Evaluation of different extraction techniques in the processing of *Anethum graveolens* L. seeds for phytochemicals recovery

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A B S T R A C T

In this study, we aim to compare essential oils from *Anethum graveolens* L. obtained by hydrodistillation, steam distillation and supercritical fluid extraction. The influence of the particle diameter was investigated for all extraction techniques considered. The effect of pressure on the supercritical fluid extraction was also evaluated. For this, a full factorial design 2^2 combined with response surface methodology was used to maximize the yield of volatile extract from the seeds of *A. graveolens* L. The mathematical modeling of each extraction method was performed using a suitable model. The gas chromatography analysis (GC) identified dillapiole, carvone and its isomers to be the major compounds.

1. Introduction

Anethum graveolens L., also known as dill, is a plant native to the Mediterranean area. It is used mainly due to its aromatic properties, *A. graveolens* L. oil contains dillapiole, carvone, and limonene as major components (Sintim et al., 2015; Stanojević et al., 2015). The pharmacological properties of *A. graveolens* L. oil, such as its antibacterial activity, have been widely reported (Chen et al., 2014; Garcez et al., 2017; Orhan et al., 2013; Rafii and Shahverdi, 2007; Tian et al., 2011).

A. graveolens L. is commonly used for flavoring foods and beverages. The oil is FEMA GRAS (2383) and Council of Europe listed and also used in seasoning blends, particularly for the use in pickles (Ashurst, 2012; Najaran et al., 2015).

Other studies have also demonstrated that the extract of *A. graveolens* L. seeds has good antioxidant and antimicrobial activities that favor the preservation of food and protection against food pathogens, as well as antifungal activity that suppresses or deteriorates some types of fungi (Karimi et al., 2016; Prakash et al., 2015; Singh et al., 2005). These various properties are the reason why *A. graveolens* has attracted the attention of the pharmaceutical and food industry for the development and manufacture of drugs and food enhancers (Tian et al., 2011).

The pharmaceutical properties of *A. graveolens* essential oils and its applicability in food products has motivated the research of extraction techniques such as steam distillation, hydrodistillation and supercritical fluid extraction (SFE) applied to its seeds.

Li et al. (2019) investigated the decoupled effects of extraction temperature, time, pressure, solvent flow and particle size of seeds for supercritical fluid extraction and for the best identified-condition yield was equal to 6.7 %. Garcez et al. (2017) investigated the combined effects of temperature, pressure and flow rate for the supercritical extraction of *A. graveolens* essential oil and for the optimal condition, the authors found a yield value of 3.16 %. Also, the olfactometric analysis of the essential oil was performed identifying the perceived aromas of this extract.

Hydrodistillation was used by Konoz et al. (2017) to obtain essential oil of *A. graveolens*. The composition was characterized by GC–MS analysis, revealing the appeal of conventional hydrodistillation for the extraction of β-phelandrene, o-cymene, thymol, dill ether, and germacrene D. Also, according to the authors, microwave-assisted hydrodistillation was more suitable for the extraction of α-pinene and α-phelandrene.

Kosar et al. (2005) also identified differences in the composition of *A. graveolens* essential oils obtained by microwave-assisted hydrodistillation and hydrodistillation methods. The extracts obtained by classical hydrodistillation had lower percentages of Myristicine, limonene, and dill apiole, while cis-isodihydrocarvone and carvone contents were increased by microwave energy.

Bowes et al. (2004) investigated the composition of *A. graveolens* essential oil from cultivars with different seeding dates and harvest stages. Steam distilled dill seed oils had the following major

compounds: α-phellandrene, limonene and carvone. The authors identified that carvone content increased as the plants matured.

Ramadan et al. (2013) also used steam distillation to obtain essential oil of *A. graveolens*, the authors presented α-terpinene, limonene, epi-α-bisabolol, carvone, and 7-α-hydroxy manool as major compounds. Moreover, they found high antioxidant activities of the extract that are attributed to the presence of polyphenols and volatiles of the essential oil.

The objective of this study was to investigate the effects of particle diameter in the steam and hydrodistillation of *A. graveolens* seeds. The effects of particle diameter and operational pressure were also investigated for supercritical extraction of the seeds using the response surface method, a technique usually employed for multivariate analysis applied to natural products (Alara et al., 2015; da Silva et al., 2015d; Belhachat et al., 2018). All the extracts had their composition determined by GC–MS.

