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Comparative analyses of the diffusion coefficients from thyme for different extraction processes

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Abstract: This work was aimed at analyzing the kinetics and mass transfer phenomena for different extraction processes from thyme (*Thymus vulgaris* L.) leaves. Different extraction processes with ethanol were studied, *i.e.*, Soxhlet extraction and ultrasound-assisted batch extraction on the laboratory scale, as well as pilot plant batch extraction with mixing. The extraction processes with ethanol were compared to the process of supercritical carbon dioxide extraction performed at 10 MPa and 40 °C. The experimental data were analyzed by a mathematical model derived from the Fick's second law to determine and compare the diffusion coefficients in the periods of constant and decreasing extraction rates. In the fast extraction period, the values of the diffusion coefficients were one to three orders of magnitude higher compared to those determined for the period of slow extraction. The highest diffusion coefficient was recorded for the fast extraction period of supercritical fluid extraction. In the cases of the extraction processes with ethanol, ultrasound, stirring and increasing extraction temperature enhanced the mass transfer rate in the washing phase. On the other hand, ultrasound contributed the most to the increase of mass transfer rate in the period of slow extraction.

Key words: *Thymus vulgaris*; ethanol extraction; supercritical extraction; extraction kinetics; modelling; diffusion coefficients.

INTRODUCTION

Common thyme (*Thymus vulgaris* L.) is a perennial shrub native to southern Europe, widely cultivated for its strong flavour, resulting from its content of thymol. Due to their antimicrobial, antioxidant and antifungal activity, flavour properties and aroma-active constituents (thymol, carvacrol, *p*-cymene, limonene and γ -terpinene), thyme essential oils and extracts have been widely applied as additives in the food and cosmetic industries thereby increasing the economic

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value of this crop worldwide.^{1,2} In recent investigations, thyme was identified as a valuable raw material for the production of antibacterial agents, whereby thyme isolates showed stronger antibacterial activity than those of sage and rosemary.³

Nowadays, different extraction techniques have been widely investigated and applied to obtain valuable natural compounds from plant material for commercial application in the food, pharmaceutical and cosmetic industries.⁴ Steam distillation is an appropriate technique for the isolation of volatile components from plant materials, such as essential oils, some amines and organic acids, as well as other, relatively volatile compounds, insoluble in water. Since it is performed at elevated temperature, it requires substantial energy consumption and may cause thermal decomposition of the components of the essential oil, resulting in flavour changes.⁵ Extraction with organic solvents or water is used for the isolation of thermolabile substances from plant materials. The organic solvents are removed from the extracts by evaporation under vacuum to obtain concretes which are further subjected to degreasing with ethanol to obtain essential oils for application in the cosmetic and perfumery industries. Processes of extraction with organic solvents are limited by the compound solubility in the specific solvent used, and hence the quality and quantity of the extracted mixture are determined by the type of extractant applied.⁴ Solvent extraction in a Soxhlet apparatus enables the isolation and enrichment of compounds of medium and low volatility and thermal stability. It allows a high recovery, but has a number of shortcomings, such as long extraction times, large consumption of solvents, cooling water and electric energy and often unsatisfactory reproducibility.⁶ These shortcomings have led to the consideration of the use of new so-called “green” separation techniques with shortened extraction time, reduced organic solvent consumption, and increased pollution prevention, such as microwave extraction, supercritical fluid extraction, ultrasound extraction, ultrafiltration, flash distillation, the controlled pressure drop process and sub-critical water extraction. Nowadays, extraction processes for the isolation of phytochemicals under extreme or non-classical conditions are constantly being developed in applied research and industry.^{7,8}

Ultrasound-assisted extraction (USE) is considered as an emerging potential technology that could improve heat and mass transfer of the solutes and increase the efficiency of the isolation of bioactive principles from plant materials. Ultrasound waves produce a cavitation effect that facilitates the erosion of the solute from the interfacial surfaces of a plant material and the release of the extractable compounds by disrupting the plant cell walls.^{6,7,9,10} The USE process thus enables high reproducibility along with a reduction of the solvent consumption and extraction time. Several classes of food components, such as aromas, pigments, antioxidants, and other organic and mineral compounds, have been efficiently isolated by a USE process from a variety of matrices (mainly animal tissues, food and plant materials).⁷ Scanning electron micrographs have provided evidence of

the mechanical effects of ultrasound, mainly shown by the destruction of cell walls and release of cell contents, leading to more effective mass transfer in solid phase as well.¹¹ The average time of ultrasonic extraction typically ranges from a few to 30 min, although it can be as long as 70 min, whereby the recoveries obtained during this time are comparable to those obtained after a dozen or so hours of Soxhlet extraction, performed at the same temperature.^{6,10} The extraction conditions could be optimized with respect to time, polarity and amount of solvent, as well as the mass and kind of sample, whereby solvent polarity and extraction time have the greatest effect on the recovery.¹² The extraction could be realised at room temperature, which makes it suitable for the extraction of thermally labile compounds. The need for the separation of the organic solvent from the extract is a disadvantage of this technique.

