fermentation

MDPI

Review

Table Olive Wastewater as a Potential Source of Biophenols for Valorization: A Mini Review

Alberto J. Huertas-Alonso [1], Diego J. Gonzalez-Serrano [1], Milad Hadidi [1,*], Manuel Salgado-Ramos [1,2], Jose C. Orellana-Palacios [1], M. Prado Sánchez-Verdú [1], Qiang Xia [3], Mario J. Simirgiotis [4], Francisco J. Barba [5], Basharat Nabi Dar [6,*] and Andres Moreno [1,*]

1 Department of Organic Chemistry, Faculty of Chemical Sciences and Technologies, University of Castilla-La Mancha, 13071 Ciudad Real, Spain; alberto.halonso@uclm.es (A.J.H.-A.); diegojesus.gonzalez@uclm.es (D.J.G.-S.); manuel.salgado@uclm.es (M.S.-R.); josecarlos.orellana@uclm.es (J.C.O.-P.); mariaprado.sanchez@uclm.es (M.P.S.-V.)
2 Department of Drug Science and Technology, University of Turin, Via P. Giuria 9, 10125 Turin, Italy
3 Key Laboratory of Animal Protein Food Processing Technology of Zhejiang Province, College of Food and Pharmaceutical Sciences, Ningbo University, Ningbo 315832, China; qiang.xia@sjtu.edu.cn
4 Institute of Pharmacy, Faculty of Sciences, Campus Isla Teja, Universidad Austral de Chile, Valdivia 5090000, Chile; mario.simirgiotis@uach.cl
5 Nutrition and Food Science Area, Preventive Medicine and Public Health, Food Science, Toxicology and Forensic Medicine Department, Faculty of Pharmacy, Universitat de València, Avda. Vicent Andrés Estellés, s/n, Burjassot, 46100 Valencia, Spain; francisco.barba@uv.es
6 Department of Food Technology, Islamic University of Science and Technology, Kashmir 192122, India
* Correspondence: milad.hadidi@uclm.es (M.H.); darnabi@gmail.com (B.N.D.); andres.moreno@uclm.es (A.M.)

check for updates

Citation: Huertas-Alonso, A.J.; Gonzalez-Serrano, D.J.; Hadidi, M.; Salgado-Ramos, M.; Orellana-Palacios, J.C.; Sánchez-Verdú, M.P.; Xia, Q.; Simirgiotis, M.J.; Barba, F.J.; Dar, B.N.; et al. Table Olive Wastewater as a Potential Source of Biophenols for Valorization: A Mini Review. *Fermentation* **2022**, *8*, 215. https://doi.org/10.3390/fermentation8050215

Academic Editor: Sathyanarayanan Sevilimedu Veeravalli

Received: 1 April 2022
Accepted: 28 April 2022
Published: 9 May 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

Abstract: The table olive industry generates high amounts of wastewater annually during the alkaline treatment, fermentation, and washing steps of olives. High conductivity and salt content, as well as the high organic and biophenol contents of these waters, is a worldwide problem, especially in the Mediterranean region, which is the major table olive producing area. There is a wide variety of bioactives found in wastewater derived from table olive processing. The main compounds of table olive wastewater, such as those derived from phenolic, hydrocarbon, and sugar fractions, can be recovered and reused. In this review, the table olive manufacturing processes and the volumes and composition of wastewater generated from the different methods of table olive processing are discussed. In addition, biophenols of table olive water and their biological activities are also introduced. The high concentrations of valuable biophenols, such as tyrosol and hydroxytyrosol, show promising potential for valorizing table olive wastewater; however, more research is needed in this area.

Keywords: wastewater; table olives; valorization; phenolic compounds; levulinic acid; oleuropein; tyrosol

1. Introduction

Annually, around 3 million tonnes of table olives are produced, with around 31% contribution from the European region. In the 2018/2019 season, the annual global table olive production was around 2.5 million tonnes (up to 2.9 million tonnes in 2019/2020) [1]. This high production results in a large amount of processing wastewater, which poses a threat to the environment due to its high salinity and conductivity, and high organic and phenolic compound contents. The wastewater problem is mainly concentrated in the Mediterranean area, where most table olives are produced. For example, countries such as Spain produce around 540,000 tonnes of wastewater [2].

This industry has a significant economic impact in the Mediterranean countries. The European Union contributes around 31% of the global olive production (approximately 900 thousand tonnes), Spain and Greece being the main contributors [2,3]. It is also worth noting that the other important production centers from the Mediterranean countries, such as Egypt, Turkey, Algeria, and Morocco, together contribute around 50% of the global production. Figure 1 shows the main producing countries of table olives during the 2019/2020 season.

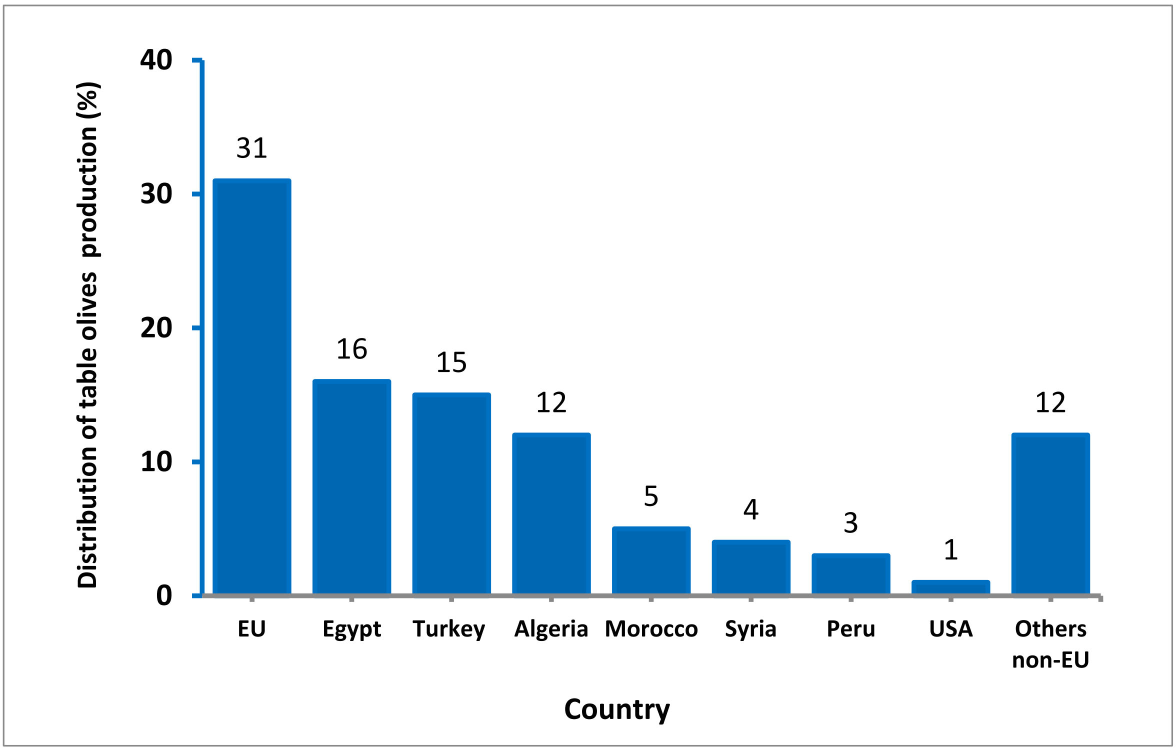

Figure 1. Main producing countries of table olives during the 2019/2020 season (Statista, 2019/2020).

