A green approach to phenolic compounds recovery from olive mill and winery wastes

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Abstract

The aim of this study was to evaluate the recovery of phenolic compounds from olive mill and winery wastes by conventional solid-liquid extraction (SLE) using water as the extraction solvent. The studied variables were extraction time (5-15 min), temperature (25-90 °C), solid-to-liquid ratio (1:10-1:100 (*kg/L*)), pH (3-10) and application of multiple extractions (1-3). The extraction efficiency was evaluated in terms of total phenolic content (TPC), determined by high performance liquid chromatography (HPLC-UV), but also from the recovery of some representative phenolic compounds. The optimized conditions were one extraction step, 10 min, 25 °C, 1:30 (*kg/L*), pH 5 for olive pomace, and one extraction step, 10 min, 70 °C, 1:100 (*kg/L*), pH 5 for winery residues. The extraction method is simple and suitable for scaling-up in industry, and the aqueous extracts are fully compatible with further purification schemes based on the use of membranes or resins. The optimized technique was applied to a set of different representative residues from olive mill and winery industries, to assess their suitability as sources for phenolic compounds recovery. The phenolic content in the extracts was evaluated by chromatographic analysis and by the Folin–Ciocalteu assay (FC). Furthermore, the antioxidant capacity was determined by 2,2-azinobis-3-etilbenzotiazolina-6-sulfonat (ABTS), 2,-diphenyl-1-picrylhydrazyl (DPPH) and ferric reducing antioxidant power (FRAP) assays. Because of their high contents in phenolic compounds and great antioxidant capacity, olive pomace and lees filters were identified as especially suited sources for phenolic compounds recovery.

Keywords: olive pomace; wine lees; phenolic compounds; solid-liquid extraction; circular economy.

1. Introduction

Agri-food industries generate large amounts of waste, and proper management and treatment of this waste has become a major challenge (Castro-Muñoz et al., 2016). In this sense, the concept of circular economy and waste valorization, by obtaining value-added products, has gained prominence, contributing to a more sustainable economy and reducing environmental problems (Roselló-Soto et al., 2015).

This work focuses on waste generated in two important sectors of the agri-food industry in southern Europe, olive oil and wine. The production of olive oil generates about 10 million tons of waste per year, which includes olive pomace (olive pulp, skin and stones) and olive mill wastewater. Regarding the production of wine, almost 20 million tons of winery by-products are discarded each year, such as wine lees, grape pomace (skin and seeds) and steams (De Bruno et al., 2018; Melo et al., 2015). Since only a small part of olive and grape phytochemicals are extracted into the final products, these

residues are an abundant source of phenolic compounds (~ 98%). Moreover, these wastes can be considered relevant raw materials since polyphenols have high nutraceutical and antioxidant power, with potential applications in the food, cosmetic, and pharmaceutical industries(Araújo et al., 2015; Dermeche et al., 2013; Ferri et al., 2020; Soberón et al., 2019). There are diverse types of phenolic compounds that can be recovered from these kind of residues, e.g. 3-hydroxytyrosol, rutin and oleuropein from olive mill wastes; gallic acid, syringic acid and hesperidin from winery wastes (Benincasa et al., 2019; Tapia-Quirós et al., 2020). The recovery of phenolic compounds from agri-food industry waste requires a first extraction stage, which can be carried out by various techniques, from the application of simple stirring, *i.e.* conventional solid-liquid extraction (SLE), to the use of additional sources of energy, such as ultrasound assisted extraction (UAE), microwave assisted extraction (MAE), or pressurized liquid extraction (PLE) (Casagrande et al., 2019; Ferri et al., 2020; Kumar et al., 2017).

In conventional SLE, the waste is in contact with appropriate solvents for a certain time. Agitation and heat can be applied to the system to speed-up and/or improve the extraction of components of interest (Zhang et al., 2018). Compared to modern techniques, such as UAE, MAE or PLE, it can be advantageous in industrial applications in terms of ease of operation, as well as of implementation and operating costs (Antónia Nunes et al., 2019).

Regardless of the extraction technique, a key point is the extraction solvent. A wide variety of solvents have been proposed for the extraction of phenolic compounds, such as ethanol, methanol, water, ethyl acetate, diethyl ether, acetone or hexane (Lamprou et al., 2020). However, in view of the application of recovered phenolic compounds in the food, nutraceutical or cosmetic fields, water and ethanol are the most compatible options (De Bruno et al., 2018; Dimou et al., 2016; Tao et al., 2014).

The extraction of phenolic compounds from agri-food wastes based on the use of water is, undoubtedly, very attractive from both environmental and economic points of view (Ansari et al., 2011; Bachtler and Bart, 2018; Benincasa et al., 2019; Borges et al., 2020; Da Rosa et al., 2019; Franco et al., 2008; Goldsmith et al., 2018; Lamprou et al., 2020; Soberón et al., 2019; Zagklis et al., 2015). Water is non-toxic, non-flammable, environmentally friendly, naturally abundant, and cheap (Benincasa et al., 2019). Moreover, the aqueous extracts are more suitable for further purification processes based on the use of membranes or resins (Antónia Nunes et al., 2019). The critical review of the published studies indicated that efforts have been mostly directed to the use of mixtures of water and ethanol or other organic solvents and accordingly, there is a lack of fundamental data on the solid-liquids extraction in water. Additionally to equilibrium and kinetic data of the solid/liquid extraction stage, the dependence on the acidity and temperature of the aqueous streams and the potential influence on the antioxidant capacity are also parameters to be known.

The present study aimed to evaluate the phenolic compounds recovery from olive mill and winery waste samples (e.g. the most relevant sectors in the Southern European agri-food industry), using conventional SLE with water to propose a simple, "green", economic, and easily scale-up system at an industrial level. The effect of extraction time, temperature, solid-to-liquid ratio, pH, and multiple steps was considered to establish optimal conditions. The efficiency of the extraction process was quantified determining both, the total phenolic content (TPC) and the concentrations of several recovered polyphenols. Finally, the aqueous extracts of a wide set of waste samples from olive oil and winery sectors were analyzed to determine the total phenolic content and antioxidant capacity of the obtained extracts, with the aim of identifying the best candidates for phenolic compounds recovery.

2. Materials and methods

2.1 Reagents

Phenolic compounds standards: rutin, gallic acid, syringic acid were obtained from Sigma Aldrich (St. Louis, USA); 3-hydroxytyrosol from TCI (Japan); oleuropein from Extrasynthese (France); hesperidin from Glentham Life Sciences (UK); 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) from Carbosynth (Berkshire, UK). Reagents used for spectrophotometric assays: folin-Ciocalteau (FC) reagent was obtained from Panreac (Barcelona, Spain); 2,20-azino-bis(3-ethylbenzothiazoline-6-sulfonic) acid (ABTS), 2,2-diphenyl-1-picrylhydrazyl (DPPH) and 2,4,6-tripyridyl-S-triazine (TPTZ)

from Alfa Aesar (Kandel, Germany); potassium peroxydisulfate from Sigma Aldrich (St. Louis, USA); sodium hydroxide, Fe(III) chloride, sodium carbonate and disodium hydrogen phosphate from Merck (Darmstadt, Germany). Solvents used were: ethanol (EtOH) HPLC grade obtained from Honeywell Riedel-de Haën™, Germany; acetonitrile (ACN) HPLC grade from Fisher Scientific, UK; dimethylsulfoxide (DMSO), formic acid (FA) 98-100% *w/w*, and hydrochloric acid (HCl) 32% *w/w* from Merck, Darmstradt, Germany. Ultrapure water was obtained from a Milli-Q system (Merck Millipore). Nylon syringe filters (13 mm, 0.22 µm) were from Filter-Lab® (Filtros Anoia, Sant Pere de Riudebitlles, Barcelona, Spain).

2.2 Samples

Olive mill and winery residue samples were provided by Spanish industries as shown in Table 1. Residue sampling was performed in the period between December 2017 and April 2019. Winery solid residues were milled and homogenized. Olive mill and winery residues were stored in the freezer at -20 °C until experiments.

Table 1. Olive mill and winery residues samples.

