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Supercritical Fluid CO_2 Extraction Technology to Produce an Innovative Healthy Product from Almond Wastes †

Franklin Chamorro [1], Javier Echave [1], Miguel. A. Prieto [1,2], Jesus Simal-Gandara [1] and Paz Otero [1,*]

[1] Nutrition and Bromatology Group, Analytical and Food Chemistry Department, Faculty of Food Science and Technology, University of Vigo, Ourense Campus, E-32004 Ourense, Spain; franklin.noel.chamorro@uvigo.es (F.C.); javier.echave@uvigo.es (J.E.); mprieto@uvigo.es (M.A.P.); jsimal@uvigo.es (J.S.-G.)

[2] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolonia, 5300-253 Bragança, Portugal

* Correspondence: paz.otero@uvigo.es

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Abstract: In this work, we studied the potential of supercritical fluid CO_2 technology to extract almond wastes and obtain a fibre product rich in minerals and phenolics without the use of an extraction co-solvent. The analysis of phenolics in the resulting extracted product was performed using liquid chromatography–tandem mass spectrometry (LC-MS/MS) and showed vanillin, catechin, and dihydroxybenzoic, vanillic, and syringic acids as main phenolic compounds (PC). In addition, the analysis of minerals carried out using inductively coupled plasma optical emission spectroscopy (ICP-OES) showed a wide range of macroelements like magnesium (Mg) and potassium (K) in quantities of up to 1.7 g/kg (Mg) and 6 g/kg (K), representing a value matrix that may be integrated into functional drinks targeting athletic people while promoting a circular economy and food up-cycling.

Keywords: supercritical fluid CO_2 extraction; almond by-products; functional foods; liquid chromatography mass spectrometry; phenolics; minerals; inductively coupled plasma optical emission spectrometry

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1. Introduction

The worldwide production of almonds, *Prunus dulcis* (Miller D.A.Webb), and their derived products such as almond oil has increased in recent years due to their important nutritional characteristics [1]. The Food and Agriculture Organization of the United Nations (FAO) reports that world almond production stood at 3,214,522 tons for the year 2020 [2], led by the United States and followed by Spain, reaching an estimated amount of 371,460 tons in 2021 according to the Spanish Ministry of Agriculture, Fisheries and Food [3]. Consequently, the increase in almond production is accompanied by a parallel increase in almond residues (shell, shell, skin, downstream). It is estimated that the almond oil industry generates up to 52% of waste weight, mainly almond cake from the shell, in relation to the material used [4]. Almond cake is a valuable source of bioactive compounds such as phenolic compounds, fatty acids, minerals, tocopherols, steroids and volatile compounds, which have demonstrated important biological activities both in vitro and in vivo [5,6], including prebiotic, antimicrobial, antioxidant, anti-inflammatory, anticancer, hepatoprotective, cardiometabolic, nootropic, anxiolytic, sedative-hypnotic, and nervous system-enhancing effects [6–8]. In fact, the use in traditional medicine of the almond and its different botanical parts is reported in the treatment of some brain disorders and respiratory and urinary tract problems [8]. The extraction of bioactive compounds from almond cake can be challenging due to their low solubility in conventional solvents and the presence of undesirable compounds [4]. In this sense, the use of supercritical fluid

CO_2 extraction (SFE-CO_2) is a promising technique to obtain high-quality and -purity compounds with unique characteristics and significant advantages. One of the main benefits of using SFE-CO_2 is its ability to obtain products with a minimal presence of residual solvents compared to conventional extraction methods [9]. In addition, SCFE-extracted compounds may have unique organoleptic and functional properties, making them suitable for use in the formulation of functional foods, dietary supplements, or cosmetic products [10]. Carbon dioxide (CO_2) is the most widely used supercritical fluid in the extraction of bioactive compounds due to its low cost, low toxicity, non-flammability, and ability to be easily removed from the final product. Furthermore, supercritical CO_2 has a high dissolving capacity, which makes it suitable for extracting a wide range of bioactive compounds from almond residues [10,11]. In the present work, the effect of SFE-CO_2 in the phenolic, mineral, and fatty acid profile of the resulting almond cake products is evaluated with the aim of obtaining ingredients rich in bioactive compounds, which can be used in various applications in the food, nutraceutical, and cosmetic industries (Figure 1).

