °C and 30 min. The increase in antioxidant activity with temperature and reaction time was also reported by Jokić et al. [36], where the maximum antioxidant activity of cocoa shell extract was determined at 220 °C and 75 min (91.69%). Similarly, high antioxidant activity (90.54%) was determined for the extract of chestnut seed shells obtained under subcritical water conditions (250 °C, 30 min), which was significantly higher than that of the extracts of chestnut seeds (54.15%) and chestnut leaves (40.39%) [38].

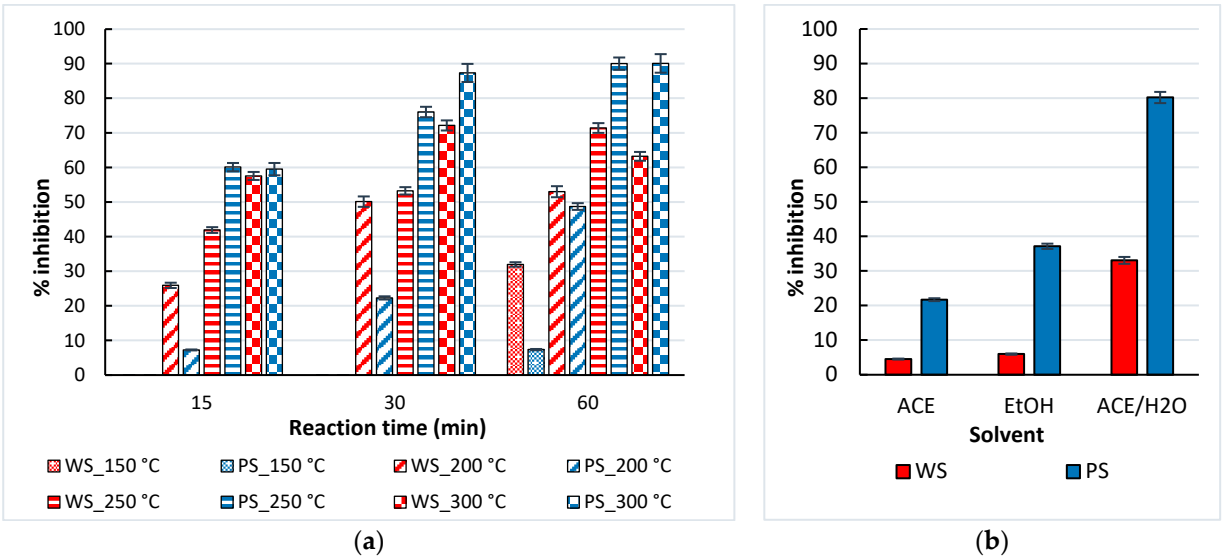


Figure 4. Antioxidant activity of pistachio and walnut shells (PS-pistachio shells; WS-walnut shells) extracts under different conditions, using (**a**) subcritical water and (**b**) conventional extraction (ACE-acetone, EtOH-ethanol, ACE/H_2O-50% acetone).

At lower temperatures and shorter reaction times, much lower antioxidant activity was observed, which can be attributed to poorer extraction of the phenolic components from the material. The lowest antioxidant activity was determined at 200 °C and 15 min and amounted to only 7.26% for pistachio shells and 26% for walnut shells. A slightly higher antioxidant activity was observed in the extracts (31.98% walnut shells and 7.38% pistachio shells) obtained at 150 °C and the longest reaction time (60 min). At higher temperatures (250 °C and 300 °C) and an extension of the reaction time to 30 or 60 min, the hydrolysis of the phenolic glycosides probably took place and phenolic aglycones were formed in the extracts, which have a higher antioxidant activity than phenolic glycosides [38].

The extracts obtained via conventional extraction generally showed lower antioxidant activities than the extracts obtained with subcritical water. Similar to the extraction with subcritical water, the extracts from pistachio shells obtained via conventional extraction (Figure 4b) showed significantly higher antioxidant activity, ranging from 20 to 80%,

compared to the activity of the conventionally obtained extracts from walnut shells, where it was only between 4 and 33%. The highest antioxidant activities (80% for pistachio shells and 33% for walnut shells) were found for extracts with a 50% aqueous solution of acetone as solvent, while the lowest values (21.7% for pistachio shells and 4.5% for walnut shells) were found for extracts obtained with acetone. A comparison of the results with published data shows that dry extracts of pistachio shells obtained via conventional extraction with 50% methanol had lower antioxidant activities (ABTS radical scavenging assay) (0.51 mmol Trolox equivalents (TE)/g dry matter (DM) of shells) than the extracts of pistachio shells obtained via extraction with subcritical water (0.68–1.2 mmol TE/g DM of shells) [20]. Meng et al. [57] also found that an extract of peanut shells obtained with 80% methanol had a high antioxidant effect (96.68%) (DPPH radical scavenging assay).

3.5. Total Phenols Content

As can be seen in Figure 5a, the content of total phenols in the extracts generally increases with increasing temperature and reaction time. The higher content of phenolic compounds in the extract could be due to the release of various phenols (gallic acid and its derivatives, flavonoids) or other bioactive components with increasing temperature [20,58]. The highest concentration of total phenols from pistachio shells was achieved at a temperature of 250 °C and a reaction time of 60 min and amounted to 31.68 mg GA/g extract (3.58 mg GA/g pistachio shells). The hydrolysis of walnut shells at 300 °C and 15 min resulted in the highest content of total phenols in the extract, namely 127.08 mg GA/g extract (21.82 mg GA/g walnut shells), but the content decreases with increasing reaction time, which probably indicates the degradation of phenolic compounds. A similar content of total phenols (130.33 mg GAE/g extract) was also found in cocoa shell extract obtained with subcritical water at 220 °C and 75 min [36].

