Supercritical Fluid Extraction of Compounds from Coriander Seeds: Experiments and Modelling

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Supercritical fluid extraction of the volatile and non-volatile fractions from coriander seeds was carried out under different conditions of pressure (90, 100 and 250 bar), temperature (40 and 50ºC), mean particle size (0.4, 0.6 and 0.8 mm) and CO_2 flow rate (2.19x10^{-4}, 3.05x10^{-4} and 4.54x10^{-4} kg/s) to understand the influence of the process parameters on the composition and extraction yield of the oil fractions. The best extraction conditions for volatile oil were at 90 bar, 40ºC, 0.6 mm and 3.05x10^{-4} kg/s and for the non-volatile oil 250 bar, 40ºC, 0.6 mm and 3.05x10^{-4} kg/s (after the removal of the volatile oil).

A model based on the concept of broken and intact cells was applied to the supercritical CO_2 extraction of the volatile oil. A good agreement was obtained between the model and our experimental measurements.

Moreover, a comparative evaluation of the antioxidant activity of the SFE extracts, of the essential oil (Hydrodistillation) and Soxhlet extract obtained with pentane, after deodorization, was performed using the 2,2-diphenyl-1-picrylhydrazyl method (DPPH).

INTRODUCTION

Coriander is an aromatic and medicinal herb widely used in Mediterranean countries. In traditional medicine seeds are employed against gastrointestinal problems and rheumatism, while in food industry leaves and seeds are used as condiment and flavour agents [1, 2].

Traditional techniques for isolation of volatile and non-volatile compounds are Hydrodistillation (HD) and Soxhlet extraction (SE), respectively, and while the first one can promote hydrolysis reactions and thermal degradation of some oil components, in the second one solvent contamination of the extract may occur. However, with supercritical fluid extraction (SFE), these problems are overcome [3]. SFE of compounds from coriander seeds was carried out in our laboratory followed by a fractional separation using two separators [4].

In recent years, Sovová has applied with success a model, based on the concept of broken and intact cells, to the extraction of plant compounds [5, 6].

An interest aim of this work was to study the influence of the process parameters (pressure, temperature, mean particle diameter and flow rate) on the extraction yield of the volatile oil. Another goal was to test the model proposed by Sovová [6, 7] using these results. Moreover, a last aim was to evaluate the antioxidant activity of the volatile oil (SFE, at 90bar and 40ºC), the essential oil (HD) and of the non-volatile fraction (SFE, at 250bar and 40ºC, and SE with pentane, after deodorization) using the 2,2-diphenyl-1-picrylhydrazyl method (DPPH).

MATERIALS AND METHODS

Plant Material

Seeds from commercial Italian coriander (L'Ortolano, Cesena, Italy) were ground and mean particle sizes of about 0.4, 0.6 and 0.8 mm were used for the extractions.

SFE Apparatus

The SFE apparatus used in this work was described elsewhere [4]. The CO_2 (99.995% purity) used in the studies was supplied by Air Liquide (Portugal).

Extraction of essential oil and volatile oil

The essential oil was isolated by HD using 40g of plant material (for 4 h, in a Clevenger apparatus). Volatile oil was obtained by SFE using 100g of plant material under the following conditions: pressure (90, 100 bar), temperature (40 and 50ºC), mean particle size (0.4, 0.6 and 0.8 mm) and flow rate (2.19×10^{-4}, 3.05×10^{-4} and 4.54×10^{-4} kg/s).

Modelling

The model proposed by Sovová has the following assumptions: (a) the temperature and the pressure are constant during the extraction; (b) the solid bed is homogeneous concerning to the initial distribution of the solute and the particle size; (c) the solvent flows axially through the bed of grinded particles; (d) the solvent is solute-free at the extractor inlet; (e) the resistance to the mass transfer is considered both in the solvent film and within the particles, which determines, respectively, the rate of extraction of the readily and the less accessible solutes; (e) the extraction may be divided into three periods, the first one controlled by the solvent film resistance, the transition period, and the last one characterized by the extraction of the solute within the particles.

Extraction of the non-volatile fraction

After the HD the plant residue was dried and submitted to a SE with pentane for 5 h (using 10 g of plant material). After the SFE at 90 bar, the same plant matrix (100 g) was submitted to a 4h extraction at 250 bar, 40ºC and 3.05×10^{-4} of CO_2 flow rate.

DPPH radical scavenging method

The free radical-scavenging activity of extracts were measured using 2,2-diphenyl-2-picrylhydrazyl (DPPH) [8]. Briefly, the absorbance of 4ml of ethanolic solution of DPPH (0.03g/l) was measured at 515nm and then 50µl of the extract (with different concentrations) was added. The decrease in absorbance of the mixture was followed during 80min. The values of EC_{50} were calculated and compared with that obtained for the synthetic antioxidant Trolox.