2. Material and methods

2.1. Plant material

The *A. graveolens* seeds used were purchased in a retail store in the city of Porto Alegre (Brazil) in 1 kg packages of dry product. The origin of seeds is Rajasthan (India) as provider information. Seeds were ground using a knife mill to obtain powders with average particle sizes of 0.5 mm, 0.7 mm and 0.9 mm. The milled seeds were divided into 100 g portions which were stored in a refrigerator at 4 °C for a maximum period of two weeks until use in extractive processes. The real particle density equal to 1.24 kg/dm^3 was determined by nitrogenium gas pycnometry (Auto Micro Ultrapyc 1200e, Quantachrome Instruments, Potsdam, Germany). The humidity level in the milled seed was settled by a moisture analyzers (Model i-Thermo 163 L, BEL Engineering, Monza, Italy) resulting in 2.10 %. This information is used to determine the yield to dry matter.

2.2. Extraction process

Extraction curves of mass *vs*. time were plotted for each extraction technique. In this study, samples were collected with a time interval of 10 min to construct the extraction curve. The experiment was finalized when the extracted mass did not increase after three consecutive measurements.

The final yields were calculated according to Eq. (1):

$$\%Yield = \frac{m_e}{m_p} * 100 \tag{1}$$

where m_e is the extracted mass collected at the end of the extraction process (g); m_p is the milled seeds dry weight initially added to the extractor vessel (g) and *%Yield* is the yield of the extraction.

2.2.1. Steam distillation (STD)

The steam distillation apparatus used includes a 4 L glass boiler heated by electric resistance, a 1.5 L glass extraction chamber, and a modified Clevenger trap with a 5 mL graduated tube. In the boiler is generated saturated steam at 373.15 K and 1.01 bar. The isolation procedure continued until the material was exhausted, the oil was dried with anhydrous sodium sulphate and experiments were performed in triplicate. The steam flow is obtained measuring the mass of condensate during a certain interval of time, in triplicate. The extractor bed porosity is obtained through the extractor volume, solid density and solid mass in the extractor.

2.2.2. Hydrodistillation (HYD)

The seeds were introduced in a round bottom flask coupled to a Clevenger type apparatus with a condenser and an oil/water separation system. The volume of water used was 500 mL and the extraction was

Table 1
Variables and their levels employed in 2^2 full factorial design for supercritical fluid extraction (SFE).

Variable			Level correspondence		
			Low (-1)	Medium (0)	High (+1)
Pressure	x_1	MPa	80	90	100
Particle diameter	x_2	mm	0.5	0.7	0.9

carried until the exhaustion of the plant material. The oil was dried with anhydrous sodium sulphate and the experiments were performed in triplicate.

2.2.3. Supercritical fluid extraction (SFE)

The acquisition of the volatile *A. graveolens* extract was carried out in a pilot plant as described in detail by Scopel et al. (2013). The experiments were conducted in a 500 mL vessel loaded with 100 g of milled *A. graveolens* seeds at different extraction conditions.

To highlight the most significant parameters and possible interactions, full factorial design 2^2 with center point design were used to create a response surface for the supercritical fluid extraction process. The influence of operational pressure (80, 90 and 100 bar) and particle diameter (0.5, 0.7 and 0.9 mm) upon the essential oil yield was studied. In Table 1, the levels of the independent variables under investigation are listed. The temperature was fixed in 308.15 K for all extractions and supercritical CO_2 at 1000 g/h was used as a solvent.

In a system involving two independent variables, the mathematical relationship of each response on theses variables can be expressed as a polynomial:

$$y = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum_{i<j} \sum \beta_{ij} x_i x_j + \sum_{j=1}^{k} \beta_{jj} x_j{}^2 \tag{2}$$

where y is the response, β_0 is a constant, β_j is the linear coefficient and β_{ij} the interaction coefficient. The coefficient β_{jj} corresponds to the regression coefficient of the quadractic term.

The optimized extraction condition was performed in triplicate and the extraction curve for the best condition was modeled.

2.3. Composition and identification of the essential oil components

The composition of the essential oil obtained was determined by GC–MS on an Agilent 7890A gas chromatograph equipped with a mass spectrometer (Agilent 5975C, Agilent Technologies, California, USA). The injector used was in split mode (1:55) at 523 K. The capillary column used was an HP-5MS (30 m x250 μm i.d., 0.25 μm phase thickness, Agilent Technologies, USA), coated with 5% phenyl-polymethylsiloxane. The oven temperature was held at 333 K for 8 min, raised to 453 K at 3 K/min rate, to 523 K at 20 K/min, then held for 10 min. The carrier gas was Helium, flow rate 0.8 mL/min; interface temperature 523 K; MS mode EI (70 eV); acquisition mass range, $40 - 450 \, m/z$. The components of the oil were identified by comparison of their mass spectra with those stored in the GC–MS databases (Adams, 2007).