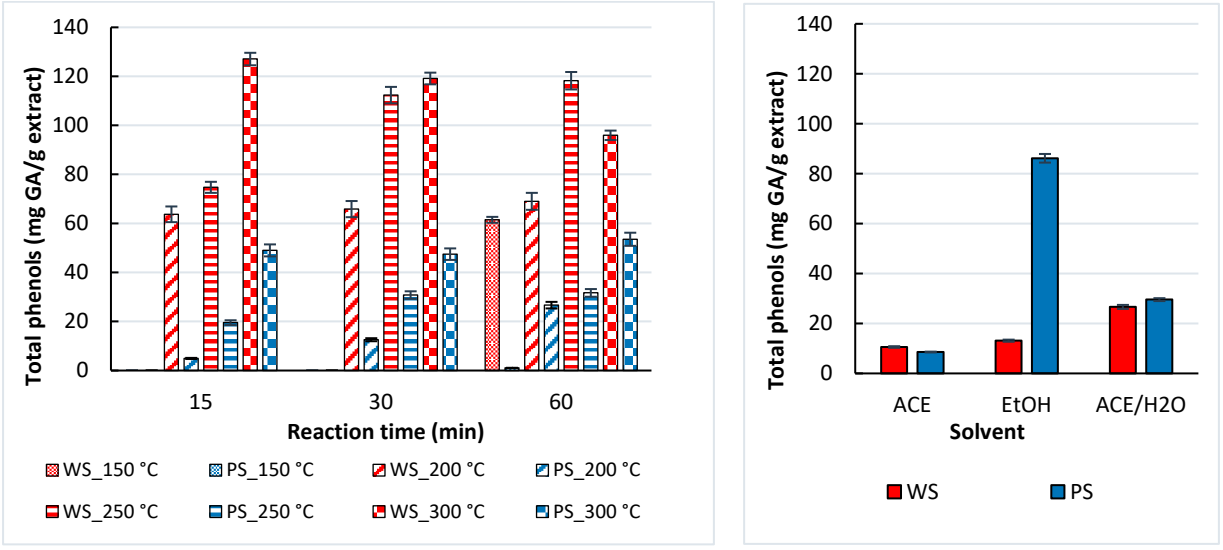


Figure 5. Content of total phenols in extracts of pistachio and walnut shells (PS-pistachio shells; WS-walnut shells) obtained via (**a**) SWE at various temperatures and reaction times and (**b**) conventional extraction with ACE-acetone, EtOH-ethanol, ACE/H_2O-50% acetone.

The lowest concentration of total phenols (Figure 5a) was determined in the extracts obtained at 150 °C and 60 min, where the content of total phenols in pistachio shell extracts was 1.05 mg GA/g extract (0.27 mg GA/g pistachio shells), while it was much higher in walnut shell extracts, amounting to 61.48 mg GA/g extract (5.02 mg GA/g walnut shells). As already known, walnut shells consist of more lignin than pistachio shells, and due to the aromatic/phenolic polymeric structure of lignin [59], the hydrolysis of the material could lead to a higher concentration of phenols than in pistachio shells. For walnut

shells, it was also found that extending the reaction time from 15 to 60 min at 250 °C resulted in a significant increase in total phenolic content, from 74.74 mg GA/g extract to 118.23 mg GA/g extract.

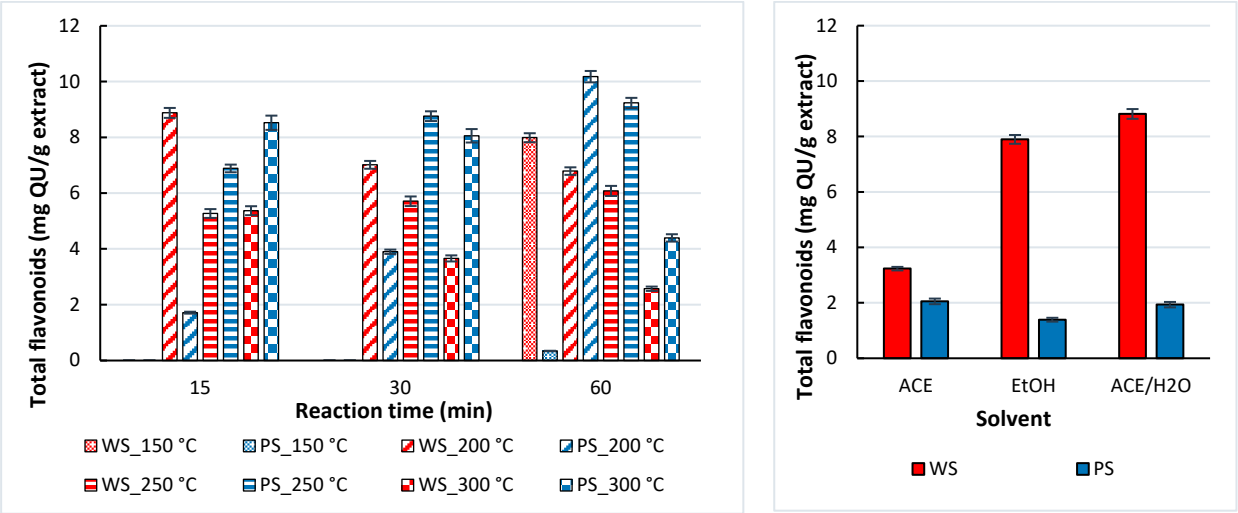
The highest content of total phenols in pistachio shell extract obtained via conventional extraction was found when ethanol was used as a solvent and amounted to 86.17 mg GA/g extract (0.20 mg GA/g pistachio shells). In this case, the content of total phenols in extracts (expressed in mg GA/g extract) from conventional ethanol extraction was significantly higher than in extracts obtained with subcritical water. However, due to the much lower yield of conventional extraction, the isolation efficiency of phenolic compounds (expressed in mg GA/g shells) from pistachio shells was more than 20 times lower than that of SWE. Cardullo et al. [23] determined a two times higher amount of total phenols isolated from pistachio shells when ethanol was used as a solvent (189 mg GAE/g extracts) compared to our results [23]. These results could be due to a longer contact time of the material with the solvent (16 h) than in our case (2 h). In general, the lowest content of total phenols in extracts (pistachio shells −8.6 mg GA/extract (0.14 mg GA/g pistachio shells) and walnut shells −10.6 mg GA/extract (0.23 mg GA/g walnut shells) was detected in both cases when acetone was used as solvent.

3.6. Total Flavonoids Content

The content of total flavonoids in the pistachio shell extract obtained with subcritical water (Figure 6a) increased at 200 and 250 °C with increasing reaction time, while it decreased at 300 °C with increasing reaction time. The highest content of total flavonoids was determined at a temperature of 200 °C and a reaction time of 60 min and amounted to 10.18 mg QU/g extract (0.98 mg QU/g pistachio shells). A similar content of total flavonoids (0.7 g/kg DM of hulls) in the extract obtained with subcritical water at 190 °C and 30 min in a semi-continuous reactor was also found in the study by Erşan et al. [20]. They also reported that the dry extract mainly contained various flavonoids such as quercetin hexosides, pentosides, glucuronides and galloylated hexcosides [20]. In our study, the content of total flavonoids in pistachio shell extract increases at 250 °C up to a reaction time of 60 min, reaching a slightly lower concentration of flavonoids (9.24 mg QU/g extract) than at 200 °C and 60 min. With a further increase in temperature to 300 °C, the content of total flavonoids in the dry extract started to decrease. Similar findings were also reported in the study of Erşan et al. [20], where the flavonoid content in subcritical water extracts of pistachio shells decreased when the temperature was increased. [20]. It is likely that further decomposition of flavonoids into other unknown products occurs at higher temperatures and longer reaction times.