2. Table Olive Manufacturing Processes

The fruit of the olive tree cannot be consumed directly once collected, since it has an extremely bitter taste. This flavor is given by a glycosylated seco-iridoid compound called oleuropein [4]. Along with oleuropein, the other seco-iridoid glycosides present in olives, although in smaller quantities, are ligstroside and demethyloleuropein (Figure 2) [4].

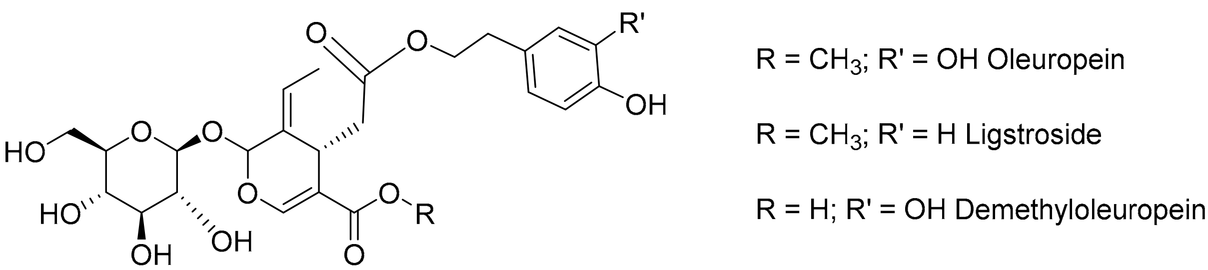

Figure 2. Structure of the main seco-iridoid glycosides present in olives.

Since the ancient times, different methods have been developed to eliminate this acidity or bitterness and make olives an edible fruit. In the early twentieth century, sodium hydroxide (NaOH) was used to hydrolyze oleuropein, which resulted in the two most important production processes: (i) the Spanish green olive process and (ii) the Californian black olive process (Figure 3).

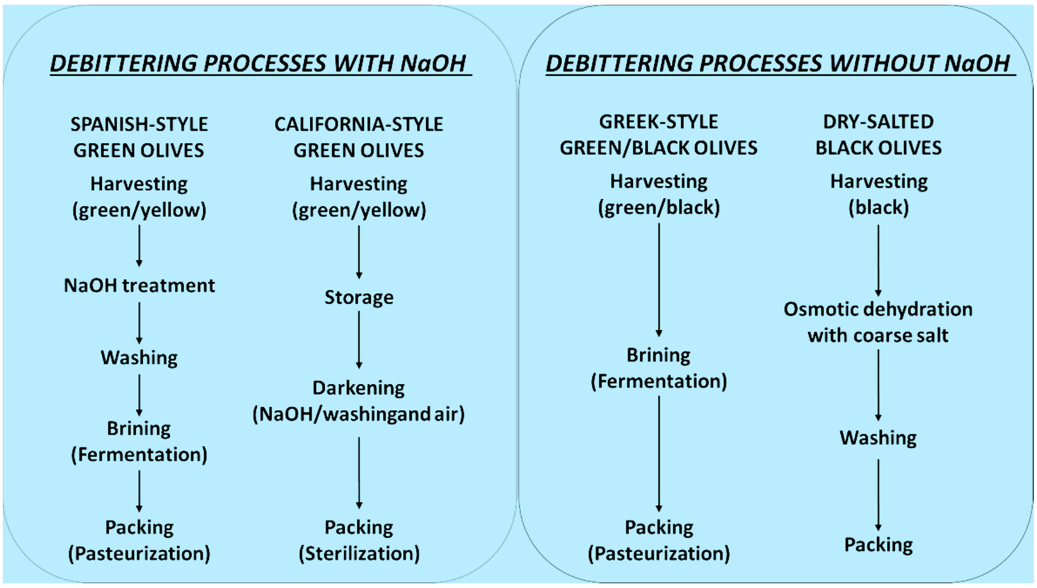

Figure 3. Different treatments for table olives [5].

The first treatment consists of immersing the olives in a solution of NaOH and, after a few days, eliminating this solution by inducing different washes to eliminate any remaining NaOH. On the other hand, the second type differs from the first treatment, as once the solution of NaOH has been removed, the olives are left in the air for 24 h before washing. The NaOH solution and the washing waters do not have any further application, and therefore, they are discarded in the two treatments, hence the great production of polluting water [5]. There are also other treatments that do not use NaOH for the acidity removal process, the Greek style being the most widely used, since it is the most economical. When the Greek style is used, the olives are placed directly in brine and left there for months or years in order to remove the bitterness completely. There is an increased use of the Greek-style treatment, as it has a low level of pollution, and it is in full agreement with the actual trends to consume products as natural and least treated as possible [6].

3. Table Olive Wastewater

Considering the large volume of table olive production, as well as the main processes used for this purpose, it is possible to form an idea that the main source of environmental pollution is that produced by the discharges of liquid effluents [5]. All of the wastewaters from table olive processing cause a serious environmental problem because of their chemical characteristics and the huge volumes produced [7].

Those involving lye treatment and extensive washings for alkali removal are the most polluting (i.e., Californian-style black-ripe, Spanish-style green, Californian-style green-ripe olives). The production of Californian-style black-ripe olives has the largest pollutant potential (maximum total volume of 6 L/kg olives produced). On the other hand, processing based on untreated olives (i.e., naturally black, green or turning-color olives) generates lesser quantities of wastewater (1 L/kg olive produced) from the fermentation brine (Figure 4). Complete information on the amounts of wastewaters produced by table olive processing should also include those derived from post-treatment (e.g., packaging) [6,8].

A few years ago, nature was responsible for eliminating or degrading the waste of this industry. However, the excessive increase in table olive production has overwhelmed this capacity for degrading these wastewaters by nature, rendering such previously innocuous wastes a threat. Water, as an essential resource for life, needs efficient use. The problem lies in the amount of water demanded by this industry, as seen above, which is estimated as 2000 m^3 per tonne of olives. In addition, companies need large areas to establish natural evaporation ponds, which could involve both authorization and administrative problems [9]. Therefore, in view of the difficulty of companies in expanding the processes, increased control and administrative sanctions, waste treatment becomes almost indispensable or mandatory. There are mainly two types of effluents: those generated in the industry, from the different processing processes, and those generated by precipitation [10]. The unbiodegradable organic load, as well as the chemical load of water produced at different stages of the industrial process, will depend on the type of processing carried out. As mentioned above, the treatment of table olive uses chemicals, such as NaOH or sodium chloride (NaCl), and large amounts of clean water for the degreasing, washing, brine and packaging phases. The chemical characteristics and high volume are the main environmental problems related to these wastewaters. Other problems to consider are pH, high conductivity due to its high saline content or waters strongly colored by the polyphenols that are part of the fruits [5]. Olives treated with NaOH need up to five times more water than those treated naturally, and they also need more energy resources and labor to be treated [10].

