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Fruit and vegetable processing wastes as natural sources of antioxidant-rich extracts: Evaluation of advanced extraction technologies by surface response methodology

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ABSTRACT

This study is focused on the recovery of polyphenols from vegetable and fruit residues and further evaluation of antioxidant features of extracts. Spinach and orange have been selected as representative matrices for a more comprehensive study since they contain significant polyphenols amount that could be used in food, pharmaceutical and/or cosmetic industries. Extraction of polyphenols from spinach and orange waste was performed using three extraction techniques: ultrasound-assisted extraction (UAE), microwave-assisted extraction (MAE), and pressurized liquid extraction (PLE). Tested factors include percentage of organic solvent (ethanol 0–80%), acidity (0–0.5% HCl), extraction time (0–30 min) and temperature (25–120 °C). Optimal extraction conditions for spinach and orange waste have been stablished by design of experiments (DoE). The performance of the extraction process has been preliminarily assessed from the overall polyphenolic content given by high-performance liquid chromatography (HPLC) and Folin–Ciocalteu index. In addition, reducing power and antiradical capacity of vegetable and fruit extracts have also been determined. For spinach, the best conditions corresponded to UAE with a mixture of ethanol/water/HCl in ratio 80/19.9/0.1 (*v/v/v*) as the solvent at 25 °C for an extraction time of 30 min, providing 0.82 mg gallic acid equivalent (GAE) per g fresh weight (fw). For the orange matrix, PLE has been chosen using 60/39.9/0.1 ethanol/water/HCl (*v/v/v*) solvent at 80 °C for 15 min, providing 3 mg GAE g^{-1} fw. However, UAE is proposed for extraction of polyphenols from spinach and orange waste at industrial scale, due to its simplicity and low cost, among other reasons.

1. Introduction

Agricultural processing inevitably generates large amounts of agri-food residues, which represent an important problem of waste disposal, most of the generated wastes are recycled as animal feed and compost, but the remaining quantities are incinerated and dumped causing greenhouse gas emissions which contributes negatively to climate change [1–3]. Specifically, the vegetable and fruit sector generate around 90 million tons of residues per year in Europe and experts estimate a rise of 40% in the next 4 years [4,5]. In Spain, vegetable and fruit processing are around the 5% of the food industry which generates almost 3 millions tonnes of residues per year [6]. Spinach is one of the most cultivated and consumed vegetables, not only in Spain but also worldwide, which generates between 13% and 25% of waste, basically corresponding to damaged leaves and solid residues from juice production [7]. On the other hand, orange is the main cultivated fruit in Spain [8] that generates around 50% of weight waste composed by peels, pulp and seeds [9].

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According to literature, a plant or vegetable residue is a good natural source of polysaccharides, bioactive molecules (e.g. polyphenols, vitamins) and carbohydrates [10]. Furthermore, according to data of spinach and orange percentage of generated waste, these matrices are attractive for the study of polyphenol recovery [7,9]. Regarding to the powerful antioxidant activity of polyphenols, epidemiological studies have pointed out that diets rich in polyphenols may help to prevent cancer, neurodegenerative and cardiovascular diseases, among others [11].

Polyphenols consist of molecules with one or more phenol groups, classified into different families: phenolic acids, flavonoids, stilbenes and lignans. Among them, phenolic acids (hydroxybenzoic and hydroxycinnamic) and flavonoids (including oligomeric tannins) are the main phenolic components of the human diet [12,13]. Spinach is rich in flavonoids such as luteolin, quercetin, apigenin, among others, whereas orange residues contain hesperidin, vanillic acid, ferulic acid, etc. [14–16].

Thus, polyphenols extracted from spinach and orange residues may be reused in food, cosmetic and pharmaceutical industries [14,17], for example to prepare natural additives, food supplements, or nutritional food ingredients, among other applications [18,19]. Nowadays, the development of a single, efficient and rapid extraction method of polyphenols from such matrices is still a great challenge. This is mainly due to the inherent limitations of various conventional extraction methods [20,21]. The extraction of polyphenols from agri-food wastes can be done using different techniques, including conventional liquid extraction (e.g., mechanical agitation, maceration and Soxhlet) as well as more efficient counterparts (e.g., ultrasound-assisted extraction (UAE), microwave-assisted extraction (MAE), pressurized liquid extraction (PLE), supercritical fluid extraction (SFE), etc.) [22–24]. UAE offers important benefits such as lower energy consumption in comparison with other techniques (MAE and PLE), being highly recommendable for extraction of polyphenols from food matrices [25,26]. MAE and PLE apply more energy during extraction process, so that higher overall yields may be achieved, but, at the same time, degradation of labile components may occur. Aqueous mixtures containing ethanol have been reported to be suitable for polyphenol extraction and safe for human health [27]. Focusing on spinach, a representative vegetable, ethanol/water mixtures have been assayed and suitable results have been reported [28,29]. Regarding residues from fruit processing, and orange residues in particular, the ethanol/water system has also been explored, showing good performance in the extraction of polyphenols [30–33].

Developing a polyphenol valorization process requires the identification of the most efficient extraction stage, where the issues of characterization of the polyphenols content and their antioxidant capacity, operating conditions and selection of compatible solvents for the subsequent separation and purification stages are critical [34].

The principal objective of the study was the revalorization of agri-food wastes as they may result in a remarkable source of raw products with increasing social and economic impact. In this context, polyphenols are possibly the most relevant group of phytochemicals from these wastes, so the study was focused on obtaining enriched mixtures of polyphenols to be the basis of by-products with great antioxidant features, with potential interest for manufacturing cosmetic and nutraceutical products. The optimization intended to recover the highest amount of phenolic components, and the overall peak area of the chromatogram was found to be a good objective response to compare the recovery yield of those fractions with remarkable antioxidant properties. Polyphenols from vegetable and fruit wastes were extracted by UAE, MAE and PLE techniques, using water-ethanol mixtures, and considering the effect of acidity, extraction time and temperature. For this purpose, factorial design approaches were employed to evaluate the impact of different experimental variables on the recovery. The efficiency of the extraction was accounted from contents of individual and overall phenolics determined by high-performance liquid chromatography with ultraviolet detection (HPLC-UV) and Folin-Ciocalteu (FC) method. Further evaluation of the antioxidant features of extracts relied on ferric reducing antioxidant power (FRAP) and Trolox equivalent antioxidant capacity (TEAC) indexes.