Sample code	Origin	Sample type	Variety
		Olive mill residues	
O1	Toledo (Spain)	Exhausted olive pomace	Arbequina, Cornicabra and Empeltre
O2	Lleida (Spain)	Olive pomace	Arbequina
O3	Huesca (Spain)	Olive pomace	Verdeña
O4	Córdoba (Spain)	Olive pomace	Hojiblanca, Picual and Arbequina
O5	Córdoba (Spain)	Olive pomace	Hojiblanca and Picual
O6	Toledo (Spain)	Olive mill wastewater	Arbequina, Cornicabra and Empeltre
		Winery residues	
W1	Barcelona (Spain)	Diatomaceous earth filter media (lees filters)	White wine (Chardonnay, Sauvignon Blanc, Xarel·lo)
W2	Ourense (Spain)	Filter waste	White wine (Merenzao and Treixadura)
W3	Ourense (Spain)	Grape pomace	White wine (Treixadura)
W4	Ourense (Spain)	Grape pomace	White wine (Merenzao)
W5	Pontevedra (Spain)	Grape pomace	White wine (Albariño)
W6	Ourense (Spain)	Grape stems	White wine (Godello)
W7	León (Spain)	Grape seeds	Red wine (Mencía)
W8	Pontevedra (Spain)	Wine lees	White wine (Albariño)
W9	León (Spain)	Grape pomace	Red wine (Mencía)
W10	Ciudad Real (Spain)	Wine lees	Red wine (Tempranillo)
W11	Pontevedra (Spain)	Grape stems	White wine (Albariño)
W12	Ciudad Real (Spain)	Wine lees	Red wine (Tempranillo)
W13	León (Spain)	Grape pomace	Red wine (Mencía)
W14	Barcelona (Spain)	Diatomaceous earth filter media (lees filters)	Red wine (Garnacha, Tempranillo, Cabernet Sauvignon, Cariñena)
W15	Pontevedra (Spain)	Winery wastewater	White wine (Albariño)
W16	Pontevedra (Spain)	Winery wastewater	White wine (Albariño)
W17	León (Spain)	Wine lees	Rose wine (Mencía)
W18	Pontevedra (Spain)	Wine lees	White wine (Albariño)
W19	Pontevedra (Spain)	Wine lees	White wine (Albariño)
W20	Pontevedra (Spain)	Wine lees	White wine (Albariño)
W21	Pontevedra (Spain)	Wine lees	White wine (Albariño)

2.3 Instruments

Phenolic compounds were determined by an HPLC-UV system, named Agilent Series 1200 (Agilent Technologies, Palo Alto, CA, USA), equipped with a quaternary pump, an automatic injection system and a diode array detector (DAD). Besides, data analysis and processing was done by the Agilent ChemStation software. Moreover, an ultra-high performance liquid chromatography-high resolution mass spectrometry (UHPLC–HRMS) system, named Accela (Thermo Scientific, Hemel Hempstead, UK), was also used for the determination of phenolic compounds. In this case, the apparatus was equipped with a quaternary pump, a thermostatic autosampler a DAD, and coupled to an LTQ Orbitrap Velos mass spectrometer (Thermo Scientific, Hemel Hempstead, UK) with an ESI source and Xcalibur Qual Browser software for HRMS data handling. A double beam Perkin Elmer UV/Vis/NIR Lambda 19 (Waltham, MA, USA) spectrophotometer with a QS quartz glass high performance cuvettes (10 mm optical path) from Hellma Analytics (Jena, Germany) was used to estimate the antioxidant and antiradical capacities of the extracts. Finally, a Vibra mix R agitator (OVAN, Badalona, Spain) was used to homogenize the mixtures. The extraction process was carried out by a SLE system, using a hot plate stirrer with temperature controller (IKA® RCT basic); and by an UAE system using an ultrasonic bath (Branson 5510, Danbury CT, USA), with a frequency of 42 kHz and power of 135 W. Once the extraction was done, the obtained extracts were centrifuged with a Labofuge 400 centrifuge (Heraeus, Hanau, Germany).

2.4 Procedures

2.4.1 High performance liquid chromatography analysis (HPLC-UV)

A Kinetex C_{18} column (Phenomenex, 100 mm x 4.6 mm x 2.6 µm, Torrance, CA, USA) was used for chromatographic analysis. Ultrapure water with 0.1% FA (A), and ACN (B) were used as mobile phase components. The gradient programs for olive oil and wine residues analysis were previously optimized (Tapia-Quirós et al., 2020). For olive oil residues the gradient program was: 0 min, 5% B; 0-38 min, 35% B; 38-40 min, 90% B; 40-42 min, 90% B; 42-42.2 min, 5% B; 42.2-50 min, 5% B; and for wine residues the gradient program was: 0 min, 5% B; 0-38 min, 45% B; 38-40 min, 90% B; 40-42 min, 90% B; 42-42.2 min, 5% B; 42.2-50 min, 5% B. The flow rate was 0.4 mL min^{-1} and the injection volume 5 µL. Chromatograms were recorded at 280, 310, 370 and 550 nm. The total phenolic content (TPC) was estimated from the total peak area in the chromatograms at 280 nm, in the time range between 5 and 36 min. TPC was expressed in terms of mg of gallic acid equivalent (GAE) per g of fresh weight (mg GAE g^{-1}) for solid samples or mg GAE L^{-1} for liquid samples. 3-hydroxytirosol, oleuropein, gallic acid, syringic acid and hesperidin were quantified from peak areas recorded at 280 nm and rutin from areas at 370 nm. Calibration curves of the analyzed compounds were constructed in the concentration range from 0.5 to 10 mg L^{-1} for gallic acid (GA), syringic acid (SYA), rutin (RUT) and hesperidin (HES); from 2 to 10 mg L^{-1} for 3-hydroxytyrosol (3-HTR); and from 3 to 10 mg L^{-1} for oleuropein (OLE).

2.4.2 Folin-Ciocalteau assay (FC)

2 mL of water, 250 µL of Folins-Ciocalteu's reagent and a proper volume of sample, were mixed in an amber glass vial. After 8 min of repose, 75 µL of 7.5% Na_2CO_3 (*w/v*) aqueous solution, and water was added to obtain a final volume of 5 mL. The reaction was developed for 2 h and the absorbance was measured at 765 nm using a reagent blank as reference. For calibration curve, the same procedure was performed using gallic acid solutions, with concentrations in the range of 1-20 mg L^{-1}, instead of samples. Phenolic compounds concentration was expressed as mg GAE g^{-1} for solid samples or mg GAE L^{-1} for liquid samples. Analyses were performed in triplicate.

2.4.3 2,2-azinobis-3-etilbenzotiazolina-6-sulfonat assay (ABTS)

An $ABTS^{\bullet+}$ stock solution was prepared with 20 mL of 7 mM ABTS and 350 µL of 140 mM potassium peroxydisulfate. The mixture was kept in the dark for at least 16 hours before being used. Daily, a working solution was prepared by diluting 300 µL of $ABTS^{\bullet+}$ stock solution in 12 mL of ethanol. The reaction was carried out by mixing 1.5 mL of

$ABTS^{\bullet+}$, a proper volume of sample and ethanol to reach a final volume of 2.5 mL. After 25 min of reaction time, the absorbance was measured at 734 nm using the $ABTS^{\bullet+}$ blank as the reference. For calibration, instead of samples, the same procedure was performed using Trolox solutions, with concentrations in the range of 0.2 to 3 mg L^{-1}. Antioxidant capacity was expressed as Trolox equivalent antioxidant capacity, mg TEAC g^{-1} in solid samples and mg TEAC L^{-1} in liquid samples. Analyses were performed in triplicate.

2.4.4 2,2-diphenyl-1-picrylhydrazyl assay (DPPH)

Before each analysis, a 0.2 mM DPPH stock solution in 50 mL ethanol was prepared and kept in the dark for 2 h. 2 mL of the DPPH solution, 0.8 mL of phosphate buffer (pH 7,4), the required volume of sample, and ethanol up to 4 mL were mixed in an amber glass vial and kept in the dark for 45 min. The absorbance was then measured at 517 nm using a reagent blank as the reference. For calibration curve, the same procedure was performed using Trolox solutions, with concentrations in the range of 0.2 to 10 mg L^{-1}, instead of samples. Antioxidant capacity was expressed as Trolox equivalent units, mg TE g^{-1} in solid samples and mg TE L^{-1} in liquid samples. Analysis were performed in triplicate.

2.4.5 Ferric reducing antioxidant power assay (FRAP)

FRAP reagent was prepared by mixing 20 mmol L^{-1} $FeCl_3$ solution, 10 mmol L^{-1} TPTZ solution (50 mmol L^{-1} HCl) and 50 mmol L^{-1} FA buffer solution, in a 1:2:10 (*v/v/v*) proportion. For the reaction, an appropriate sample volume was mixed with 300 µL of FRAP reagent and water to reach a final volume of 2.5 mL. After 5 minutes of reaction, the absorbance was measured at 595 nm using a reagent blank as reference. For calibration curve, the same procedure was performed using Trolox solutions, with concentrations in the range of 0.2 to 5 mg L^{-1}, instead of samples. Antioxidant capacity was expressed as Trolox equivalent units, mg TE g^{-1} in solid samples and mg TE L^{-1} in liquid samples. Analysis were performed in triplicate.