The lowest content of total flavonoids in pistachio shell extract (0.34 mg QU/g extract) was determined at a temperature of 150 °C and a reaction time of 60 min. Flavonoids are a group of phenolic compounds [60], so it is to be expected that the lowest content of total flavonoids is also the lowest content of total phenols (Figure 5). A similar content of total flavonoids was found in dry extracts of walnut shells, with the exception that the content of total flavonoids decreased with increasing temperature at a constant reaction time, and at 200 °C and 300 °C it decreased with increasing reaction time at constant temperature. The highest content (8.9 mg QU/g extract) was found at 200 °C and 15 min, while the lowest content was obtained at 300 °C and 60 min (2.57 mg QU/g extract). At the lowest reaction conditions (150 °C and 60 min) the content of total flavonoids was 7.99 mg QU/g extract. The extraction of walnut shells with ethanol (7.9 mg QU/g extract) and 50% acetone solution (8.8 mg QU/g extract) resulted in a similar content of total flavonoids in the dry extract compared to extraction with subcritical water at low temperature (150–200 °C). Ethanol has already proven to be a good solvent for the extraction of flavonoids from walnut shells (Figure 6b). Yang et al. [61] determined a slightly higher yield of total flavonoids (18.97 mg rutin equivalents (REs)/mg extract), which is probably due to the higher extraction temperature (50 °C) compared to our study.

Sultanova et al. [62] reported that 90% ethanol contributes to a higher concentration of flavonoids (quercetin and catechin).



(**a**) (**b**)

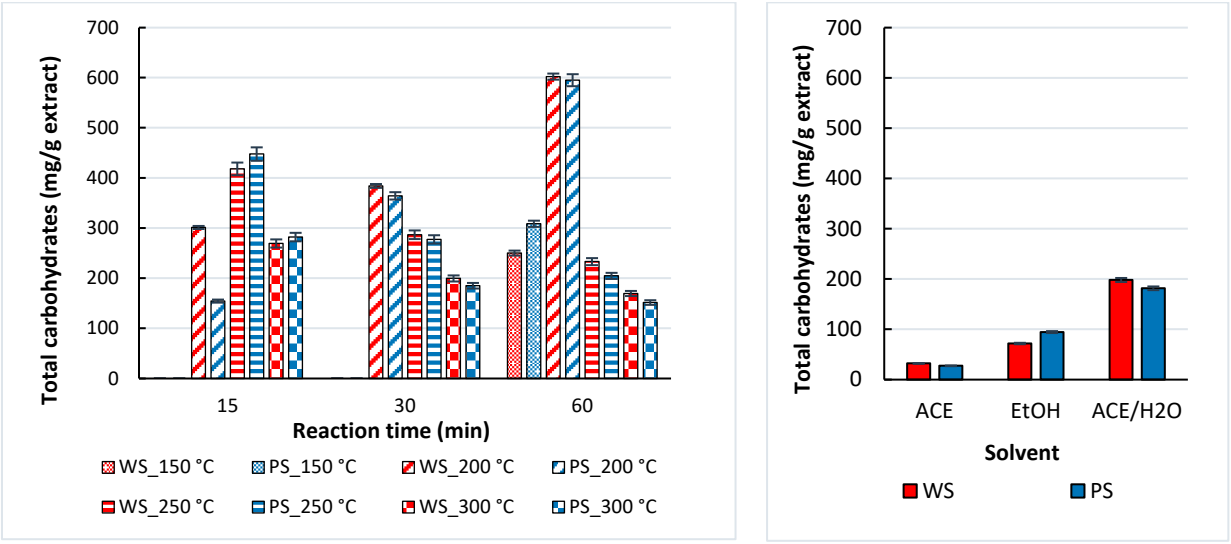
Figure 6. Content of total flavonoids in extracts of pistachio and walnut shells (PS-pistachio shells; WS-walnut shells) obtained via (**a**) SWE at various temperatures and reaction times and (**b**) conventional extraction with ACE-acetone, EtOH-ethanol, ACE/H_2O-50% acetone.

3.7. Total Carbohydrates Content

Carbohydrates can be completely dissolved in subcritical water due to the similar polarity of the medium, but this requires close monitoring of the reaction parameters, especially the temperature [30,63]. Using water as a medium, the hemicellulose in the biomass can be degraded to carbohydrates at low temperatures (190–210 °C) [64]. At this temperature, the hemicellulose in the biomass is completely decomposed. The residue after hydrolysis is rich in cellulose and lignin, which can be further utilised. Yang et al. [5] reported that the optimal conditions for the recovery of carbohydrates (about 400 mg TCH/g walnut shells) from walnut shells with subcritical water are 200 °C and 15 min. The residue from the walnut shells was used to produce a biodegradable foam by mixing it with corn starch. The biodegradable foam thus produced was a promising material that could take the place of plastic products in the future [5]. Gagić et al. also reported that the amount of carbohydrates (87.22 mg TCH/g shells) extracted from the shells of chestnut seeds was the highest at 200 °C and 15 min [38].

In our study, the total carbohydrate content in the extracts obtained from pistachio and walnut shells at 150 °C and 60 min was 250.13 mg TCH/g extract for walnut shells and 308.54 mg TCH/g extract for pistachio shells. At the temperature of 200 °C the total carbohydrate content in the extracts increased with increasing reaction time up to 60 min (Figure 7a), while it decreased with increasing reaction time at higher temperatures. Thus, the maximum content of total carbohydrates in dry extracts was determined at 200 °C after 60 min and amounted to 595 mg TCH/g extract in the case of the pistachio shells and 602 mg TCH/g extract in the case of the walnut shells. The highest isolation efficiency of carbohydrates for walnut shells was also achieved at 200 °C and 60 min and amounted to 190.34 mg TCH/g walnut shells, while in the case of pistachio shells it was achieved at 250 °C and 15 min (93.66 mg TCH/g pistachio shells). In general, the lowest content of total carbohydrates in the extract and the lowest extraction efficiency were determined in both cases at 300 °C and 60 min (151 mg TCH/g extract (12.01 mg/g pistachio shells) for pistachio shells and 169 mg TCH/g extract (24.85 mg TCH/g walnut shells) for walnut shells). It can be concluded that the decrease in carbohydrate content at temperatures above 200 °C and longer reaction times (>15 min) is due to the hydrolysis of poly- or

oligosaccharides and the higher decomposition rate of monosaccharides, which is due to the high ionic product of water at these temperatures [5].