The process of supercritical fluid extraction (SFE) has gained a lot of attention for the extraction of bioactive principles from herbs and spices, especially in the field of high value added compounds, such as pharmaceuticals and nutraceuticals. In order to isolate essential oil rich extracts from aromatic herbs and spices, the SFE process is optimally performed under mild pressure (9–10 MPa) and temperature (40–50 °C) conditions.¹³ The SFE process is superior to the conventional extraction processes in a variety of ways: speed of extraction, completeness of extraction, elimination of organic solvents, suitability for thermally sensitive compounds, simplified procedure, selectivity, reduced environmental hazard/non-toxicity and cost savings. Due to their low viscosity and higher diffusivity compared to liquids, supercritical fluids have better transport properties than liquids, and can diffuse through solids more easily.

Knowledge of the mechanism and kinetics of extraction processes is generally needed for optimizing the operating conditions and extraction process design. Independent of the type of plant material or solvent polarity, two extraction periods could be observed: a) a rapid increase in the concentration of the extractable substances in the solvent in the initial stage of the process, known as the washing or the fast extraction period and b) a slow increase in the concentration of the extractable substances in the solvent with increasing progress of the extraction, known as the slow extraction period. Mathematical modelling of extraction processes from different herbaceous materials has been of great importance for design purposes because it allows generalization of the experimental results and successful prediction of the extraction kinetics. A mathematical model based on the second Fick's Law, which was introduced by Crank,¹⁴ has been widely used to describe the process of unsteady diffusion in the solid phase for different extraction processes and particle geometries.^{14–20}

In this study, a model based on the Fick's Second Law¹⁴ was used to estimate and compare the diffusion coefficients for different extraction processes from thyme leaves. The method proposed by Osburn and Katz,¹⁸ which considers

two parallel diffusion processes in the solid, was used to determine and compare the diffusion coefficients in the periods of so-called fast and slow extraction. Comparative analysis of diffusion coefficients was provided in order to investigate and quantify the influence of the extraction temperature, ultrasound and stirring on the mass transfer rate during ethanol extraction as well as to compare different extraction processes with ethanol and supercritical carbon dioxide with respect to the diffusion coefficients.

EXPERIMENTAL

Materials

Dried leaves of *Thymus vulgaris* L. (crop 2009) were supplied by the Institute for Medicinal Plant Research "Dr. Josif Pančić" (Belgrade, Serbia). The moisture content of the air-dried plant material, determined by Karl Fischer volumetric titration, was 10.9 mass %. The ground plant material (average particle diameter of 0.4 mm) was used for the extractions. Ethanol (96 %, Alba, Novi Sad, Serbia) and demi water (NIS Petrol Rafinerija nafte, Novi Sad, Serbia) were used to prepare the solvent mixture of ethanol and water (70:30 v/v) for the solvent extractions. Commercial carbon dioxide (99 % purity) supplied by Messer-Tehnogas (Serbia) was used for the supercritical extraction.

Soxhlet extraction

Ground dried thyme leaves (50 g) were placed in a thimble-holder and continuously filled with condensed fresh solvent from a distillation flask filled with 600 ml of ethanol aqueous solution (70 % v/v) for approximately 16 h (the solvent to feed ratio was 12:1). Each time when the liquid reached the overflow level, the solution in the thimble-holder was siphoned back into the distillation flask, carrying the extracted solutes into the bulk liquid. After each extraction cycle, 5 ml of the solution was taken from the flask, filtered and evaporated to the dryness using a rotary vacuum evaporator (Devarot, Elektromedicina, Ljubljana, Slovenia).

The mass of the extract was determined and the extraction yield (Y) was calculated from the formula:

$$Y (\%, w / w) = 100 \frac{m_e}{m_{pm}} \quad (1)$$

where m_e is the mass of the extract and m_{pm} is the mass of the raw material.