2. Materials and methods

2.1. Chemicals and reagents

Polyphenols used as standards were as follows: 2-(3,4-dihydroxyphenyl) ethyl alcohol (dihydroxytyrosol), resveratrol, myricetin and catechin from TCI (Japan); 2-(4-hydroxyphenyl) ethanol (hydroxytyrosol), 2,5-dihydroxybenzoic acid, 3,4-dihydroxybenzaldehyde, 3,4-dihydroxybenzoic acid, 4-hydroxybenzoic acid, chlorogenic acid, epicatechin, ethyl gallate, ferulic acid, gallic acid, naringenin, *p*-coumaric acid, quercetin, rutin, syringic, caffeic and vanillic acid from Sigma Aldrich (St. Louis, USA); apigenin and caftaric acid from Chengdu Biopurify Phytochemicals (China); hesperidin and kaempferol from Glentham Life Sciences (UK); homogentisic acid from Extrasynthese (France); luteolin from Carbosynth (USA).

Reagents to be used for the extraction process, HPLC method and spectrophotometric indexes were as follows: acetonitrile (ACN, HPLC grade) was purchased from Fisher Scientific (UK). Ethanol (EtOH, HPLC grade), formic acid (98–100%, w/w), hydrochloric acid (32%, w/w), sodium hydroxide, Fe(III) chloride, sodium carbonate and disodium hydrogen phosphate were obtained by Merck (Darmstadt, Germany). Methanol (MeOH, UHPLC Supergradient, ACS) was purchased from Panreac (Spain). Water was purified with a Milli-Q equipment (Merck Millipore). Reagents for antioxidant indexes were potassium peroxodisulfate from Merck, Folin-Ciocalteu (FC) reagent from Panreac, 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic) acid (ABTS), 2-diphenyl-1-picrylhydrazyl (DPPH), and 2,4,6-tripyridyl-S-triazine (TPTZ) from Alfa Aesar (Germany).

2.2. Samples

Spinach, carrot, kale, celery, beet, broccoli, orange, kiwi, strawberry, white grape and red grape samples were purchased from local markets in Barcelona. Industrial solid wastes from fruit and vegetable juices were simulated using the following procedure recommended by the researchers from fruit juice company. Thus, fruits and vegetables were processed with a domestic juicer and the solid residues were used as the samples. No significant differences in terms of physical, chemical and morphological properties were expected among lab wastes and those obtained at industrial scale. Subsequently, solid wastes were milled with a blender to increase the homogeneity of the samples until obtaining a homogeneous paste. Each wet sample was distributed in various containers that were stored in the freezer at −20 °C until use.

2.3. Instruments and apparatus

The determination of the total phenolics content by HPLC-UV was carried out with an Agilent Series 1200 HPLC Chromatograph (Agilent Technologies, Palo Alto, California, USA) with a quaternary pump (G1311A), a degasser (G1322A), an automatic injection system (G1392A) and a diode array detector (G1315B). The Agilent ChemStation software was used for instrument control and data processing.

A double beam Perkin Elmer UV/Vis/NIR Lambda 19 spectrophotometer was used to estimate the antioxidant and antiradical capacities of vegetable and fruit extracts. QS quartz glass high performance cuvettes (10 mm optical path) from Hellma Analytics (Jena, Germany) were used.

The UAE of polyphenols was conducted using an ultrasonic bath (Branson 5510, USA). MAE experiments were performed using a microwave laboratory system (Ethos E, Milestone S.r.l, Italy). Finally, a Dionex ASE 350 apparatus (Dionex Corp., USA) was used for PLE assays. In all the cases, the resulting extracts were centrifuged with a Rotina 420

centrifuge (Hettich, Tuttlingen, Germany).

2.4. Extraction procedures

2.4.1. Ultrasound-assisted extraction (UAE)

Extractions were performed with different ethanol and HCl percentages: ethanol (40%, 60% and 80%) and HCl (0%, 0.1% and 0.5%) in water. Briefly, 1 g of sample was mixed with 20 mL of solvent and was sonicated for 30 min at 25 °C (frequency of 42 kHz and power of 135 W). To minimize the effect of potential heterogeneity of the distribution of ultrasonic waves on each experimental plan, the different replicates of each extraction condition were placed randomly in a proper rack located in the bath. After that, the mixture was centrifuged for 15 min at 3500 rpm and the supernatant was filtered through 0.45 μm nylon membrane (Whatman, Clifton, NJ, USA). To minimize the influence of the adsorption of compounds on the filter, the initial filtered fraction (about 1 mL) was discarded. Subsequently, ca. 1.5 mL of filtrate was collected in an injection vial and was stored at 4 °C until the analyses. In these conditions, extracts were stable for, at least, two weeks. Assays were carried out in triplicate.

Because of the highest simplicity of UAE with respect to the other extraction techniques, the best experimental conditions from this technique were used as the reference for the comparison of the extraction performance of MAE and PLE.

2.4.2. Microwave-assisted extraction (MAE)

The samples were treated under various experimental conditions: ethanol/water mixtures (0%, 40% and 60% ethanol and 0.1% of HCl); temperature (60, 90 and 120 °C) and extraction time (5 and 15 min). In each experimental assay, 1 g of waste sample was mixed with 20 mL of solvent and was placed in an extraction vessel. After MAE treatment, the resulting extracts were centrifuged for 15 min at 3500 rpm. The supernatant was filtered using a nylon filter of 0.45 μm and stored at 4 °C until the analysis as explained in 2.4.1. Extractions were performed in triplicate.

2.4.3. Pressurized liquid extraction (PLE)

Briefly, 1 g of waste sample was mixed with 2 g of diatomaceous earth and then the mixture was placed into a 5 mL extraction cell containing a cellulose filter at the bottom. Different experimental factors were tested, including solvent composition (40%, 60% and 80% ethanol with 0.1% of HCl in water), temperature (80, 100 and 120 °C), extraction time (5, 10 and 15 min) and number of cycles (1 or 2 cycles). Pressure was 145 psi (about 10 bar). Other conditions such as preheating time (5 min), flush volume (60%) and purge time (60 s) were prefixed according to previous studies [35,36]. After PLE, the volume of each extract was adjusted to 20 mL with the extraction solvent. The solutions were centrifuged for 15 min at 3500 rpm, and were processed and stored as explained in 2.4.1. Extractions were made in triplicate.

2.5. Determination of polyphenols by HPLC-UV

Samples were analyzed by HPLC-UV to determine total polyphenols content (TPC) associated to phenolic acids and flavonoids. Working conditions were adapted from the fully validated method by Aznar et al. [37]. A Kinetex C18 column (100 mm × 4.6 mm of internal diameter and 2.6 μm particle size) from Phenomenex (Torrance, CA, USA) was used. The mobile phase was composed of 0.1% formic acid in Milli-Q water (solvent A) and ACN (solvent B). The gradient elution program was as follows: 0 min, 5% B; 25 min, 50% B; 27 min, 90% B; 29 min, 90% B; 29.2 min, 5% B; 35 min, 5% B. The flow rate was 1 mL min^{-1} and the injection volume was 5 μL. UV detection was performed at 280, 310 and 370 nm for a more specific monitoring of target analytes. In more detail, 280 was used for the detection of hydroxybenzoic acids, flavanols and flavanones (e.g. 4-hydroxybenzoic acid, vanillic acid, hesperidin, etc.); 310 for hydroxycinnamic acids (e.g. coumaric and ferulic acids), and 370 nm for other flavonoid families including flavonols, flavones and isoflavones (e.g. quercetin, rutin, etc.). Compounds were quantified using the corresponding pure standards.