2.4. Mathematical modeling

The mathematical models were selected based on the main aspects of each technique and the most suitable hypothesis for each case. Mathematical models in which differential mass balances are performed for solid and fluid phases in an extraction bed can be used for both SFE and steam distillation, as in both cases solvent flow is passign through a bed of seeds with the same steps of mass transfer and equilibrium hypotheses (Xavier et al., 2011). Steam distillation and supercritical fluid extraction curves were fitted by the Reverchon (1996) and Sovová

(2005) models. Hydrodistillation was conducted by a batch process so a specific mathematical model (Sovová and Aleksovski, 2006) was used to generate the extraction curve for this technique.

The model proposed by Reverchon (1996) was originally used on the modeling of supercritical extraction of sage oil. The author considers the essential oil as a single compound, and only a small fraction of oil is available on the surface of the particles after the milling process. The mass transfer is controlled by internal resistance only, and mass transfer related to the external resistance is neglected in the model. This model is also frequently used to model steam distillation extraction (Rossa et al., 2018).

In this model the extract concentration in the fluid phase, C, and the extract content in the aromatic plant, q, has two independent variables, extraction time (t) and extractor length (z). The mass balance in the fluid and solid phases are presented in Eqs. (3) and (4), respectively

$$\frac{\partial C(z, t)}{\partial t} = -\upsilon \frac{\partial C(z, t)}{\partial z} - \frac{(1 - \varepsilon)}{\varepsilon} \rho_s \frac{\partial q(z, t)}{\partial t} \tag{3}$$

$$\frac{\partial q(z, t)}{\partial t} = -k_{TM}(q(z, t) - q(z, t)^*) \tag{4}$$

where υ is the interstitial velocity of the fluid, ε is the bed porosity, and ρ_s is the plant density. The previous differential equations satisfy the initial conditions described by $C(z, 0) = 0$ and $q(z, 0) = q_0$ for all z, and the following boundary conditions $C(0, t) = 0$ for all t and $\partial C(z, t)/\partial z = 0$ at $z = H$. A linear relationship is used due to the lack of experimental phase aiming to represent the equilibrium data.

$$q(z, t)^* = K_p C(z, t) \tag{5}$$

where K_p (m³/kg) is the volumetric partition coefficient of the extract between the solid and the fluid phases at equilibrium.

The model Sovová (2005) is similar to the other models proposed by the same author, and basically simulates two periods of extraction, being suitable for the case of essential oil extraction, whose equilibrium is characteristically controlled by the interaction solute-matrix. The author considers that the resistance to mass transfer within the fluid is null and the initial amount of free solute is not enough to saturate the solvent. This model has been used efficiently to fit SFE data into various reports (Barroso et al., 2011; Coelho et al., 2012; Martín et al., 2011; Scopel et al., 2016).

The mathematical model equations (Sovová, 2005) are the following:

$$e = q \frac{Kx_u}{1 + K(\gamma/r)} \, for \, 0 \leq q \leq q_c \tag{6}$$

$$e = x_u [1 - C_1 exp(-C_2 q)] \, for \, q > q_c \tag{7}$$

e is the extraction yield, q the relative amount of the passed solvent, K (y^*/x_t) the partition coefficient, x_u is the concentration in the untreated solid, C_1 and C_2 are model constants, q_c is the relative amount of the passed solvent in the transition, γ the solvent-to-matrix ratio in the bed (Eq. 8), and r the grinding efficiency (Equation 9).

$$\gamma = \frac{\rho_f \varepsilon}{[\rho_s (1 - \varepsilon)]} \tag{8}$$

where ε is the bed void fraction, $\dot{Q}$ the solvent flow rate, N_m the charge of insoluble solid, a_s is the specific area between the regions of intact and broken cells, and k_s is the solid phase mass transfer coefficient.

$$r = 1 - C_1 exp(-C_2 q_c) \tag{9}$$

$$k_s a_s = \frac{(1 - r)(1 - \varepsilon)\dot{Q}C_2}{N_m [1 - ((1 - r)C_2/K)]} \tag{10}$$