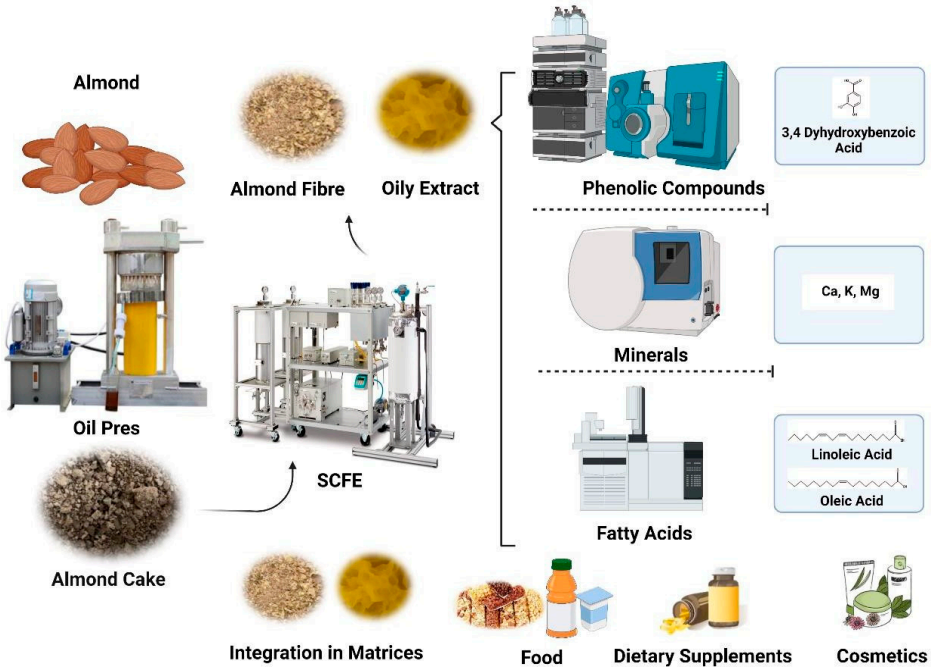

Figure 1. Schematic representation of this work's objectives.

2. Material and Method Section

2.1. By-Products Sample Preparation and Supercritical Fluid Extraction (SFE-CO_2)

Almond press cake was provided by Spanish nut oil processing industries in 2021. Once in our facilities, the press cake was submitted to a dehydration process in an evaporator with 800 L of capacity, coupled with vacuum equipment. Thus, a final dried product was obtained with humidity below 10%, which was submitted to an SFE-CO_2 extraction process to obtain an oily extract and a fibre ingredient, which were nutritionally evaluated because of their content of phenolics, minerals, and fatty acids. SFE-CO_2 experiments were performed in an HA220-40-48 System (HuaAn Supercritical Extraction Co., Ltd. Nantong, China) composed of a conditioner, pumps for CO_2, filters, heaters, and 2 extractor cells with 24 L of volume each. The temperature of the extraction system was fixed at 40 °C, the CO_2 flow was 210 L/h and the extraction time was 45 min. Two pressures were tested, 20 and 24 MPa. The most important parameters in SFE-CO_2 extraction are the pressure and temperature inside the cell. The equipment allows an extraction pressure of up to 40 MPa and an extraction temperature of up to 85 °C, respectively. In this work, the pressure and temperature were adjusted by a pressure regulator and a temperature controller to experimental conditions. Moreover,

the characteristics of the matrix to be extracted, such as its degree of humidity, were controlled by a humidity analyser (PCE Instruments, Meschede, Germany).

