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

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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 fiber product rich in minerals and phenolics without the use of extraction co-solvent. The analysis of phenolics in the resulting extracted product was performed by 13 liquid chromatography tandem mass spectrometry (LC-MS/MS) and showed vanillin, catechin and the acids dihydroxybenzoic, vanillic and syringic as main phenolic compounds (PC). In addition, the analysis of minerals carried out by Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES) showed a wide range of macroelements like Magnesium (Mg) and Potassium (K) in quantities up to 1.7g/kg (Mg) and 6 g/kg (K), so that represent a value matrix to be integrated into functional drinks targeting sporty people while promoting the circular economy and the 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. 1. Introduction

The world production of almond *Prunus dulcis* (Miller D.A.Webb) and their derived products such as almond oil, has increased in recent years, due to its 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], leading by the United States and followed by Spain, reaching an estimated amount of 371,460 tons in 2021, according to Spanish Ministry of Agriculture, Fisheries and Food [3]. Consequently, the increase of almond production is accompanied by a parallel increase of almond residues (shell, shell, skin, downstream). It is estimated that the almond oil industry generates up to 52% of waste weigh, 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, respiratory and urinary tract problems [8]. 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 its ability to be easily removed from the final product. Furthermore, supercritical CO2 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 industry (Figure 1).

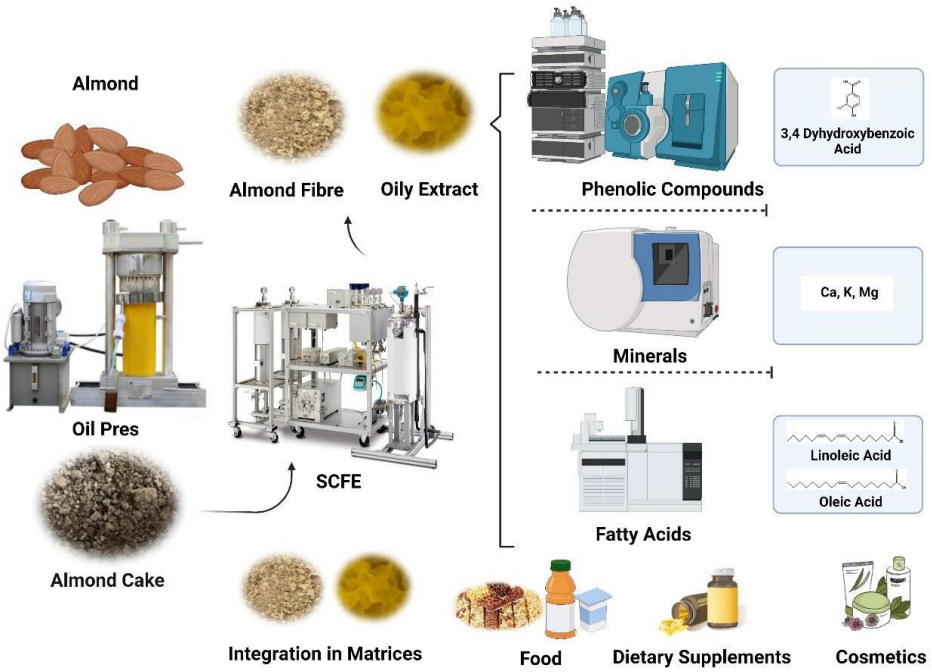

Figure 1. Schematic representation of work objectives

2. Material and Method section

2.1. By-products sample preparation and Supercritical Fluid Extraction (SFE-CO_2)

Almond press cake were 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 concentration of 800 L of capacity, coupled to a vacuum equipment. Thus, it was obtained a final dried product with a humidity below to 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 a HA220-40-48 System (HuaAn Supercritical Extraction Co., Ltd. Nantong, China), composed of conditioner, pumps for CO_2, filters, heaters and 2 extractor cells of 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 a SFE-CO2 extraction are the pressure and temperature inside the cell. The equipment allows an extraction pressure up to 40 MPa and an extraction temperature 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, characteristics of matrix to be extracted such as its degree of humidity was controlled by a humidity analyzer (PCE Instruments).