2.4.6 Phenolic compounds extraction with water

Ultrapure water was used as the extraction solvent and the stirring rate was set at 300 rpm. First, the extraction was done at 90 °C, 1:20 *kg/L* solid-to-liquid ratio, and with the natural pH of the samples (pH 5). Then, for the optimization of extraction, variables such as extraction time (5, 10 and 15 min), temperature (25, 50, 70 and 90 °C), solid-to-liquid ratio (1:10, 1:20, 1:30, 1:50 and 1:100 *kg/L*), pH (3, 5 and 10) and multiple extraction stages (1-3) were evaluated. For each assayed condition, experiments were performed in triplicate. After each experiment, the samples were centrifuged for 15 min at 3500 rpm, filtered with nylon syringe filters (13 mm, 0.22 µm) and stored at 4 °C until analysis.

2.4.7 Ultrasound assisted extraction (UAE) with ethanol-water

For comparative purposes, UAE experiments were performed according to a previously optimized procedure (Tapia-Quirós et al., 2020). Briefly, 1 g of sample and 20 mL of 50:50 ethanol:water (*v/v*) were mixed in a 45 mL Falcon tube and vortexed. The tubes were then placed into an ultrasonic bath at room temperature (20 °C) for 30 min, the final temperature being 24 °C. Then, the samples were centrifuged, filtered and stored at 4 °C until analysis. Extractions were performed in triplicate.

2.5 Data analysis

One-factor analysis of variance (ANOVA) with replication was applied at 95% confidence level ($p < 0.05$) to check statistically the significance of effects. *p* values are collected in Tables S1, S2 and S3 (Supplementary Material).

3. Results and discussion

3.1 Optimization of phenolic compounds extraction by using water as extraction solvent

In a preliminary study (Tapia-Quirós et al., 2020), different extraction techniques and extraction solvents were investigated to determine the optimum conditions for polyphenols extraction. However, in the second step of validating the technology at pilot scale, many concerns arisen when considering the use of i) an extracting system containing an organic solvent and ii) advanced technologies using microwaves, ultrasounds or pressurized solvents. Although such approaches are applied at analytical scale, when sustainability and economic feasibility aspects are considered, organic solvents and advanced techniques are recommended to be avoided. Besides, the differences in extraction efficacies did not justify the use of such approaches. In this context, the extraction of polyphenols using water and mechanical stirring was explored. Based on previous results (Tapia-Quirós et al., 2020; Montenegro-Landívar et al., 2021), the extraction parameters were evaluated as independent, since no interaction effects were found between them.

Samples O5 and W14 were used in the optimization study, due to they were evaluated in previous experiments and were identified as a rich source of phenolic compounds (8.00 ± 0.12 and 5.85 ± 0.03 mg GAE g^{-1}, respectively) (Tapia-Quirós et al., 2020). Sample O5 was an olive pomace, whereas sample W14 consisted of diatomaceous earth filters used to retain lees during wine processing steps (lees filters). The extraction efficiency was evaluated in terms of TPC, determined by HPLC-UV (section 2.4.1). Furthermore, for olive pomace (Figure 1a), 3-hydroxytyrosol (3-HTR), rutin (RUT) and oleuropein (OLE) were also selected as characteristic compounds to evaluate their extractions by SLE (section 2.4.6) with a concentration of 0.09, 0.07 and 0.65 mg g^{-1}, respectively. On the other hand, for lees filters, apart from TPC data, the compounds chosen were gallic acid (GA), syringic acid (SYA) and hesperidin (HES), with a concentration of 0.16, 0.28 and 0.30 mg g^{-1}, respectively (Figure 1b). The identity of the selected compounds had been previously confirmed by UHPLC–HRMS (Tapia-Quirós et al., 2020), and their chemical structures are shown in Figure 2.

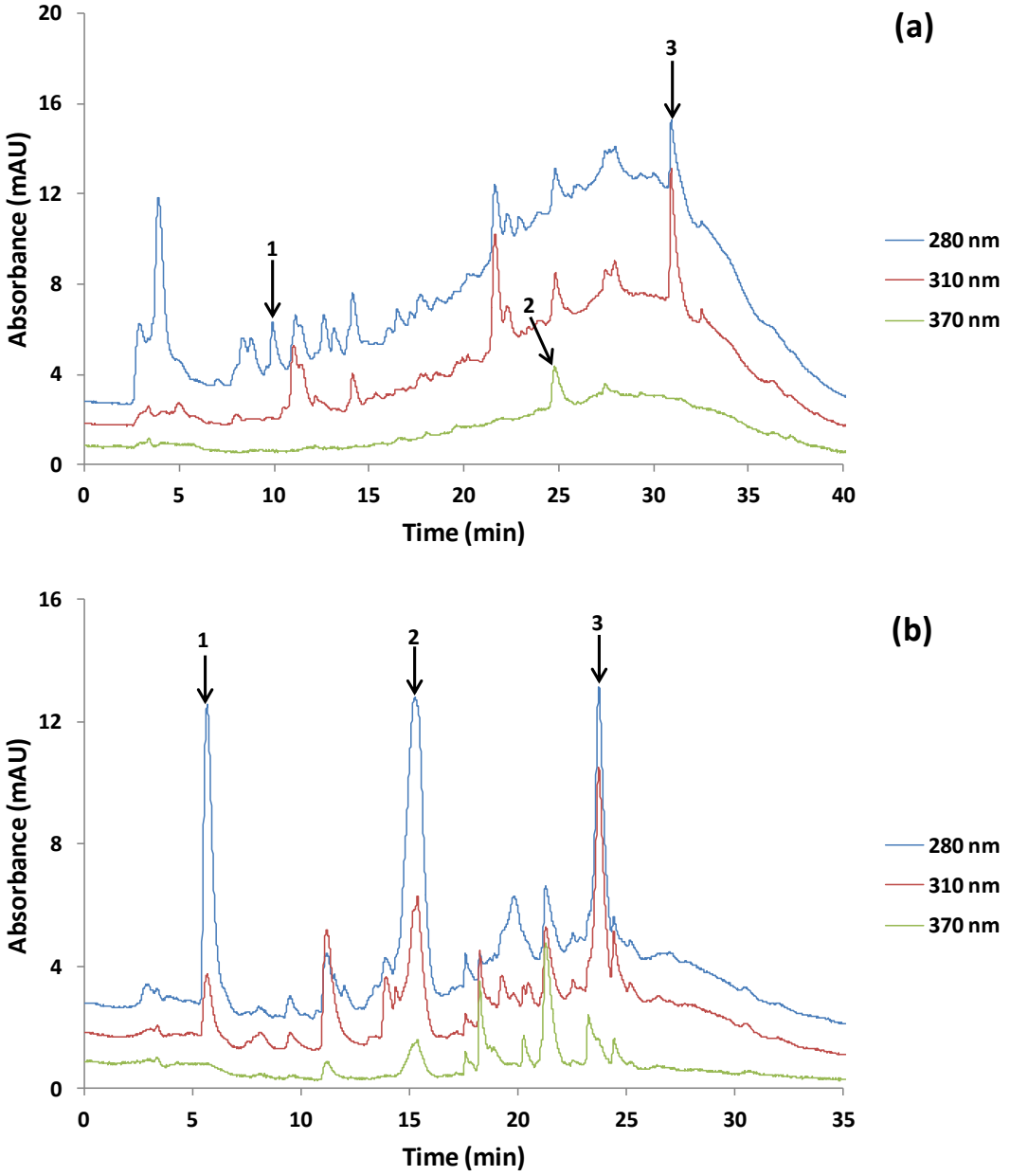

Figure 1. (a) Olive pomace HPLC chromatograms at 280, 310 and 370 nm; peak assignment: 1= 3-hydroxytyrosol, 2= rutin, 3= oleuropein. (b) Lees filters HPLC chromatograms at 280, 310 and 370 nm; peak assignment: 1= gallic acid, 2= syringic acid, 3= hesperidin.

