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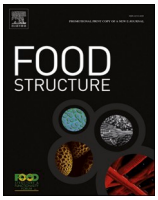

Using different physical treatments to modify the structure and improve the technofunctional properties of clementine by-products

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ABSTRACT

Clementine by-products are an important source of dietary fiber, which has different technofunctional properties depending on its chemical composition and structure. These properties can be modified through different treatments. In this work, the impact of treatments such as hot air drying (HAD), homogenization (HOM), freeze drying (FD), and extrusion (EXT) was evaluated on the structure and technofunctional properties of clementine by-products' powders, to promote their use as ingredients in food development as a way of valorization. The structure of by-products was studied using microscopy (Light Microscopy and Field Emission Scanning Electron Microscopy) and vibrational spectroscopic (FTIR and FT-Raman) techniques. The technofunctional properties, water and oil holding capacities, water solubility, swelling capacity, and emulsifying capacity, as well as particle size were evaluated. HOM and EXT showed a more stratified and porous structure than HAD and FD. FTIR and FT-Raman showed that the by-products mainly comprised pectin and cellulose. Regarding technofunctional properties, HOM powders had high water retention and swelling capacities, and good emulsifying capacity even when using high amounts of oil in an emulsion (75 %). FD powders showed the highest oil retention capacity and EXT powders the highest water solubility.

1. Introduction

Clementines (*Citrus clementina* Hort. ex Tan.) are one of the most consumed fruits worldwide, with a global production of approximately 42 million tons in 2021 (FAO, 2021). It is an immensely appreciated citrus variety due to its sweet flavor, absence of seeds, easy to peel skin, and small size (Cebadera et al., 2020). Despite these features that make clementine an ideal fruit for fresh consumption, approximately 30 % of production is used for juice extraction (Barboni et al., 2010; Marín et al., 2007). Because juice extraction by-products of clementines are approximately 50 % of the weight of fresh fruits, they can become a pollution problem if they are under-used. Clementine by-products, mainly peel and pulp, are a potential source of dietary fiber that can be valuable in the food industry (Cebadera et al., 2020; Liu et al., 2022). They have typically been used for animal feed and fuel production (de Moraes Barros et al., 2012) but have also been directly discarded into the environment (Garcia-Castello et al., 2015). Dietary fiber may have different technofunctional properties depending on its chemical composition and structure (Garau et al., 2007). Some of these properties, such as water and oil holding capacities (WHC and OHC, respectively), solubility in water (WS), and swelling and emulsifying capacities (SC and EC, respectively), can be related to structural features such as the surface area or the porosity of the particles. For example, high WS was related to higher porosity and surface area in citrus "Hallabong" powders (Lee et al., 2012), and high SC was related to higher surface area in *Polygonatum odoratum* root powders (Lan et al., 2012). These technofunctional properties impart food quality parameters, such as viscosity, oil loss during cooking, or satiating effect during digestion (de Moraes Crizel et al., 2013; Martínez-Las Heras et al., 2017; Perez-Pirotto et al., 2022). The technofunctional properties may also have physiological effects on the human body. The high hydration properties of soluble dietary fibers decrease the diffusion of glucose in the human gut and improve postprandial blood glucose metabolism, reducing the risk of type 2 diabetes (Miehle et al., 2022). High oil or fat absorption rates and high emulsifying capacities of dietary fibers increase the adsorption of oil or bile acids, increase excretion of feces, limit their absorption in

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the small intestine, and reduce plasma cholesterol (Lan et al., 2012; Wang et al., 2015). The particle size of dietary fibers is also relevant in colon function because it affects transit time, fermentation, and fecal bulking (Guillon & Champ, 2000; Tosh & Yada, 2010). Improving the technofunctional properties of the dietary fiber in the by-products for its use in the design and formulation of foods increases the possibilities for valorizing these by-products, expanding their beneficial properties.

Hot air drying (HAD) has traditionally been used to obtain stable, dried powders of fruit and vegetable by-products (Bas-Bellver et al., 2020; Mehadi Galib et al., 2022). However, alternative techniques have been studied to modify the technofunctional properties of dietary fibers and improve their nutraceutical functionalities. Extrusion (EXT) is one of the most promising processes for improving these features by applying high pressure and temperature to samples. Garcia-Amezquita et al. (2019) and Larrea et al. (2005) showed that EXT improved orange peel and pulp hydration properties, respectively, obtaining higher values of WHC and SC. Freeze drying (FD) treatment has also been shown to improve the functionality of dietary fibers compared to HAD treatments. For example, the FD method for the preparation of citrus "Hallabong" powders improved the WS values compared to the HAD (Lee et al., 2012). FD mango fiber concentrates showed higher SC, WHC, and OHC than HAD ones (Mehadi Galib et al., 2022). Que et al. (2008) obtained pumpkin flours with higher OHC values after FD treatment. Homogenization (HOM) treatment under normal pressure has also been used to obtain pectin-rich dietary fiber from the citrus peel with improved functional properties, such as WHC and SC, and smaller particle sizes (Huang et al., 2021). Although research has been conducted applying treatments to citrus peel or pulp separately, no research exists on the effect of treatments on clementine by-products comprising peel and pulp. Therefore, this work aimed to compare the impact of treatments, such as hot air drying, homogenization, freeze drying, and extrusion, on clementine by-product powders' structure and technofunctional properties to promote their use in food development while opening new ways for the revalorization of these by-products.