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 the previous study [12]. Briefly, the amount of 1 g of sample were extracted with 30 mL of MeOH: W (80:20) in a continuously magnetic agitation (300 rpm) for 1 hour 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 LC-MS/MS analysis. High Performance Liquid Chromatography-Mass Spectrometry (HPLC-MS, 1260 Series, Agilent) coupled to a compact Mass Detector equipment (TRIPLE QUAD 3500; AB SCIEX INSTRUMENTS) 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. Mobile phase was composed of 0.1% formic acid in water (A), and 0.1% formic acid in acetonitrile (B), using a gradient. 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, initial conditions were kept from the minute 15 and held for 6 min. 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; interface heater, on. Phenolic compounds were identified and quantified employing standard solutions and constructing the calibration curves for each compound. The transition 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), phallic 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, remaining phenolics in negative mode. Results were 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 constant weight. Minerals were analyzed 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, 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, 0.25g 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 standard were used to construct the corresponding calibration curves. Results were reported as mg/kg.

2.4. Fatty acid analysis

FAs were analyzed using a GC–FID system (Agilent Technologies, Loveland, CO 80537, USA). The amount of 1g of sample was extracted and derivatized according 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 caried gas was Helium at flow 1.8 mL/min. Oven temperature started at 50◦C, increased to 210◦C at 20◦C increase per min and hold for 18 min. Then, temperature was further increased to 230◦C at 20◦C increase per min and kept at 230◦C for 13 min. The injection volume was 1μL in splitless mode. Inlet temperatures was set at 260◦C and MS ion source and interface temperatures were230◦C and 280◦C respectively. Data were acquired in a full scan from 40 to 500 m/z and 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. Almond cake were predominantly composed of polyphenols like 3,4-dihydroxybenzoic acid, vanillic acid, syringic acid, protocatechuic acid and in lesser extent, we also found salicylic, ferulic, *p*-coumaric and phthalic acids. These results concord with previous studies in which hydroxybenzoic, vanillic, protocatechuic and syringic acids are the predominant phenolic acids in almond wastes [4,16]. In this sense, almond cake here analysed show 54.4 mg/kg of 3,4-hydroxybenzoic acid, 7.06 mg/kg of vanillic acid and 2 mg/kg of syringic acid and 0.64 mg/kg of protocatechuic acid. In addition, almond cake also showed flavonoids like rutin, quercetin, vanillin and luteolin, from 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 the circular economy and the 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 7 varieties of almond hulls (*Prunus dulcis* L.) showed that chlorogenic acid, catechin, and protocatechuic acid were the most important polyphenols in 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 fibre ingredient. While the quantity of these bioactive compounds analysed in the oily extracts is scarce or very low. And comparing pressures, in general terms, 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 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 SCFE process (mg/kg)

COMPOUND	ABREV.	Almond Cake	*SCFE of Almond cake*			
			Fibre Ingredient 20 MPa	Fibre Ingredient 24 MPa	Oily Extract 20 MPa	Oily Extract 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
Salycilic 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
Phalic 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. Results showed the content of Ash were homogenous for three products tested and in the range of 2.63-2.74 % (table 2). Then, the identification and quantification of macroelements and microelemtnos in all almond wastes was carried out by ICP-OES and results are included in table 2. Almond cake contains high amounts of essential minerals. The content of macroelements in g/kg, decrease as follows: K (6.00) > Ca (2.84) > P (2.80) > Mg (1.63) > Na (0.34). And the amount of microelements in mg/kg kept 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 bibliography which show that almond 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 is carried out at the lower pressure of 24 MPa.

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

		SCFE of Almond cake			
MINERAL	Almond Cake	Fibre Ingredient 20 MPa	Fibre Ingredient 24 MPa	Extract 20 MPa	Extract 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

*SCFE: Supercritical Fluid Extraction

3.2. 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). Results showed that fibre ingredient obtained from almond cake contain up to 4 times less of 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 24MPa and 28.92 mg/kg in that obtained at 20MPa. It is worthy to mention that the content of SFA was also reduced in both fibres obtained after SCFE up to 4 times (10.22 mg/kg FA, 24 MPa).

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

FA	Almond Cake	*SCFE of Almond cake*			
		Fibre Ingredient 20 MPa	Fibre Ingredient 24 MPa	Oily Extract 20 MPa	Oily Extract 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: polyunsaturated 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, solid fraction was extracted by SFE-CO2 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 drive dominance of sports and energy drinks in functional foods and beverages. In this sense, the SCFE technology allowed to obtain a high-quality product from almond press cake, *i.e.* a defatted and natural antioxidant fibre ingredient with up to 4 times less fat than the almond cake, with 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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