2.2. Analysis of Phenols by LC-MS/MS

Liquid chromatography–mass spectrometry (LC-MS/MS) was used for the analysis of phenolic compounds as reported by a previous study [12]. Briefly, an amount of 1 g of sample was extracted with 30 mL of MeOH:W (80:20) under continuous magnetic agitation (300 rpm) for 1 h at 40 °C. Then, the extracts were centrifuged, and the extraction was repeated twice. After that, the samples were dried, frozen, lyophilized, and dissolved in 2 mL of MeOH prior to LC-MS/MS analysis. High-performance liquid chromatography–mass spectrometry (HPLC-MS, 1260 Series, Agilent, Hong Kong, China) coupled with compact mass detector equipment (TRIPLE QUAD 3500; AB Sciex Instruments, Framingham, MA, USA) was used for the analysis in a C18 column (PHENOMENEX LUNA, 150 mm × 2 mm and 3 µm) at 40 °C. The flow rate was 0.3 mL min−1 and the injection volume was 10 µL. The mobile phase was composed of 0.1% formic acid in water (A) and 0.1% formic acid in acetonitrile (B), using a gradient. The initial conditions (98% A and 2% B) were held for 4 min before ramping to 20% B at 7 min and 90% B at 14 min. Then, the initial conditions were kept from minute 15 and held for 6 min. The instrument parameters were as follows: curtain gas (CUR), 25 psi; collision gas (CAD), 7 psi; ion spray voltage (IS), −4500 V; temperature (TEM), 400 °C; ion source gas 1 (GS1), 55 psi; ion source gas 2 (GS2), 55 psi; and interface heater, on. Phenolic compounds were identified and quantified employing standard solutions and constructing the calibration curves for each compound. The transitions used for quantification were vanillin (VA, *m/z* 166.7 > 122.9), cinnamic acid (CA, *m/z* 147.0 > 103.0), dihydroxibenzoic acid (DA, *m/z* 152.9 > 109.0), ferulic acid (FA, *m/z* 195.0 > 176.9), *p*-coumaric acid (*p*-CA, *m/z* 162.0 > 119), phthalic acid (PA, *m/z* 164.8 > 77.0), syringic acid (SA, *m/z* 199.0 > 140), *m*-toulic acid (M-TA, *m/z* 134.9 > 91.0), luteolin (LU, *m/z* 285.0 > 133), syringaldehyde (SY, *m/z* 183.0 > 77.0), quercetin (QE, *m/z* 301.0 > 150), vanillin (VN, *m/z* 150.7 > 108), rutin (RU, *m/z* 609 > 300), tyrosol (TYR, *m/z* 137.0 > 106.0), hydroxytyrosol (HTYR, *m/z* 153.0 > 123.0), ligstroside (LIG, *m/z* 522.8 > 360.0), oleacin (OLE, *m/z* 318.8 > 195), oleuroside (OLS, *m/z* 538.9 > 307), and oleuropein (OLP, *m/z* 538.9 > 377). FA, SA, and SY were detected in positive mode and the remaining phenolics in negative mode. The results are reported as mg/kg.

2.3. Ash Content and Analysis of Minerals by ICP-OES

The ash content was determined thermogravimetrically [13]. Briefly, 10 mg of water and volatile matter-free samples were ignited at 900 °C beneath a flow of an O_2-rich gas (30 mL/min) until reaching a constant weight. Minerals were analysed by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Perkin–Elmer Optima 4300 DV spectrometer (Shelton, CT, USA) equipped with an AS-90 autosampler, an axial system, a high dynamic range detector, and a cross-flow-type nebulizer for pneumatic nebulization. The ICP-OES assessment was performed following the procedure described by Millos et al. (2009) [14]. Briefly, 0.25 g of sample were digested with nitric acid and hydrogen peroxide using a Multiwave 3000 oven (Anton Paar, Graz, Austria) equipped with eight digestion vessels. For quantification, standard stock solutions with the addition of internal standards were used to construct the corresponding calibration curves. The results are reported as mg/kg.

2.4. Fatty Acid Analysis

FAs were analysed using a GC–FID system (Agilent Technologies, Loveland, CO 80537, USA). An amount of 1 g of sample was extracted and derivatized according to the method of Miller and Berger as mentioned in Otero et al. [15]. The column used was an Agilent HP-5MS UI capillary column (30 m × 0.250 mm × 0.25 um). The carried gas was helium at a flow rate of 1.8 mL/min. The oven temperature started at 50 °C, was increased to

210 °C at a 20 °C increase per min, and was held for 18 min. Then, the temperature was further increased to 230 °C at a 20 °C increase per min and kept at 230 °C for 13 min. The injection volume was 1 µL in splitless mode. The inlet temperature was set at 260 °C and the MS ion source and interface temperatures were 230 °C and 280 °C, respectively. Data were acquired in a full scan from 40 to 500 m/z and the results are expressed as a relative percentage (%).