2. Materials & methods

2.1. Materials

The clementine pomace was donated by the Zumos Valencianos del Mediterráneo S.L. company. The pomace was mainly composed by peel and pulp. Once received in laboratory facilities, the clementine pomace was minced at 1400 rpm in an emulsifying mincer CUP 8Tr (Eurofred, Barcelona, Spain) for 10 min before being processed into clementine pomace powder.

2.2. Processing of clementine pomace powder

Four treatments were performed to obtain clementine pomace powder.

2.2.1. Hot air drying (HAD)

The clementine pomace was dried at 65 °C in a hot air dryer FED 260 model (Binder, Tuttlingen, Germany) until a constant weight.

2.2.2. Homogenization (HOM)

Homogenization treatment was performed according to Huang et al. (2021), with some modifications. The clementine pomace was homogenized at 5800 rpm for 5 min in a Thermomix TM31 (Vorwerk, Wuppertal, Germany). The sample was transferred to beakers, and 96° ethanol was added at 1:2 (v/v). The pH of the mixture was adjusted to 7 with NaOH 1 M. The sample was stirred magnetically for 30 min and then centrifuged (SORVALL SUPER T21, Ramsey, MN, USA) at 8000×*g* for 10 min. The supernatant was discarded and the remaining pellet was HAD at 65 ºC until a constant weight.

2.2.3. Freeze drying (FD)

Clementine pomace was frozen immediately at −20 ºC after mincing and being freeze-dried in a Telstar Lioalfa-6 Lyophyliser (Telstar, Terrassa, Spain) at 10^{-2} Pa and −45 ºC for 72 h.

2.2.4. Extrusion (EXT)

The extrusion treatment was conducted according to Huang & Ma (2016) and Larrea et al. (2005). The moisture of the clementine pomace was adjusted to 15 % and then extruded using a Kompakextruder 19/25 DN (Brabender GmbH & Co. KG, Duisburg, Germany), with a 19-mm diameter barrel and a barrel length/diameter ratio of 25/1. A 3:1 screw was used at a speed of 130 rpm; the die diameter was 4 mm. The temperature of the extruder die zone was 130 ºC. The extruded clementine pomace was dried by HAD at 60 ºC until a constant weight.

After the four treatments, the samples were ground for 1 min at 10,200 rpm in a Thermomix TM31 (Vorwerk), packed under vacuum (EDESA, Granollers, Spain), and stored in the dark in a desiccator until use. The moisture content of the powders was HAD 2.7 ± 0.9 g/ 100 g; HOM 2.0 ± 0.6 g/ 100 g; FD 2.5 ± 0.9 g/ 100 g; EXT 3.6 ± 0.5 g/ 100 g.

2.3. Microstructure

Samples were observed by Light Microscopy (LM) and Field Emission Scanning Electron Microscopy (FESEM).

For LM, the sample was placed on a glass slide and observed using a Nikon Eclipse 80i® light microscope (Nikon Co. Ltd., Tokyo, Japan) with a FlexaCam C3 camera (Leica Microsystems, Weztlar, Germany). Images were captured and stored at 4000 × 3000 pixels using the microscope software Leica Application Suite X (Leica Microsystems).

For FESEM, the sample was adhered to the stub using double-sided carbon tape and sputtered with a thin platinum layer. The samples were photographed (Ultra 55 FESEM, Zeiss, Oberkochen, Germany) with an acceleration voltage of 2 kV.

2.4. Vibrational spectroscopic measurements

Fourier-transformed infrared (FTIR) spectra of the clementine pomace were measured on a Nicolet 6700 FTIR spectrometer (ThermoFisher Scientific, Waltham, MA, USA) in KBr pellets at 400–4000 cm^{-1}, with a resolution of 2 cm^{-1}, and 64 scans. Vibrational spectra were recorded and processed by Omnic 8.0 software (ThermoFisher Scientific).

Fourier-transformed (FT) Raman spectra of clementine pomace were measured on a Nicolet iS50 with the FT-Raman Module (ThermoFisher Scientific), Nd:YAG laser (λ_{ex} = 1064 nm, power 500 mW), CaF_2 beam splitter and InGaAs detector. Vibrational spectra were recorded and processed with Omnic 9.2 software (ThermoFisher Scientific).

FTIR and FT-Raman spectra were exported in ASCII format to Origin Pro 18 software (OriginLab, Northampton, MA, USA) for further processing (smoothing, baseline correction, and intensity scale normalization). The positions of overlapped bands (shoulders) were determined using the second derivative logarithm.

2.5. Particle size analysis

The particle size of the samples was determined in wet conditions by laser light scattering using a Mastersizer 2000 coupled to a Hydro 2000 unit (Malvern Instruments, Malvern, U.K.). The refractive index was set at 1.52, the refractive index of the dispersant (water) was 1.33 and the particle absorption index was 0.1. The results are the mean of three replicates and are given as particle volume-weighted mean diameter (D [4,3]), particle surface-weighted mean diameter (D [3,2]), size distributions, span, and specific surface area.