The TPC of extracts was estimated according to Tapia-Quirós et al. [38] from the total peak area of the chromatograms at 310 nm with a bandwidth of 33 nm, in the time range of 5–20 min, thus giving simultaneous information on a wide range of phenolic acid and polyphenolic families. The TPC was expressed in terms of gallic acid equivalent (GAE) per g fresh weight (fw), using gallic acid standard solutions to build the calibration curve in the range of concentrations 1–10 mg L^{-1}.

2.6. Identification of targeted polyphenols by HPLC-HRMS

Various phenolic compounds present in the extracts were identified by high performance liquid chromatography-high resolution mass spectrometry (HPLC-HRMS) with an Accela chromatograph coupled to a LTQ Orbitrap Velos mass spectrometer (Thermo Scientific, Hemel Hempstead, UK). The separation was performed with the Kinetex C18 column (100 mm × 4.6 mm of internal diameter and 2.6 μm particle size) and an elution program based on increasing the methanol percentage. MS detection relied on electrospray ionization (ESI) in negative mode. Mass spectra were acquired in the *m/z* range 100–1500 at a mass resolution of 30,000 full width at half-maximum (FWHM) at *m/z* 200. Data was analyzed with XCalibur software v2.0.7 (Thermo Fisher Scientific, USA). Other experimental conditions have been detailed in Ref. [38].

2.7. Determination of antioxidant indexes

Folin-Ciocalteu (FC), ferric reducing antioxidant power (FRAP), 2,2-diphenyl-1-picrylhydrazyl (DPPH) and 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic) acid (ABTS) methods have been described in detail elsewhere [39]. In any case, spectrophotometric measurements were carried out at the selected wavelengths (765 nm for FC, 595 nm for FRAP, 517 nm for DPPH and 734 nm for ABTS) using a double-beam system in which test and blank solutions were placed in the sample and reference holders, respectively.

2.8. Experimental design and statistical analysis

The influence of experimental variables on the extraction of polyphenols from waste matrices using the proposed techniques (UAE, MAE and PLE) was assessed by factorial design. Depending on the cases, 2- and 3-factor at 2- or 3-level full designs were created to deal with the main effects as well as the possible interactions. In general, variables under study comprised solvent percentage, HCl percentage, temperature and time. Data resulting from these studies were further evaluated statistically to find out the optimal conditions.

All the experiments were performed in triplicate and results were expressed as mean ± standard derivation (SD). The average values of TPC obtained by UAE, MAE and PLE, determined by HPLC-UV, were subjected to analysis of variance (ANOVA) to ascertain the significance of factors and their potential interactions. Mean values of representative cases were also compared using Student's *t*-test. In any case, $p \leq 0.05$ was considered as the significance criterion.

Extraction values were further processed according to the response surface methodology (RSM) to visualize simultaneously the influence of the experimental factors. The RSM approach was applied to each individual target compound (e.g. hesperidin, ferulic acid, coumaric acid, etc.) as well as to the TPC resulting from the contribution of all the compounds. Extraction values from each studied design were fitted to multilinear expressions including quadratic terms. In the case of the simultaneous influence of ethanol and HCl percentages, for instance, the equation used was $R = a_0 + a_1\ \text{ethanol\%} + a_2\ \text{HCl\%} + a_3\ \text{ethanol\%} + a_4\ \text{ethanol\%}^2 + a_5\ \text{HCl\%}^2$, being a_0, a_1, a_2, a_3 a_4 and a_5 the coefficients to be

fitted, and ethanol% the experimental value of the ethanol percentage, HCl% the HCl percentage, and ethanol%^{2} and HCl%^{2} the corresponding quadratic terms. Subsequently, the significance of the regression and each coefficient were statistically evaluated, and the final model was built including only those relevant terms.

3. Results and discussion

3.1. Extraction of phenolic compounds from spinach waste

Polyphenols were extracted from spinach leave waste using hydro-organic solutions. The optimal working conditions were defined as those leading to the highest total polyphenols recovery. The study of the influence of the experimental variables (extraction time, solvent composition and temperature) on the extraction yield was evaluated for UAE, MAE and PLE techniques.

The principal factors under study were the solvent composition (including solvent type, solvent percentage and HCl percentage), processing temperature and time. Other specific factors, such as number of cycles, were also considered in PLE. With so many factors involved, a full factorial design at several (two or three) levels was considered quite unreasonable because a huge number of experimental runs was required; this was even more dramatic with replicated experiments. Anyway, preliminary evidences suggested that chemical (solvent