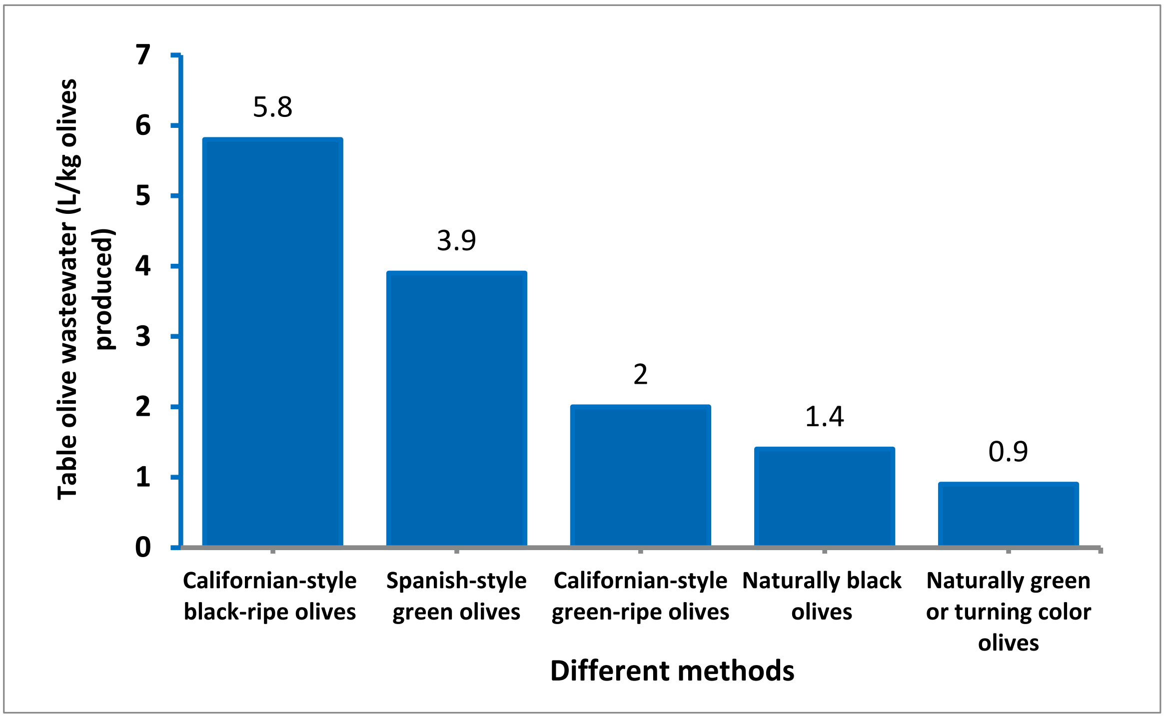

Figure 4. Average volumes of wastewaters generated from the different methods of table olive processing [6].

In general, the streams of water formed in the different processes are mixed and stored in evaporation ponds. This technique has several associated problems, such as bad odors, insect proliferation and underground aquifer contamination. Although they are not permitted facilities, in Spain, for example, they are still operational [3]. There is a current trend to change the way human beings are acting in order to do as little damage to the environment as possible. Possible solutions are summarized in two ways: control of water consumed and control of waste produced. To carry out the control of the water consumed, it is necessary to know, on the one hand, the water consumed at each point of the process, and on the other hand, the volume of the effluent produced. In factories that possess a high level of efficiency, around 2–3 L of water per kilogram of olives are employed, while in the least efficient ones, it is possible to reach up to 15 L per kilogram of olives [11]. Among the different measures for the reduction in waste and according to different studies, the processes with most industrial applications in the reduction or elimination of these pollutants are the following:

- Reuse of cooking bleach: it is a simple operation and requires few complementary installations, as a pump and an auxiliary tank are sufficient. It is a very profitable process, as it takes advantage of the high amounts of NaOH that would be lost. This reduces the volume of discharges, saves water and avoids a large amount of polluting matter.
- Washing elimination: it has been seen that the use of a single washing step could provide a fermentation and a final product that do not differ from those obtained by performing more washes.
- Purification and reuse of brines: until now, the reuse of brines has not been very successful in the industry, as they present suspended solids that give it turbidity (mainly by lactic fermentation). Considering the high polluting power of fermentation brines, which have a large amount of lactic acid, the regeneration of these has been studied for later use.
- Two systems have been developed to remove suspended solids and color:
- Adsorption on active carbon and tangential filtration. One of the main advantages of this method is its versatility, since the properties of the treatment can be adjusted according to the purpose that will be given to the generated brine, thus making the cost as fair as possible and without additional costs [12]. If the brine is intended for packaging, all color must be removed, which demands more amounts of active carbon. However, if it is used for other procedures in the same industry, filtration would be enough, which would be conducted with less active coal. Likewise, the type of coal is decisive, since the chosen one will have one behavior or another. An example is the number of polyphenols that retain each other [13].
- Ultrafiltration through a membrane of a certain pore size (most commonly used on an industrial level). The essential part of this type of treatment is the type of filter membrane, as well as its pore size [14–16]. In order to achieve a good rinsing of the brine, it is necessary to use a pore size equal to or less than 1 kDa. Some variables to consider when using this technique are pressure (permeation increases with pressure, operating as much as possible), initial concentration of suspended solids (more, less flow) and temperature (increasing this decreases viscosity, and therefore, favors filtration).

Wastewaters produced during acidity removal and washing processes occur in a very short period of time (between September and November) and in small geographical areas, while wastewaters obtained in the fermentation process are obtained throughout the year in packaging plants. Because of this and the different chemical characteristics they possess (the former have high pH values, whereas fermentation waters have low pH values, together with each stream possessing different amounts of suspended oils, polyphenols, etc.), it is necessary to perform different treatments for each wastewater stream [17–19].

Nowadays, biorefineries include a wide range of technologies to separate the main components of waste generated in industrial and agri-food processes (carbohydrates, proteins, fats, etc.), which are considered renewable raw materials that can be reused or recycled to produce energy (biofuels) or to obtain other high-value-added chemicals that meet environmental needs [18–20]. Within Europe and North America, it has been estimated that each person generates around 280–300 kg of food waste per year. These crop-derived residues (such as wheat, barley, rye, oats, or maize) could help to meet energy needs. However, the main drawback of using this waste is that crops have time variations or limitations. It is therefore logical to also consider waste from other sources, such as forest waste, which is the most important source of renewable energy in Europe [21]. Therefore, the waste generated in the processes, both industrial and agri-food, represents an alternative, since it is a renewable source. Proper treatment of waste to obtain high-value-added compounds requires a deep understanding of its chemical composition and structure for successful fractionation [22,23]. The following section addresses the identification of the main components found in these wastewaters and which value-added products could be obtained from them [24].

4. Composition of Table Olive Wastewater

As mentioned above, the olive industry generates large volumes of wastewater, characterized by high biochemical oxygen demand (BOD) and chemical oxygen demand (COD). On the other hand, these waters contain significant amounts of food components (proteins, fats, sugars, fiber, phenolic compounds, etc.) with remarkable nutritional, biological, and functional properties [25].