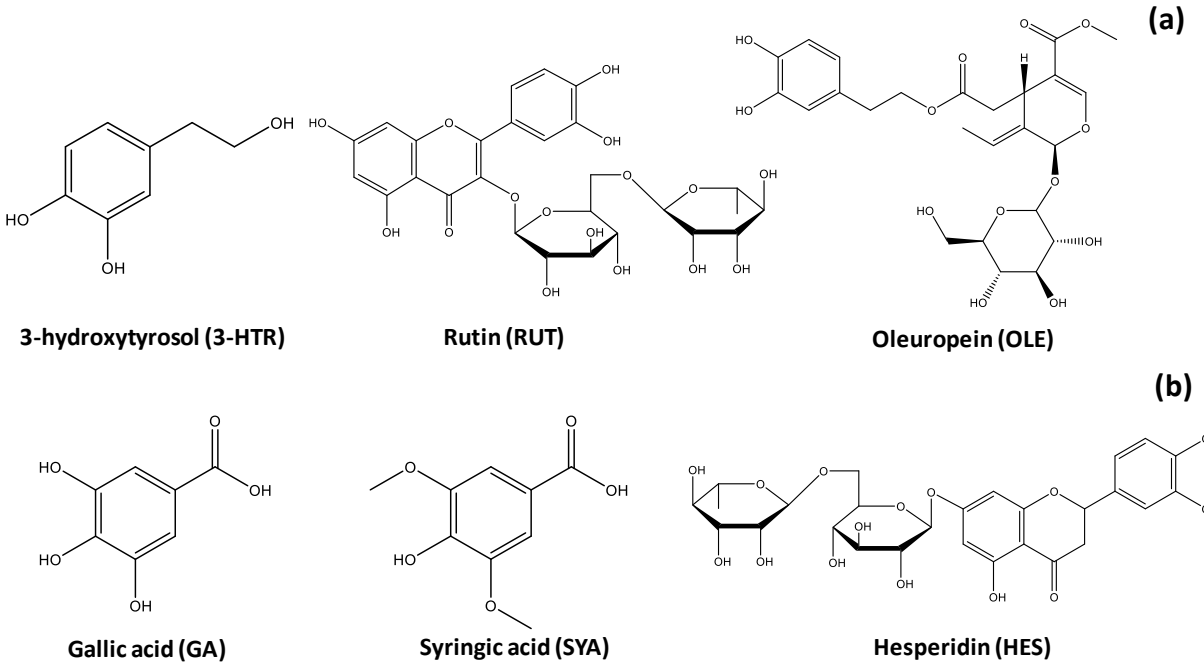

Figure 2. Chemical structures of the selected compounds for (a) olive pomace and (b) lees filters.

3.1.1 Olive pomace matrix

SLE optimization results for olive pomace matrix are shown in Figure 3. Also, results of reviewed studies with SLE and similar samples are compiled in Table 2.

Extraction time. TPC increased from 5 to 10 min (*ca.* 20%); however, increasing the extraction time to 15 min did not provide any advantage (Figure 3a). Regarding individual phenolic compounds, OLE showed the same pattern of behavior as TPC; however, in the extraction of 3-HTR and RUT, there was no significant increase in extraction with time ithin the evaluated time interval. Usually, the limiting step of solid liquid extraction is internal diffusion (Wang and Weller, C. L., 2006), which can led to low extraction kinetics. In this system, however, the extraction kinetics is fast, and overall, 10 min is an adequate time for the extraction of this type of samples. In contrast, other authors have proposed 30 min of extraction time with dimethyl sulfoxide as extraction solvent for olive pomace samples (Romero et al., 2018).

Extraction temperature. Temperature can be important, since it may help to disrupt cellular membranes, increase their permeability, or disrupt interaction of polyphenols with matrix components (Jovanovic et al., (2017). When studying the influence of temperature it was found that it was not relevant, neither when considering TPC nor the compounds individually (Figure 3b). Therefore, the extraction can be carried out at room temperature, as other authors have also proposed for aqueous SLE of olive leaves (Benincasa et al., 2019). Regarding TPC recovery from olive pomace with organic solvents, other authors have also proposed room temperature extraction (Benincasa et al., 2019; De Bruno et al., 2018; Lafka et al., 2011; Ramos et al., 2013; Romero et al., 2018).

Solid-to-liquid ratio. A slight increase in extracted TPC was observed as the volume of water increased (Figure 3c). When considering the specific compounds, the effect was significant for 3-HTR, but not for RUT or OLE. This behavior could be related to the log P values: 0.11, -0.90 and -0.87 respectively (values estimated with Advanced Chemistry Development Software, V11.2), with the compounds with a less favorable, a priori, extraction would be more susceptible to an increase of the volume of water. Considering the results, the 1:30 (*kg/L*) ratio was a good option. Working with a higher volume of water may provide a greater recovery for certain compounds (e.g. 3-HTR), but it would also lead to the management of higher volumes of extract. Other authors have proposed similar solid-to-liquid ratio

(1:25.2 and 1:30 *kg/L* for TPC and OLE recovery, respectively), for olive leaves SLE with water-sulfuric acid (Lamprou et al., 2020).

pH. Depending on the polyphenol, changes of pH speciation occur in the assayed range (between 3 and 10), that could affect extraction; however no significant effect of the pH factor on the TPC extraction was observed, nor for 3-HTR, RUT or OLE compounds (Figure 3d). Therefore, the extraction can be performed without adjusting the pH, proceeding at the natural pH provided by the sample itself. In contrast, Ansari et al. (Ansari et al., 2011) obtained a higher extraction efficiency of OLE from olive leaves at pH 3 (OLE being in the neutral form), also by SLE using water. The different behavior could be related to different interactions of the target compounds with the matrix components.

Multiple extractions. In terms of TPC extraction, after a second extraction, an improvement of only about 10% was achieved (Figure 3e). When considering specific compounds, for 3-HTR the increase of the extraction yield was 37%, and for OLE 20%, but no increase was observed for RUT. A third extraction step did not contribute to increase phenolic compounds recovery in any case (*i.e.* TPC, 3-HTR or OLE). From these results, it can be concluded that, in terms of TPC, a single extraction step would be the option of choice, but for specific target compounds (e.g. 3-HTR) a two-extraction scheme could be considered. A three step extraction, as has been proposed (Soberón et al., 2019), does not improve the analyte recoveries for this kind of systems.