Sovová and Aleksovski (2006) proposed a model specific for hydrodistillation based on the concept of broken and intact cells. These types of models divide the extraction process into two periods: first, the easily accesssible solute is swiftly extracted; later, the solute inside the

intact cells diffuses gradually to the surface of the matrix, then it is extracted. The mathematical representation of the solution of this model is presented in Eq. (11).

$$Y = Y_\infty \left[1 - fexp\left(-\frac{t}{T_1}\right) - (1 - f)exp\left(-\frac{t}{T_2}\right) \right], \, T_2 > T_1 \tag{11}$$

where Y is the essential oil yield; Y_∞ is the total extraction yield; f is the relative ratio of broken cells to the total number of cells; and T_1 and T_2 are model time constants.

The non-linear regression of the equations was performed in the curve fitting tool-box on Matlab, R2014a (The MathWorks, Inc., MA, USA). The unknown parameters of the models were estimated through optimization by minimizing the sum of square errors between experimental data and calculated data through the Nelder–Mead simplex method (Lagarias et al., 1998).

2.5. Statistical data analysis

The data obtained were presented as means of three replicate determinations ± standard deviation. Results were submitted to analysis of variance to compare means with one-way ANOVA and Tukey post hoc test ($p < 0.05$), using software STATISTICA software (version 10, StatSoft Inc., Tulsa, USA). To evaluate the factorial design with the center point the same software was used for statistical treatment of the results. Means were also compared by *t*-test when relevant.

Moreover, correlations among essential oil composition from each extraction technique were evaluated using a principal component analysis, which is a multivariate statistical method that, when applied to a given number of data, groups these data by similarity. Its foundations can be found in Jackson (2003) and Mackiewicz and Ratajczak (1993). The method has been used in different areas of knowledge as can be seen in the works of González-Coloma et al. (2006); Silvestre et al. (1997) and Christensen et al. (2005). The PCA was used to cluster the extracts according to the volatile compounds profile, using the STATISTICA software (version 10, StatSoft Inc., Tulsa, USA). The essential oils obtained by STD and HYD were compared by particle diameter and extraction technique, while the only oil obtained by SFE evaluated was the one obtained at the optimized condition.

3. Results and discussion

3.1. Steam and hydrodistillation

The extraction time for both techniques were very similar, about 160 min for each run. There was no statistical difference between the means of essential oil obtained from each technique for the different particle diameters (Table 2). The final essential oil yield for the same particle size was similar when comparing STD and HYD.

The similarity between these results was expected, due to the proximity of the process experimental conditions. The slightly lower yield obtained for HYD can be attributed to the hydrocracking of some polar compounds due to hot liquid water contact.

Table 2
Essential oil yields for steam distillation (STD) and hydrodistillation (HYD) for the different particle diameters.

Particle diameter (mm)	Yield (% w/w)	
	Steam distillation	Hydrodistillation
0.5	0.86[a] ± 0.04	0.84[a] ± 0.04
0.7	1.05[a] ± 0.01	0.92[b] ± 0.04
0.9	1.19[b] ± 0.01	1.14[b] ± 0.01

[a] Mean of three replicates ± standard error; Means in the same column with different lowercase letters (a and b) are significantly different ($p < 0.05$) as determined by Tukey's post hoc test.

The results for the hydro and steam distillation yields are higher when particles with larger diameters were used. The decrease of the particle size implies an increase of surface area for mass transfer, which consequentially increases the amount of extract removed from the raw material. However, it has been observed in previous reports that this does not always occur and can be attributed to the adsorption of the solute on the surface of the particle and consequent difficulty of removal of this solute adsorbed (Li et al., 2009; Zhang et al., 2012). Another cause of this behavior is associated with bed compaction being favored by the use of particles with smaller diameters and thus preventing the passage of solvent through the bed reducing the proper flow rate (Wang and Weller, 2006). In our study, bed compaction occurred when smaller particles were used and the formation of preferential paths made extraction more difficult.

3.2. Supercritical fluid extraction

The effects of operational pressure (x_1) and particle diameter on extract yield from *A. graveolens* L. were evaluated by response surface methodology. The coded and decoded values of independent variables and the responses obtained in the multivariate study are shown in Table 3. Within the experimental space considered, the total yields ranged from 0.81 % to 3.08 % (w/w).