3. Results and Discussion

3.1. Analysis of Phenolic Family Compounds

Table 1 shows the phenolic profile analysed in almond cake and the resulting products obtained after SCFE. The almond cake was predominantly composed of polyphenols like 3,4-dihydroxybenzoic acid, vanillic acid, syringic acid, protocatechuic acid, and, to a lesser extent, we also found salicylic, ferulic, *p*-coumaric, and phthalic acids. These results accord with previous studies in which hydroxybenzoic, vanillic, protocatechuic, and syringic acids were the predominant phenolic acids in almond wastes [4,16]. In this sense, the almond cake here analysed shows 54.4 mg/kg of 3,4-hydroxybenzoic acid, 7.06 mg/kg of vanillic acid, 2 mg/kg of syringic acid, and 0.64 mg/kg of protocatechuic acid. In addition, the almond cake also showed flavonoids like rutin, quercetin, vanillin, and luteolin, among which vanillin was the most predominant, with quantities of 13.5 mg/kg and aldehydes like syringaldehyde in quantities of 5.57 mg/kg. Almonds are a rich source of phenolics [17] and, consequently, their wastes can be used for the development of new nutraceuticals while promoting a circular economy and food upcycling. Almond skins present between 70 and 100% of the total phenols present in the whole almond fruit [4]. The characterization of polyphenolics carried out in seven varieties of almond hulls (*Prunus dulcis* L.) showed that chlorogenic acid, catechin, and protocatechuic acid were the most important polyphenols in the almond hull and up to 220 mg/kg of PCA is reported [18]. Comparing data before and after SCFE, we observed that phenolic acids, flavonoids, and aldehydes remained in the solid part called the fibre ingredient, while the quantity of these bioactive compounds analysed in the oily extracts was scarce or very low. Comparing pressures, in general terms, a high amount of phenolic family compounds is obtained when SCFE is carried out at the lower pressure tested of 20 MPa instead of 24 Mpa. So far, information about the extraction of compounds from almond wastes is scarce and only focused on oil extraction from the fruit. There is no information about the use of almond press cake for high-end markets.

Table 1. Main phenolics found in almond wastes before and after the SCFE process (mg/kg).

			SCFE of Almond Cake			
COMPOUND	**ABREV.**	**Almond Cake**	**Fibre Ingredient**	**Fibre Ingredient**	**Oily Extract**	**Oily Extract**
			20 MPa	**24 MPa**	**20 MPa**	**24 MPa**
			Phenolic acids			
3,4-dihydroxybenzoic acid	DA	54.40	57.40	35.00	1.65	4.18
Vanillic acid	VA	7.06	7.41	5.06	6.88	6.15
Syringic acid	SA	1.99	2.01	1.60	0.35	0.10
Protocatechuic acid	PTA	0.64	0.62	0.48	nd	nd
Salicylic acid	SAA	0.22	0.24	0.17	nd	nd
Ferulic acid	FA	0.25	0.25	0.21	0.34	0.44
p-coumaric acid	P-CA	0.13	0.13	0.09	0.30	0.63
Phthalic acid	PA	0.25	0.24	0.16	0.04	0.04
			Flavonoids			
Rutin	RU	0.54	0.554	0.422	nd	nd
Quercetin	QE	0.12	0.12	0.13	0.16	0.05
Vanillin	VN	13.50	16.49	9.23	0.55	0.39
Luteolin	LU	0.01	0.01	0.02	0.04	0.01
			Aldehydes			
Syringaldehyde	SY	5.57	6.34	4.04	1.54	0.81

SCFE: Supercritical fluid extraction.