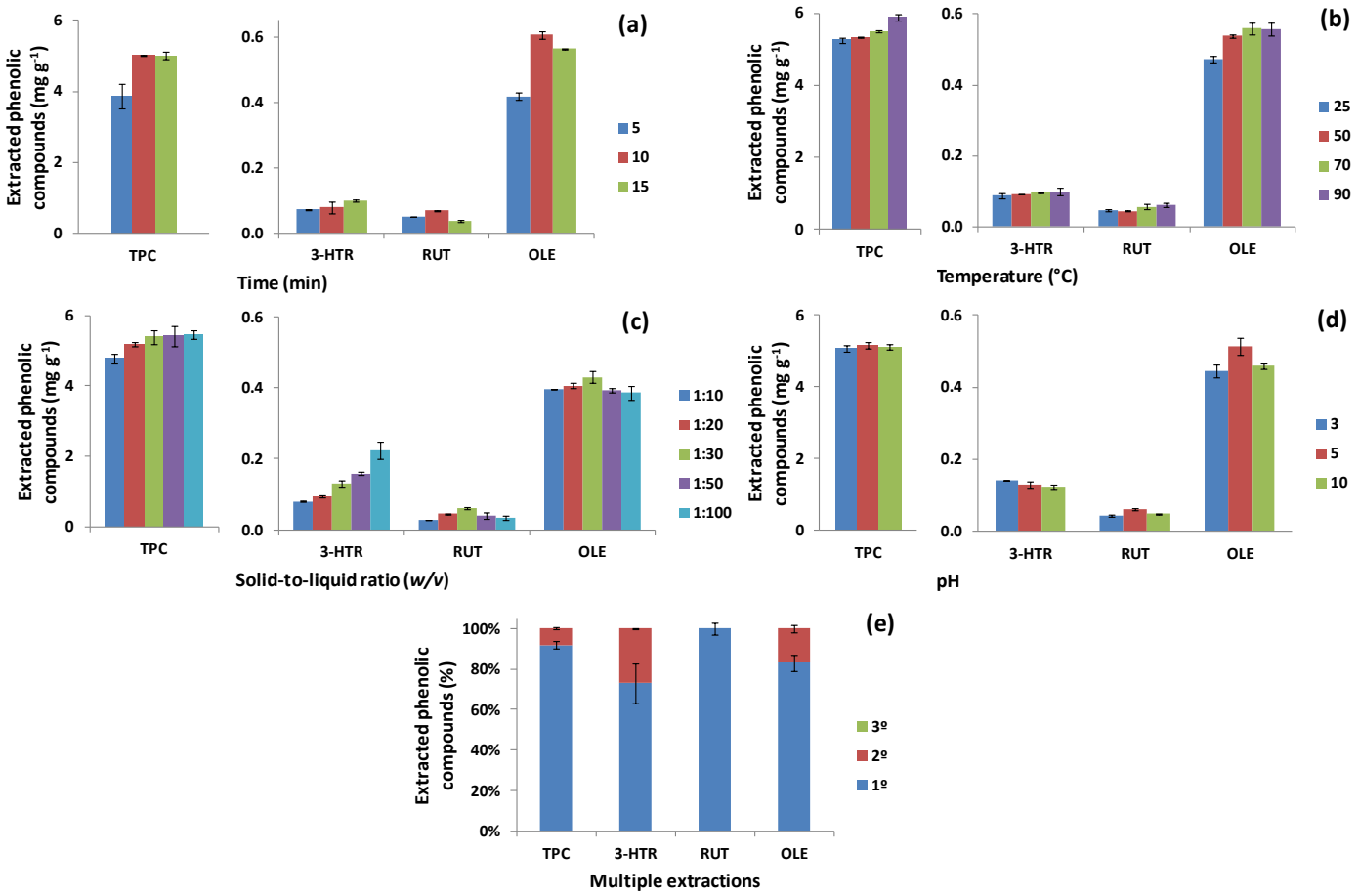

Figure 3. Effect of (a) extraction time, (b) extraction temperature (°C), (c) solid-to-liquid ratio (*kg/L*), (d) pH and (e) multiple extractions, on the phenolic compounds recovery (mg g^{-1}) from olive pomace samples by SLE.

Table 2. SLE experiments and optimized conditions for olive mill residues.

Sample	Solvent	Experimental conditions	Polyphenols concentration	Reference
Olive pomace	Methanol	1:25 *kg/L*, 70 °C, 12 h	4.37 mg GAE g^{-1}	(Alu'datt et al., 2010)
Olive pomace	Ethanol	1:5 *kg/L*, 25 °C, 180 min, pH 2	1.23 ± 0.21 caffeic acid equivalents (CAE)	(Lafka et al., 2011)
Olive pomace	Methanol	1:10, *kg/L*, 180 °C, 90 min	45.2 mg CAE g^{-1}	(Aliakbarian et al., 2011)
Olive pomace	Water	1:15 *kg/L*, 25 °C, 40 min	25 mg GAE g^{-1}	(Ramos et al., 2013)
Olive pomace	Dimethyl sulfoxide	1:3 *kg/L*, 25 °C, 30 min	1.3 g kg^{-1}	(Romero et al., 2018)
Olive pomace	Ethanol:water 80:20 *v/v*	1:2 *kg/L*, 25 °C, 120 min	171 ± 4 mg GAE 100 g^{-1}	(De Bruno et al., 2018)
Olive leaves	Dimethyl sulfoxide	1:15 *kg/L*, 25 °C, 30 min	50 g kg^{-1}	(Romero et al., 2018)
Olive leaves	Water	6:50 *kg/L*, 25 °C, 10 days	753, 1139, 3.6, 134, 1331, 400 mg kg^{-1} oleuropein, hydroxytyrosol, tyrosol, verbacoside, rutin and luteolin, respectively	(Benincasa et al., 2019)
Olive leaves	Water	1:60 *kg/L*, 90 °C, 70 min	38.25 mg GAE g^{-1}	(Goldsmith et al., 2014)
Olive leaves	Water	1:8 *kg/L*, 60 °C, 4 h, pH 3	13 mg g^{-1} oleuropein	(Ansari et al., 2011)
Olive leaves	Water:6.4% sulfuric acid	1:25.2 *kg/L*, 31.9 °C, 5 h	86.4 mg GAE g^{-1}	(Lamprou et al., 2020)
Olive leaves	Water:2% sulfuric acid	1:30 *kg/L*, 40 °C, 5 h	43.1 mg g^{-1} oleuropein	(Lamprou et al., 2020)
Olive leaves	Ethanol:water 50:50 *v/v*	1:6 *kg/L*, 55 °C, 90 min	27.5 mg GAE g^{-1}	(Gullón et al., 2018)
Olive stone	Methanol	1:2 *kg/L*, 40 °C, 90 min	210 mg GAE kg^{-1} TPC; 24.3, 0.7, 33.2 mg kg^{-1} hydroxytyrosol, syringic acid and oleuropein, respectively	(Nakilcioğlu-Taş and Ötleş, 2019)
Olive tree pruning	Ethanol:water 50:50 *v/v*	1:6 *kg/L*, 55 °C, 90 min	23.85 mg GAE g^{-1}	(Gullón et al., 2018)

3.1.2 Lees filters matrix

SLE optimization results for lees filters matrix are shown in Figure 4, and examples of SLE studies with similar samples are shown in Table 3.

Extraction time. The TPC improved significantly from 5 to 10 min of extraction time (*ca.* 70%); nevertheless, increasing the extraction time to 15 min did not enhance the TPC extraction (Figure 4a). The same behavior pattern was shown by GA, SYA, and HES. Therefore, 10 min of extraction time was found suitable for the recovery of phenolic compounds from this type of samples, as it was for olive pomace, showing a fast kinetics extraction. In contrast, Casagrande et al. (Casagrande et al., 2019), recovered higher values of phenolic compounds at 15 min of extraction time from grape pomace of juice production using acetone at 60 °C.

Extraction temperature. Unlike what was observed in the olive pomace study, the effect of temperature on the extraction from lees filters was significant (Figure 4b). The TPC in the aqueous extract increased *ca.* 60% when temperature rose from 25 to 90 °C; SYA and HES showed the same behavior. This trend suggests that the raise of temperature contributes to the interruption of the interaction of polyphenols with matrix components, which facilitates the extraction. Due to the small improvement observed when temperature was increased from 70 to 90 °C (*ca*. 10% TPC increase), and considering the energy cost, 70 °C was selected for extraction. Bachtler and Bart (Bachtler and Bart, 2018), as well as Franco et al. (Franco et al., 2008), also reported that an increase in the extraction temperature leads to an improvement of the phenolics extraction yield from other winery wastes (e.g. grape pomace or vine leaves).

Solid-to-liquid ratio. The solid-to-liquid ratio had a significant effect on the TPC, as well as on the evaluated compounds (Figure 4c). The TPC increased about 50% when the ratio increased from 1:10 to 1:100 (*kg/L*); GA, SYA and HES also showed the same pattern, which can be related to the saturation of the extraction medium (Jovanovic et al, 2017). These results pointed out that a high solid-to-liquid ratio (1:100 *kg/L*) was recommendable for the recovery of phenolic compounds in this type of samples. Tomaz et al. (Tomaz et al., 2016), have also used a high solid-to-liquid ratio (1:80 *kg/L*), for the SLE of grape skins using acetonitrile:water:formic acid (20:79:1 *v/v/v*) at 50 °C and 1 h of extraction time.

pH. In addition to the natural pH of the aqueous extracts (pH 5), extraction at pH 3 and 10 was considered. In terms of TPC pH did not affect the extraction yield (Figure 4d). In this sense, Batchler and Bart (Bachtler and Bart, 2018) also found that acidity does not significantly influence the extraction of phenolic compounds from red grape leaves. On the other side, when considering individually GA, SYA and HES, the extraction yields do depend on the pH. At pH 3 GA and SYA are mainly in the neutral form, whereas at pH 5 the prevalent species are anionic, which contributes to the improvement of the extraction into water. In addition, changes in the interactions of these polyphenols with components of the matrix could occur when pH increases from 3 to 5, also contributing to the improvement of extraction. The enhacement of HES extraction cannot be explained in terms of changes in speciation, since HES is in the neutral form at pH 3 and 5, but as a consequence of disruption of HES interactions with the matrix. Lastly, the extraction yields at pH 10 are lower than under acidic conditions, possibly due to poor stability under basic conditions (Honda et al., 2019). Summarizing, it is no necessary to adjust the pH, since the pH provided by the sample is appropriate for the extraction.

Multiple extractions. Performing more than one extraction step did not improve the recovery of phenolic compounds, neither for the TPC nor for the individual compounds (Figure 4e). After the second extraction step, the concentration of phenolic compounds in the extracts were below the HPLC-UV limit of quantification, meaning that all the target compounds were quantitatively extracted in a first extraction. In contrast, Jurčević et al. (Jurčević et al., 2017) used three extraction cycles for polyphenols recovery from wine lees using methanol/2 % HCl (95:5 *v/v*).