(**a**) (**b**)

Figure 7. Total carbohydrate content (TCH) in the dry extract (PS—pistachio shells; WS—walnut shells) obtained via (**a**) subcritical water at different reaction conditions and via (**b**) conventional extraction (ACE-acetone, EtOH-ethanol, ACE/H_2O-50% acetone).

The total carbohydrate content in the extracts obtained by conventional extraction (Figure 7b) was lower than in the extracts obtained with subcritical water. The conventional extraction of walnut shells with 50% acetone gave the highest amount of total carbohydrates (198.11 mg TCH/g extract) in the dry extract. Under these conditions, the extraction yield was quite low and amounted to only 2.53%. The lowest total carbohydrate content in the extract was 27.33 mg TCH/g extract and was obtained with the acetone extraction.

3.8. Sugars and Derivatives

Sugars and sugar derivatives were detected with HPLC. Cellobiose, glucose, fructose and lactose were the main sugars in the extract solutions (Table 2). Cellobiose was detected after hydrothermal degradation of pistachio and walnut shells at 150 °C, 200 °C and 250 °C for all reaction times. The highest amount of cellobiose was detected in walnut shell extract at 200 °C and 15 min and amounted to 83.39 mg/g extract. The concentration of cellobiose in walnut shell extract decreased with increasing temperature and reaction time. At 250 °C and 60 min it was still present in the extract solution, while at 300 °C it could no longer be detected. In pistachio shell extracts, the cellobiose concentration was very low at 200 °C (up to 2 mg/g extract), while at 250 °C it was only present at 15 min. No cellobiose was detected when the extract solutions were prepared from pistachio and walnut shells using conventional extractions. In subcritical water, cellobiose was converted to glucose [63], which reached the maximum concentration in the walnut shell extract at 250 °C and 60 min (51.3 mg/g extract), while in the pistachio shell extract the maximum amount of glucose (17.9 mg/g extract) was detected earlier, namely at 200 °C and 60 min. In conventional extraction, the maximum glucose concentration was detected in the extract from pistachio shells (6.3 mg/g extract), which was obtained with 50% acetone. Glucose is converted to fructose in subcritical water by an isomerization reaction [48]. The highest amount of fructose (117.10 mg/g extract) in the extract from walnut shells was achieved at 250 °C and 15 min. In conventional extraction, similar to glucose, a high concentration of fructose (8.7 mg/g extract) was also detected in the extract from pistachio shells obtained with 50% acetone. Lactose was determined in low concentrations (2.65 mg/g extract) only in the pistachio shell extract, which was obtained at 200 °C and 15 min, and in the ethanol extract

(2.3 mg/g extract). The lactose was probably converted from cellobiose via an isomerization reaction [63].

Table 2. The content of sugars and sugar derivatives in extracts of pistachio and walnut shells obtained via SWE and via conventional extraction (mg component/g extract).

Conditions	Cellobiose	Glucose	Fructose	Lactose	1,6-AG *	5-HMF *	F *	MF *	LA *
Walnut shells									
150 °C, 60 min	11.21	8.69	12.75	/	/	2.15	9.32	0.74	3.15
200 °C, 15 min	83.39	10.32	92.08	/	/	4.28	36.90	2.49	1.85
200 °C, 30 min	14.34	24.13	86.62	/	4.18	8.69	42.18	5.14	5.40
200 °C, 60 min	2.76	25.76	60.39	/	5.32	12.07	59.02	8.11	15.15
250 °C, 15 min	13.66	29.9	117.10	/	8.1	19.99	30.62	5.28	22.25
250 °C, 30 min	3.69	44.03	94.5	/	37.68	18.7	11.6	7.46	29.15
250 °C, 60 min	3.7	51.3	54.16	/	52.11	16.9	9.5	2.95	37.33
300 °C, 15 min	/	14.94	7.1	/	55.01	5.6	5.4	1.79	53.61
300 °C, 30 min	/	6.09	3.04	/	13.6	2.68	1.25	1.74	40.54
300 °C, 60 min	/	1.18	1.9	/	5.9	1.15	0.99	1.96	56.39
ACE	/	/	1.52	/	/	/	/	/	/
ACE/H_2O	/	5.6	11.84	1.61	/	/	/	/	/
EtOH	/	2.8	3.6	/	/	/	/	/	/
Pistachio shells									
150 °C, 60 min	/	0.39	49.30	0.18	/	1.17	6.13	0.08	/
200 °C, 15 min	0.49	/	21.28	2.65	/	3.55	71.8	4.44	3.15
200 °C, 30 min	1.06	1.72	42.12	/	/	10.25	167.6	3.85	9.31
200 °C, 60 min	1.71	17.9	61.26	/	3.24	60.6	430.2	13.59	25.83
250 °C, 15 min	0.48	10.21	4.45	/	4.24	101.4	167.8	6.03	48.17
250 °C, 30 min	/	7.70	4.31	/	16.36	124.7	126.8	9.74	53.19
250 °C, 60 min	/	5.71	2.13	/	66.07	47.7	67.7	8.89	56.1
300 °C, 15 min	/	/	/	/	39.2	28.3	63.5	12.13	25.39
300 °C, 30 min	/	/	/	/	12.9	6.7	57.6	6.92	48.63
300 °C, 60 min	/	/	/	/	4.2	0.06	37.68	5.10	65.26
ACE	/	1.68	4.11	/	/	/	/	/	/
ACE/H_2O	/	6.3	8.7	/	/	/	/	/	/
EtOH	/	2.37	3.22	2.3	/	/	/	/	/

* 1,6 AG—1,6-anhydroglucose, 5-HMF—5-hydrohxmethylfufrural, F—furfural, MF—methylfurfural, LA—levulinic acid.