3.2. Analysis of Ash Content and Minerals

First, the content of ash in almond cake and in the obtained fibre ingredients after SCFE at both pressures 24 MPa and 27 MPa was calculated. The results show that the content of ash was homogenous for the three products tested and in the range of 2.63–2.74% (Table 2). Then, the identification and quantification of macroelements and microelements in all almond wastes were carried out by ICP-OES and the results are included in Table 2. Almond cake contains high amounts of essential minerals. The content of macroelements, in g/kg, decreased as follows: K (6.00) > Ca (2.84) > P (2.80) > Mg (1.63) > Na (0.34). And the amounts of microelements in mg/kg were in the following order: Fe (290.2) > Zn (22.7) > Mn (18.8) > Cu (15.5). These results are in line with others found in the literature which show that almonds contain around 1.2–2.7 g/kg of Mg, 1.9–5.2 g/kg of P, 5.2–7.6 g/kg of K, and up to 0.053 g/kg of Fe [19]. Comparing data before and after SCFE, we observed that minerals found in the almond cake remained in the fibre ingredient after the SCFE process. The content of those minerals in the oily extracts is much lower. And comparing pressures, higher amounts of minerals were obtained when SCFE was carried out at a lower pressure of 24 MPa.

Table 2. Ash content (%) and elements in the almond cake before and after SCFE processes.

		SCFE of Almond Cake			
MINERAL	**Almond Cake**	**Fibre Ingredient**	**Fibre Ingredient**	**Extract**	**Extract**
		20 MPa	**24 MPa**	**20 MPa**	**24 MPa**
Ash (%)	2.63	2.74	2.72	-	-
		***Macroelements* (g/kg)**			
Ca	2.84	3.02	1.64	0.030	0.012
K	6.00	6.08	5.91	0.001	0.001
Mg	1.63	1.74	1.46	0.001	0.003
P	2.80	2.95	1.39	0.001	0.007
Na	0.34	0.32	0.46	1.11	0
		***Microelements* (mg/kg)**			
Mn	18.8	19.2	0.9	0.05	0.14
Fe	290.2	299.7	299	1.83	8.96
Cu	15.5	11.9	0.2	0.29	0.29
Zn	22.7	23.3		0.82	0.72

3.3. Analysis of Fatty Acids

Next, the analysis of fatty acids was carried out by GC-FID. Each fatty acid was quantified with their respective standard and then expressed as the summary of total saturated fatty acids (SFAs), total monounsaturated fatty acids (MUFAs), and total polyunsaturated fatty acids (PUFAs) for each almond by-product in mg per kg (Table 3). The results show that the fibre ingredient obtained from almond cake contains up to four times less FA content. For example, almond cake showed 81.29 mg/kg of FA, while 19.61 mg/kg were found in the fibre ingredient after SCFE at 24 MPa, and 28.92 mg/kg was found in that obtained at 20 MPa. It is worth mentioning that the content of SFA was also reduced in both fibres obtained after SCFE up to four times (10.22 mg/kg FA, 24 MPa).

Table 3. Fatty acid quantities in the almond cake before and after the SCFE process (mg/kg).

		SCFE of Almond Cake			
FA	**Almond Cake**	**Fibre Ingredient**	**Fibre Ingredient**	**Oily Extract**	**Oily Extract**
		20 MPa	**24 MPa**	**20 MPa**	**24 MPa**
Total SFAs	42.53	15.17	10.22	676.91	633.45
Total MUFAs	27.93	10.09	6.91	453.65	437.22
Total PUFAs	10.83	3.66	2.48	153.00	119.77
Total FA	81.29	28.92	19.61	1283.56	1190.44

SCFE: Supercritical fluid extraction. SFA: saturated fatty acids. (MUFAs: monounsaturated fatty acids. PUFA: poly-unsaturated fatty acids.

4. Conclusions

In this work, the use of almond wastes is proposed to obtain ingredients from an alternative source through technologies that will enable upcycling companies to diversify their product ranges and make higher profits. After drying the almond cake, a solid fraction was extracted by SFE-CO_2, employing two pressures. As a result of this process, oily extracts and a defatted fibre ingredient were obtained. Due to the prevalence of lifestyle diseases and the growing geriatric population, consumers across the globe are becoming health-conscious. Also, the increasing number of health and fitness clubs drives the dominance of sports and energy drinks in functional foods and beverages. In this sense, the SCFE technology allowed us to obtain a high-quality product from almond press cake, i.e., a defatted and natural antioxidant fibre ingredient with up to four times less fat than the almond cake, with a high content of minerals and phenolics, which could be used in novel fortification food applications. The SCFE technology has several advantages over traditional extraction technologies in that they can be more efficient and more cost-effective. In addition, there is also increasing concern regarding the use of solvents that, despite being food-grade, can leave chemical residues.

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