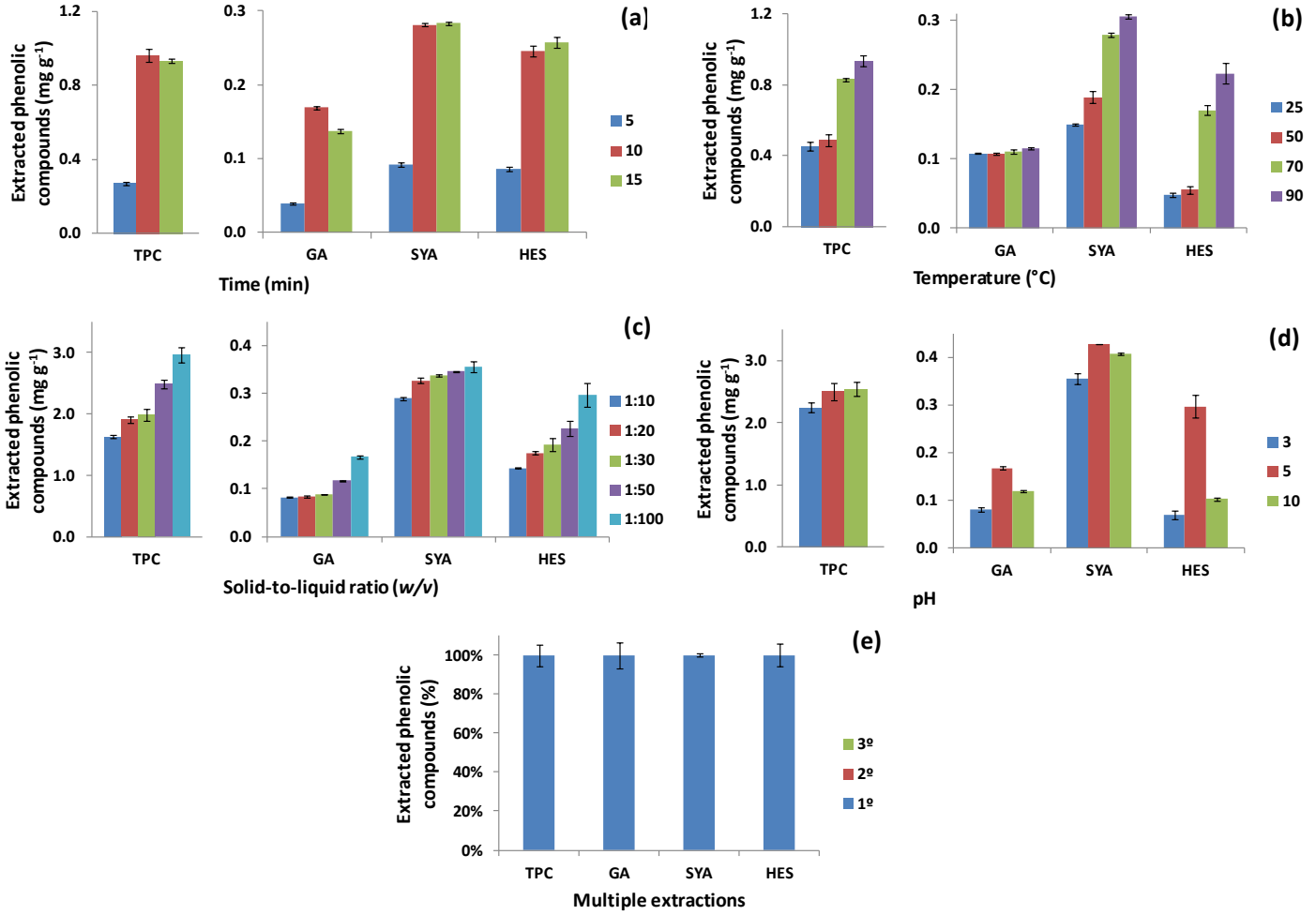

Figure 4. Effect of (a) extraction time, (b) extraction temperature (°C), (c) solid-to-liquid ratio (*kg/L*), (d) pH and (e) multiple extractions, on the phenolic compounds recovery (mg g^{-1}) from lees filters samples by SLE.

Table 3. SLE experiments and optimized conditions for winery residues.

Sample	Solvent	Experimental conditions	Polyphenols concentration	Reference
Grape pomace	Ethanol:water 50:50 *v/v*	1:25 *kg/L*, 60 °C, 2 h	196.2 ± 22.7 mg GAE g^{-1}	(Antoniolli et al., 2015)
Grape pomace	Ethyl acetate	1:10 *kg/L*, 25 °C, 6 h	70.5 ± 0.03 mg GAE g^{-1}	(Pintać et al., 2018)
Grape pomace	Acetone	1:12.5 *kg/L*, 60 °C, 45 min	31.25 mg GAE g^{-1}	(Casagrande et al., 2019)
Grape marc	EtOH:water:HCl 50:49:1 *v/v/v*	1:5 *kg/L*, 25 °C, 15 min, two extraction steps	0.44 g GAE L^{-1}	(Zagklis and Paraskeva, 2015)
Grape marc	Ethanol:water 50:50 *v/v*	1:50 *kg/L*, 60 °C, 30 min	22 mg GAE g^{-1}	(Sant'Anna et al., 2012)
Grape skins	Acetone 51.46% *v/v*	0.1:32.25 *kg/L*, 90 min	39.57 mg GAE g^{-1}	(Medouni-Adrar et al., 2015)
Grape skins	Ethanol	0.10:1 *kg/L*, 25 °C, 19 h	3.22 mg GAE g^{-1}	(Casazza et al., 2012)

Grape skins	Acetonitrile:water:formic acid 20:79:1 *v/v/v*	1:80 *kg/L*, 50 °C, 1 h	44406.82, 3302.85, 223.64 mg kg^{-1} of anthocyanins, flavonol glycosides and flavan-3-ols, respectively	(Tomaz et al., 2016)
Grape seeds	Ethanol 74.33% *v/v*	0.1:70.86 *kg/L*, 65 min	96.56 mg GAE g^{-1}	(Medouni-Adrar et al., 2015)
Wine lees	Methanol/2% HCl (95:5 *v/v*)	1:5 *kg/L*, 25 °C, 60 min, three extraction cycles	2316.6 ± 37.9 mg GAE 100 g^{-1}	(Jurčević et al., 2017)

3.2 Extraction of phenolic compounds: SLE with water vs. UAE with ethanol:water (50:50 v/v)

According to the results obtained in the SLE optimization, the best extraction conditions were selected for each waste matrix. In summary, the extraction consists of a 10 min step at pH 5. No pH adjustment was necessary, as the samples provide the required pH. For the olive pomace sample, it is proposed to carry out the extraction at room temperature (25 °C) and with a solid-to-liquid ratio 1:30 (*kg/L*), while for the lees filters 70 °C and 1:100 (*kg/L*) are selected.

The conventional SLE was compared with UAE (see section 2.4.7), which had been previously optimized (Tapia-Quirós et al., 2020) and used ethanol:water (50:50 *v/v*) as the extraction solvent. The two methods were applied to samples O5 (olive pomace) and W14 (lees filters), and the results are shown in Figure 5. Moreover, in Figure S1 (supplementary material) the chromatograms comparison of the samples obtained with the different extraction techniques are provided.

For olive pomace matrix, SLE had a better performance, with a higher extraction yield for TPC (24%), and OLE (62%) (Figure 5a); for RUT and 3-HTR, there was no significant differences between the recoveries provided by the two extraction techniques.

For the lees filters sample, SLE provided higher extraction yields of TPC (67%), GA (34%) and SYA (37%) (Figure 5b), while for HES similar recoveries were obtained with the two extraction techniques.

For all the above, SLE was more effective when compared to UAE. Extraction with water has shown to be a good approach, specially for the lees sample, which polyphenolic profile has a strong contribution of hydroxycinnamic acids.