Ultrasonic-assisted extraction

The batch ultrasonic-assisted extraction was performed in an open rectangular ultrasonic cleaner bath (Bandelon Sonorex, RK 52, 60 W, internal dimensions: 150 mm×140 mm×100 mm, Bandelon Electronic, Munich, Germany) using the indirect sonication mode at 35 kHz. Ground plant material (20 g) was added into round bottom flask filled with 240 ml of ethanol aqueous solution (70 % v/v) and subjected to ultrasound-assisted extraction (solvent to feed ratio 12:1). The flask with the sample was partially immersed into the ultrasonic bath, filled with water and sonicated for 90 min at 40 °C (± 1.0 °C). In specific time intervals (5, 10, 15, 25, 35, 45, 60, 75 and 90 min), 4 ml of the solution were taken from the flask, filtered and evaporated to the dryness using a rotary vacuum evaporator. The mass of the extract was determined and the yield of extraction was calculated by Eq. (1).

Pilot-scale extraction

The pilot-scale extraction (PSE) from thyme was performed in a self-made batch apparatus presented in Fig. 1. The batch extractor was filled with 600 g of the ground plant material and 7.2 dm³ of ethanol aqueous solution (70 % v/v) (solvent to feed ratio 12:1). The extractions were performed at 40 °C and at the boiling temperature of the ethanol aqueous solution (80.5 °C) for 2 h. The temperature of the water bath was regulated and maintained at a constant level (± 0.5 °C). In specific time intervals (10, 30, 60, 120, 180 and 240 min), 30 ml of the solution were taken from the flask and filtered. The solvent was removed from the filtered samples using a rotary vacuum evaporator and the differential mass of the extract was determined. The extraction yield was calculated by Eq. (1).

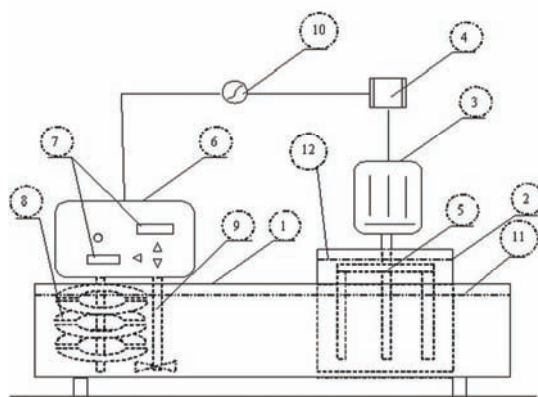


Fig. 1. Scheme of the pilot-scale extraction apparatus: 1 – water bath; 2 – extraction vessel; 3 – electromotor; 4 – frequency regulator; 5 – mixer; 6 – thermoregulation unit; 7 – temperature indicator controller; 8 – heaters; 9 – water bath mixer; 10 – electric power source; 11 – water level in the bath; 12 – level of the solvent and plant material in the vessel.

Supercritical CO₂ extraction

Extraction with supercritical carbon dioxide was performed in an Autoclave Engineers SCE Screening System with a 150 cm³ extractor, which was previously described in detail.²¹ The extractions were performed at 10 MPa and 40 °C in order to isolate the essential oil rich extracts and to minimize the yield of higher molecular weight compounds.¹³ The initial mass of the plant material used for the extraction was 32 g. At the beginning of the SFE, the plant material was exposed to the influence of the supercritical fluid for one hour under the extraction conditions (without flow of the supercritical carbon dioxide) as a pre-treatment. The chosen pre-treatment of the herbaceous matrix enhances the rate of the SFE due to the glandular trichomes cracking during the exposure to supercritical fluid.²² After one hour of pre-treatment, continuous flow of supercritical fluid was established. Extraction was realized until total exhaustion of the plant material and maximal extraction yield was determined after consumption of 94.3 kgCO₂ kg⁻¹ plant material (*i.e.*, after 5 h of extraction). The mass flow rate of the CO₂ was 0.66 kg h⁻¹. The experiment was performed in triplicate.

Mathematical model

Chosen extraction processes were analyzed with the diffusion model proposed by Crank,¹⁴ which is derived from the Fick's Second Law.¹⁴

The model used in this study was based on the following assumptions:¹⁵⁻¹⁸ a) the solid particles are considered as spheres with a diameter of $2R$; b) the solute is initially homogeneously contained in the solid; c) the solute content in the solid varies with time and distance; d) the extraction of solute occurs in a two-step process, *i.e.*, a constant rate and a decreasing rate stage; e) thermodynamic equilibrium is established at the interface and f) the porous solid is considered as a pseudo-homogeneous medium.