To investigate the main factors and interactions influencing the extraction of *A. graveolens* L., and their tendencies due to the variation of the factors within the ranges considered, a polynomial regression was fitted following the response surface methodology (RSM). Table 4 shows the regression coefficients obtained using the coded variables from Table 3. The determination coefficients (R^2 and R^2_{adj}) for the full model are also presented.

The non-significant coefficients ($p > 0.05$) were removed from the general polynomial (Eq. 1). The final models were refitted and they are presented in decoded variables in Table 5. The interactive effects of operational parameters on *A. graveolens* extraction, the three-dimensional profiles of the regression models are illustrated in Fig. 1.

For these experiments, the extraction yields were more responsive to the operational pressure ($p = 0.005$) than the particle diameter ($p = 0.014$). According to the RSM analyses, the increase in operational pressure and small particle diameters enhance the extraction yield. The interaction of both parameters does not affect significantly the extraction. In the supercritical fluid extraction, smaller particle diameters result in a larger surface area and more broken cells, which improves the solvent penetration in the vegetal matrix. In this type of extraction, the solvent flow is high and the condition of the solvent is not favorable to the formation of bed compaction, which justifies the increase of surface area due to the decrease of the particle diameter to promote the higher extract yield. Also, the solvent capacity to solubilize analytes increases at higher pressures. The best condition, within the sample analyzed, was 10 MPa and 0.5 mm.

Table 3

2^2 full factorial design with a center point for supercritical fluid extraction (SFE).

Sample	Decoded variables		Coded variables		Response
	Pressure (bar)	Diameter (mm)	x_1	x_2	(% w/w)
1	100	0.9	1	1	1.97
2	90	0.7	0	0	2.05
3	90	0.7	0	0	2.1
4	80	0.9	−1	1	0.81
5	100	0.5	1	−1	3.08
6	80	0.5	−1	−1	1.44
7	90	0.7	0	0	2.25

Table 4

Regression codified coefficients (cc) of the quadratic model given by Eq. (1), their individual significance (p) at 95 % confidence level, and determination coefficients for the full model.

Regressed coefficients	SFE	
	cc	p
β_0	2.133	< 0.005
β_1	0.700	0.005
β_2	−0.435	0.014
β_{12}	−0.120	0.147
β_{11}	−0.308	0.060
R^2	0.9927	
R^2_{adj}	0.9703	

Table 5

Response surface model for supercritical fluid extraction (SFE) with extraction yield y, pressure x_1 and particle size x_2.

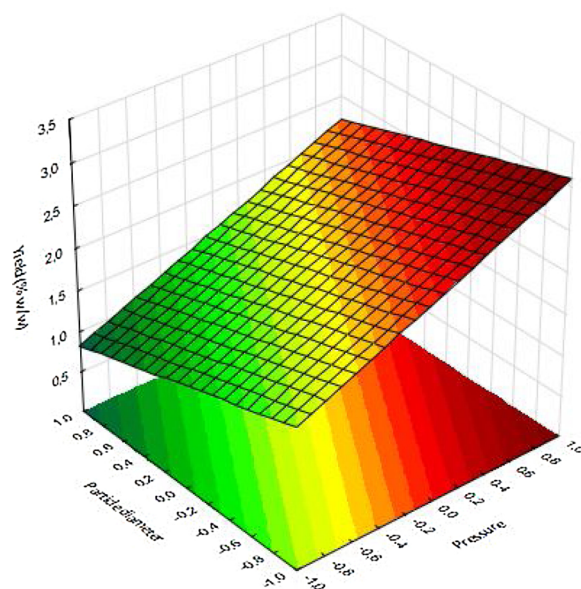| Reduced experimental models	R^2	R^2adj
y = 1.96 + 0.70*x_1 − 0.43*x_2	0.9181	0.8772

Fig. 1. Effect of particle size and pressure on the extraction yield of supercritical fluid extraction (SFE) of *A. graveolens* seeds.

Table 6

GC/MS of volatile oil extracted by steam distillation (STD) and hydrodistillation (HYD).