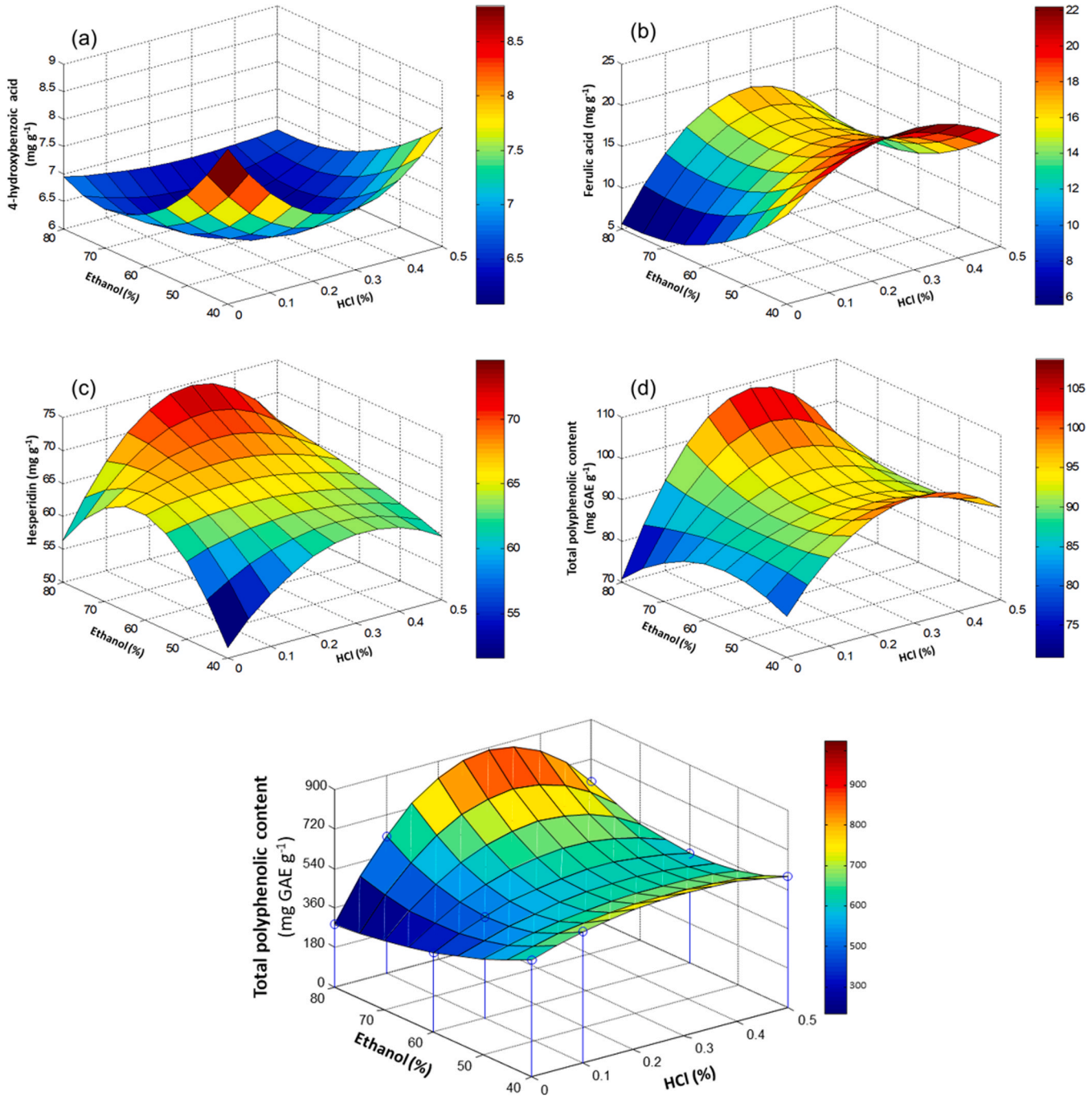

Fig. 1. Surface response depicting the extraction behavior of various individual polyphenols and the total polyphenols content (mg GAE g^{-1} fw) by UAE as a function of ethanol and HCl percentages for spinach waste using UAE. (a) 4-hydroxybenzoic acid; (b) ferulic acid; (c) hesperidin; (d) overall phenolic amount from the addition of each individual compound; (e) total phenolic amount from the overall area at 280 nm. Extraction time: 30 min.

composition) and physical (temperature and time) factors were not interrelated, so independent studies to check the influence of chemical and physical variables on the extraction were designed.

In general, we applied factorial designs (2-factor at 3-level) to explore the influence of the working conditions on the phenolic recovery, so that, a total of 9 experimental conditions were assayed (considering triplicates, 27 runs in each design).

This design was highly versatile and reasonable from the point of view of the experimental effort required as well as the quality of the information provided (it is ideal for the evaluation of the significance of effects and interactions, and data can easily be fitted to multilinear models). Levels and working ranges under study were selected according to our previous experience on the extraction of polyphenols from fruit matrices. These studies were performed at lab scale to propose extraction protocols for further scaling up experiments.

For each extraction technique, the response surface methodology combined with multicriteria decision approach was used to try to find the optimum extraction conditions. For this purpose, each individual compound was considered to fit its surface response. Furthermore, overall responses were established according to two complementary approaches, as a way to estimate the best extraction conditions considering all the polyphenols under study as follows: (i) Combined response considering the amounts of each target compound (here, the addition of the concentrations of 4-hydroxybenzoic acid, coumaric acid, ferulic acid and hesperidin) and (ii) the TPC of extracts was estimated according to the total peak area at 310 nm, in the time range of 5–20 min, which was related to a wide range of phenolic compounds detected under these conditions [38].

Preliminary, spinach extracts were analyzed by LC-HRMS to identify some relevant compounds. 4-hydroxybenzoic acid, coumaric acid, ferulic acid and hesperidin were found thanks to the exact *m/z* values of the corresponding $[M\text{-}H]^-$ ions. The identity of these polyphenols was further confirmed by using standards.

3.1.1. UAE

Initial experiments were performed at room temperature using an extraction time of 30 min [40]. Results of the influence of the ethanol percentage (40%, 60% and 80%, *v:v*) and HCl content (0%, 0.1% and 0.5%, *v:v*) on the extraction of various individual phenolic compounds (4-hydroxybenzoic acid, ferulic acid and hesperidin), on the global phenolic concentration and on the TPC value estimated from the overall area at 310 nm are shown in Fig. 1. As can be seen, the extraction behavior was different depending on the type of compound, being the more polar species better extracted at lower ethanol percentages (e.g. 4-hydroxybenzoic acid, at 40%, see Fig. 1a) while the less polar ones were better recovered at higher percentages (e.g. hesperidin, at 80%, *v:v*, see Fig. 1c). Regarding to the HCl percentage, its influence was noticeable for coumaric and ferulic acids, and the best extraction yields were obtained at intermediate HCl concentrations (see Fig. 1b). These findings were statistically evaluated according to the RSM approach and results given in Table S1 (Supplementary material) confirmed that ethanol percentage was an influencing factor in the extraction of 4-hydroxybenzoic acid and hesperidin, while HCl percentage was relevant for the aforementioned hydroxycinnamic acids.

When the information of compounds belonging to the different families was combined, the best compromise to obtain the maximum extraction recovery has been attained at 80% ethanol and 0.1% HCl (Fig. 1d). This conclusion was in agreement with results from the use of the overall peak area as the data (Fig. 1e). In general, TPC increased with increasing ethanol concentration, whereas the maximum of TPC for HCl was attained at 0.1%. Thus, it was found that higher ethanol concentration and moderate acidity help to increase polyphenols extraction from spinach waste. The optimum UAE conditions for the extraction of polyphenols were 80% ethanol and 0.1% HCl (*v:v*), leading to a TPC of 820 ± 20 mg GAE kg^{-1} fw. Qiu et al. [41] studied the effect of extraction solvent, extraction time, and temperature on Okinawa spinach leaves extraction efficiency, obtaining optimal conditions of 40% ethanol, 30 min extraction time and 40 °C; the TPC under these conditions was 10,380 mg GAE kg^{-1} of dry matter.

A chromatogram showing the polyphenolic profile under the selected extraction conditions is depicted in Fig. 2. The occurrence of various phenolic acids (e.g. 4-hidroxybenzoic, ferulic and *p*-coumaric acids) and hesperidin as relevant components has been confirmed by HPLC-HRMS. Table S2 (Supplementary material) reports the concentration of each one under optimal conditions. These findings were in accordance with data reported in literature indicating that ferulic and *p*-coumaric acids were quite abundant in fresh spinach leaves extracts [42].