2.6. Technofunctional properties

2.6.1. Water holding capacity (WHC)

Water holding capacity was measured according to Wang et al. (2015), with minor modifications. Briefly, 0.5 g of sample were mixed in a falcon tube with 20 mL of distilled water at room temperature (20 ºC) for 24 h. The samples were centrifuged at 10,678 ×*g* for 10 min, and the pellet was weighed. The WHC was calculated using Eq. 1:

$$WHC(g/g) = W_1/W \quad (1)$$

where W_1 is the weight of the pellet and W is the weight of the sample.

2.6.2. Oil holding capacity (OHC)

The oil holding capacity was measured according to Reißner et al. (2019). Briefly, 0.5 g of sample were mixed with 10 mL of sunflower oil in falcon tubes at room temperature (20 ºC) for 18 h. The samples were centrifuged at 10,000 ×*g* for 30 min and the pellet was weighed. The OHC was calculated using Eq. 2:

$$OHC(g/g) = W_1/W \quad (2)$$

where W_1 is the weight of the pellet and W is the weight of the sample.

2.6.3. Water solubility (WS)

The water solubility was determined following the method described by Wang et al. (2015), with some modifications. Briefly, 0.5 g of sample were mixed with 25 mL of distilled water and vortexed for 30 s. Subsequently, the samples were stirred in a thermostatic water bath at 90 ºC for 30 min. After being cooled down, samples were centrifuged at 10,678 ×*g* for 10 min; the supernatant was collected, freeze-dried, and weighed. The WS was calculated using Eq. 3:

$$WS(\%) = W_1/W \times 100 \quad (3)$$

where W_1 is the weight of the freeze-dried supernatant and W is the weight of the sample.

2.6.4. Swelling capacity (SC)

The swelling capacity was evaluated based on the method described by Reißner et al. (2019). Concisely, 1.8 g of sample were placed in a graduated tube and mixed with 10 mL of distilled water. The samples were left to hydrate for 18 h at room temperature (20 ºC), and the volume in mL of swollen sample was recorded. SC was calculated using Eq. 4:

$$SC(mL/g) = V/W \quad (4)$$

where V is the volume of the swollen sample and W is the weight of the sample.

2.6.5. Emulsifying capacity (EC)

The EC was determined according to Dick et al. (2019). The solutions of the treated clementine pomace powders at 1 %, 2.5 %, and 5 % were prepared in distilled water and stirred for 2 h. Subsequently, solutions were left overnight at 4 ºC for total hydration. Oil-in-water emulsions were prepared in 10:90, 25:75, 50:50, and 75:25 v/v ratios (oil:solution). The solution was homogenized at 10,000 rpm for 2 min with a high-speed homogenizer Ultraturrax T-18 (IKA, Staufen, Germany) while slowly adding sunflower oil. Emulsions were centrifuged at 1300×*g* for 5 min, and the emulsion layer volume and the total volume were measured. The EC was calculated using Eq. 5:

$$EC(\%) = EV_1/V_T \times 100 \quad (5)$$

where EV_1 is the volume of the emulsion layer and V_T is the total volume.

2.7. Statistical analysis

The analytical values of the experiments are shown as mean ± standard deviation. Statistical analysis of the results was performed using the Statgraphics Centurion XVIII software (Statgraphics Technologies, Inc., The Plains, VA, USA). A one-way analysis of variance (ANOVA) was performed for particle size analysis, WHC, OHC, WS, and SC, where the factor analyzed was the treatment applied to the clementine pomace: HAD, HOM, FD, and EXT. To determine the significant differences between the samples, the honest significant difference (HSD) test was used at a significance level of 95 %. A multi-factorial ANOVA was performed for EC, where the factors analyzed were the treatment, % of clementine pomace, and the oil:solution ratio.

3. Results and discussion

3.1. Microstructure

Fig. 1 shows the microstructure, observed by LM and FESEM, of the clementine pomace obtained using the four treatments. The HAD treatment produced particles with an irregular polygonal structure of different sizes and shapes (Fig. 1A). The surface of these particles was homogeneous and smooth (SM in Fig. 1), probably due to the high degree of fusion and close contact of the components that constitute the powder structure (Fig. 1E). HOM treatment led to smaller and more elongated particles (Fig. 1B) than HAD treatment. These particles showed a stratified fibrous structure (ST in Fig. 1) with porous orography (Fig. 1F). The high degree of stratification could be related to strong mechanical shearing, hydraulic friction, and tearing of the particles, as observed by Huang et al. (2021) when processing citrus peel by homogenization. FD treatment also produced smaller particles (Fig. 1C) than HAD treatment. Particles had a smooth and homogeneous surface; nevertheless, stratified areas were also observed (Fig. 1G), although to a lesser extent than the HOM samples. The EXT treatment led to smaller but more heterogeneous sized particles (Fig. 1D) than the other treatments. The surface of these particles showed a high degree of stratification and porosity but also a smooth orography with a fusion of components in some areas (Fig. 1H). The high number of holes in the extruded particles could be due to the combination of shear stress, temperature, and hydrostatic pressure that occurred during extrusion, as Chen et al. (2014) showed when processing soluble dietary fiber from soybean residues by extrusion.