Olive is a fruit characterized by a low sugar content, a high concentration of oil, and a bitter taste caused by oleuropein. Due to the high phenolic compound content of olives, wastewaters from both olive oil production and table olive processing can be sources of species with a high antioxidant capacity (Table 1). These phenolic compounds are of great interest to the food, pharmaceutical, and cosmetic industries due to their antioxidant properties [26]. They can mitigate the effect of reactive species involved in ageing and inflammatory, coronary, and degenerative diseases, as well as being potential antitumor compounds [27]. The concentration and types of phenols are highly variable in wastewater from table olive processing, as these depend on factors such as harvest, region, variety, treatment, etc. Thus, it is complicated to predict what type of phenols are present in these waters. For this reason, most authors who deal with the management of these wastewaters do not measure free phenolic compounds but rather the global parameters that are taken into account in their entirety, such as total phenols and antioxidant capacity. Total phenols are measured spectrophotometrically according to the Folin–Ciocalteu method, and the results are expressed in mg/L of gallic acid or in mg/L of tyrosol, while antioxidant capacity is measured by total antioxidant activity (TAA) or DPPH (2,2-diphenyl-1-picrylhydrazyl) radical-scavenging activity [28].

Table 1. Physicochemical parameters and chemical analysis of wastewater corresponding to the three stages of processing of Spanish green olives [25].

Parameters	Debittering Process Wastewaters	Washing Process Wastewaters	Fermentation Process Wastewaters
COD (mg/L)	9390	13,630	18,910
BOD_5 (mg/L)	3115	4640	6050
pH	12.99	11.52	4.30
Conductivity (ms/cm)	11.13	10.17	53.10
Color	1.96	1.44	0.49
Total phenols (mg/L)	211.2	446.1	182.1
Total phenolic compounds (mg/L)	80.39	117.23	76.41
Benzoic acid	0.93	1.50	0.80
2-Phenoxyethanol	1.39	2.76	0.27
Cinnamic acid	1.67	1.23	N.D
Tyrosol	16.33	47.40	16.83
Phenylacetic acid	8.09	1.79	1.69
3,4-Dimethoxybenzoic acid	1.86	10.91	3.96
Vanillic acid	5.55	5.43	2.69
Hydroxytyrosol	9.69	16.21	6.09
3,4-Dihydroxybenzoic acid	10.26	1.52	0.26
Syringic acid	N.D	10.25	4.59
4-Hydroxycinnamic acid	4.18	6.00	1.33
Dibutyl phthalate	7.03	9.71	32.82
Gallic acid	5.09	0.96	3.89

Table 1. *Cont.*

Parameters	Debittering Process Wastewaters	Washing Process Wastewaters	Fermentation Process Wastewaters
Ferullic acid	2.00	1.56	1.00
Caffeic acid	6.32	N.D	0.19
Total organic acids (mg/L)	27.38	27.20	157.23
Total amino acids (mg/L)	31.82	46.31	13.74
Total sugars (mg/L)	149.33	193.4	63.99

With respect to phenolic compounds, their concentration is usually measured by high-resolution liquid chromatography (HPLC). In table olive processing water, tyrosol and hydroxytyrosol are the predominant polyphenols. The oleuropein molecule is hydrolyzed in the acidity reduction process, generating hydroxytyrosol and elenolic acid glucoside. Regarding tyrosol, it is obtained to a lesser extent from the hydrolysis of ligstroside (Figure 5). Therefore, we do not find either oleuropein or ligstroside in wastewater equivalents [3]. The levels of elenolic acid glucoside decrease rapidly due to the conversion of this compound into elenolic acid and glucose (Figure 5) through the acidic conditions produced by the microbial action (it is a substrate for lactic acid bacteria) [29]. In previous study, Huertas-Alonso et al. (2021) observed that the hydroxytyrosol content of table olive wastewaters was between 2 to 6 times higher than the tyrosol content, depending on washing time after alkaline treatment. Furthermore, the first washing wastewater sample contained higher tyrosol content than the debittering wastewater (48 mg/L residue vs. 126 mg/L residue) [10]. Biophenols from Greek-style olive oil and table olive wastewater were concentrated and recovered by an adsorption resin. The main phenols found in the table olive wastewater were hydroxytyrosol, tyrosol, hydroxytyrosol4-O-glucoside, and 11-methyl-oleoside [30].

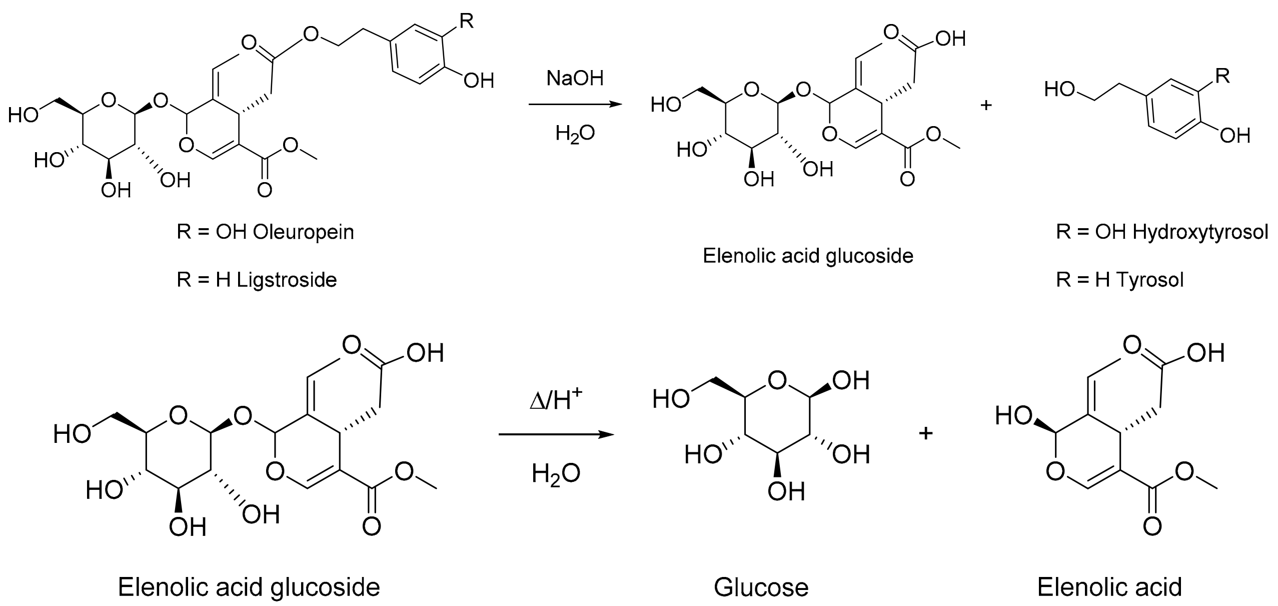

Figure 5. Oleuropein, ligstroside, and elenolic acid glucoside hydrolysis [31].