3.1.2. MAE

MAE extraction was also investigated with mixtures containing water, ethanol and hydrochloric acid from a factorial design. Levels under study were 0%, 40% and 60% for ethanol *v:v*, 60, 90 and 120 °C for temperature and 5 and 15 min for extraction time (see Table 1). For 5 min, results indicated that TPC improved with the increasing ethanol content, whereas for 15 min the TPC increased in the range of 0–40% ethanol and declined from 40% to 60%. Anyway, no significant ($p > 0.05$) improvement in the extraction yield was observed when increasing extraction time. These results agreed with Fiorito et al. [43], suggesting that a high percentage of ethanol improved the recovery of polyphenols using MAE. This was attributed to the higher solubility of less polar compounds in higher ethanol percentages. For temperature, the extraction yield increased from 60 °C to 90 °C, while decreased at 120 °C. This finding suggested that compound degradation may occurs at high temperatures for this matrix. Therefore, selected MAE conditions for the spinach matrix were ethanol/H_2O/HCl (60/39.9/0.1, *v/v/v*) as the solvent, a temperature of 90 °C and an extraction time of 5 min. The TPC obtained under these conditions was 950 ± 7 mg GAE kg^{-1} fw.

3.1.3. PLE

PLE factors under study comprised solvent composition (40%, 60% and 80% ethanol), temperature (80, 100 and 120 °C), time (5 and 15 min) and number of cycles (1 and 2). Recovery results in terms of overall peak area of polyphenols and PLE/UAE area ratio are summarized in Table 2 for a better comparison of the extraction performance with respect to UAE. ANOVA and t-student tests demonstrated that the effects of temperature, time and solvent composition in the ranges studied were negligible ($p > 0.05$). Therefore, working conditions, selected under the basis of saving solvent, energy and time, were solvent composition of ethanol/H_2O/HCl (40/59.9/0.1, *v/v/v*), temperature of

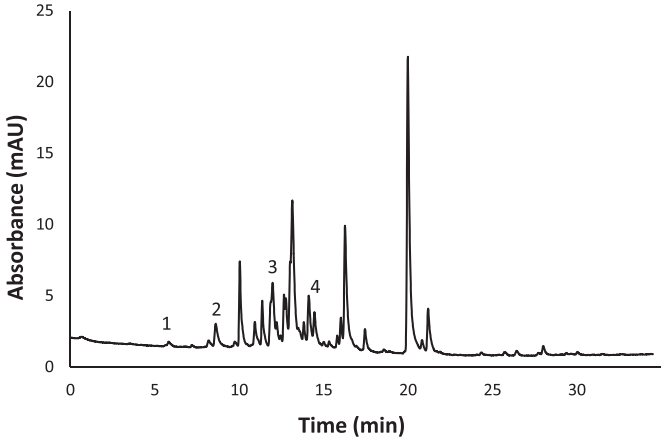

Fig. 2. Chromatogram at 310 nm of the spinach leaf waste extracted by UAE using ethanol/H_2O/HCl (80/19.9/0.1, *v/v/v*) for 30 min of extraction time. Peak assignment: 1 = 4-hidroxybenzoic acid, 2 = *p*-coumaric acid, 3 = ferulic acid, 4 = hesperidin.

Table 1
Results for the experimental design of MAE of spinach matrix. Average of the total area ($n = 3$) with the corresponding standard derivation and MAE/UAE ratio.

Experiment	EtOH (%, *v:v*)	Temperature (°C)	Time (min)	Overall peak area (Average ± SD)	MAE/ UAE
1	0	60	5	330 ± 110	0.49
2			15	350 ± 50	0.52
3		90	5	350 ± 20	0.53
4			15	240 ± 40	0.36
5		120	5	280 ± 80	0.41
6			15	560 ± 440	0.84
7	40	60	5	550 ± 110	0.82
8			15	640 ± 20	0.95
9		90	5	670 ± 70	1.00
10			15	710 ± 170	1.05
11		120	5	610 ± 14	0.90
12			15	580 ± 20	0.87
13	60	60	5	400 ± 70	0.60
14			15	390 ± 140	0.58
15		90	5	780 ± 20	1.16
16			15	630 ± 110	0.94
17		120	5	640 ± 110	0.95
18			15	560 ± 5	0.84

Table 2
Results for the experimental design of PLE of spinach matrix. Average of the total area ($n = 3$) with the corresponding standard derivation and MAE/UAE ratio.

Experiment	EtOH (%, *v:v*)	Temperature (°C)	Overall peak area (Average ± SD)	PLE/ UAE
1	40	80	3600 ± 400	1.23
2		100	3400 ± 200	1.16
3		120	3400 ± 100	1.14
4	60	80	3600 ± 300	1.21
5		100	2980 ± 60	1.00
6		120	2900 ± 200	0.99
7	80	80	3500 ± 200	1.18
8		100	3140 ± 80	1.06
9		120	3300 ± 400	1.12

80 °C and extraction time of 5 min. Besides, the application of further cycles did not improve the recovery yields so that 1 extraction cycle was chosen (see Fig. S1). Hence, a TPC of 1000 ± 130 mg GAE kg^{-1} fw was obtained, being the most effective extraction of polyphenols from spinach leaf waste. Similar conditions (ethanol/H_2O (50/50, *v/v*), temperature of 80 °C and extraction time of 10 min) were reported by Jaime et al. [44] for the extraction by PLE of polyphenols from spinach leaves extract.

3.1.4. Comparison of UAE, MAE and PLE under optimal conditions

In order to evaluate the extraction performance as a function of the extraction technique, recoveries from each option under selected conditions were compared. ANOVA and t-student tests using the TPC values obtained by UAE, MAE and PLE indicated that differences among techniques were statistically not significant ($p > 0.05$). Accordingly, there was not a noticeable improvement in the extraction efficiently of total polyphenols recovery from spinach leaves. Thus, UAE processing could be a simpler and more convenient approach for further scaling up, having an industrial potential, due to its low operating costs [45,46]. In this sense, Talmaciu et al. [47] compared the cost of UAE, MAE and supercritical fluid extraction (SFE) for polyphenol extraction, and concluded that UAE provided the lowest capital cost.

3.2. Extraction of phenolic compounds from orange waste

As for the spinach leave waste, UAE, MAE and PLE were also used to evaluate the extraction of polyphenols from fresh samples of orange peel and seeds. In a similar way, different experimental variables, such as extraction time, solvent composition, and temperature were studied under DoE approaches in order to stablish the optimal conditions and total amount of polyphenols extracted.

