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Properties of *Portulaca oleracea* seed oil via supercritical fluid extraction: Experimental and optimization

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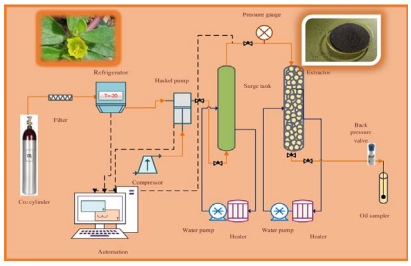
GRAPHICAL ABSTRACT



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ABSTRACT

Extraction of oil from *Portulaca oleracea* seeds via supercritical fluid was carried out for the first time. Response surface methodology was applied to evaluate the effect of operating variables, namely pressure, temperature, particle size and extraction time. Optimum conditions were found to be pressure of 23.50 MPa, temperature of 333 K, particle size of 0.8 mm, and dynamic extraction time of 210 min. The highest recovery achieved was 91.88 ± 1.60%, under the optimum conditions, and 92.94%, from RSM. The fatty acid content of the oil was found to be composed of unsaturated (79%) and saturated (20.7%) compounds. Major fatty acids included linolenic, linoleic, and oleic acids. Experiments were performed on physicochemical properties of the oil samples; these included saponification, iodine, peroxide and acid contents, specific extinctions, total phenol content, antioxidant activity, TGA and stability tests. The results indicated high levels of omega-3, making it a good candidate for pharmaceutical and food industries.

1. Introduction

Portulaca oleracea L. *(P. oleracea, purslane*) is a yearly green plant in the family Portulacaceae [1]. *P. oleracea L.* grows in some areas in Europe and Asia. This plant is traditionally utilized as an edible herbal treatment [2,3]. It has many medicinal effects such as hypolipidemic, anti-aging, anti-inflammatory [4], anti-oxidant, analgesic, wound-healing [5,6], anti-bacterial [7,8], hypoglycaemic, hypocholesterolaemic, and anti-tumour effects [9]. The main active ingredients of *P. oleracea* are unsaturated fatty acids [10], terpenoids [11], coumarins, flavonoids [12], and alkaloids [13–15]. In addition to these valuable components, purslane is a major source of omega-3 fatty acid [16–20].

Nowadays, with scientific advances attained in the scope of public health, alternatives to organic solvents used in oil extraction process are proposed. It is worth mentioning that, toxic organic residues represent a

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serious problem in the solvent-based extraction [21]. Several new and clean extraction methods such as supercritical fluid extraction (SFE), microwave extraction, and ultra-sonication assisted extraction have been developed for the extraction of essential oil or oil from plant seeds [22]. Among the mentioned methods, supercritical extraction has been introduced as a significant alternative to conventional oil extraction techniques. SFE has been proved to be capable of achieving extraction recovery comparable to those obtained by conventional Soxhlet extraction, such as *n*-hexane. Commonly, carbon dioxide (CO_2) has been the fluid of choice for supercritical fluid extraction processes, because of its special thermodynamic and heat transfer properties. Additionally, CO_2 is non-toxic, non-flammable, cost-efficient, easily available, and environment-friendly. Although CO_2 has a moderate critical temperature and pressure, but it is a non-polar solvent, making it suitable for extracting oils or hydrocarbons [23–28].

To the best of our knowledge, no comprehensive report has been published on the optimized extraction of oil from *P. oleracea* seeds via supercritical carbon dioxide (SC-CO_2). Even though a U.S. patent has been referred to in related literature, none of its results are accurate, having many unacceptable and significant errors [37]. Therefore, the main objective of this work is to design experiments and develop an empirical statistical model to predict cumulative recovery of this extraction process. Experimental data and model predictions are compared to one another to find out optimum operating conditions. Moreover, in order to characterize the extracted oil, its physiochemical properties are determined.

2. Material and methods

2.1. Materials

Pressurized cylinders of carbon dioxide gas (99.90% purity, Fadak Gas Factory, Iran) were used for supercritical fluid extraction. Chemicals used for the analysis included *n*-hexane and ethanol (Merck, German Company), 2, 2-Diphenyl-1-picrylhydrazyl (DPPH) radical (Sigma–Aldrich Chemie, Germany), gallic acid (Sigma–Aldrich Chemie, Germany), Folin–Ciocalteu's phenol reagent and sodium carbonate (Merck, Germany). All of the chemicals and reagents were of analytical grade. Also, *P. oleracea* seeds were purchased from Pakan Bazr Co. (Esfahan, Iran).