Sugar derivatives, namely 1,6-anhydroglucose, levulinic acid, 5-hydroxymethylfurfural (5-HMF), furfural (F) and methylfurfural (MF) were also formed in the aqueous phase during the hydrolysis of pistachio and walnut shells in subcritical water (Table 2), whereas these components were not formed during conventional extraction with organic solvents. 1,6-Anhydroglucose was first detected at 200 °C and 30 min in the case of walnut shells. 1,6-Anhydroglucose is formed via the dehydration of glucose. As shown in Table 2, the concentration of 1,6-anhydroglucose increased, while the glucose content decreased with increasing temperature and reaction time. The maximum concentration of 1,6-anhydroglucose in the extract is reached at 250 °C and 60 min in the case of pistachio shells (66.07 mg/g extract) and at 300 °C and 15 min in the case of walnut shells (55.01 mg/g extract). Furfurals (5-HMF, furfural and 5-MF) are the main degradation products of sugars. 5-HMF can be produced from glucose or fructose via glucose isomerization, while furfural is formed when 5-HMF loses the formyl group [65]. The content of furfurals (5-HMF, furfural and 5-MF) increased with increasing temperature and reaction time, reaching the highest value at 250 °C and 30 min for 5-HMF (124.7 mg/g extract) and at 200 °C and 60 min for furfural (430.2 mg/g extract) and for 5-MF (13.59 mg/g extract) in the case of pistachio shells. The high content of furfurals in the extract is a consequence of the higher content of total carbohydrates. In addition, the pistachio shells consist of a low lignin content and a high content of hemicellulose and cellulose, so more carbohydrates and furfural are

formed during hydrolysis than in the walnut shells. In comparison to the literature, the highest yield of furfurals was also determined in the chestnut shell at 200–250 °C for up to 30 min [38]. Another sugar derivative detected in the dry extracts of pistachio and walnut shells is levulinic acid, the main product of the hydrolysis of 5-HMF. The concentration of levulinic acid increased with increasing temperature up to 300 °C, with the maximum concentration in the dry extract being reached after 60 min (walnut shells—56.39 mg/g extract, pistachio shells—65.26 mg/g extract). Levulinic acid and furfurals (5-HMF and furfural) were also determined in the study in which the walnut shells were hydrolyzed via microwave-assisted autohydrolysis. At 210 °C and a reaction time of 10–55 min, the concentrations of the compounds were between 0.46 g/L and 0.85 g/L for levulinic acid, between 0.6 g/L and 2.24 g/L for 5-HMF and between 2.14 and 0.40 g/L for furfural [22].

3.9. The Electricity Costs of the Chemical Conversion of Waste Biomass into Valuable Products in Subcritical Water

It has been estimated that the electricity consumption for the chemical conversion of pistachio and walnut shells with subcritical water on a laboratory scale at 200 °C and a reaction time of 15 min and 60 min is about 9 kWh and 28 kWh per kg of shells, respectively, while the electricity costs would increase accordingly at 300 °C and amount to 22 kWh and 57 kWh per kg of walnut and pistachio shells, respectively. Increasing the reactor capacity (200–10,000 L) would reduce electricity costs. In a 200 L pilot reactor at 200 °C and at a reaction time of 15 min and 60 min, the electricity costs would be 1.2 kWh and 3.8 kWh per kg of shells, respectively, while at 300 °C the electricity costs would be 3.2 kWh and 8.3 kWh per kg of shells, respectively.

By using an industrial reactor (10,000 L), the electricity costs would decrease further and would be 0.95 kWh per kg of shells after 15 min and 2.9 kWh per kg of shells after 60 min at 200 °C, while at 300 °C they would amount to 2.4 kWh per kg of shells after 15 min and 6.3 kWh per kg of shells after 60 min of reaction time.

4. Conclusions

Bioactive and valuable components from pistachio and walnut shell waste were obtained via SWE at different temperatures (150–300 °C), three different reaction times (15 min, 30 min, 60 min) and a material:solvent ratio of 1:10 (g/mL). The conventional extraction was carried out for 2 h at 40 °C with three different solvents (acetone, ethanol and a 50% aqueous solution of acetone) and a material:solvent ratio of 1:20 (g/mL).

It was found that the extraction yield of pistachio and walnut shells with subcritical water was significantly higher (from 8% to 41%) than extraction with conventional solvents (0.23 to 2.85%), which is due to the decomposition of the material in subcritical water during processing. The extracts obtained with subcritical water at 300 °C have excellent antioxidant properties, reaching an antioxidant activity of up to 91% for pistachio shells, while a slightly lower value of 72% is obtained for walnut shells. When the waste material was extracted with 50% acetone, high (80%) antioxidant activity was also observed in the extract from pistachio shells. The extract of walnut shells obtained with subcritical water contains significantly higher amounts of total phenols (127.08 mg GA/g extract) than the extract of pistachio shells (53.52 mg GA/g extract), while the ethanol extract of pistachio shells achieves a slightly higher content of total phenols (86.17 mg GA/g extract). The extracts also contain low concentrations of total flavonoids (up to 10.18 mg QU/g extract).

The content of total carbohydrates and sugars (glucose, fructose and lactose) in the extracts obtained with SWE was significantly higher than in the extracts obtained by conventional extraction with organic solvents, while cellobiose and sugar derivatives, namely 1,6-anhydroglucose, levulinic acid, 5-hydroxymethylfurfural, furfural and methylfurfural were detected only in the extracts obtained with subcritical water. Namely, in conventional extractions, the decomposition reactions of the material that lead to the formation of these components do not take place. The highest carbohydrate content, which can be a good source for the production of bioethanol, was obtained from the waste shells (595 mg TOH/g

extract in the case of pistachio shells and 602 mg TOH/g extract in the case of walnut shells) at the lowest temperature (200 °C). In general, glucose and fructose were the most represented sugars in all extracts, while furfurals dominated among the derivatives, which are a valuable component as they are widely used in various industries (plastics, paints, pharmaceuticals, agriculture and chemicals).

In any case, it can be confirmed that subcritical water is an excellent and environmentally friendly medium that can efficiently hydrolyze lignocellulosic biomass and, by modifying and optimizing the process parameters to obtain the desired products, can extract valuable components such as phenolic compounds and sugars in higher yields compared to organic solvents and also valuable degradation products such as furfurals and levulinic acid. In further research, it would be necessary to investigate possible methods for separating the individual compounds.

