A comparison between the solvent extraction and supercritical fluid extraction to obtain polyphenolic compounds using the orange peel as raw material

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Extended Abstract.

Oranges worldwide are an important crop [1], mainly used to obtain juice and oils [2]. However, large quantities of residues are generated during the processing of this citrus fruit, representing between 44-60% of the processed orange fruit mass [1]. Orange processing residues are composed of peel, rag (segment membranes and cores), juice sacs, and seeds [3], where the peel is the major component with 50% of the weight of fresh fruit [4]. In orange, it is possible to find polyphenolic compounds such as hydroxycinamic acid and flavonoids, where the most prevalent are flavanones as hesperidin, a citrus flavonoid, with many therapeutic properties [5]. Among these, it is possible to find anti-inflammatory, antihypertensive, diuretic, analgesic, and hypolipidemic activities [6]. In addition, the polyphenolic compounds greatly interest the wine, food, and pharmaceutical industries [7], [8]. The extraction of the polyphenolic compounds uses technologies as solvent extraction (SE) and supercritical fluid extraction (SFE). The technology selection involves considerations such as the solubility of interest component, technical-economic, energetic, and environmental factors. The combinations of these factors can impact in different Sustainable Development Goals (SDG) as promoting sustainable agriculture (Goal 2), promoting, inclusive, and sustainable economic growth (goal 8), and promoting inclusive and sustainable industrialization and foster innovation (goal 9). So, this work proposes a comparison between the SE and SFE using orange peel as raw material to obtain hesperidin as the main component in the extract. Additionally, based on the experimental results, the simulations are proposed to perform the energetic (based on exergetic assessment) and economic assessment. The methodology used to achieve this objective is divided into five parts: (i) orange peel characterization, (ii) estimation of extraction conditions based on solubility analysis, (iii) process extraction (SE and SFE), (iv) quantification and extract characterization, and (v) simulation and assessment.

First stage: orange peel characterization: The physicochemical characterization of raw material is performed with three repetitions. The moisture, extractives (NREL/TP-510-42619), ash (NREL/TP-510-42622), holocellulose (ASTM D1104), cellulose (T203 os-74 ASTM 1695-77) and lignin (T222). The contents are determined according to international norms and methods [9]–[11]. The pectin quantification was carried out using the method proposed by Yu et al. [12].

Second stage: estimation of extraction conditions based on solubility analysis: The Peng–Robinson equation of state with the Stryjek Vera modification (PRSV equation of state) with the Van der Waals and Wong–Sandler (WS) mixing rules have been used to calculate solubility of hesperidin in CO_2 [13]. In addition, the UNIFAC DORTMUND model is used to estimate the parameters required by the WS mixing rules [14]. The equation used to calculate the solubility of a solid in gas is:

$$y_2 = \frac{P_2^{subli}\varphi_2^{subli}}{P\varphi_2}\exp\left[\frac{V_2^s}{RT}\left(P - P_2^{subli}\right)\right]$$

P_2^{subli} corresponds to the sublimation pressure, V_2^s is the solid molar volume, φ_2^{subli} is the sublimation fugacity coefficient and φ_2 is the fugacity coefficient in the supercritical phase.

Third stage: process extraction (SE and SFE): From the solubility analysis it is possible to estimate the best conditions of temperature, pressure, and co-solvent concentration (for SFE). In this work ethanol is considered as solvent (SE) and co-solvent (SFE) for CO_2 in concentrations of 100%, 70%, 50%, 30%, and 0%. The other parameters required for the extraction processes are presented in **Table 1**.

Table 1. Conditions considered for the process extraction

Technology	Solvent	Co-solvent	Time extraction [min]	Concentration
SE	Ethanol	-	30	0.2 g/mL
SFE	CO_2	Ethanol	30	0.2 g/mL

Fourth stage: quantification and extract characterization: In the obtained extracts are quantified the Total Phenolic Compounds (TPC) [15], the Flavonoid content (FLA), hesperidin concentration (HES) [16], naringenin concentration (NAN), reducing sugars (DNS), antioxidant activity using DPPH and ABTS methods [17], [18]. The equipment used is an LC-2010A HT (SHIMADZU), with a liquid chromatograph, a UV-visible detector, a quaternary pump, a vacuum-degasifier, and an automatic sampler. The chromatographic separation was performed in column C18 with a size of 150 mm x 4.6 mm and a particle size of 5 µm. The conditions for the flavonoids quantification are reported by Faraneh Zareiyanab y Habibollah Khajehsharifia [19].