Compounds[a]	RI[b]	STD (%A)[c]			HYD (%A)[c]		
		L	M	S	L	M	S
Limonene	1028	2.38	1.07	0.44	3.63	1.44	1.78
cis-Dihydro carvone	1196	7.07	6.73	5.80	6.91	7.30	6.62
trans-Dihydro carvone	1203	3.83	3.18	1.65	3.89	3.54	1.85
Carvone	1246	23.85	22.58	22.46	23.25	23.78	22.89
Anethole	1285	0.56	0.59	3.06	0.40	0.63	3.05
Myristicin	1522	0.56	0.43	0.79	0.50	0.45	0.71
Dillapiole	1633	61.75	65.43	65.79	61.42	62.86	63.11

[a] : compounds identified with the library Adams (2007).
[b] : retention index calculated for a range of alkanes.
[c] : percent area of each peak relative to the total area of the identified compounds in the chromatogram. L: largest particle diameter (0.9 mm). M: medium particle diameter (0.7 mm). S: smallest particle diameter (0.5 mm).

Table 7
GC/MS of volatile oil extracted by supercritical fluid extraction (SFE).

Compounds[a]	RI[b]	(%A)[c]						
		1	2	3	4	5	6	7
cis-Dihydro carvone	1196	1.72	3.35	3.18	1.46	2.61	2.14	2.81
trans-Dihydro carvone	1203	0.78	1.23	1.14	–	–	–	1.06
Carvone	1246	8.16	11.83	11.41	6.67	10.95	9.23	10.49
Anethole	1285	–	0.48	–	–	1.87	1.63	–
Myristicin	1522	–	0.46	–	–	–	–	–
Elemicin	1559	–	0.42	–	–	–	–	–
Dillapiole	1633	89.34	82.22	84.26	91.88	84.58	87.00	85.64

[a] : compounds identified with the library Adams (2007).
[b] : retention index calculated for a range of alkanes.
[c] : percent area of each peak relative to the total area of the identified compounds in the chromatogram.
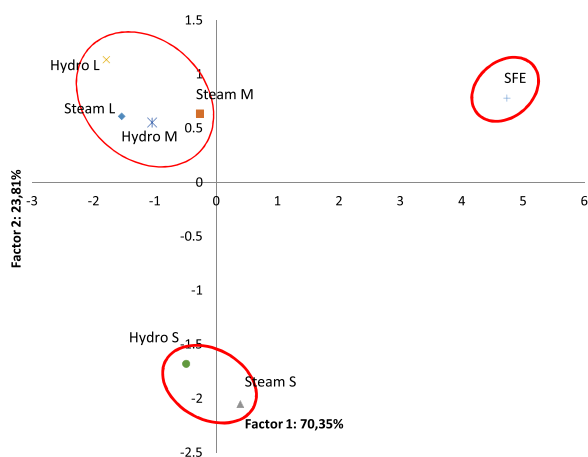

Fig. 2. Results of Principal Components Analysis - Grouping by the similarity of the composition of the extracts obtained by steam distillation (STD), hydro-distillation (HYD) and supercritical fluid extraction (SFE).

Table 8
Parameters estimated using the Sovová e Aleksovski (2006) model.

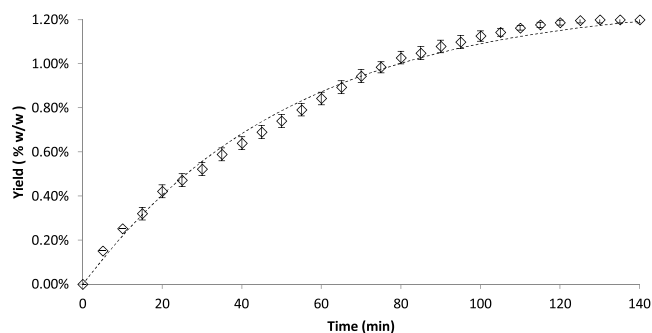| Parameters		
f	–	0.020
T_1	min	2.171
T_2	min	79.138

Fig. 3. The yield curve of essential oil obtained by hydrodistillation (HYD) of *A. graveolens* L. seeds (% $g_{oil}\ g_{plant}^{-1}$): mathematical model (_ _) and experimental data (◊).

Table 9
Parameters estimated using the Reverchon (1996) model for steam distillation (STD) and supercritical fluid extraction (SFE).

Parameters			
		STD	SFE
k_p	$m^3\ kg^{-1}$	9.71×10^{-3}	9.48×10^{-3}
K_{tm}	s^{-1}	3.26×10^{-4}	3.38×10^{-4}

Table 10
Parameters estimated using the Sovová (2005) model for steam distillation (STD) and supercritical fluid extraction (SFE).