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References

1. Herrera, R.; Hemming, J.; Smeds, A.; Gordobil, O.; Willför, S.; Labidi, J. Recovery of Bioactive Compounds from Hazelnuts and Walnuts Shells: Quantitative-Qualitative Analysis and Chromatographic Purification. *Biomolecules* **2020**, *10*, 1363. [CrossRef] [PubMed]
2. Pistachios: Global Production 2022/23. Available online: https://www.statista.com/statistics/933073/pistachio-global-production/ (accessed on 18 August 2023).
3. Walnut Production Worldwide 2022/23. Available online: https://www.statista.com/statistics/675967/walnut-production-worldwide/ (accessed on 18 August 2023).
4. Han, H.; Wang, S.; Rakita, M.; Wang, Y.; Han, Q.; Xu, Q. Effect of Ultrasound-Assisted Extraction of Phenolic Compounds on the Characteristics of Walnut Shells. *Food Nutr. Sci.* **2018**, *9*, 1034–1045. [CrossRef]
5. Yang, W.; Shimizu, I.; Ono, T.; Kimura, Y. Preparation of Biodegradable Foam from Walnut Shells Treated by Subcritical Water. *J. Chem. Technol. Biotechnol.* **2015**, *90*, 44–49. [CrossRef]
6. Robles, E.; Izaguirre, N.; Martin, A.; Moschou, D.; Labidi, J. Assessment of Bleached and Unbleached Nanofibers from Pistachio Shells for Nanopaper Making. *Molecules* **2021**, *26*, 1371. [CrossRef]
7. Marett, J.; Aning, A.; Foster, E.J. The Isolation of Cellulose Nanocrystals from Pistachio Shells via Acid Hydrolysis. *Ind. Crops Prod.* **2017**, *109*, 869–874. [CrossRef]
8. Wartelle, L.H.; Marshall, W.E.; Toles, C.A.; Johns, M.M. Comparison of Nutshell Granular Activated Carbons to Commercial Adsorbents for the Purge-and-Trap Gas Chromatographic Analysis of Volatile Organic Compounds. *J. Chromatogr. A* **2000**, *879*, 169–175. [CrossRef]
9. Khoshraftar, Z.; Ghaemi, A. Evaluation of Pistachio Shells as Solid Wastes to Produce Activated Carbon for CO_2 Capture: Isotherm, Response Surface Methodology (RSM) and Artificial Neural Network (ANN) Modeling. *Curr. Res. Green Sustain. Chem.* **2022**, *5*, 100342. [CrossRef]
10. Harini, K.; Chandra Mohan, C. Isolation and Characterization of Micro and Nanocrystalline Cellulose Fibers from the Walnut Shell, Corncob and Sugarcane Bagasse. *Int. J. Biol. Macromol.* **2020**, *163*, 1375–1383. [CrossRef]
11. Barczewski, M.; Sałasińska, K.; Szulc, J. Application of Sunflower Husk, Hazelnut Shell and Walnut Shell as Waste Agricultural Fillers for Epoxy-Based Composites: A Study into Mechanical Behavior Related to Structural and Rheological Properties. *Polym. Test.* **2019**, *75*, 1–11. [CrossRef]
12. Thiagarajan, A.; Velmurugan, K.; Sangeeth, P.P. Synthesis and Mechanical Properties of Pistachio Shell Filler on Glass Fiber Polymer Composites by VARIM Process. *Mater. Today Proc.* **2021**, *39*, 610–614. [CrossRef]
13. Aydin, H.; Baysal, G.; Bulut, Y. Utilization of Walnut Shells (*Juglans regia*) as an Adsorbent for the Removal of Acid Dyes. *Desalination Water Treat.* **2009**, *2*, 141–150. [CrossRef]
14. Şentürk, İ.; Alzein, M. Adsorptive Removal of Basic Blue 41 Using Pistachio Shell Adsorbent—Performance in Batch and Column System. *Sustain. Chem. Pharm.* **2020**, *16*, 100254. [CrossRef]