According to the study of Osburn and Katz,¹⁸ who investigated the kinetics of extraction from lamina soybean flakes, it was necessary to consider the presence of two parallel diffusion processes inside the solid; one faster and one slower. This method can also be applied to describe of the extraction from different particle geometries (spheres or flat plates).¹⁵⁻¹⁸ The mass transfer from the spherical particles is described by the following equation:^{15,16,18}

$$\frac{c_{\infty} - c}{c_{\infty}} = F_1 \exp\left\{\frac{-\pi^2 D_1 t}{R^2}\right\} + F_2 \exp\left\{\frac{-\pi^2 D_2 t}{R^2}\right\} \quad (2)$$

where: $F_1 = 6f_1/\pi^2$ and $F_2 = 6f_2/\pi^2$ are the fractions of the solute that are extracted with diffusion coefficients D_1 and D_2 , respectively, f_1 and f_2 are constants, t is the extraction time and R is the radius of the spherical particles. In the later stages of the extraction, only the second term on the right hand side of Eq. (2) remains significant. Therefore, the parameter D_2 could be obtained from the slope and the parameter f_2 from the intercept of the curve when $\ln(c_{\infty}/(c_{\infty} - c))$ is plotted as function of t . In the earlier stages of the extraction, the second exponential term is close to unity and D_1 and f_1 could be determined from the same plot.¹⁵

RESULTS AND DISCUSSION

Extraction kinetics study

The determined extraction yields obtained by the employed methods are presented in Table I. The extraction yields for the extraction processes with ethanol are plotted as function of the extraction time in Figs. 2 and 3. The extraction curve for the supercritical extraction process is presented as a plot of extraction yields *vs.* specific amount of supercritical carbon dioxide consumed (m_{CO_2}) in Fig. 4.

TABLE I. The yields obtained by laboratory and pilot-scale extraction from thyme leaves

Extraction type	Notation	$T/^\circ\text{C}$	t/h	t_{90}^a/h	V_3^b/l	Ultrasound	Stirring	$Y^c/\%$
Laboratory scale								
Soxhlet	SE	80.5	15	10.0	0.60	No	No	29.80±2.16
Ultrasonic	USE	40.0	1.5	1.25	0.24	Yes	No	18.5±0.75
Supercritical	SFE	40.0	5.0	1.60	4.8	No	No	1.15±0.15
Pilot plant scale								
Batch solvent	PSE1	40.0	2.0	1.40	7.2	No	Yes	21.23±0.52
	PSE2	80.5	2.0	0.66	7.2	No	Yes	27.60±0.37

^aTime required for the achievement of 90 % recovery of extractable substances in the given process; ^bvolume of solvent (70 % v/v aqueous solution of ethanol or supercritical carbon dioxide); ^caveraged values of extraction yields determined in triplicate with the absolute deviation

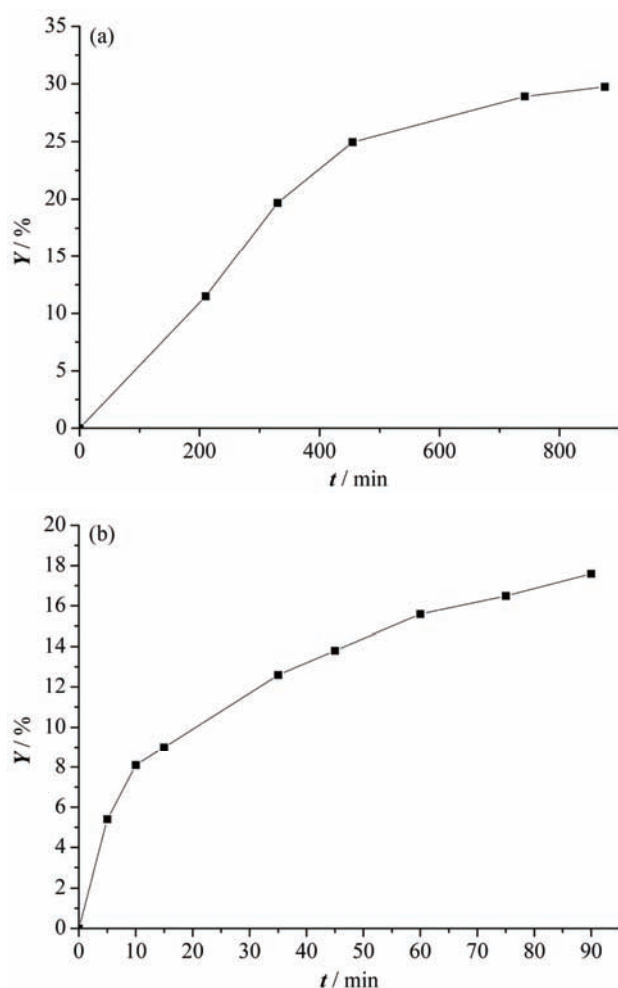


Fig. 2. Kinetics of thyme extraction a) in the Soxhlet apparatus and b) by ultrasonic-assisted extraction.