Orange extracts were analyzed by HPLC-HRMS to identify the most abundant compounds. In this case, 4-hydroxybenzoic acid, vanillic acid, syringic acid, coumaric acid, ferulic acid, rutin and hesperidin were detected via exact *m/z* values of $[M\text{-}H]^-$ ions. As in the spinach case, the tentative identification was confirmed by using standards. These results agree with some studies of polyphenols in citrus wastes (including orange), in which ferulic acid, *p*-coumaric acid, rutin, vanillic acid and 4-hydroxybenzoic acid were identified as relevant compounds [14, 48–51]. Moreover, Magwaza et al. [52] reported hesperidin as the major flavanone in citrus fruits.

3.2.1. UAE

First studies were focused on the assessment of the solvent composition, in which the ethanol/H_2O/HCl system was studied at 3 levels as follows: 40, 60, 80% (*v:v*) ethanol, and 0, 0.1, 0.5% (*v:v*) HCl. Extractions were carried out at room temperature for an extraction time of 30 min and the extraction performance was evaluated in terms of the TPC.

As in the spinach case, the extraction of individual polyphenols was first studied using RSM. Results summarized in Table S3 (Supplementary material) indicated that ethanol percentage was relevant for the extraction of hydroxybenzoic acids such as vanillic and syringic acids, and the best yields were obtained at low ethanol percentages (40% *v:v* ethanol). Conversely, the influence of HCl percentage was not relevant in this case. For the flavonoids, which are less polar compounds, the ethanol percentage was also noticeable, and the best extractions were attained at 80% ethanol, while the influence of HCl was less important. The extraction behavior of ferulic and coumaric acids was, in this case, dependent on both ethanol and HCl factors. The overall extraction response resulting from the combination of the concentrations of the target compounds also showed the influence of these experimental factors. Results shown in Fig. 3, either from the combined response from each compound (Fig. 3a) or from the TPC values estimated with the total chromatographic area at 310 nm (Fig. 3b), indicated that the maximum recovery corresponded to ethanol/H_2O/HCl (60/39.9/0.1, *v/v/v*), thus giving a TPC value of 400 ± 100 mg GAE kg^{-1} fw by UAE.

Fig. 4 shows the chromatogram obtained from the orange matrix and Table S2 (Supplementary material) reports the concentration of the identified polyphenols in extract obtained under the optimal conditions by UAE (60%, *v:v* ethanol and 0.1%, *v:v* HCl, 30 min extraction time).

3.2.2. MAE

The optimization of the orange waste extraction by MAE was planned in the same way as for the spinach waste. DoE was designed to explore the influence of ethanol (0%, 40% and 60%, *v:v*), temperature (60, 90 and 120 °C) and time (5 and 15 min). In this case, compared with UAE, MAE provided a noticeable increase of extraction, which was attributed to the rupture of the vegetal cells induced by the radiation [31]. The results for orange matrix are summarized in Table 3.

It was found that the extraction improved with the increase of the ethanol content (from 0% to 60%) and temperature (from 60 °C to 120 °C). Time also had a positive effect on this process and, in general, higher TPC values were obtained with 15 min. These conclusions were statistically supported by ANOVA and t-student tests, indicating that the factors studied have a positive influence on the extraction ($p < 0.05$). As a result, selected MAE conditions corresponded to ethanol/H_2O/HCl ratio of 60/39.9/0.1 (*v/v/v*) at 120 °C and with 15 min of extraction time, leading to TPC of 2000 ± 130 mg GAE kg^{-1} fw. At these conditions, the extraction yield improvement was more than 4-fold using MAE with respect to UAE.

Unlike spinach, in this matrix, no degradation of compounds was

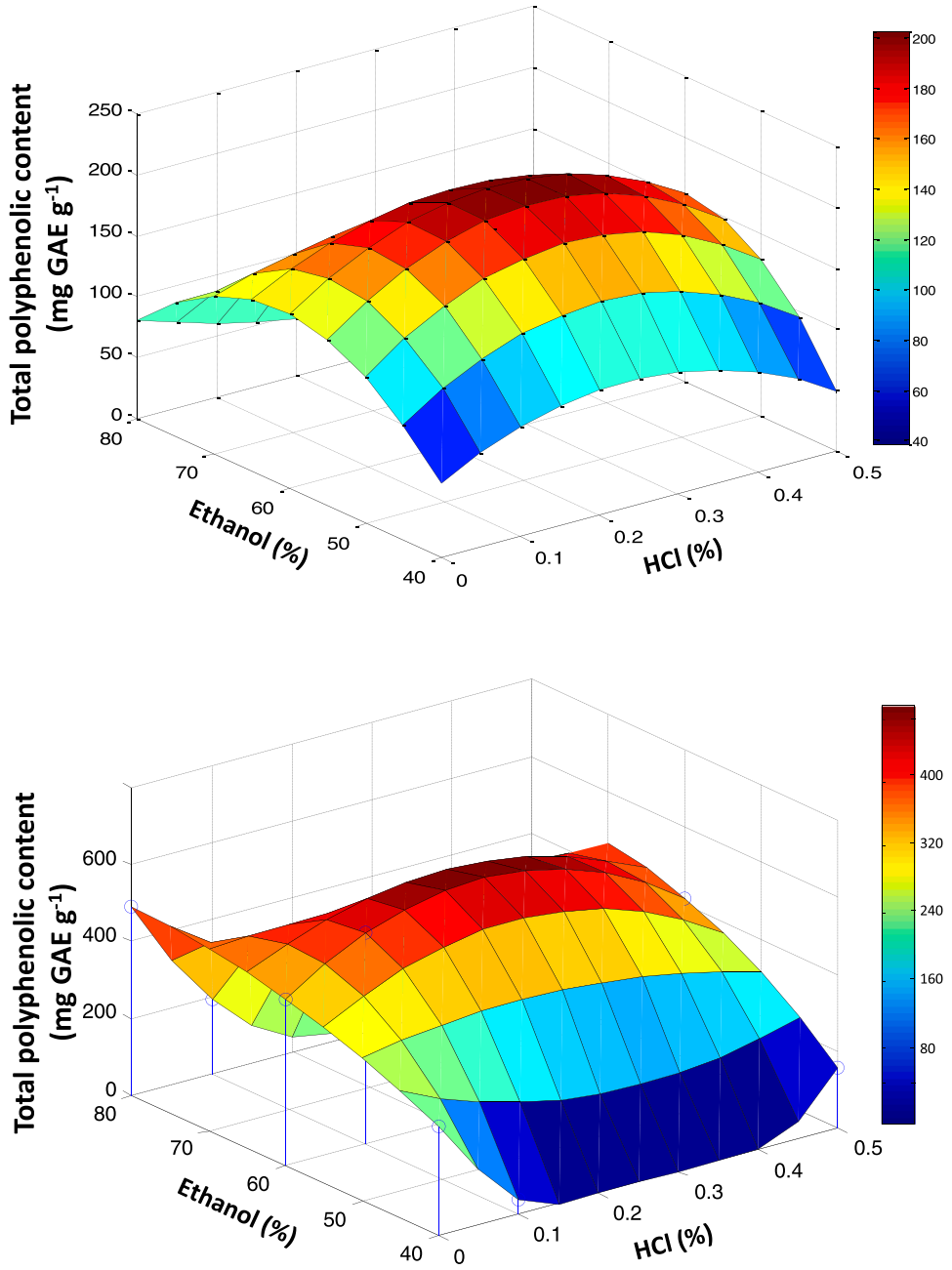

Fig. 3. Surface response of total polyphenols content (mg GAE g^{-1} fw) by UAE as a function of ethanol and HCl percentages for orange waste using UAE. (a) overall phenolic amount from the addition of each individual compound; (b) total phenolic amount from the overall area at 280 nm. Extraction time: 30 min.

observed (it can be mentioned that degradation occurs depending on the nature of the phenolic compounds and of the matrix), even at higher temperatures (120 °C).