3.2. Structural characterization: FTIR and FT-Raman

The FTIR and FT-Raman spectra of clementine pomace after different treatments are shown in Figs. 2 and 3. The assignment of vibrational bands is supported by the appropriate literature (Chien et al., 2022; de Oliveira et al., 2009; Duan et al., 2022; Saletnik et al., 2022; Synytsya et al., 2003; Zannini et al., 2021). The spectral differences between the samples of clementine pomace are discussed in terms of physical and chemical changes caused by the treatments, i.e., heating for HAD, HOM, and EXT and the loss of ethanol-soluble low molecular compounds for HOM.

The FTIR spectra of all treated pomace samples showed a high similarity, but several differences in band positions and intensities were still found. The broad band centered at 3419–3408 cm^{-1}, and the narrow band at 2926 cm^{-1} arose from O–H and C–H stretching vibrations, respectively. The band at 1743–1740 cm^{-1} is related to the C═O stretching vibration of methyl ester groups in pectins. Two narrow bands at 1645–1643 and 1520–1522 cm^{-1} arose from C═O and C═C stretching vibrations of phenylpropanoid compounds, including phenolic acids, whereas two broad shoulders near 1608 and 1420 cm^{-1} originated from antisymmetric and symmetric stretching vibrations of carboxylate anions COO^- that could be from pectins. Clementine peels are abundant in polyphenols, including phenolic acids, and contain

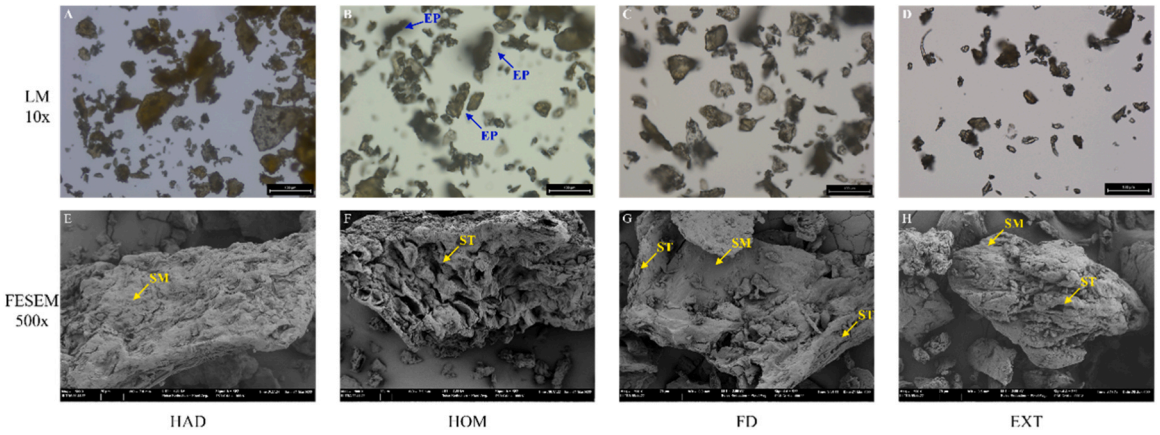

Fig. 1. Light Microscopy (LM) (A–D: ×10 magnification) and Field Emission Scanning Electron Microscopy (FESEM) (E–H: ×500 magnification) images of clementine pomace obtained by different treatments: hot air drying (HAD), homogenization (HOM), freeze drying (FD), and extrusion (EXT). Yellow arrows mark smooth (SM) and stratified (ST) areas. Blue arrows mark elongated particles (EP).

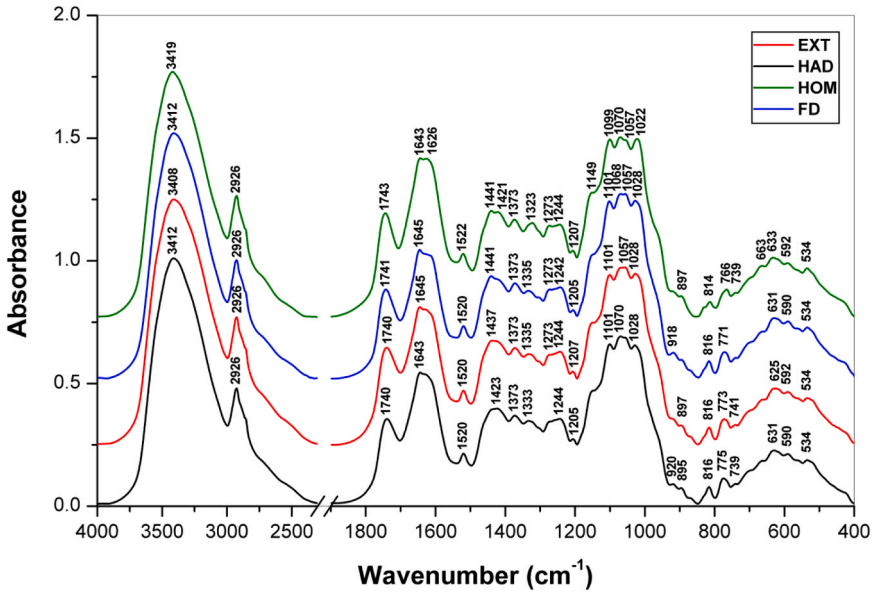

Fig. 2. FTIR spectra of clementine pomace obtained by different treatments: hot air drying (HAD), homogenization (HOM), freeze drying (FD), and extrusion (EXT).