As expected, much higher extraction yields were obtained by the solvent extractions due to the lower selectivity of the aqueous ethanolic solution compared to that of supercritical carbon dioxide. According to the presented results, 1.5 h of ultrasonic extraction at 40 °C enabled 85 % recovery of thyme extract achieved by the Soxhlet extraction at a higher temperature (80.5 °C) and for a much longer extraction time (≈ 15 h) with the same solvent. This can be explained by the beneficial effects of ultrasound waves to the extraction efficiency that have been assigned to mass transfer intensification, cell disruption, improved penetration and capillary effects.^{9–11}

Considering the kinetic plots (Figs. 2–4), the presence of two extraction stages were noticed: a constant rate stage followed by a stage of decreasing rate. Namely, transfer of the extractable substances from thyme included: a) a solid to

liquid (or supercritical carbon dioxide) phase transfer, corresponding to the extraction of the easy available solute, from exogenous glands disrupted by milling, by simple washing, and b) a molecular diffusion of the inaccessible fraction of solute (intact glandular trichomes) throughout the porous herbaceous matrix.

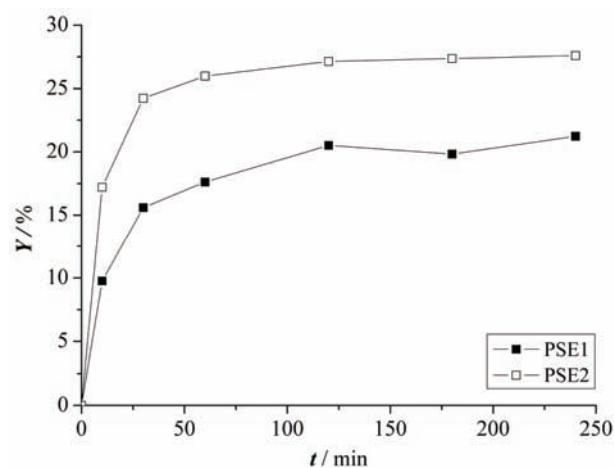


Fig. 3. Influence of temperature on the kinetics of thyme extraction by the ethanol-water mixture on the pilot-scale.

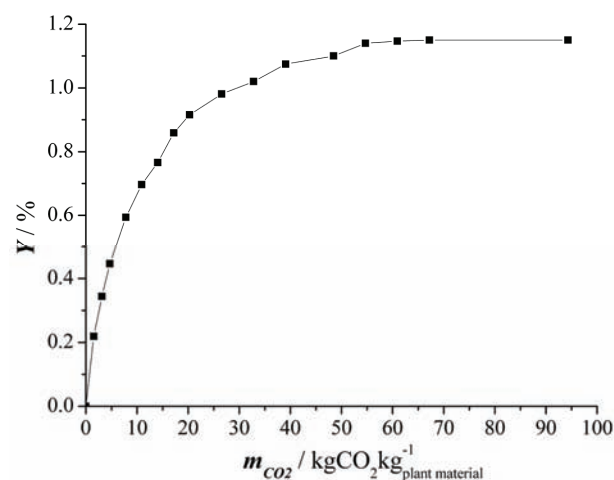


Fig. 4. Extraction yield as a function of the specific amount of supercritical carbon dioxide for the SFE at 10 MPa and 40 °C.

The shape of extraction curves in the Figs. 2b and 3 and the results presented in the Table I indicated that the rate of solvent extractions within the initial washing stage was enhanced by increasing temperature, stirring and ultrasound. Moreover, the rate of solvent extraction during the slow extraction period was particularly enhanced by ultrasound. As for the SFE process, the applied pre-treatment of the plant material (exposure to supercritical carbon dioxide) led to the cracking of additional glandular trichomes, which contributed to an increase of the extraction rate within the early stage of the SFE process.

According to the presented kinetic data, the time required for achievement of satisfactory recovery of extractable substances (90 % recovery), denoted as t_{90} , can be determined (Table I). The rate of achievement of a satisfactory yield of extract was noticeably affected by the nature of the employed solvent. The highest recovery rate was achieved in the supercritical extraction process (1.60 h). An increase of the extraction temperature in the case of the pilot plant extraction also increased the rate of achievement of a satisfactory extraction yield (0.66 instead of 2 h).