2.2. Preparation of P. oleracea

After drying the seeds in shadow at 22–27 °C for one day, residual water content of the seeds was dried in oven at 95–105 °C for 10 h before placing the samples in desiccator to have their moisture content dropped below 4%. The dried seeds were chopped in a domestic mixer grinder and then graded into five different ranges of particle size by a vibratory sieve shaker, as reported in Table 1. The dried samples were stored in a sack in a cool and dry place until analysis.

2.3. Methods

2.3.1. Oil extraction via conventional method

P. oleracea seed (sample) oil was extracted using standard Soxhlet apparatus with *n*-hexane as the solvent. Extraction process was performed with 20 g of seed sample along with 500 ml of *n*-hexane in a glass thimble at 78 °C for 8 h. Excess solvent was removed under vacuum at 40 °C utilizing a rotary vacuum evaporator. Once the solvent was evaporated totally, mass of the oil was quantified gravimetrically and the oil sample was stored in a dark vial [24].

Table 1
Coded and uncoded values of the independent variables used in the experimental design.

Independent variables	Level of factor				
Coded levels	−2	−1	0	1	2
Pressure (x_1,MPa)	8	12	16	20	24
Temperature (x_2, K)	313	318	323	328	333
Particle size (x_3, mm)	0.45	0.60	0.75	0.90	1.05
Dynamic time (x_4, min)	30	75	120	165	210

2.3.2. Supercritical fluid extraction procedure

The SFE pilot plant used in this study consisted of an extraction vessel of 74 ml in capacity, 0.025 m in internal diameter, and 0.15 m in height, a cylinder filled with liquefied CO_2, a high-pressure pump (Haskel, maximum pressure = 600 bar) to pressurize the liquefied CO_2 to the desired pressure, a surge tank and a packed bed vessel (extraction vessel) (both of which were made of 316-stainless steel), a shell-and-tube heat exchanger where hot water was circulated within the shell at fixed temperature, and a back-pressure valve to control the extraction pressure, into which a heating element was incorporated to avoid freezing. In the present work, 5 g of sample was introduced into the extraction cell. Carbon dioxide from a gas cylinder (standard cylinder) was passed to the refrigerator unit where CO_2 was cooled and liquefied. The liquefied CO_2 was then pressurized by the high-pressure pump. The compressed CO_2 was introduced into the surge tank and then transferred to the main extraction column. A shell-and-tube heat exchanger, wherein water was circulated within the shell at constant temperature, provided the required temperature for extraction process. A packed bed vessel of sufficient volume was filled with the sample and glass beads, so as to prevent flow channeling in the packed bed while avoiding dead volume. Operating pressure and temperature were kept within desired ranges. Static time was determined for all experiments by closing the back-pressure valve for about 30 min, and dynamic conditions were adjusted by opening the back-pressure valve. During the dynamic time, the extraction cell temperature was held at 0 °C by using an ice bath chamber. In order to keep the back-pressure valve from freezing, it was heated by an electrical heating jacket. The obtained oil was collected carefully, since it was sensitive to light. Once weighed, the samples were stored in sealed murky vials in a cool place (e.g. fridge) until analysis. The extracted oil was then measured to calculate the extraction recovery. For each extract sample obtained at a particular set of experimental conditions, tests were performed in triplicate and mean values were reported [24,29,30]. The used SC-CO_2 apparatus is shown in Fig. 1. Total recovery of the SC-CO_2 extraction can be calculated by dividing weight of the obtained oil by the total oil extracted using Soxhlet. The extraction recovery was calculated according to Eq. (1):

$$\text{Recovery}(\%) = \frac{\text{Amount of extracted oil (g)}}{\text{Amount of total oil ininitial ground sample (g)}} \times 100 \quad (1)$$

2.3.3. Experimental design and statistical analysis

Response surface methodology (RSM) was employed to optimize the process and determine effects of independent factors on the recovery of extraction. The experimental design and statistical analysis were accomplished by Design Expert 7.0.0 software. Preliminary experiments were performed to obtain optimal operating conditions. Central composite design (CCD) was utilized to evaluate effects of independent variables (input parameters) and their impacts on the recovery. In this case, input parameters included pressure, temperature, particle size and dynamic time. Studied ranges of the independent variables, coded and non-coded values of them, and their units are given in Table 1. The relationship between recovery (R) and process variables (coded) was obtained by fitting a model onto experimental data; this relationship is given by the following second-order polynomial function:

$$R = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{44} x_4^2 \quad (2)$$