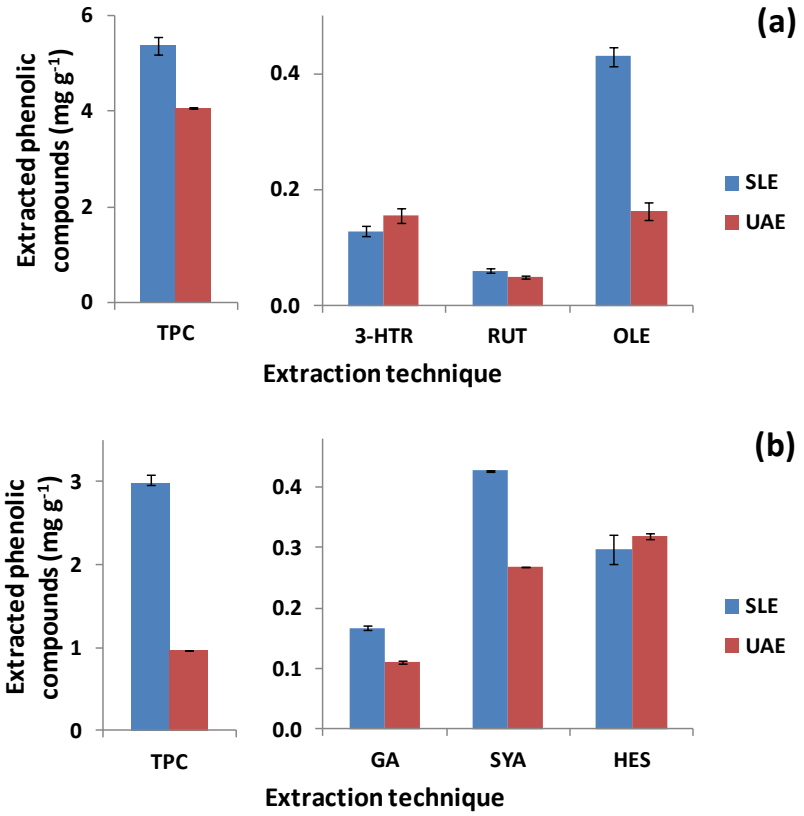

Figure 5. Solid-liquid extraction technique comparison for phenolic compounds recovery as TPC and individual phenolic contents (mg g^{-1}) in (a) olive pomace and (b) lees filters.

3.3 TPC and antioxidant capacity in olive mill and winery production wastes

A wide set of waste samples from olive oil mills and wineries was characterized in terms of TPC and antioxidant capacity after the extraction of polyphenols using the selected SLE conditions (Table 4); for the liquid wastes (O6 and W15-21) only filtration was performed before analysis.

HPLC-UV and FC methods were used to estimate TPC. The approach based on HPLC-UV assumes that the total area of the chromatogram at 280 nm, within the time window from 5 to 36 min, is mainly due to the contributions of the polyphenol peaks. On the other hand, FC is based on a redox reaction, and it is assumed that in this type of samples, polyphenols are the main reducing agents that react with the FC reagent. Both HPLC-UV and FC results are expressed in terms of gallic acid equivalent (GAE) concentration.

The antioxidant capacity was determined by the FRAP, ABTS and DPPH methods. FRAP is based on a redox reaction involving the reduction of a Fe(III) complex to the Fe(II) form, whereas ABTS and DPPH are based on reactions between a radical species and a reducing agent. Again, it is assumed that phenolic compounds are the major reducing agents. All results of antioxidant capacity have been expressed in terms of Trolox equivalent antioxidant capacity (TEAC).

The results obtained for HPLC-UV, FC, FRAP, ABTS and DPPH assays are collected in Table 4. Also, Table 5 shows some reviewed studies of TPC and antioxidant capacity of olive mill and winery residues.

Table 4. TPC and antioxidant capacity of olive mill and winery residues.

Sample code	TPC (mg GAE kg^{-1})		Antioxidant capacity (mg TEAC kg^{-1})		
	HPLC-UV	FC	ABTS	DPPH	FRAP
Olive mill residues					
O1	27 ± 0.01	69 ± 0.01	350 ± 0.02	596 ± 0.06	52 ± 0.01

O2	30 ± 0.01	62 ± 0.01	3725 ± 0.13	1699 ± 0.01	378 ± 0.01
O3	527 ± 0.04	1670 ± 0.20	10937 ± 0.45	365 ± 0.04	2806 ± 0.08
O4	5673 ± 0.07	2787 ± 0.23	25770 ± 0.37	23608 ± 0.09	9773 ± 0.40
O5	5906 ± 0.05	2817 ± 0.24	26269 ± 2.5	11219 ± 0.81	12043 ± 1.7
O6*	1862 ± 24	2265.5 ± 3.0	541 ± 42	1863 ± 12	4721 ± 48
Winery residues					
W1	52 ± 0.01	80 ± 0.01	151 ± 0.01	529 ± 0.14	31 ± 0.01
W2	69 ± 0.01	241 ± 0.02	576 ± 0.01	1351 ± 0.15	90 ± 0.01
W3	74 ± 0.01	151 ± 0.02	568 ± 0.02	393 ± 0.02	35 ± 0.01
W4	76 ± 0.01	236 ± 0.02	1167 ± 0.01	1047 ± 0.24	149 ± 0.01
W5	81 ± 0.01	200 ± 0.01	3499 ± 0.11	4364 ± 0.10	590 ± 0.01
W6	99 ± 0.01	107 ± 0.01	891 ± 0.01	390 ± 0.17	34 ± 0.01
W7	128 ± 0.01	406 ± 0.01	811 ± 0.01	1050 ± 0.07	159 ± 0.01
W8	172 ± 0.01	318 ± 0.07	707 ± 0.01	1345 ± 0.15	65 ± 0.01
W9	187 ± 0.01	270 ± 0.02	817 ± 0.01	1359 ± 0.03	128 ± 0.01
W10	205 ± 0.01	341 ± 0.01	1177 ± 0.01	1115 ± 0.07	114 ± 0.01
W11	233 ± 0.01	24005 ± 7.0	3235 ± 0.01	7058 ± 0.04	206 ± 0.01
W12	273 ± 0.01	534 ± 0.20	1037 ± 0.01	1329 ± 0.06	709 ± 0.01
W13	459 ± 0.02	21957 ± 3.2	4418 ± 0.24	5064 ± 0.19	550 ± 0.01
W14	620 ± 0.01	1446 ± 0.50	7176 ± 0.81	3857 ± 0.11	1453 ± 0.01
W15*	1.03 ± 0.01	0.09 ± 0.01	0.71 ± 0.19	8.2 ± 3.0	0.21 ± 0.06
W16*	11.98 ± 0.28	387 ± 20	37 ± 3	30.4 ± 3.4	4.31 ± 0.07
W17*	14.35 ± 0.03	48 ± 6	69 ± 3	78.9 ± 1.7	17.73 ± 0.61
W18*	36.02 ± 0.60	1080 ± 2	84 ± 7	27.7 ± 1.3	17.14 ± 0.71
W19*	38.71 ± 0.68	1107 ± 1	97 ± 27	320 ± 14	25.38 ± 0.06
W20*	84.68 ± 0.47	97 ± 3	277 ± 2	389 ± 20	104.1 ± 4.8
W21*	99.42 ± 0.23	2844 ± 29	155 ± 26	345 ± 12	46.0 ± 2.1

*Liquid sample. HPLC-UV and FC expressed in terms of mg GAE L^{-1} and FRP, ABTS and DPPH in terms of mg TEAC L^{-1}.

The phenolic yield of the different oil mill wastes (O1-O6) was very diverse (Table 4), varying from 27 to 5906 mg GAE kg^{-1} as determined by HPLC-UV; this can be attributed to the type of waste, but also to varietal issues (Carranco et al., 2018; Farrés-Cebrián et al., 2016). The extracts from the olive pomace samples O4 and O5 were the ones that presented the highest TPC and TEAC values. In fact, both olive pomace residues were obtained from wineries located in the same region (Córdoba, Spain) and from the same olive varieties: Hojiblanca and Picual. On the other hand, the mill wastewater (sample O6) also yielded high results. It has been previously reported that oil mill wastewater may be richer in phenolic compounds and antioxidant capacity than olive pomace extracts (Leouifoudi et al., 2015). Goldsmith et al. (Goldsmith et al., 2018), obtained 28070 mg TEAC kg^{-1} from olive pomace aqueous extracts using DPPH assay which is similar to that obtained for O4 sample. Regarding the winery waste, a wide range of TPC values and antioxidant activity were also obtained. Sample W14, a lees filter of diatomaceous earth, and sample W13, a grape pomace from Mencia variety, were the richest in phenolics. Again, in global terms, TPC and antioxidant activity were directly correlated, and samples W13 and W14 had high TEAC vales. Figure S2 (supplementary information) shows normalized data of the spectrophotometric assays and HPLC-UV technique from olive mill and winery residues. Overall, samples having high values for TPC also show high values for antioxidant capacity, although there is not a simple relationship. Actually, antioxidant capacity is related to phenolic content, but it should be taken into account that the samples are complex, with different phenolic profiles, each component contributing to a different extent to the response of the different methods (Alcalde et al., 2019). Using

water as extractant is an additional advantage for the antioxidant capacity; comparing the results of antioxidant capacity (ABTS) with those obtained in a previous work with organic solvent (ethanol:water 50:50 *v/v*) and UAE, it can be seen that mostly the same samples had a highest antioxidant capacity with water as extraction solvent (Tapia-Quirós et al., 2020).