Evaluation of the diffusion coefficients

Equilibrium concentrations (or saturation concentrations) of thyme extracts in ethanol aqueous solution or supercritical carbon dioxide at infinite time (c_{∞}) represent concentrations of solute in solvent when all resistances are overcome. Since the ethanol extractions are batch processes and SFE is characterized by a continuous flow of the supercritical fluid, different procedures were used to determine c_{∞} . Equilibrium concentrations of extractable substances for extraction with ethanol at a given temperature were determined by exhaustion of the plant material. In the case of the SFE process, c_{∞} was determined by the following procedure: milled plant material was placed in the extractor vessel and pressurized to the extraction conditions. Sudden fast depressurization followed in order to disrupt the untouched glandular trichomes and plant cells and to minimize cell wall resistance in the extraction process. The extraction vessel was pressurized again and the solubility of saturation was determined from the slope of the extraction curve in the early stages of extraction. The obtained c_{∞} values are presented in Table II.

TABLE II. Corresponding values of c_{∞} of extractable substances from thyme for laboratory and pilot-scale extraction processes

Extraction type	Notation	$c_{\infty} / \text{kg m}^{-3}$
Laboratory scale		
Soxhlet	SE	27.1
Ultrasonic	USE	16.9
Supercritical	SFE	0.90
Pilot plant scale		
Batch solvent	PSE1	24.0
	PSE2	27.0

The corresponding plots of the function $\ln(c_{\infty}/(c_{\infty} - c))$ against the extraction time are presented in Figs. 5–7 for the fast stage as well as for the slower stage of the chosen extraction processes.

During the SFE process, the concentration of extractable substances in the supercritical carbon dioxide, which flows continuously, decreased with time due

to exhaustion of the plant material, and therefore the function $\ln(c_{\infty}/(c_{\infty} - c))$ against t had a downward trend (Fig. 7). However, this function had an upward trend for USE, SE and PSE as batch processes due to the enrichment of ethanol with solute over time (Figs. 5 and 6).

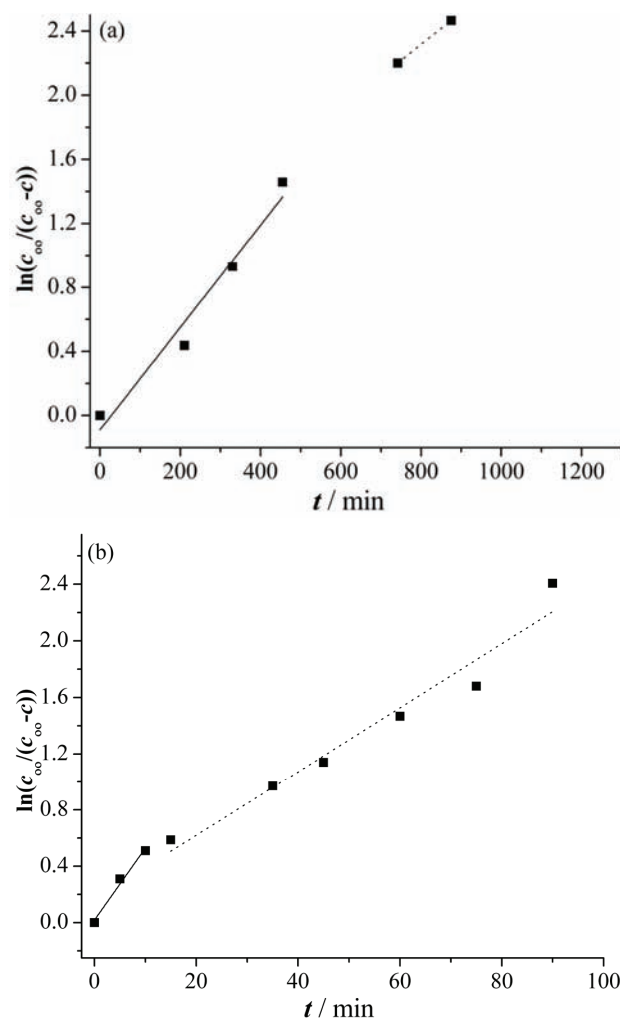


Fig. 5. Plot of the function $\ln(c_{\infty}/(c_{\infty} - c))$ against time for the fast first and the later slower second stage of the laboratory-scale a) Soxhlet extraction at 80.5 °C, and b) ultrasonic-assisted extraction (USE) of thyme at 40 °C (— fast extraction; ---- slow extraction).