In view of the compounds obtained after the hydrolysis of oleuropein, the valorization of these waters can be divided into two pathways. On the one hand, (i) obtaining phenolic compounds, such as hydroxytyrosol and tyrosol, and on the other hand, (ii) the valorization of the sugar-rich fraction, in which one of the compounds is elenolic acid glucoside, whose structure contains a glucose molecule [32].

5. Biological Activities

Based on the literature data, the biological activities, including antioxidant, antimicrobial, cytotoxicity, and anti-inflammatory activities, of the wastewater streams derived from table olive processing are shown in Table 2. The biological activities of olive phenols, such as oleuropein, verbascoside, hydroxytyrosol, tyrosol, luteolin, and apigenin 7-O-glycosides, as well as phenolic acids, which are minor constituents of olive fruits, have been widely evaluated [33]. In the phenolic fraction of table olive wastewater, the main compounds are hydroxytyrosol and tyrosol. Hydroxytyrosol is a phenolic compound found in olive leaves and ester-shaped fruit or after degradation, in its free form. The main activity of this compound is as antioxidant, being one of the highest among polyphenols [34]. Antioxidant implies that it will be a powerful free radical scavenger, which is formed in different metabolic processes of cells and is a very reactive chemical species [3]. Free radicals are highly reactive and unstable chemical species (millisecond life), characterized by having one or more uneven electrons. They are formed as reaction intermediates from a homolytic rupture of a bond. Excess of free radicals can induce lipid and protein oxidation, altered cell membrane integrity, and DNA damage, causing serious pathologies, such as cancer (particularly mouth, pharynx, and oesophagus), Parkinson's, diabetes, or Alzheimer's. Therefore, applying an external source of antioxidants can provide substantial help in preventing cellular oxidative stress and its consequences [35]. Free radicals are generated in the body due to the presence of oxygen, although their production is increased by environmental pollution, smoking, high-fat diets, excessive exposure to solar radiation, etc. [36]. For instance, polyphenols are of great interest to the food [37], pharmaceutical [27], packaging [38], and cosmetic (sun creams) [39] industries due to their particular characteristics. The way these free radicals act is well known. They react with other molecules by snatching an electron to stabilize themselves, causing the other molecules to become a radical. This molecule will react with another molecule following the chain. Thus, this process can cause major changes in species, such as DNA or proteins. Bouaziz et al. [40] reported the ethyl acetate extract of olive table wastewater showed high hydroxytyrosol and tyrosol concentrations of 690 and 98 mg g/L dry weight extract, respectively. DPPH and ABTS (2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid)) scavenging radical activities of table olive wastewater extract were 8.91 IC_{50} (µg/mL) and 2.06 (TEAC (Trolox equivalent antioxidant capacity) mmol). In addition, the extract had growth inhibition effects on human cells in a dose-dependent manner. HeLa and DG75 cell lines showed the highest sensitivity to the cytotoxic actions of the extract [40]. In a similar study, Belaqziz et al. [41] observed table olive processing wastewater extracts had high DPPH radical scavenging activities. The extract had high antibacterial activity against S. aureus at a concentration of 5 mg [41].

Table 2. Main biophenols in table olive wastewater and their respective biological activity.

Biological Activity	Remarks	[Ref]
Antioxidant	Hydroxytyrosol was isolated from table olive effluents (4127 µmol of Trolox/mmol of active molecule)	[42]
	DPPH and ABTS scavenging radicals activities of table olive wastewater extract were 8.91 IC_{50} (µg/mL) and 2.06 (TEAC mmol)	[40]
	Table olive processing wastewaters extracts had high DPPH radical scavenging activities	[41]
Cytotoxicity	Table olive wastewater extract had growth inhibition effects on human cells in a dose-dependent manner. HeLa and DG75 cell lines showed the highest sensitivity to the cytotoxic actions of the extract	[40]
Anti-inflammatory	Hydroxytyrosol isolated from table olive effluents inhibited the gene expression of any pro-inflammatory cytokine	[42]
Antimicrobial	Positive activity against *S. aureus* was demonstrated from table olive processing wastewaters	[41]
	Table olive wastewaters showed in vitro antimicrobial activity against the bacteria *Erwinia amylovora* and *Pseudomonas syringae*, and the *Oomycota Phytophthora* sp	[43]

6. Identification of Phenolic Compounds in Olive Waste

Chromatographic techniques, including gas chromatography (GC) and HPLC, are the major separation methodologies to quantify phenolics in both olive oil and table olive processing wastewaters. Although in some cases these methods are employed directly to detect those fractions, which are known to be present in samples using an external standard, the comprehensive and accurate profiling of phenolic composition requires further identification processes [41]. There have been multiple identification techniques established for the structural determination of phenolic compounds in olive-related products, which tend to be hyphenated techniques, integrating separation and quantification, such as gas chromatography–mass spectrometry (GC-MS), capillary electrophoresis mass spectrometry, and liquid chromatography mass spectrometry (LC-MS). Mass spectrometry (MS) shows the advantages in analyzing phenolics, such as high accuracy and sensitivity. Particularly, the Fourier transform ion cyclotron resonance MS (FT-ICR-MS) is able to identify the compounds and compare their abundance without sample pre-treatments, including separation and purification steps. Although it is less sensitive than MS [44,45], nuclear magnetic resonance (NMR) spectroscopy is capable of simultaneously detecting numerous metabolites through readily sampling pre-treatment procedures in a non-invasive, selective, and fast way. In addition, it also shows superior structural elucidating capability, especially the ability to provide information about isomeric and isobaric compounds [46].

^{1}H- and ^{13}C-NMR spectroscopy, involving one-dimensional (1D) and two-dimensional (2D) techniques, has been employed for the analysis of complex mixtures, such as olive oil, olive fruit, and olive mill wastewater [47] for characterization, authentication, and discrimination purposes. For example, the structure elucidation by comprehensive ^{1}H/^{13}C-NMR spectroscopy revealed that the major phenolic components of representative green olive drupes from Italy and Greece included tyrosol, hydroxytyrosol, vanillin, vanillic acid, phloretic acid, (+)-pinoresinol, (+)-1-acetoxypinoresinol, and dehydrodiconiferyl alcohol [48]. The detection of the olive-derived phenolic components is performed according to the chemical shifts of multiple model compounds assigned.

^{1}H-NMR is used to analyze the polar polyphenols and to provide information about lipid fractions, including fatty acid composition and unsaturation degrees, as well as some other minor components, while ^{13}C-NMR can help characterize the stereochemistry information of unsaturation. Relative to ^{1}H- and ^{13}C-NMR spectroscopy, ^{31}P-NMR requires the derivatization step for detecting and quantifying phenolic compounds. A relatively wide range of ^{31}P chemical shifts contributes to simplifying the analysis process of ^{31}P-NMR spectra. In addition, the 100% natural abundance of the ^{31}P and the use of a known amount of internal standard allow the measurement of absolute concentration of compounds, thus making normalization unnecessary [49]. Based on the identification of the phosphitylated phenolics through the reaction of hydroxyl and carboxyl groups of polyphenols with the phosphitylating reagent (Figure 6), Christophoridou et al. employed ^{31}P-NMR spectroscopy to quantify phenolic compounds of olive oil using phosphitylated cyclohexanol as internal standard [50]. However, there are some drawbacks encountered during the analysis of NMR spectrometry, which causes ambiguous assignments, such as strong signal overlapping and variation in intensities owing to the presence of a wide range of chemical components with different concentration distributions [10].