From the data shown in Table 4, it can be inferred that pomace from olive oil production can be a valuable resource for polyphenols recovery, but olive variety seems to have a strong influence. Conversely, concerning winery waste, lees residues are specially interesting, once more with an influence of grape variety. A study to characterize these large differences is currently under development.

Table 5. Reviewed studies of TPC and antioxidant capacity of olive mill and winery residues.

			Antioxidant capacity		
Sample	**Solvent**	**TPC**	**Assay**	**Concentration**	**Reference**
Olive pomace	Ethanol:water (80:20 *v/v*)	57 - 171 mg GAE 100 g^{-1}	ABTS	50 mM TEAC g^{-1}	(De Bruno et al., 2018)
Olive pomace	Water	13.76 mg GAE g^{-1}	DPPH	28.07 mg TEAC g^{-1}	(Goldsmith et al., 2018)
Grape pomace	Ethanol:water (60:40 *v/v*)	5.29 - 8.50 g CE kg^{-1}	DPPH	87.13 - 135.17 µmol TEAC g^{-1}	
			ABTS	75.83 - 77.36 µmol TEAC g^{-1}	
rape pomace	Water, ethanol	920 - 2276 mg GAE kg^{-1} dw	ABTS	2922 mg AA L^{-1}	
Grape pomace	Ethanol:water (80:20 *v/v*)	69.3 - 131.7 mg GAE g^{-1}	DPPH	0.52 - 1.09 mmol TEAC g^{-1}	(Tournour et al., 2015)
Grape seeds	Methanol, ethanol, acetone	139.92 - 211.63 mg GAE kg^{-1} dw	FRAP	219.84–289.02 mg $FeSO_4$ kg^{-1} dw	(Nakilcioğlu-Taş and Ötleş, 2019)
Wine lees	Ethanol:water (75:25 *v/v*)	254 mg GAE g^{-1} dw	FRAP	2197 µmol TEAC g^{-1} dw	(Romero-Díez et al., 2018)

$FeSO_4$: reduced iron equivalents

AA: Ascorbic acid equivalents

3.4 Perspectives on the implementation of a water extraction stage in the green processing of winery and olive oil wastes.

The growing role of circular economy in the industry is promoting the valorization of food by-products which are still underestimated and mainly considered as a problem due to their management cost and their environmental effects, induced by their disposal. The large volumes of wastes guide the need to develop scalable technologies for industrial applications with high recovery, reducing processing times, with low capital and operation costs and using green solvents. The review of the state of the art indicates that most of the present proposals are centered in the integration of mixtures of aqueous, benign organic solvents and CO_2(g) with advanced physical methods (Pagano et al., 2021). However, the recovery ratios of polyphenols obtained in the present work (see above sections), demonstrated that a combination of water and temperature are providing competitive advantages than extraction approaches using advanced extraction technologies (e.g. UAE, MAE, PLE and Supercritical CO_2 extraction, among others). Thus, the results of this work aim to reconsider the use of water as main solvent and also temperature for the polyphenols extraction stage. Chemat et al. (Chemat et al., 2019) formulated the concept of a green extraction of natural products as any approach "*based on design of extraction processes which will reduce or eliminate energy consumption and petroleum solvents, while ensuring a safe extract and quality*". This proposal is totally oriented to many of the objectives identified as Sustainable Development Goals (SGD) of the United Nations ("United Nations Sustainable Development," n.d.) to meet the challenges of the 21st century protecting both our environment and consumers, and it is totally aligned with new paradigms as the Circular Economy tools supporting the industry development in the

next decades. From the basis of the postulation of the twelve principles of green chemistry (Anastas and Warner, 1998) and the twelve principles of green engineering (Anastas and Zimmerman, 2003), the basis of the "green extraction" was defined under the basis of six principles (Chemat et al., 2012). Probably, the most important unit operation in the polyphenol recovery process is the solid-liquid extraction, particularly when it is not optimized, since it is often time and energy consuming, inducing the use of huge amount of solvent (e.g. water or organic compounds, harmful for the environment and users) and generating large quantity of waste (Makris, 2018). In this context, Chemat et al. (Chemat et al., 2019) identified as the objective "*to obtain higher extraction efficiency and higher quality extract while reducing extraction time, number of unit operations, global energy consumption, quantity of solvent in the process, environmental impact, economical costs and quantity of waste generated*". Taking into account these principles, the extraction processes studied in this work were evaluated under these principles. Tapia-Quirós et al. (Tapia-Quirós, 2021) analyzed different advanced extraction techniques, such as UAE, MAE and PLE. In that thesis, results demonstrated that PLE provided higher efficiency for olive oil wastes and MAE for olive oil wastes, although UAE performance was also satisfactory. The economic evaluation of different advanced technologies, in terms of capital investment and operational cost, developed by Talmaciu et al. (Talmaciu et al., 2015) concluded that between them, UAE is the one with lower values. In the same direction, Croxatto Vega el al. (Croxatto Vega et al., 2021) combined the techno-economic and life cycle assessment for the extraction of polyphenols from red wine pomace. They concluded that PLE had higher capital, operational expenses and environmental concerns. On the other hand, scarce data could be found for supercritical CO_2(g), although some pilot scale results were reported by Fernandez-Ponce et al (Fernández-Ponce et al., 2016), any economic analysis was provided. Hence, considering the extraction performance and simplicity, but also the investment and operational costs, UAE was considered as reference technology for comparative issues. Thus, the key performance indicators achieved with aqueous-based extraction systems were compared with those obtained by UAE.

All in all, it is worth mentioning that extraction processes using organic volatile solvents render them incompatible with the development of green extraction processes. Thus, efforts of solvent substitution have been done. According to the sustainable development goals, green extraction processing routes should be characterized by: i) the use of non-hazardous compounds, ii) reusable solvents, and iii) low energy demand. Additionally, they use should not be affecting the quality of the final products and being environmentally benign, to facilitate the integration in process intensification as promising paths towards a sustainable industrial production. Typically, most of the green approaches were postulated in base of the use of bioethanol, which is a bio-solvent produced through fermentation of starch and sugar, containing agri-food and beverage wastes (Sarris and Papanikolaou, 2016). Besides, ethanol blended with an appropriate amount of water as extraction solvent (from ratios of 80 to 20 %(v/v)) has shown to be very effective. However, when such approaches are used, final recovery stages, e.g. using evaporation stages, should be integrated, while in the proposed approach in this study such energy intensive stage will be avoided.

4. Conclusions

Conventional solid-liquid extraction using water as a solvent is very suitable for the extraction of phenolic compounds from residues of olive mills and winery companies. This is highly interesting from an industrial perspective, because SLE is a simple technique, easy to implement and to scale up. In addition, using water as extraction solvent is very advantageous environmentally, but also in terms of operational costs, and the aqueous extracts are fully compatible with purification schemes relying on membranes and/or resins-based processes. This green technique can be applied to the treatment of industrial residues of olive mill and winery industries, contributing to the environmental protection.

Similar extraction conditions can be applied to both investigated matrices (olive pomace and lees filters). The proposed conditions were a 10 min single extraction step at the sample natural pH (*ca.* 5), at room temperature (25 °C) for olive pomace and at 70 °C for winery wastes. As to sample-to-solvent ratio, 1:30 and 1:100 (*kg/L*) are proposed for olive pomace and winery wastes, respectively.

Olive mill and winery wastes are suitable sources for phenolic compounds recovery in a circular economy perspective. Large differences between the total phenolic content have been observed among the wastes evaluated in this study. In particular, olive mill wastewaters and wine lees were especially rich in phenolic compounds and showed high antioxidant capacities.

On the basis of polyphenol recovery results of this study, future research efforts should be directed towards (i) testing allegedly "green" processes, based in aqueous solvents, (ii) the integration of advanced separation technologies to reduce unit operations, which in turn would reduce the associated chemicals and energy requirements, (iii) the evaluation and assessment of potential technologies to ascertain suitability for a given objective and (iv) the designed scale-up procedures that would drive to the deployment of industrial applications on polyphenols production.

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