Parameters			
		STD	SFE
r		0.821	0.571
y^*	$kg_{solute}\ kg_{solvent}^{-1}$	8.65×10^{-2}	8.50×10^{-4}
k_S	$m\ s^{-1}$	5.66×10^{-9}	2.27×10^{-8}
x_t		0.0051	0.0143

3.3. Volatile composition

The major volatile compounds identified in essential oils from STD and HYD are presented in Table 6. Table 7 presents the volatile compounds in SFE extracts in the same order previously shown in Table 3.

The major compounds identified in all techniques were the same: carvone and dillapiole. For STD and HYD, the sum of those two compounds represents 85 % of the extract, while for the SFE extract they represent 95 %. Limonene, present in STD and HYD, was absent in the extract obtained by SFE. That may be because lighter compounds are usually carried by the supercritical CO_2 during the extraction. These results are in accordance with previous works from other authors (Orhan et al., 2013; Singh et al., 2005; Sintim et al., 2015).

3.4. Principal component analysis

Seven extracts were compared by using PCA analysis to give an overview of the influence of different extraction techniques on *A. graveolens* L. oils. The oils obtained in the different diameters employed for STD and HYD were compared, and for SFE only the extraction condition that presented the best yield (10 MPa and 0.5 mm) was considered.

The points in the plot are the data observations. The nearest the spot, the similar data and when further apart are dissimilar. The plot shows the possible presence of atypical observations, groups, similarities, trends, and other patterns in the data.

In the score plot (Fig. 2), two clusters can be observed. The largest one consists in oils from STD and HYD from larger and medium sized-particle diameters, with similar compositions from all compounds. The second cluster consists of oils from the smaller particle diameters; this cluster presented anethole and myristicin in major composition. The SFE extract stands visible apart from the essential oils, with a larger amount of dillapiole, a smaller amount of carvone and a clear lack of some minor compounds.

3.5. Mathematical modeling

3.5.1. Hydrodistillation

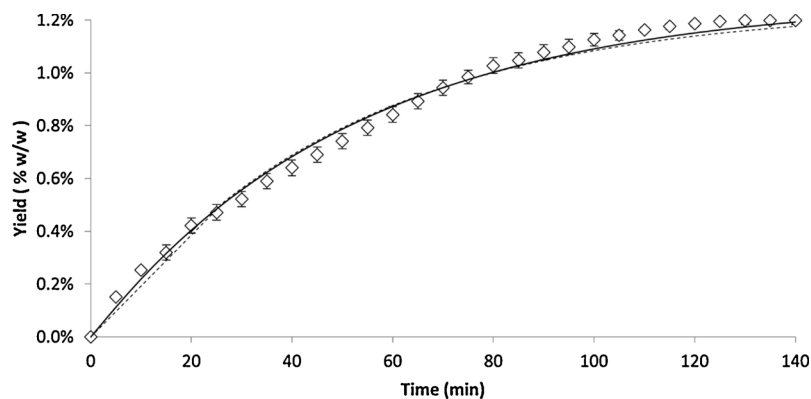The model proposed by Sovová and Aleksovski (2006), which was

Fig. 4. The yield curve of essential oil obtained by steam distillation (STD) of *A. graveolens* L. seeds (% $g_{oil} g_{plant}^{-1}$): Sovová (2005) model (_ _ _), Reverchon (1996) model (——) and experimental data (◊).
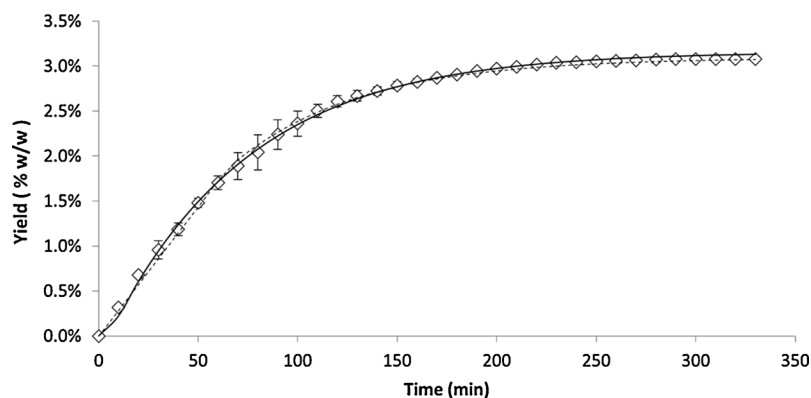