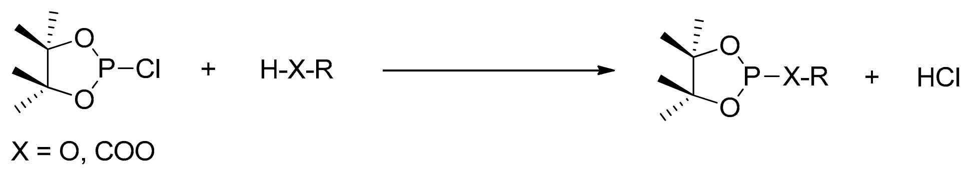

Figure 6. The derivatization of the hydroxyl and carboxyl groups of polyphenols with 2-chloro-4,4,5,5-tetramethyldioxaphospholane.

To deal with the problems mentioned above, chromatographically coupled NMR technologies have been developed and optimized [46]. Chromatography technologies, such as preparative or semipreparative LC, column chromatography, and thin-layer chromatography, were first employed to isolate polyphenols, followed by the subsequent off-line analysis by means of NMR spectroscopy. For example, Owen et al. employed semipreparative HPLC to isolate and purify the phenolic compounds of brined olives, and then the purified compounds were subjected to structure elucidation using ^{1}H- and ^{13}C-NMR spectroscopies [51]. However, the fractionation and separation procedures followed by off-line NMR analysis is time and labor consuming. Thus, the online hyphenation of NMR-based structure elucidation and the powerful separation technique has been proposed, and its applicability has been widely evaluated in different types of sample matrices [52], concluding that the LC-NMR systems and their mode selection rely on the specific samples. A major improvement in the NMR spectroscopy sensitivity has been obtained by incorporating a solid-phase extraction (SPE) system after LC separation and before NMR analysis. Christophoridou et al. used LC-SPE-NMR to achieve the simultaneous determination of four types of oleuropein and the identification of new phenolic compounds, which have not been reported previously [53].

7. Conclusions

The olive production is approximately 800 thousand tonnes worldwide, with Spain and Greece being the main contributors in the Mediterranean, but the use of water in the industrial process is huge, at 2000 m^3 per tonne of olives, which makes the wastewater generated a great threat to the environment but also a source of organic compounds that can be recovered and used. Some solutions to avoid the water contamination problem, such as better control or reuse of the water consumed and control of the waste generated, were revised. The processes for the recovery of biophenols in the waste were discussed. Furthermore, some uses were proposed, as well as the generation and use of high-value products from the recovered organic fractions, such as those derived from phenolic, hydrocarbon, and sugar fractions, were elaborated. Finally, the techniques for the identification and quantification of biophenols in olive-related products were revised.

Author Contributions: Conceptualization: A.M. and M.H.; methodology, D.J.G.-S., J.C.O.-P. and A.J.H.-A.; formal analysis and resources: M.P.S.-V., M.S.-R., F.J.B., B.N.D. and M.J.S.; writing—original draft preparation, A.J.H.-A., D.J.G.-S., Q.X., J.C.O.-P. and M.H.; writing—review and editing: A.J.H.-A., D.J.G.-S. and M.H.; validation and supervision: A.M., M.H., B.N.D. and F.J.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no specific grant.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding authors.

Acknowledgments: The authors thank the P320RT0186-BIOLATES project for supporting this review.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Olive Global Production Share by Country 2018/2019 | Statista. Available online: https://www.statista.com/statistics/937256/share-of-table-olive-production-by-country-global/ (accessed on 1 March 2022).
2. Rincón-Llorente, B.; de la Lama-Calvente, D.; Fernández-Rodríguez, M.J.; Borja-Padilla, R. Table Olive Wastewater: Problem, Treatments and Future Strategy. A Review. *Front. Microbiol.* **2018**, *9*, 1641–1664. [CrossRef] [PubMed]
3. Álvarez-Blanco, S.; Mendoza-Roca, J.A.; Corbatón-Báguena, M.J.; Vincent-Vela, M.C. Valuable Products Recovery from Wastewater in Agrofood by Membrane Processes. In *Sustainable Membrane Technology for Water and Wastewater Treatment*; Figoli, A., Criscuoli, A., Eds.; Springer: Singapore, 2017; pp. 295–318. ISBN 978-981-10-5621-5 978-981-10-5623-9.