The corresponding diffusion coefficients for the periods of constant and decreasing extraction rate, D_1 and D_2 , respectively, are presented in Table III. Diffusion coefficients in the initial washing period were one to three (in the case of the SFE process) orders of magnitude higher compared to those for the period of slow extraction. Moreover, the calculated value of the diffusion coefficient for the SFE process in the washing period was two or three orders of magnitude

higher compared to those reported for the extraction processes with ethanol. This was expected since supercritical fluids penetrate into samples of plant material almost as well as gases, due to their low viscosity. At the same time, their dissolving power is similar to those of liquids.⁶ In addition, there was a higher content of lower molecular weight compounds in the thyme supercritical extract (mainly essential oil with thymol as the most abundant compound^{3,23,24}) than in the thyme ethanol extracts, which also contributes to faster diffusion rate of the solute in the case of the thyme SFE. Recently, phenylindolizine was identified as main component of the thyme ethanol extract.²⁵

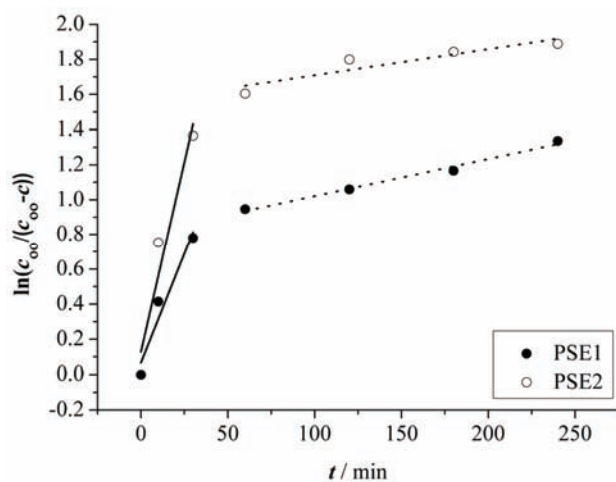


Fig. 6. Plot of the function $\ln(c_{\infty}/(c_{\infty}-c))$ against time for the fast first and the later slower second stage of the pilot-scale extraction of thyme at different temperatures (PSE1 and PSE2); — fast extraction; ---- slow extraction).

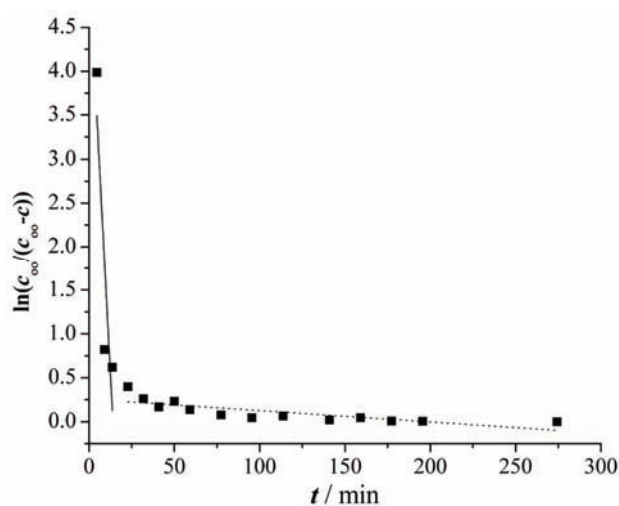


Fig. 7. Plot of the function $\ln(c_{\infty}/(c_{\infty}-c))$ against time for the fast first and the later slower second stage of SFE (— fast extraction; ---- slow extraction).

Considering the solvent extractions, the mass transfer rate described by D_1 could be increased by ultrasound, temperature increase or by stirring within the initial washing phase, while ultrasound particularly affected the mass transfer rate during the slow period of extraction (described by D_2) (Table III).

TABLE III. Diffusion coefficients of solute obtained for different extraction processes of thyme

Extraction method	f_1	f_2	F_1	F_2	$D_1 \times 10^{10} / \text{m}^2 \text{ s}^{-1}$	$D_2 \times 10^{11} / \text{m}^2 \text{ s}^{-1}$
Laboratory scale						
SE	0.842	0.802	0.512	0.488	0.13	0.81
USE	0.253	1.392	0.153	0.846	2.07	9.18
SFE	0.370	1.274	0.225	0.775	15.0	0.523
Pilot plant scale						
PSE1	0.910	0.732	0.554	0.446	4.04	3.41
PSE2	1.298	0.346	0.790	0.210	7.04	2.43

During the batch extraction of thyme with ethanol on the pilot plant scale, a temperature increase from 40 to 80.5 °C enhanced the extraction efficiency due to its positive effect on the solubility of the solutes. The temperature increase also enhanced the mass transfer rate in the washing phase due to the reduced viscosity at elevated temperatures. Agitation enabled enhancement of the mass transfer of solute particularly in the period of fast extraction (washing period), which was confirmed by the one order of magnitude higher diffusion coefficients for the PSE compared to the SE process at the same temperature (80.5 °C) (Table III).