15. Kali, A.; Amar, A.; Loulidi, I.; Jabri, M.; Hadey, C.; Lgaz, H.; Alrashdi, A.A.; Boukhlifi, F. Characterization and Adsorption Capacity of Four Low-Cost Adsorbents Based on Coconut, Almond, Walnut, and Peanut Shells for Copper Removal. In *Biomass Conversion and Biorefinery*; Springer: Berlin/Heidelberg, Germany, 2022. [CrossRef]
16. Siddiqui, S.H.; Ahmad, R. Pistachio Shell Carbon (PSC)—An Agricultural Adsorbent for the Removal of Pb(II) from Aqueous Solution. *Groundw. Sustain. Dev.* **2017**, *4*, 42–48. [CrossRef]
17. Pavlovič, I.; Knez, Ž.; Škerget, M. Hydrothermal Reactions of Agricultural and Food Processing Wastes in Sub- and Supercritical Water: A Review of Fundamentals, Mechanisms, and State of Research. *J. Agric. Food Chem.* **2013**, *61*, 8003–8025. [CrossRef] [PubMed]
18. Knez, Ž.; Hrnčič, M.K.; Čolnik, M.; Škerget, M. Chemicals and Value Added Compounds from Biomass Using Sub- and Supercritical Water. *J. Supercrit. Fluids* **2018**, *133*, 591–602. [CrossRef]
19. Jalili, A.; Heydari, R.; Sadeghzade, A.; Alipour, S. Reducing Power and Radical Scavenging Activities of Phenolic Extracts from *Juglans regia* Hulls and Shells. *Afr. J. Biotechnol.* **2012**, *11*, 9040–9047. [CrossRef]
20. Erşan, S.; Güçlü Üstündağ, Ö.; Carle, R.; Schweiggert, R.M. Subcritical Water Extraction of Phenolic and Antioxidant Constituents from Pistachio (*Pistacia vera* L.) Hulls. *Food Chem.* **2018**, *253*, 46–54. [CrossRef]
21. Ganesapillai, M.; Mathew, M.; Singh, A.; Simha, P. Influence of Microwave and Ultrasound Pretreatment on Solvent Extraction of Bio-Components from Walnut (*Julgans regia* L.) Shells. *Period. Polytech. Chem. Eng.* **2016**, *60*, 40–48. [CrossRef]
22. Ahorsu, R.; Cintorrino, G.; Medina, F.; Constantí, M. Microwave Processes: A Viable Technology for Obtaining Xylose from Walnut Shell to Produce Lactic Acid by Bacillus Coagulans. *J. Clean. Prod.* **2019**, *231*, 1171–1181. [CrossRef]
23. Cardullo, N.; Leanza, M.; Muccilli, V.; Tringali, C. Valorization of Agri-Food Waste from Pistachio Hard Shells: Extraction of Polyphenols as Natural Antioxidants. *Resources* **2021**, *10*, 45. [CrossRef]
24. Capaldi, G.; Binello, A.; Aimone, C.; Mantegna, S.; Grillo, G.; Cravotto, G. New Trends in Extraction-Process Intensification: Hybrid and Sequential Green Technologies. *Ind. Crops Prod.* **2024**, *209*, 117906. [CrossRef]
25. Zhang, J.; Wen, C.; Zhang, H.; Duan, Y.; Ma, H. Recent Advances in the Extraction of Bioactive Compounds with Subcritical Water: A Review. *Trends Food Sci. Technol.* **2020**, *95*, 183–195. [CrossRef]
26. Zakaria, S.; Mustapa Kamal, S. Subcritical Water Extraction of Bioactive Compounds from Plants and Algae: Applications in Pharmaceutical and Food Ingredients. *Food Eng. Rev.* **2015**, *8*, 23–34. [CrossRef]
27. Cheng, Y.; Xue, F.; Yu, S.; Du, S.; Yang, Y. Subcritical Water Extraction of Natural Products. *Molecules* **2021**, *26*, 4004. [CrossRef] [PubMed]
28. Akiya, N.; Savage, P.E. Roles of Water for Chemical Reactions in High-Temperature Water. *Chem. Rev.* **2002**, *102*, 2725–2750. [CrossRef] [PubMed]
29. Gbashi, S.; Adebo, O.A.; Piater, L.; Madala, N.E.; Njobeh, P.B. Subcritical Water Extraction of Biological Materials. *Sep. Purif. Rev.* **2017**, *46*, 21–34. [CrossRef]
30. Ravber, M.; Knez, Ž.; Škerget, M. Hydrothermal Degradation of Fats, Carbohydrates and Proteins in Sunflower Seeds after Treatment with Subcritical Water. *Chem. Biochem. Eng. Q.* **2015**, *29*, 351–355. [CrossRef]
31. Toor, S.S.; Rosendahl, L.; Rudolf, A. Hydrothermal Liquefaction of Biomass: A Review of Subcritical Water Technologies. *Energy* **2011**, *36*, 2328–2342. [CrossRef]
32. Chemat, F.; Vian, M. *Alternative Solvents for Natural Products Extraction*; Springer: Berlin/Heidelberg, Germany, 2014; ISBN 978-3-662-43627-1.
33. Cravotto, C.; Grillo, G.; Binello, A.; Gallina, L.; Olivares-Vicente, M.; Herranz-López, M.; Micol, V.; Barrajón-Catalán, E.; Cravotto, G. Bioactive Antioxidant Compounds from Chestnut Peels through Semi-Industrial Subcritical Water Extraction. *Antioxidants* **2022**, *11*, 988. [CrossRef]
34. Shitu, A.; Izhar, S.; Tahir, T.M. Sub-Critical Water as a Green Solvent for Production of Valuable Materials from Agricultural Waste Biomass: A Review of Recent Work. *Glob. J. Environ. Sci. Manag.* **2015**, *1*, 255–264. [CrossRef]
35. Kapoor, S.; Sachdev, P. Drying Method Affects Bioactive Compounds and Antioxidant Activity of Carrot. *Int. J. Veg. Sci.* **2014**, *21*, 141217142840007. [CrossRef]
36. Jokić, S.; Gagić, T.; Knez, Ž.; Šubarić, D.; Škerget, M. Separation of Active Compounds from Food By-Product (Cocoa Shell) Using Subcritical Water Extraction. *Molecules* **2018**, *23*, 1408. [CrossRef] [PubMed]
37. Pinto, D.; Vieira, E.F.; Peixoto, A.F.; Freire, C.; Freitas, V.; Costa, P.; Delerue-Matos, C.; Rodrigues, F. Optimizing the Extraction of Phenolic Antioxidants from Chestnut Shells by Subcritical Water Extraction Using Response Surface Methodology. *Food Chem.* **2021**, *334*, 127521. [CrossRef] [PubMed]
38. Gagić, T.; Knez, Ž.; Škerget, M. Subcritical Water Extraction of Horse Chestnut (*Aesculus hippocastanum*) Tree Parts: Scientific Paper. *J. Serbian Chem. Soc.* **2021**, *86*, 603–613. [CrossRef]
39. Zhu, G.; Zhu, X.; Xiao, Z.; Zhou, R.; Zhu, Y.; Wan, X. Kinetics of Peanut Shell Pyrolysis and Hydrolysis in Subcritical Water. *J. Mater. Cycles Waste Manag.* **2013**, *16*, 546–556. [CrossRef]
40. Gur, C.S.; Dunford, N.T.; Gumus, Z.P. Cytotoxicity of Subcritical Water Extracts Obtained from Byproducts Generated at Commercial Pecan Shelling Operations on Cancer Cells. *Bioresour. Bioprocess.* **2023**, *10*, 47. [CrossRef]
41. Liu, A.; Park, Y.; Huang, Z.; Wang, B.; Ankumah, R.O.; Biswas, P.K. Product Identification and Distribution from Hydrothermal Conversion of Walnut Shells. *Energy Fuels* **2006**, *20*, 446–454. [CrossRef]