4. Cardoso, S.M.; Falcão, S.I.; Peres, A.M.; Domingues, M.R.M. Oleuropein/Ligstroside Isomers and Their Derivatives in Portuguese Olive Mill Wastewaters. *Food Chem.* **2011**, *129*, 291–296. [CrossRef] [PubMed]
5. Brenes, M.; Ramírez, E.; García, P.; Medina, E.; de Castro, A.; Romero, C. *New Developments in Table Olive Debittering*; International Society for Horticultural Science (ISHS): Leuven, Belgium, 2018; pp. 483–488.
6. Papadaki, E.; Mantzouridou, F.T. Current Status and Future Challenges of Table Olive Processing Wastewater Valorization. *Biochem. Eng. J.* **2016**, *112*, 103–113. [CrossRef]
7. Ayed, L.; Asses, N.; Chammem, N.; ben Othman, N.; Hamdi, M. Advanced Oxidation Process and Biological Treatments for Table Olive Processing Wastewaters: Constraints and a Novel Approach to Integrated Recycling Process: A Review. *Biodegradation* **2017**, *28*, 125–138. [CrossRef]
8. de Castro, A.; Brenes, M. Fermentation of Washing Waters of Spanish-Style Green Olive Processing. *Process Biochem.* **2001**, *36*, 797–802. [CrossRef]
9. Caporaso, N.; Formisano, D.; Genovese, A. Use of Phenolic Compounds from Olive Mill Wastewater as Valuable Ingredients for Functional Foods. *Crit. Rev. Food Sci. Nutr.* **2017**, *58*, 2829–2841. [CrossRef]
10. Huertas-alonso, A.J.; Gavahian, M.; González-serrano, D.J.; Hadidi, M.; Salgado-ramos, M.; Prado Sánchez-Verdú, M.; Simirgiotis, M.J.; Barba, F.J.; Franco, D.; Lorenzo, J.M.; et al. Valorization of Wastewater from Table Olives: NMR Identification of Antioxidant Phenolic Fraction and Microwave Single-Phase Reaction of Sugary Fraction. *Antioxidants* **2021**, *10*, 1652. [CrossRef]
11. Ferrer-Polonio, E.; Mendoza-Roca, J.A.; Iborra-Clar, A.; Alonso-Molina, J.L.; Pastor-Alcañiz, L. Biological Treatment Performance of Hypersaline Wastewaters with High Phenols Concentration from Table Olive Packaging Industry Using Sequencing Batch Reactors. *J. Ind. Eng. Chem.* **2016**, *43*, 44–52. [CrossRef]
12. Achak, M.; Hafidi, A.; Ouazzani, N.; Sayadi, S.; Mandi, L. Low Cost Biosorbent “Banana Peel” for the Removal of Phenolic Compounds from Olive Mill Wastewater: Kinetic and Equilibrium Studies. *J. Hazard. Mater.* **2009**, *166*, 117–125. [CrossRef]
13. Sabbah, I.; Marsook, T.; Basheer, S. The Effect of Pretreatment on Anaerobic Activity of Olive Mill Wastewater Using Batch and Continuous Systems. *Process Biochem.* **2004**, *39*, 1947–1951. [CrossRef]
14. El-Abbassi, A.; Kiai, H.; Raiti, J.; Hafidi, A. Application of Ultrafiltration for Olive Processing Wastewaters Treatment. *J. Clean. Prod.* **2014**, *65*, 432–438. [CrossRef]
15. Kiai, H.; García-Payo, M.C.; Hafidi, A.; Khayet, M. Application of Membrane Distillation Technology in the Treatment of Table Olive Wastewaters for Phenolic Compounds Concentration and High Quality Water Production. *Chem. Eng. Process. Process Intensif.* **2014**, *86*, 153–161. [CrossRef]
16. Hadidi, M.; Khaksar, F.B.; Pagan, J.; Ibarz, A. Application of Ultrasound-Ultrafiltration-Assisted Alkaline Isoelectric Precipitation (UUAAIP) Technique for Producing Alfalfa Protein Isolate for Human Consumption: Optimization, Comparison, Physicochemical, and Functional Properties. *Food Res. Int.* **2020**, *130*, 108907. [CrossRef] [PubMed]
17. Ferrer-Polonio, E.; Carbonell-Alcaina, C.; Mendoza-Roca, J.A.; Iborra-Clar, A.; Álvarez-Blanco, S.; Bes-Piá, A.; Pastor-Alcañiz, L. Brine Recovery from Hypersaline Wastewaters from Table Olive Processing by Combination of Biological Treatment and Membrane Technologies. *J. Clean. Prod.* **2017**, *142*, 1377–1386. [CrossRef]
18. Hadidi, M.; Majidiyan, N.; Jelyani, A.Z.; Moreno, A.; Hadian, Z.; Khanegah, A.M. Alginate/Fish Gelatin-Encapsulated Lactobacillus Acidophilus: A Study on Viability and Technological Quality of Bread during Baking and Storage. *Foods* **2021**, *10*, 2215. [CrossRef] [PubMed]
19. Aghamohammadi, B.; Morshedi, A.; Akbarian, M.; Akbarian, A.; Hadidi, M.; Moayedi, F. Effect of high pressure processing of food characteristics: A review of quality aspect. *Int. J. Biosci.* **2014**, *4*, 193–205. [CrossRef]
20. Kamm, B.; Gruber, P.R.; Kamm, M. *Biorefineries-Industrial Processes and Products; Status Quo and Future Directions*; Wiley-VCH Verlag GmbH & Co: Weinheim, Germany, 2006.
21. Matharu, A.S.; de Melo, E.M.; Houghton, J.A. Opportunity for High Value-Added Chemicals from Food Supply Chain Wastes. *Bioresour. Technol.* **2016**, *215*, 123–130. [CrossRef]
22. Majidiyan, N.; Hadidi, M.; Azadikhah, D.; Moreno, A. Protein Complex Nanoparticles Reinforced with Industrial Hemp Essential Oil: Characterization and Application for Shelf-Life Extension of Rainbow Trout Fillets. *Food Chem. X* **2022**, *13*, 100202. [CrossRef]
23. Hesami, G.; Darvishi, S.; Zarei, M.; Hadidi, M. Fabrication of Chitosan Nanoparticles Incorporated with Pistacia Atlantica Subsp. Kurdica Hulls’ Essential Oil as a Potential Antifungal Preservative against Strawberry Grey Mould. *Int. J. Food Sci. Technol.* **2021**, *56*, 4215–4223. [CrossRef]
24. Corma, A.; Iborra, S.; Velty, A. Chemical Routes for the Transformation of Biomass into Chemicals. *Chem. Rev.* **2007**, *107*, 2411–2502. [CrossRef]
25. Parinos, C.S.; Stalikas, C.D.; Giannopoulos, T.S.; Pilidis, G.A. Chemical and Physicochemical Profile of Wastewaters Produced from the Different Stages of Spanish-Style Green Olives Processing. *J. Hazard. Mater.* **2007**, *145*, 339–343. [CrossRef] [PubMed]
26. Zahi, M.R.; Zam, W.; el Hattab, M. State of Knowledge on Chemical, Biological and Nutritional Properties of Olive Mill Wastewater. *Food Chem.* **2022**, *381*, 132238. [CrossRef] [PubMed]
27. Obied, H.K.; Allen, M.S.; Bedgood, D.R.; Prenzler, P.D.; Robards, K.; Stockmann, R. Bioactivity and Analysis of Biophenols Recovered from Olive Mill Waste. *J. Agric. Food Chem.* **2005**, *53*, 823–837. [CrossRef] [PubMed]
28. Haghani, S.; Hadidi, M.; Pouramin, S.; Adinepour, F.; Hasiri, Z.; Moreno, A.; Munekata, P.E.S.; Lorenzo, J.M. Application of Cornelian Cherry (*Cornus mas* L.) Peel in Probiotic Ice Cream: Functionality and Viability during Storage. *Antioxidants* **2021**, *10*, 1777. [CrossRef]