Fig. 5. The yield curve of the volatile extract obtained by supercritical fluid extractions (SFE) of *A. graveolens* L. seeds (% $g_{oil} g_{plant}^{-1}$): Sovová (2005) model (_ _ _), Reverchon (1996) model (——) and experimental data (◊).

specifically developed to describe HYD processes, presented good adherence to the experimental data. To be able to solve the model equations, no further fluid or solid-phase properties were necessary, only the experimental curve. Parameters evaluated from the extraction curves were f (ratio of broken and intact cells), T_1 (time constant for the diffusion in broken cells), and T_2 (time constant for the diffusion in intact cells) and are shown in Table 8. Fig. 3 shows the extraction curve for HYD with seeds of 0.9 mm particle diameter. The largest particle diameter was chosen because it resulted in the best experimental extraction yield.

3.5.2. Steam distillation and supercritical fluid extraction

The two mathematical models, proposed by Reverchon (1996) and by Sovová (2005), are based on a differential mass balance through the fixed bed, each one being solved by a different method. The first one is solved numerically and the second one analytically, with different assumptions. For each extraction method, the fluid properties vary accordingly to the conditions (*P, T*), as well as the bed porosity changes with the different extractor geometries.

To solve the two model equations, the following parameters were experimentally determined for the STD process: steam flow (Q_v) 13.4 g h^{-1} and bed porosity (ε_{SD}) of 0.62. To determine the steam (ρ_{steam} = 0.59 kg m^{-3}) and CO$_2$ (ρ_{CO_2} = 650.49 kg m^{-3}) specific mass, the Peng-Robinson equation was used (Reid et al., 1987). The solid specific area (a_s) is 5147.9 m^{-1} and the density of the solid phase (ρ_s) 1.24 kg dm^{-3} are equal for both extraction methods. The bed porosity for the supercritical fluid extraction is (ε_{SFE}) 0.78.

The two parameters fitted using the Reverchon (1996) model are the diffusion coefficient (K_{tm}) and the equilibrium constant (k_p), presented in Table 9. Regarding the Sovová (2005) model, the parameters fitted from the experimental data are the grinding efficiency (r), the equilibrium fluid-phase concentration (y^*), the solid-phase mass transfer coefficient (k_s), and dimensionless transition concentration (x_t), which are shown in Table 10. Fig. 4 shows the extraction yield for

steam distillation with seeds of 0.9 mm particle diameter, along with the two fitted models. The fitted models presented good accuracy to describe the experimental data for both extraction methods.

The experimental data obtained from steam distillation produced value for the internal mass transfer coefficient with the same order of magnitude found in the study by Rossa et al. (2018) on the extraction of *Piper hispidinervum* essential oil.

The same procedure is followed for the supercritical fluid extraction; the two models are fitted to the experimental data, presenting good adherence. Fig. 5 shows the SFE yields at 100 bar, 308.15 K, 2.78 × 10^{-4} kg s^{-1} solvent flow and 0.5 mm particle diameter.

The values obtained for the adjusted parameters concerning SFE show orders of magnitude very similar to those presented in other reports (Bernardo-Gil and Casquilho, 2007; Coelho et al., 2012; Mezzomo et al., 2009; Scopel et al., 2016). The difference between the equilibrium coefficients (y^*) for each extraction method is due to the different solvent flow at each process, even if the yields for the SFE process are higher than the one for the STD process.

Mathematical models play a key role in the development, design, and control of industrial processes because, when well-adjusted, they eliminate or reduce time-consuming design steps and experiments. In this sense, information on the unknown parameters of the models employed in the representation of the physical phenomenon may help further research involving the extraction operations considered here when the raw material is dill seed. The similarity in the order of magnitude between the parameters determined in this article and other studies available in the literature strengthens the confidence in the results obtained for these parameters.

4. Conclusion

Regarding the STD and HYD, the particle diameter lightly affects the composition of the essential oils. There was found no influence of the particle diameter on the extraction yields for these two techniques even

though particles with an average diameter of 0.9 mm have shown a slightly higher yield than the other conditions tested. SFE presented a higher extraction yield (approximately 2.6 times higher) and distinct composition extract. Pressure and particle diameter presented significance on the SFE result. The statistical method of response surface methodology showed the tendency of the SFE yield to increase with higher pressures (P = 100 bar) and smaller particles (d$_p$ = 0.5 mm). The mathematical models evaluated from the extraction yield curves showed a good fit to the experimental data, and useful parameters associated with the mass transfer phenomenon in the extraction process were obtained.

Declaration of Competing Interest

None.

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