3.2.3. PLE

Ethanol percentage, temperature, time and number of cycles were here the variables under study. The DoE design, analogous to that of the spinach case, is detailed in Table 4. In the same table, TPC results indicated that the increase of ethanol percentage slightly increased the extraction yield. However, the influence of temperature was, in general, quite irrelevant. The highest TPC values were obtained at intermediate to high ethanol percentages (60–80% *v:v*) and low to intermediate temperatures (80–100 °C).

Additional studies on process time (see Fig. S2 in Supplementary material) revealed that the extraction increased significantly with time from 5 to 15 min ($p < 0.05$). Besides, the application of further extraction cycles did not improve significantly ($p > 0.05$) the recovery yield (see Fig. S2 in Supplementary material). The same behavior was observed by M'hiri et al. [53], who reported that there is no significant effect of the cycles on the TPC; thus, one cycle is sufficient for polyphenols extraction from orange waste. As a result, conditions selected for the extraction of polyphenols from orange matrix by PLE were as follows: ethanol/H_2O/HCl in ratio of 60/39.9/0.1 (*v/v/v*) as the solvent, 80 °C, 15 min extraction time and 1 extraction cycle. Under these circumstances, TPC of 3000 ± 70 mg GAE kg^{-1} fw was obtained. These results agree with Barrales et al. [33], who determined similar optimal conditions for PLE of polyphenols from orange peels, at 65 °C, ethanol 75% (*v/v*) and extraction time of 20 min.

Finally, the fact that a large extraction time did not decrease the TPC values suggested that polyphenols recovered from the orange matrix

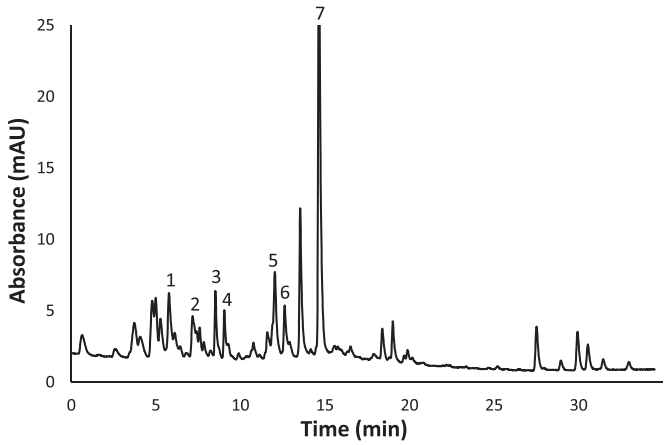

Fig. 4. Chromatogram at 310 nm for the orange matrix extracted by UAE (ethanol:water:HCl 60:39.9:0.1, *v/v/v* and 30 min of extraction time). Peak assignment: 1 = 4-hydroxybenzoic acid, 2 = vanillic acid, 3 = syringic acid, 4 = *p*-coumaric acid, 5 = ferulic acid, 6 = rutin, 7 = hesperidin.

Table 3
Results for the experimental design of MAE of orange matrix. Average of the total area ($n = 3$) with the corresponding standard derivation and MAE/UAE ratio.

Experiment	EtOH (%, *v:v*)	Temperature (°C)	Time (min)	Overall peak area (Average ± SD)	MAE/ UAE
1	0	60	5	780 ± 40	0.51
2			15	800 ± 20	0.52
3		90	5	3000 ± 1000	2.06
4			15	1900 ± 620	1.28
5		120	5	2070 ± 70	1.36
6			15	3000 ± 1000	2.21
7	40	60	5	2600 ± 100	1.70
8			15	2620 ± 60	1.72
9		90	5	2600 ± 200	1.75
10			15	2560 ± 20	1.67
11		120	5	2900 ± 120	1.92
12			15	3100 ± 120	2.04
13	60	60	5	3000 ± 200	1.98
14			15	3300 ± 160	2.21
15		90	5	4100 ± 160	2.73
16			15	4200 ± 180	2.79
17		120	5	5000 ± 400	3.26
18			15	6700 ± 400	4.40

Table 4
Results for the experimental design of PLE of orange matrix. Average of the total area ($n = 3$) with the corresponding standard derivation and MAE/UAE ratio.

Experiment	EtOH (%, *v:v*)	Temperature (°C)	Overall peak area (Average ± SD)	PLE/ UAE
1	40	80	8000 ± 400	4.71
2		100	9500 ± 500	5.63
3		120	10,000 ± 200	5.90
4	60	80	11,500 ± 200	6.76
5		100	10,000 ± 1000	6.01
6		120	10,800 ± 200	6.41
7	80	80	10,500 ± 600	6.21
8		100	11,600 ± 300	6.83
9		120	9000 ± 1000	5.47

were not affected by degradation processes.

3.2.4. Comparison of UAE, MAE and PLE under optimal conditions

A comparison of the three optimized procedures (UAE, MAE and PLE) was performed to propose the most efficient methodology for the extraction of polyphenols from orange wastes of agri-food industry. The TPC values of the extracts obtained by UAE, MAE and PLE were significantly different compared between them ($p < 0.05$). Comparing MAE (2000 ± 130 mg GAE kg^{-1} fw) with UAE (400 ± 100 mg GAE kg^{-1} fw), MAE provided a significant increase ($p < 0.05$) of the extraction (ca. 4-fold higher TPC) without a remarkable alteration of the compositional patterns. In a similar way, PLE yields were ca. 7 times higher than those of UAE ($p < 0.05$), with 3000 ± 70 mg GAE kg^{-1} fw.