Fifth stage: Simulation and assessment: The SE and SFE process design considered the experimental results and conditions used in the experimental part (see **Table 1**). The simulation is performed using Aspen plus v.9. software. The thermodynamic model used in the SFE process is the Predictive Soave-Redlich-Kwong (PSRK) model used to estimate the equilibrium phase in supercritical conditions [20]. In the SE process, the thermodynamic model is the Non-Random Two-Liquids (NRTL), the model recommended by Bitchikh et al. and Luo et al., [21], [22]. The mass flow of orange peel considered in the simulations in this work is 19 kg/h. The economic assessment is based in the work of Solarte et al. [23]. The costs and prices used for the economic assessment are presented in the **Table 2**. The energetic assessment is based on previously obtained mass and energy balance based on the of Restrepo et al. [24]. As last aspect to compare the technologies, is performed an environmental assessment based on the Life Cycle Assessment (LCA). The methodology for the LCA is reported in the ISO 14040.

Table 2. Cost for raw material, reagents, utilities, and product sale

Raw material, reagents, and supplies			**Utilities**		
Component	**Costs and prices**	**Ref.**	**Component**	**Price**	**Ref.**
Orange peel	0.022 USD/kg*		Electricity	0.13	[25]
Ethanol	0.72 USD/kg	[26]	LP steam	7.89 USD/ton	[27]
CO_2	0.55 USD/kg	[28]	**Product prices**		
Water	0.326 USD/cum	[29]	Extract rich in flavonoids	14 USD/kg	[28]

* Estimated transport cost taking into account transport in a six-axle truck at a distance of 20 km

Results.

The orange peel used for this work has an extractive content of 24.79%, where 22.35% corresponds to water-soluble components. Additionally, it presents percentages of cellulose, hemicellulose, lignin, pectin, ash, and fats of 17.53%, 20.33%, 11.38%, 21.28%, 2.18%, and 2.52%, respectively. Secondly, the solubility of hesperidin is analyzed, where it was identified that this flavonoid is very poorly soluble in CO_2. Hence, an SFE process requires the addition of a co-solvent to improve its solubility. Hesperidin is highly soluble in polar solvents such as acetone and ethanol. The solubility of hesperidin in ethanol decreases with temperature and pressure. From this analysis, the selected conditions for extracting hesperidin from the orange peel are 100 bar and 30°C. In the third stage (extraction), yields between 2.53% and 22.53% are obtained for SE and 2.86% and 6.24% for SFE. The ethanol concentration maximized the extraction of polyphenolic compounds such as hesperidin is 50% for both SE and SFE. SE with 50% ethanol obtained TPC, HES, DPPH, FLA, ABTS, DNS, and NAN values of 5,620.59 mg GAE/100 g, 44.43 mg/g, 8.94 ug/mL, 1,852.33 mg quercetin/100 g, 288.24 µmol Trolox/100 g, 4.59 g sugars/100 g, and 21.24 mg/ 100g, respectively. While with SFE, these values correspond to 822.93 mg GAE/100 g, 6.89 mg/g, 10.09 ug/mL, 665.27 mg quercetin/100 g, 182.18 µmol Trolox/100 g, 3.11 g sugars/100 g, and 3.75 mg/100 g, respectively. These results show that with the addition of a co-solvent in the SFE, the solubility of the flavonoids in the orange peel is not comparable to that in processes such as SE. So, for obtaining flavonoids from citrus wastes it is advisable not to use processes such as SFE. The SE and SFE processes decrease the extractives concentration in the orange peel by 24.27% and 44.24%, respectively. These processes allowed the concentration of orange peel polysaccharides, facilitating their valorization under biorefinery schemes.

When simulating SE and SFE, yields of 21.89% and 6.24%, respectively, are obtained. The energy consumption in both processes corresponds to around 50% in the extract purification stage. In contrast, the extraction stage presented the highest exergy values, representing destruction and modifications in the orange peel matrix. On the economic side, the most representative costs correspond to the costs of raw materials and utilities. Where the costs of utilities and inputs such as CO_2 in SFE make this technology not economically viable. Additionally, it should be considered that SE presents extraction yields and higher concentrations of flavonoids in the extracts compared to SFE. In the environmental area, SFE has lower yields and uses CO_2, which has a greater environmental impact than SE.

Conclusion.

The extraction of flavonoids such as hesperidin from orange peel is a process that must use low pressures. As evidenced in this work, the use of SFE leads to a decrease in the concentration of polyphenolic compounds in the extract obtained, especially flavonoids. In addition, it is found that the use of 50% EtOH gives the best yields for obtaining flavonoids from orange peel.

The main polyphenolic compounds in orange peel correspond to flavonoids such as hesperidin and naringenin. The solubility of these flavonoids decreases with increasing pressure and temperature. Therefore, the use of technologies such as SE is recommended for extracting flavonoids from orange peel. By using a 50% ethanol solution, a yield of 21.89% is presented, which is one of the highest yields. However, compared to other ethanol concentrations, 50% ethanol allows the extraction of 1,592.73 mg GAE/100 g, more than a 70% solution with the highest yield (22.53%).

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