42. Safari, F.; Salimi, M.; Tavasoli, A.; Ataei, A. Non-Catalytic Conversion of Wheat Straw, Walnut Shell and Almond Shell into Hydrogen Rich Gas in Supercritical Water Media. *Chin. J. Chem. Eng.* **2016**, *24*, 1097–1103. [CrossRef]
43. Safari, F.; Tavasoli, A.; Ataei, A. Gasification of Iranian Walnut Shell as a Bio-Renewable Resource for Hydrogen-Rich Gas Production Using Supercritical Water Technology. *Int. J. Ind. Chem.* **2017**, *8*, 29–36. [CrossRef]
44. Demirbas, A. Hydrogen-Rich Gas from Fruit Shells via Supercritical Water Extraction. *Int. J. Hydrogen Energy* **2004**, *29*, 1237–1243. [CrossRef]
45. Čolnik, M.; Knez, Ž.; Škerget, M. Sub- and Supercritical Water for Chemical Recycling of Polyethylene Terephthalate Waste. *Chem. Eng. Sci.* **2021**, *233*, 116389. [CrossRef]
46. Čolnik, M.; Kotnik, P.; Knez, Ž.; Škerget, M. Hydrothermal Decomposition of Polyethylene Waste to Hydrocarbons Rich Oil. *J. Supercrit. Fluids* **2021**, *169*, 105136. [CrossRef]
47. Talmaciu, A.I.; Ravber, M.; Volf, I.; Knez, Ž.; Popa, V.I. Isolation of Bioactive Compounds from Spruce Bark Waste Using Sub- and Supercritical Fluids. *J. Supercrit. Fluids* **2016**, *117*, 243–251. [CrossRef]
48. Gagić, T.; Perva-Uzunalić, A.; Knez, Ž.; Škerget, M. Hydrothermal Treatment of Sugars to Obtain High-Value Products. *J. Serbian Chem. Soc.* **2020**, *85*, 97–109. [CrossRef]
49. El Hamdouni, Y.; El Hajjaji, S.; Szabó, T.; Trif, L.; Felhősi, I.; Ab, K.; Labjar, N.; Hermouche, L.; Shaban, A. Biomass Valorization of Walnut Shell into Biochar as a Resource for Electrochemical Simultaneous Detection of Heavy Metal Ions in Water and Soil Samples: Preparation, Characterization, and Applications. *Arab. J. Chem.* **2022**, *15*, 104252. [CrossRef]
50. Yang, H.; Yan, R.; Chen, H.; Lee, D.H.; Zheng, C. Characteristics of Hemicellulose, Cellulose and Lignin Pyrolysis. *Fuel* **2007**, *86*, 1781–1788. [CrossRef]
51. Kaya, M.; Şahin, Ö.; Saka, C. Preparation and TG/DTG, FT-IR, SEM, BET Surface Area, Iodine Number and Methylene Blue Number Analysis of Activated Carbon from Pistachio Shells by Chemical Activation. *Int. J. Chem. React. Eng.* **2018**, *16*, 20170060. [CrossRef]
52. Açıkalın, K. Thermogravimetric Analysis of Walnut Shell as Pyrolysis Feedstock. *J. Therm. Anal. Calorim.* **2011**, *105*, 145–150. [CrossRef]
53. Okonkwo, C.E.; Hussain, S.Z.; Onyeaka, H.; Adeyanju, A.A.; Nwonuma, C.O.; Bashir, A.A.; Farooq, A.; Zhou, C.; Shittu, T.D. Lignin Polyphenol: From Biomass to Innovative Food Applications, and Influence on Gut Microflora. *Ind. Crops Prod.* **2023**, *206*, 117696. [CrossRef]
54. Gagić, T.; Knez, Ž.; Škerget, M. Hydrothermal Hydrolysis of Sweet Chestnut (*Castanea sativa*) Tannins. *J. Serbian Chem. Soc.* **2019**, *85*, 108. [CrossRef]
55. Dizhbite, T.; Telysheva, G.; Jurkjane, V.; Viesturs, U. Characterization of the Radical Scavenging Activity of Lignins—Natural Antioxidants. *Bioresour. Technol.* **2004**, *95*, 309–317. [CrossRef] [PubMed]
56. You, S.; Xie, Y.; Zhuang, X.; Chen, H.; Qin, Y.; Cao, J.; Lan, T. Effect of High Antioxidant Activity on Bacteriostasis of Lignin from Sugarcane Bagasse. *Biochem. Eng. J.* **2022**, *180*, 108335. [CrossRef]
57. Meng, W.; Shi, J.; Zhang, X.; Lian, H.; Wang, Q.; Peng, Y. Effects of Peanut Shell and Skin Extracts on the Antioxidant Ability, Physical and Structure Properties of Starch-Chitosan Active Packaging Films. *Int. J. Biol. Macromol.* **2020**, *152*, 137–146. [CrossRef] [PubMed]
58. Anjum, S.; Gani, A.; Ahmad, M.; Shah, A.; Masoodi, F.A.; Shah, Y.; Gani, A. Antioxidant and Antiproliferative Activity of Walnut Extract (*Juglans regia* L.) Processed by Different Methods and Identification of Compounds Using GC/MS and LC/MS Technique. *J. Food Process. Preserv.* **2017**, *41*, e12756. [CrossRef]
59. Paysepar, H.; Venkateswara Rao, K.T.; Yuan, Z.; Shui, H.; Xu, C. Production of Phenolic Chemicals from Hydrolysis Lignin via Catalytic Fast Pyrolysis. *J. Anal. Appl. Pyrolysis* **2020**, *149*, 104842. [CrossRef]
60. Balasundram, N.; Sundram, K.; Samman, S. Phenolic Compounds in Plants and Agri-Industrial by-Products: Antioxidant Activity, Occurrence, and Potential Uses. *Food Chem.* **2006**, *99*, 191–203. [CrossRef]
61. Yang, J.; Chen, C.; Zhao, S.; Ge, F.; Liu, D. Effect of Solvents on the Antioxidant Activity of Walnut (*Juglans regia* L.) Shell Extracts. *J. Food Nutr. Res.* **2014**, *2*, 621–626. [CrossRef]
62. Sultanova, M.; Dalabayev, A.; Saduakas, A.; Nurysh, A.; Akzhanov, N.; Yakiyayeva, M. The Potential of Non-Traditional Walnut Shells Waste for the Production of Antioxidant Reach Extracts Intended for the Food Industry. *Potravinarstvo Slovak J. Food Sci.* **2023**, *17*, 391–404. [CrossRef]
63. Gagić, T.; Perva-Uzunalić, A.; Knez, Ž.; Škerget, M. Hydrothermal Degradation of Cellulose at Temperature from 200 to 300 °C. *Ind. Eng. Chem. Res.* **2018**, *57*, 6576–6584. [CrossRef]
64. Mok, W.S.L.; Antal, M.J., Jr. Uncatalyzed Solvolysis of Whole Biomass Hemicellulose by Hot Compressed Liquid Water. *Ind. Eng. Chem. Res.* **1992**, *31*, 1157–1161. [CrossRef]
65. Rasmussen, H.; Sørensen, H.R.; Meyer, A.S. Formation of Degradation Compounds from Lignocellulosic Biomass in the Biorefinery: Sugar Reaction Mechanisms. *Carbohydr. Res.* **2014**, *385*, 45–57. [CrossRef] [PubMed]