approximately 0.26 mg g^{-1} of *p*-coumaric acid and 0.44 mg g^{-1} of *trans*-ferulic acid (Gómez-Mejía et al., 2023). The shoulder near 1468 cm^{-1} and the bands at 1441 and 1373 cm^{-1} were assigned to CH_2 scissoring and CH_3 antisymmetric and symmetric bending vibrations, respectively. The band at 1335–1333 cm^{-1} (C–H bending vibration) and shoulder near 833 cm^{-1} (out-of-plane C–OH vibration) are typical for pectins; these features were more pronounced for the homogenized sample (HOM), possibly because of the removal of small molecules and thus increasing contribution of polysaccharides. The bands near 1272 and 1244 cm^{-1} arose from C–O–C and C–O vibrations in methyl esters and carboxylic groups. According to the second derivatives of the FTIR spectra, the bands/shoulders of methyl ester groups near 2960, 1740, 1441, 1370, 1278, and 1236 cm^{-1} decreased after heating for samples HAD and EXT so that partial de-esterification can occur. In contrast, despite heating, these bands even increased for HOM, which could be due to changes in composition after ethanol treatment. Several intense overlapped bands in the range of 1150–950 cm^{-1} arose predominantly from C–O–C, C–O, and C–C stretching vibrations that prove the presence of cell wall polysaccharides. The shoulder near 1150 cm^{-1} arose from C–O–C stretching vibrations in glycosidic bonds of pectins, whereas the bands near 1100, 1070, 1057, and 1028–1022 cm^{-1} originated from coupled C–O and C–C stretching and C–OH bending vibrations in pyranoid rings. The bands/shoulders at 1150, 110, 1070, 983, and 954 cm^{-1} are typical of pectins (HG and RG-I), whereas the bands/-shoulders at 1057 and 897 cm^{-1} indicated the presence of cellulose. The skeletal vibration band at 775–766 cm^{-1} was sensitive to the treatment of raw material and successively shifted to higher wavenumbers in the order: HOM - FD - EXT - HAD.

The assignment of Raman bands observed in the range 1800–200 cm^{-1} was supported by the appropriate literature (de Oliveira et al., 2009; Hu et al., 2022; Saletnik et al., 2022; Synytsya et al., 2003). The broad band at 1741–1737 cm^{-1} assigned to C═O stretching vibrations from methyl esters decreased or disappeared after heating for EXT and HAD samples. In contrast to FTIR, FT-Raman is sensitive to vibrations of unsaturated and aromatic compounds, and the doublet at 1629 and 1604 cm^{-1}, pronounced for the freeze-dried sample, is typical for phenylpropanoids. The bands at 1648, 1336, and 1265 cm^{-1} were assigned to C═O, C═C, and C–O stretching and =CH bending vibrations in phenylpropanoids and unsaturated fatty acids (Saletnik et al., 2022). The bands at 1529, 1155, and 1004 cm^{-1} were assigned to C═C stretching, C–C stretching, and C–CH_3 rocking vibrations of carotenoids, respectively (de Oliveira et al., 2009). All of these bands of unsaturated

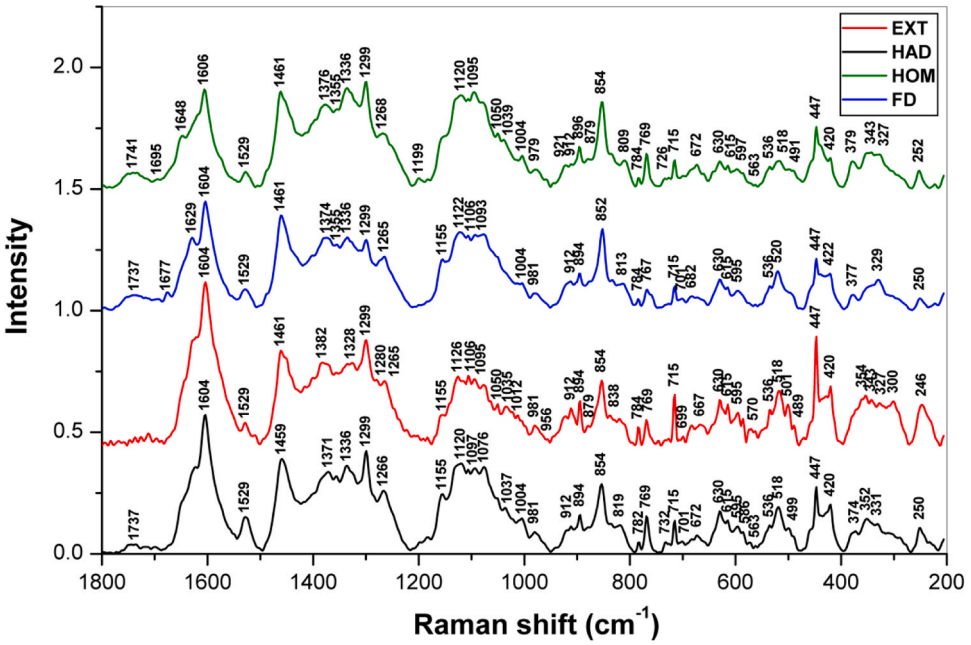

Fig. 3. FT-Raman spectra of clementine pomace obtained by different treatments: hot air drying (HAD), homogenization (HOM), freeze drying (FD), and extrusion (EXT).