RESULTS AND DISCUSSION

A detailed analysis of the experimental results of SFE extraction of volatile oil from coriander seeds showed that the best extraction conditions were at 90 bar, 40 ºC, 0.6 mm and 3.05×10^{-4} kg/s [9].
Table 1 shows the different parameters obtained with these results when the model proposed by Sovová [6, 7] is applied. From the analysis of the mean deviation it was shown a good agreement with the experimental results and the model.

Table 1: Values of the optimized Sovová's model parameters.

P (bar)	T (ºC)	ϕ(mm)	Fl (kg/s)	x_0*10^3 (kg/kg)	x_k*10^3 (kg/kg)	yr*10^3 (kg/kg)	F*10^3	S*10^4	MD(%)
90	40	0.6	3.05x10^{-4}	4.45	2.70	0.80	4.70	1.94	7.33
100	40	0.6	3.05x10^{-4}	4.45	3.23	0.70	6.11	2.40	2.76
90	50	0.6	3.05x10^{-4}	4.45	3.45	0.30	8.98	0.19	4.32
90	40	0.4	3.05x10^{-4}	4.45	2.60	0.90	7.45	3.38	1.05
90	40	0.8	3.05x10^{-4}	4.45	3.11	0.70	3.88	1.42	9.44
90	40	0.6	2.19x10^{-4}	4.45	3.20	0.70	4.22	3.57	1.90
90	40	0.6	4.54x10^{-4}	4.45	3.00	0.70	47.44	1.64	8.18

MD%= (100/N)*[Σ[abs(experimental yield-calculated yield)/experimental yield]]
x_0, initial solute content in the solid (kg extract/kg CO_2); x_k, solute fraction inside the particle (kg extract/kg solute-free feed); yr, apparent solubility (kg extract/kg CO_2); F, parameter of the fast extraction period (dimensionless); S, parameter of the slow extraction period (dimensionless); MD%, mean deviation. P, T, ϕ and Fl are, respectively, the pressure, the temperature, the mean particle size and the flow rate.

The model parameters F and S describe, respectively, the initial and the final part of the extraction curve. F is proportional to the fluid phase mass transfer coefficient (k_f) and S to the solid mass transfer coefficient (k_s). Concerning to the CO_2 density, F and S increased with the pressure (for the same temperature), while the opposite was observed for the temperature (at the same pressure), indicating that the higher is the density, the lower is the resistance to the mass transfer of the volatile oils to the CO_2. The mean particle size has also some influence, since the model parameters increased when the mean particle diameter decreased. Taking into account the flow rate, an increase on it had a great influence on F, comparing to S, indicating that the mass transfer within the particle is almost independent of the flow rate.
Furthermore, concerning to the antioxidant activity, all extracts presented high EC_{50} (between 87 and 320g extract/g DPPH), which means that they are weak scavengers of free radicals (Table 2). These values are much higher than that obtained for Trolox (0.2g extract/g DPPH). The weak antioxidant activity of different extracts (obtained with different solvent mixtures) of coriander seeds and leaves has been reported earlier [10, 11]. The effect seems to be more active in extracts from leaves than from seeds [11].

Table 2: EC_{50} values (expressed as g antioxidant/g DPPH) for the different extracts tested. S1- 1st separator; S2- 2nd separator

Extract	Extraction yield % (g extract/g plant material)	EC_{50} (g extract/g DPPH)
SFE-90bar	0.4	319.6
HD	0.4	272.7
SFE-250bar, S1 (after deodorization)	2.4	-
SFE-250bar, S2 (after deodorization)	1.6	256.6
SE-pentane (after deodorization)	4.9	87.1

However, the extract obtained in the first separator in the SFE carried out at 250bar showed a pro-oxidant activity, since its scavenger capacity increased when the concentration decreased. Consequently, this is the reason why the EC_{50} is not presented in table 2.
These results show, effectively, that the Soxhlet extraction is most efficient in obtaining antioxidants from coriander seeds since this extract has the lower EC_{50}. However, the contamination of the extract

with pentane becomes this extract not suitable for food applications, being preferable a toxic solvent free extract. Moreover, the two step supercritical fluid extraction allowed to isolate the pro-oxidant fraction from the all extract, which is an advantage in a future industrial applications.

CONCLUSION

A SFE study of the volatile and non-volatile fractions from coriander seeds was presented under different conditions of pressure, temperature, mean particle size and CO_2 flow rate. The best extraction conditions were at 90 bar, 40ºC, 0.6 mm and $3.05x10^{-4}$ kg/s.

The mass-transfer coefficients for the fluid and solid phases for the extraction of the volatile oil of coriander seeds were calculated using the model proposed by Sovová. A good agreement was obtained between the model and the experimental results.

Moreover, it was also showed that the extracts isolated by different procedures employed in this study have weak antioxidant activity, although one extract presented an inverse behaviour as the higher concentration the lower its ability to scavenge the DPPH radical. This is of particular interest when formulating new aromatized food products.

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