Finally, PLE was more efficient than MAE in terms of TPC extraction, providing TPC values in PLE extracts ca. 1.5-fold higher than in MAE extracts. Therefore, in the case of the orange matrix, PLE provided a higher extraction yield of polyphenols, followed by MAE. The use of intensive conditions (ethanol/H_2O/HCl 60/39.9/0.1 (*v/v/v*), 80 °C, 15 min and 1 extraction cycle) was recommendable for the recovery of polyphenols for this matrix. However the scaling of PLE or MAE currently has not been depth studied [54]. On the other side, when considering simplicity, as well as investment and operational costs UAE is the technique of choice [38,47]. For this reason, UAE is proposed as an achievable operational technique for industrial scale-up.

3.3. Antioxidant features of fruit and vegetable waste extracts

The identification of the agri-food wastes with the richest contents of bioactive phytochemicals was the main objective of this paper. Fruit and vegetable extracts could be the basis of by-products with great antioxidant features, with potential interest for manufacturing food supplements and nutraceuticals with increasing social and economic impact. Under this approach, and although UAE conditions chosen above for spinach and orange selected as representatives for vegetable and fruit samples might differ slightly from the optimal ones required for other fruits and vegetables, they could reasonably be extended to other waste matrices to explore the potential of the valorization.

Hence, spinach, carrot, kale, celery, beet, broccoli, orange, kiwi, strawberry, white grape and red grape wastes were processed in the same way as follows. 1 g of each sample residue was extracted with 20 mL solvent solution consisting of 80% (*v:v*) ethanol and 0.1% (*v:v*) HCl. Samples were sonicated for 30 min at room temperature, the supernatant solutions were centrifuged for 15 min at 3500 rpm and were filtered through the nylon membrane. Samples were extracted in duplicate.

The extract solutions from each residue were analyzed chromatographically and spectroscopically according to the different phenolics, antioxidant and antiradical indexes described in Section 2.6. HPLC and FC method were used to determine the TPC in terms of mg GAE kg^{-1} fw, FRAP accounted the reducing power expressed as Trolox equivalent (mg Trolox kg^{-1} fw) and DPPH and ABTS indexes provided an estimation of the antiradical capacity of the samples (also expressed as Trolox equivalent). According to Dzah et al. [55], these assays are used to test the conservation of antioxidant activity of plants extracts after UAE.

Results from these assays are given in Table 5. As can be seen, the values provided by each index differ from the others (even when referred to the same standard). This finding was attributed to the different nature of the redox and antiradical reactions involved. ANOVA was applied to assess the occurrence of significant differences among samples and indexes. Statistical results showed that antioxidant contents differed depending on the samples ($p < 10^{-35}$) since all of them showed different compositional profiles. For the indexes, results were seldom comparable in terms of overall antioxidant capacity ($p < 10^{-17}$). Besides, the interaction between samples and indexes was significant as well ($p < 10^{-19}$), meaning that values from each index depended on the type of sample. These results suggested that understanding the overall antioxidant capacity of fruit and vegetable wastes is still a challenging issue.

Besides, the HPLC method accounts for all absorbing compounds at 310 nm, mainly phenolic compounds although other aromatic molecules may also be detected, thus providing in some cases an

Table 5
TPC, antioxidant and antiradical indexes of the agri-food residues under study. Standard deviations are given in parenthesis.

Sample	HPLC[a]	FC[a]	FRAP[b]	DPPH[b]	ABTS[b]
Spinach	3100 (100)	630 (40)	83 (10)	1005 (80)	1090 (90)
Carrot	360 (20)	60 (1)	14 (10)	*nd*	15 (2)
Kale	3490 (600)	1100 (300)	1192 (1)	108 (2)	1600 (100)
Celery	290 (100)	68 (5)	23 (10)	*nd*	18 (1)
Beet	180 (50)	580 (6)	990 (30)	1450 (30)	1560 (70)
Broccoli	280 (100)	370 (20)	95 (6)	420 (40)	240 (2)
Orange	820 (300)	690 (30)	990 (20)	2700 (200)	570 (30)
Kiwi	390 (10)	200 (20)	144 (10)	890 (40)	305 (9)
Strawberry	1750 (100)	950 (100)	350 (1)	3400 (40)	4900 (100)
Whyte grape	330 (20)	1200 (200)	1360 (50)	6750 (200)	4040 (400)
Black grape	4900 (300)	3450 (20)	5900 (50)	10,600 (600)	8900 (300)

[a] HPLC and FC method data expressed as mg GAE kg^{-1} fw.
[b] FRAP, DPPH and ABTS data expressed as mg Trolox kg^{-1} *fw*; *nd*, non detected.

overestimation of active compounds. Anyway, despite the different scales of assays, results from all these methods were in agreement when comparing the set of samples under study, meaning that those rich in antioxidants displayed high index values for all the methods and vice versa. In the case of vegetables, spinach, kale and beet residues seem to be great sources of antioxidant compounds. In the case of fruit by-products, grape and strawberry matrices provided extracts with high phenolic concentrations.

4. Conclusions

This study is developed in the frame of a more general research project focused on the revalorization of industrial wastes resulting from fruit and vegetable juice processing. Polyphenols have been identified as the most relevant group of phytochemicals from these wastes as a source of antioxidant by-products. The optimization of the extraction conditions has been carried out based on experimental design approaches, multicriteria decision making and response surface methodology. The recovery of remarkable target compounds, such as 4-hydroxybenzoic acid, vanillic acid, coumaric acid and hesperidin, has been successfully evaluated, and specific conditions have been stablished. Anyway, more global criteria have been defined to assess the content of active antioxidant species. In this regard, the overall chromatographic area has been found to be an excellent descriptor of the global phenolic content.

The investigated water-ethanol mixtures, which are permitted by the food industry, showed a good efficiency for the extraction of phenolic compounds from spinach and orange wastes by UAE, MAE and PLE. The comparison of the extraction yields pointed out UAE was a convenient approach for spinach matrix while PLE provided higher performance for the orange matrix, in which ca. 5-fold increase was obtained compared with UAE. Anyway, considering simplicity and operational cost UAE was eventually recommended for industrial waste processing, especially for dealing with labile sample components.

The endorsed procedure was applied to other vegetable and fruit by-products and the resulting ethanolic extracts were analyzed by HPLC and spectrophotometric indexes. Various residues were identified as potential targets of antioxidant compounds, including spinach, kale, grape, strawberry and orange, among others.

CRediT authorship contribution statement

María Fernanda Montenegro-Landívar: Investigation, Formal analysis, Methodology, Writing - original draft. **Paulina Tapia-Quirós**: Investigation, Methodology. **Xanel Vecino**: Conceptualization, Supervision, Writing - review & editing. **Mònica Reig**: Conceptualization, Writing - review & editing. **César Valderrama**: Conceptualization, Supervision, Writing - review & editing. **Mercè Granados**: Conceptualization, Writing - review & editing. **José Luis Cortina**: Resources, Funding acquisition, Writing - review & editing. **Javier Saurina**: Conceptualization, Supervision, Formal analysis, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2021.105330.

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