compounds were sensitive to the treatment of clementine pomace. The carotenoid bands were less pronounced for the extruded sample due to partial thermal destruction of these compounds, and the increase of the band at 1604 cm^{-1} for EXT and HAD can be explained by chemical modification of polyphenols by heating, possibly oxidative polymerization and covalent attachment to polysaccharides. The bands at 1336 and 1299 cm^{-1} were assigned mainly to in-plane bending vibrations in the pyranoid ring of carbohydrates (Saletnik et al., 2022). Two bands at 1126–1120 and 1097–1093 cm^{-1} represented the symmetric and asymmetric stretching modes of C–O–C in the glycosidic bond of cellulose; following cellulose bands found at 1050, 896–894, 520–518, and 379–374 cm^{-1} (Szymańska-Chargot et al., 2011). Further bands at 1050, 1039–1035, and 854–852 cm^{-1} resulted from C–C and C–O stretching and skeletal deformation vibrations of pectins (Synytsya et al., 2003).

3.3. Particle size analysis

The effect of the four treatments on the particle size of the clementine pomace is summarized in Table 1 and Fig. 4. Regardless of using the same milling conditions, significant differences ($p < 0.05$) were found in D [4,3] and D [3,2] when clementine pomace powder was prepared using different treatments. The HAD treatment led to particles with significantly ($p < 0.05$) higher values of D [4,3] and D [3,2], whereas the EXT treatment produced particles with significantly ($p < 0.05$) lower values. The particles obtained through HOM and FD treatments had intermediate values with no significant ($p > 0.05$) differences. The decrease in particle size of the HOM clementine pomace compared to HAD could be related to the high turbulent flow speed and shear stress applied during treatment, as observed by Ma & Mu (2016) in de-oiled cumin dietary fiber treated with a high-speed shear emulsifying method. EXT treatment halved the particle size and almost doubled the span of the clementine pomace powder when compared to HAD treatment. The specific surface area is inversely related to the particle size and directly to the size and number of pores; mechanical treatments such as extrusion can affect it (Duque et al., 2017). According to the FESEM images (Fig. 1E–1H), where the pores of the particles are shown and with the particle size analysis, the HOM, FD, and EXT treatments led to higher specific surface areas compared to the HAD treatment

Table 1
Particle size and technofunctional properties results of hot air-dried (HAD), homogenized (HOM), freeze drying (FD), and extruded (EXT) clementine pomace.

Parameter	HAD	HOM	FD	EXT
Particle size				
D [4,3] (μm)	353 ± 12^{c}	198 ± 9^{b}	200 ± 4^{b}	148 ± 10^{a}
D [3,2] (μm)	77 ± 2^{c}	58 ± 1^{b}	57 ± 2^{b}	41 ± 1^{a}
Span (-)	2.5 ± 0.1^{a}	3.5 ± 0.2^{b}	2.9 ± 0.1^{a}	4.3 ± 0.4^{c}
Specific surface area (m^2 g^{-1})	0.078 $\pm 0.003^{a}$	0.103 $\pm 0.002^{b}$	0.105 $\pm 0.003^{b}$	0.146 $\pm 0.002^{c}$
Technofunctional properties				
WHC (g water g^{-1}) *	6.7 ± 0.5^{b}	10.6 ± 0.3^{c}	7.0 ± 0.2^{b}	6.0 ± 0.3^{a}
OHC (g oil g^{-1}) *	2.2 ± 0.3^{a}	2.2 ± 0.1^{a}	2.6 ± 0.1^{b}	2.1 ± 0.1^{a}
WS (g soluble compounds 100 g^{-1}) *	39 ± 3^{b}	27 ± 1^{a}	45 ± 4^{c}	49 ± 1^{d}
SC (mL g^{-1}) *	4.6 ± 0.3^{a}	11.4 ± 1.1^{c}	9.6 ± 0.8^{b}	10.7 ± 0.5^{c}

Different letters in the same row mean significant differences ($p < 0.05$). *Dry matter-related content.

($p < 0.05$). According to the span values and Fig. 4, mechanical treatments such as HOM and EXT gave broader distributions ($p < 0.05$) than non-mechanical treatments (HAD and FD). Despite these differences, heterogeneous powders were obtained after the four treatments, as their span values were greater than 1 in all cases.

3.4. Technofunctional properties

The WHC, OHC, WS, and SC of the clementine pomace were measured (Table 1) to evaluate the treatments' effect on the technofunctional properties.