29. Ramírez, E.; Brenes, M.; de Castro, A.; Romero, C.; Medina, E. Oleuropein Hydrolysis by Lactic Acid Bacteria in Natural Green Olives. *LWT-Food Sci. Technol.* **2017**, *78*, 165–171. [CrossRef]
30. Mousouri, E.; Melliou, E.; Magiatis, P. Isolation of Megaritolactones and Other Bioactive Metabolites from "Megaritiki" Table Olives and Debittering Water. *J. Agric. Food Chem.* **2014**, *62*, 660–667. [CrossRef]
31. Cavaca, L.A.S.; Rodrigues, C.A.B.; Simeonov, S.P.; Gomes, R.F.A.; Coelho, J.A.S.; Romanelli, G.P.; Sathicq, A.G.; Martínez, J.J.; Afonso, C.A.M. Valorization of Oleuropein via Tunable Acid-Promoted Methanolysis. *ChemSusChem* **2018**, *11*, 2300–2305. [CrossRef]
32. de Marco, E.; Savarese, M.; Paduano, A.; Sacchi, R. Characterization and Fractionation of Phenolic Compounds Extracted from Olive Oil Mill Wastewaters. *Food Chem.* **2007**, *104*, 858–867. [CrossRef]
33. Alagna, F.; Mariotti, R.; Panara, F.; Caporali, S.; Urbani, S.; Veneziani, G.; Esposto, S.; Taticchi, A.; Rosati, A.; Rao, R.; et al. Olive Phenolic Compounds: Metabolic and Transcriptional Profiling during Fruit Development. *BMC Plant Biol.* **2012**, *12*, 162. [CrossRef]
34. Rodríguez-Gutiérrez, G.; Duthie, G.G.; Wood, S.; Morrice, P.; Nicol, F.; Reid, M.; Cantlay, L.L.; Kelder, T.; Horgan, G.W.; Fernández-Bolaños Guzmán, J.; et al. Alperujo Extract, Hydroxytyrosol, and 3,4-Dihydroxyphenylglycol Are Bioavailable and Have Antioxidant Properties in Vitamin E-Deficient Rats—A Proteomics and Network Analysis Approach. *Mol. Nutr. Food Res.* **2012**, *56*, 1131–1147. [CrossRef]
35. Giacomazza, D.; D'Andrea, D.; Provenzano, A.; Picone, P.; Provenzano, F.; Guarrasi, V.; Raimondo, M.; San Biagio, P.L.; Passantino, R.; Mangione, M.R.; et al. The Precious Content of the Olive Mill Wastewater: The Protective Effect of the Antioxidant Fraction in Cell Cultures. *CyTA-J. Food* **2018**, *16*, 658–666. [CrossRef]
36. Ghio, A.J.; Carraway, M.S.; Madden, M.C. Composition of Air Pollution Particles and Oxidative Stress in Cells, Tissues, and Living Systems. *J. Toxicol. Environ. Health Part B* **2012**, *15*, 1–21. [CrossRef] [PubMed]
37. Chasekioglou, A.N.; Goula, A.M.; Adamopoulos, K.G.; Lazarides, H.N. An Approach to Turn Olive Mill Wastewater into a Valuable Food By-Product Based on Spray Drying in Dehumidified Air Using Drying Aids. *Powder Technol.* **2017**, *311*, 376–389. [CrossRef]
38. Hadidi, M.; Jafarzadeh, S.; Forough, M.; Garavand, F.; Alizadeh, S.; Salehabadi, A.; Khaneghah, A.M.; Jafari, S.M. Plant Protein-Based Food Packaging Films; Recent Advances in Fabrication, Characterization, and Applications. *Trends Food Sci. Technol.* **2022**, *120*, 154–173. [CrossRef]
39. Galanakis, C.M.; Tsatalas, P.; Galanakis, I.M. Implementation of Phenols Recovered from Olive Mill Wastewater as UV Booster in Cosmetics. *Ind. Crops Prod.* **2018**, *111*, 30–37. [CrossRef]
40. Bouaziz, M.; Lassoued, S.; Bouallagui, Z.; Smaoui, S.; Gargoubi, A.; Dhouib, A.; Sayadi, S. Synthesis and Recovery of High Bioactive Phenolics from Table-Olive Brine Process Wastewater. *Bioorg. Med. Chem.* **2008**, *16*, 9238–9246. [CrossRef] [PubMed]
41. Belaqziz, M.; Tan, S.P.; El-Abbassi, A.; Kiai, H.; Hafidi, A.; O'Donovan, O.; McLoughlin, P. Assessment of the Antioxidant and Antibacterial Activities of Different Olive Processing Wastewaters. *PLoS ONE* **2017**, *12*, e0182622. [CrossRef]
42. Fernández-Prior, Á.; Bermúdez-Oria, A.; Millán-Linares, M.D.C.; Fernández-Bolaños, J.; Espejo-Calvo, J.A.; Rodríguez-Gutiérrez, G. Anti-Inflammatory and Antioxidant Activity of Hydroxytyrosol and 3,4-Dihydroxyphenyglycol Purified from Table Olive Effluents. *Foods* **2021**, *10*, 227. [CrossRef]
43. Brenes, M.; de Los Santos, B.; Aguado, A.; de Castro, A.; García, P.; Romero, C. Assessment of the Antimicrobial and Fertilizing Activity of Table Olive Concentrated Waste Streams During Their Shelf Life. *Waste Biomass Valorization* **2021**, *13*, 2083–2093. [CrossRef]
44. Ogrinc, N.; Košir, I.J.; Spangenberg, J.E.; Kidrič, J. The Application of NMR and MS Methods for Detection of Adulteration of Wine, Fruit Juices, and Olive Oil. A Review. *Anal. Bioanal. Chem.* **2003**, *376*, 424–430. [CrossRef]
45. Lisec, J.; Schauer, N.; Kopka, J.; Willmitzer, L.; Fernie, A.R. Gas Chromatography Mass Spectrometry–Based Metabolite Profiling in Plants. *Nat. Protoc.* **2006**, *1*, 387–396. [CrossRef] [PubMed]
46. Gebretsadik, T.; Linert, W.; Thomas, M.; Berhanu, T.; Frew, R. LC–NMR for Natural Product Analysis: A Journey from an Academic Curiosity to a Robust Analytical Tool. *Science* **2021**, *3*, 6. [CrossRef]
47. Belaid, C.; Khadraoui, M.; Mseddi, S.; Kallel, M.; Elleuch, B.; Fauvarque, J.F. Electrochemical Treatment of Olive Mill Wastewater: Treatment Extent and Effluent Phenolic Compounds Monitoring Using Some Uncommon Analytical Tools. *J. Environ. Sci.* **2013**, *25*, 220–230. [CrossRef]
48. Khallouki, F.; Hull, W.E.; Würtele, G.; Haubner, R.; Erben, G.; Owen, R.W. Isolation of the Major Phenolic Compounds in the Pits of Brined Green Olive Drupes: Structure Elucidation by Comprehensive 1H/13C-NMR Spectroscopy. *Nat. Prod. Commun.* **2019**, *14*, 203–221. [CrossRef]
49. Dais, P.; Boskou, D. Detection and Quantification of Phenolic Compounds in Olive Oil, Olives, and Biological Fluids. In *Olive Oil Minor Constituents and Health*; Boskou, D., Ed.; CRC PressTaylor and Francis Group: Boca Raton, FL, USA, 2009; pp. 55–107. ISBN 978-1-4200-5993-9.
50. Christophoridou, S.; Dais, P. Novel Approach to the Detection and Quantification of Phenolic Compounds in Olive Oil Based on 31P Nuclear Magnetic Resonance Spectroscopy. *J. Agric. Food Chem.* **2006**, *54*, 656–664. [CrossRef] [PubMed]
51. Owen, R.W.; Haubner, R.; Mier, W.; Giacosa, A.; Hull, W.E.; Spiegelhalder, B.; Bartsch, H. Isolation, Structure Elucidation and Antioxidant Potential of the Major Phenolic and Flavonoid Compounds in Brined Olive Drupes. *Food Chem. Toxicol.* **2003**, *41*, 703–717. [CrossRef]

52. Sandvoss, M.; Roberts, A.D.; Ismail, I.M.; North, S.E. Direct On-Line Hyphenation of Capillary Liquid Chromatography to Nuclear Magnetic Resonance Spectroscopy: Practical Aspects and Application to Drug Metabolite Identification. *J. Chromatogr. A* **2004**, *1028*, 259–266. [CrossRef]
53. Christophoridou, S.; Dais, P.; Tseng, L.-H.; Spraul, M. Separation and Identification of Phenolic Compounds in Olive Oil by Coupling High-Performance Liquid Chromatography with Postcolumn Solid-Phase Extraction to Nuclear Magnetic Resonance Spectroscopy (LC-SPE-NMR). *J. Agric. Food Chem.* **2005**, *53*, 4667–4679. [CrossRef]