The WHC of the HOM clementine pomace was significantly ($p < 0.05$) higher than those of the other samples studied in this work, which could be due to its smaller particle size and porous microstructure (Fig. 1F). A similar effect was observed in HOM treated citrus fibers by Huang et al. (2021), although lower values of WHC were obtained in this work. The significantly ($p < 0.05$) lower values of WHC obtained in the

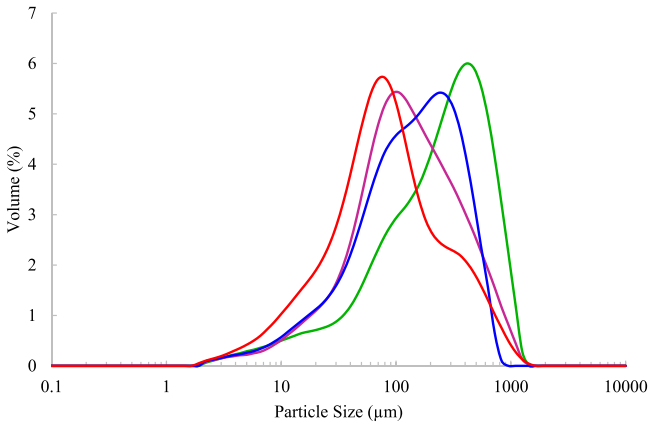

Fig. 4. Particle size distribution of hot air-dried (■), homogenized (■), freeze-dried (■), and extruded (■) clementine pomace.

other treatments (HAD, FD, and EXT) can be related to their more compact orography and the higher degree of fusion of their components, as seen in Fig. 1E, 1G, and 1H, that would hamper the water uptake. The reduction of WHC after the EXT treatment could be due to the breakdown of the fiber matrix that may occur as a consequence of the treatment and the losses of soluble dietary fiber removed along with the soaking water during WHC determination (Zhong et al., 2019).

FD treatment led to significantly ($p < 0.05$) higher OHC than the other treatments. This increase may be due to a less disrupted and porous structure so that the powder can retain more oil (Martínez-Las Heras et al., 2017). Similar results for OHC were found in orange (Garau et al., 2007; Perez-Pirotto et al., 2022), persimmon (Martínez-Las Heras et al., 2017), and carambola by-products (Chau et al., 2006).

Significant differences ($p < 0.05$) were found in the WS of the clementine pomace after applying the four treatments. The HOM clementine pomace showed the lowest WS value (27 %), which could be because of the removal of some soluble components in the ethanolic solution used during the treatment. The differences in WS between HAD (39 %) and FD (45 %) treatments can be explained by the difference in particle size and specific surface area, and they were also found by Lee et al. (2012) in their work with citrus "Hallabong" powders. The decrease in particle size and the increase in the specific surface area, shown in FD treatment, resulted in a higher contact surface available to transfer water to the particles; therefore, the WS of the FD particles increased. Treatment with EXT led to the highest WS, consistent with other work in orange by-products (Garcia-Amezquita et al., 2019; Huang & Ma, 2016; Larrea et al., 2005), where higher WS values were related to the presence of low molecular weight compounds. Garcia-Amezquita et al. (2019) observed that the high temperature and high pressure applied during extrusion treatment allowed degradation and solubilization of polysaccharides; this could occur in clementine pomace in our study, increasing the WS of the extruded sample.

The lowest significant ($p < 0.05$) values of SC were found in HAD samples, followed by the FD samples. The highest values of SC corresponded to the HOM and EXT treatments, but no significant ($p > 0.05$) differences were found between them. Some studies conducted on dietary fiber from citrus peel (Huang et al., 2021) and *P. odoratum* root (Lan et al., 2012) have shown that higher SC is related to smaller particle size and greater surface area. In this work, all HOM, FD, and EXT treatments produced smaller particle sizes (Table 1) and doubled the SC of clementine pomace regarding HAD treatment. The last treatment led to a larger particle size and a lower specific surface area (Table 1). Therefore, its lowest SC value followed the results reported in literature (Chen et al., 2018; Huang & Ma, 2016; Qiao et al., 2021). The HOM and EXT highest values obtained for SC could be because of the mechanical processing that caused a higher exposure of polar groups and hydrogen bonds and to the higher number of holes and pores, also shown in the FESEM images (Fig. 1F and 1H).

3.4.1. *Emulsifying capacity*

The EC of the clementine pomace is presented in Fig. 5. Multifactorial ANOVA showed significant interactions ($p < 0.05$) between the factors: treatment - oil:solution ratio (Fig. 5A), treatment - % of clementine pomace (Fig. 5B), and oil:solution ratio - % of clementine pomace (Fig. 5C).

A maximum EC, greater than 80 %, was observed in HOM clementine pomace regardless of the oil:solution ratio (Fig. 5A) and of the % of clementine pomace (Fig. 5B). Regarding the oil:solution ratio used for the emulsion's preparation (Fig. 5A), HOM treatment led to higher EC values at low oil amounts (10:90 oil:solution ratio) if compared to the other treatments. From concentrations of oil equal to and greater than 25 %, no significant ($p < 0.05$) differences were found between HOM and FD treated samples, which gave the highest values of EC. The high EC values obtained when using HOM and FD clementine pomaces can be attributed to the higher pectin content (Fig. 2) and the WHC and OHC values (Table 1). Likewise, Huang et al. (2020) showed in their study, orange pulp and peel fiber powders with higher content in pectin and greater WHC and OHC had improved emulsifying abilities. Higher OHC prevented the coalescence of oil droplets, and more pectin promoted the steric or electrostatic effects responsible for the EC of the orange fiber powders (Ngouémazong et al., 2015). Regarding the % of clementine pomace used for emulsion preparation (Fig. 5B), the best treatment to maximize the EC was HOM, regardless of the clementine pomace proportion used. In contrast, HAD treatment led to the lowest EC values for the entire clementine pomace range.

Evaluation of the interactions between the % of clementine pomace and the oil:solution ratio (Fig. 5C) showed interesting results. The increase in the % of clementine pomace had no significant effects ($p > 0.05$) in the EC for the 10:90 oil:solution ratio, with an EC approximately 65 %. Adding more clementine pomace (from 1 % to 2.5 %) to the solution led to a significantly ($p < 0.05$) higher EC for the 25:75 and 50:50 oil:solution ratio values. However, no significant ($p > 0.05$) differences were found when increasing the % of clementine pomace from 2.5 % to 5 %. In contrast, the use of 5 % clementine pomace and a 75:25 oil:solution ratio caused a significant reduction ($p < 0.05$) in the EC (<40 %).

The highest EC was achieved using HOM clementine pomace at any % of clementine pomace and any oil:solution ratio values. When using a large amount of oil in an emulsion (75:25 oil:solution ratio), a lower % of clementine pomace led to better EC.

4. Conclusions

Treatment of clementine pomace by different methods, such as hot air drying, homogenization, freeze drying, and extrusion, enables obtaining functionalized ingredients suitable for food design and elaboration. The technofunctional properties of these ingredients change depending on the treatment applied, and they are related to the structure observed after the treatments. Homogenization and extrusion gave place to more stratified and porous particles than hot air drying and freeze drying.

Homogenization would be the most suitable treatment to obtain an ingredient with high water retention and swelling capacities, due to the smaller size and porous structure of these particles; whereas to improve the oil retention capacity, a freeze drying treatment would be recommended. Among the treatments carried out, extrusion would be chosen to obtain powders with high water solubility. If a good emulsifying capacity is desired, the preferred treatment would be homogenization. This treatment allows the design of emulsions prepared using different amounts of oil and clementine pomace, even with the highest amounts used in this work (75 % and 5 %, respectively). Therefore, the role of

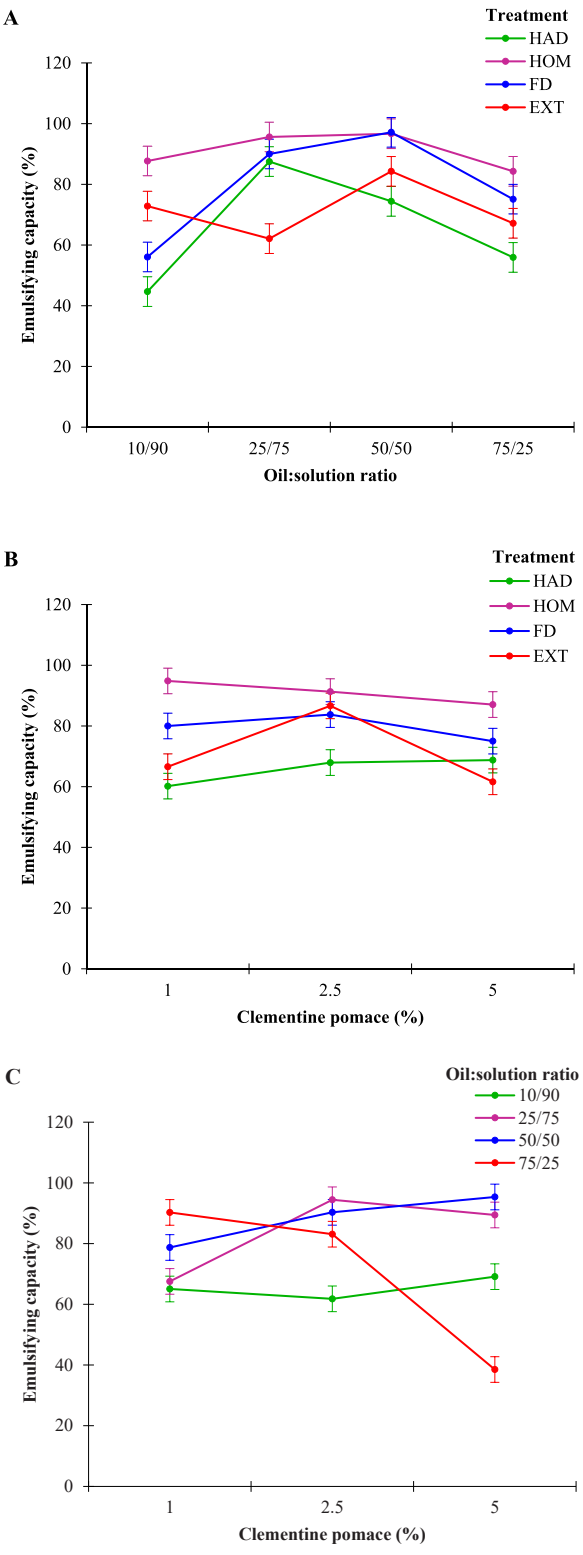

Fig. 5. Means and interaction plots with Tukey HSD intervals for emulsifying capacity (%). A, B, and C: interactions between treatment - oil:solution ratio, treatment - clementine pomace (%), and oil:solution ratio - clementine pomace (%), respectively. Treatments: hot air drying (HAD), homogenization (HOM), freeze drying (FD), and extrusion (EXT).

clementine pomace as an excellent emulsifying and stabilizing agent is demonstrated. This work paves the way for using juice industry by-products to obtain ingredients using physical treatments, allowing these ingredients to be labeled as "clean label" for the food industry.

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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