To the best of our knowledge, there are no data available in the open literature on the values of the diffusion coefficients in extraction processes from thyme, except in one previously published study²³ in which the diffusion coefficient for the mass transfer through the glandular trichomes membrane in the SFE process was determined using mathematical modelling on the micro-scale.²² Obtained value of the diffusion coefficient through the peltate gland membrane was $3.5 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$.²³ This diffusion coefficient corresponds to the diffusion coefficient in the process of the slow extraction (after the easily accessible oil is exhausted), which was determined in this study to be $5.32 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ (Table III) using the mathematical model based on the Fick's Second Law. The similar values of the diffusion coefficients can be explained by the same extraction conditions (10 MPa and 40 °C), as well as by the similar chemical composition of the extracts, mainly composed of essential oil.

Herodež *et al.*¹⁷ investigated the kinetics of extraction from balm (*Melissa officinalis* L.) belonging to the same plant family as thyme (Lamiaceae) with an ethanol:methanol:2-propanol ratio 90:5:5 v/v in an ultrasonic bath for 1 h at room temperature. The authors used the same mathematical model as applied in this study except they considered the solid particles as flat plates with a thickness of $2L$ and reported one order of magnitude lower diffusion coefficients of carnosic,

ursolic and oleanolic acids for the period of the fast extraction (order of magnitude $10^{-11} \text{ m}^2 \text{ s}^{-1}$) as well as for the period of slow extraction (10^{-13} – $10^{-12} \text{ m}^2 \text{ s}^{-1}$) compared to the values obtained in this investigation. The reason for this lies in the fact that the higher molecular weight compounds present in the balm leaves (carnosic, ursolic and oleanolic acid with molecular weight of 332.43–456.71 kg kmol^{-1}) need more time to diffuse from the solid particle than the compounds present in the thyme ethanol extract. Reportedly,^{24,25} the thymol (molecular weight 150.22 kg kmol^{-1}) content in a thyme ethanol extract was still very high (8 %) and phenylindolizine (molecular weight 193.25 kg kmol^{-1}) was identified as the most abundant component. The lower values of diffusion coefficients reported by Herodež *et al.*¹⁷ could be also result from performing the ethanol extraction at a lower temperature (room temperature) than the temperatures applied in this study (40 and 80.5 °C).

CONCLUSIONS

An analysis of the mass transfer phenomena in the extraction of phytochemicals on the laboratory and pilot plant scale is necessary for process design. This work provides new data on the values of the diffusion coefficients in different extraction processes from thyme. In the fast extraction period, the diffusion coefficients were one to three orders of magnitude higher compared to those in the period of slow extraction. The highest diffusion coefficient was reported for the early stage of the SFE process, which was due to the physical properties of supercritical carbon dioxide. Concerning the solvent extractions, the mass transfer rate in the period of fast extraction and the corresponding diffusion coefficient can be enhanced by a temperature increase, ultrasound and stirring. The mass transfer rate and corresponding diffusion coefficients in the period of slow extraction was most affected by ultrasound.

NOMENCLATURE

c	Concentration of solute in the solution at time t , kg m^{-3}
c_{∞}	Concentration of the solute in the solution at infinite time ($t \rightarrow \infty$), kg m^{-3}
D_1	Diffusion coefficient in the constant extraction rate period, $\text{m}^2 \text{ s}^{-1}$
D_2	Diffusion coefficient in the decreasing extraction rate period, $\text{m}^2 \text{ s}^{-1}$
F_1, F_2	Fractions of the solute, which are extracted with diffusion coefficients D_1 and D_2 , respectively
f_1, f_2	Parameters obtained from the intercept of the curve when $\ln(c_{\infty}/(c_{\infty}-c))$ is plotted as a function of the extraction time t
m_e	Mass of the extract, g
m_{CO_2}	Specific amount of supercritical carbon dioxide consumed, $\text{kg CO}_2 \text{ kg}^{-1}_{\text{plant material}}$
m_{pm}	Mass of the plant material
R	Radius of the spherical particles, mm
T	Temperature, °C
t	Extraction time, min

t_{90}	Extraction time required for the achievement of 90 % recovery of the extractible substances under the given extraction conditions and extractant
V_s	Volume of solvent (70 % v/v aqueous solution of ethanol or supercritical carbon dioxide)
Y	Extraction yield, mass %.

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ИЗВОД

УПОРЕДНА АНАЛИЗА КОЕФИЦИЈЕНАТА ДИФУЗИЈЕ ЗА РАЗЛИЧИТЕ ПРОЦЕСЕ ЕКСТРАКЦИЈЕ ИЗ ТАМЈАНА

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Циљ овог рада била је анализа кинетике и феномена преноса масе за различите процесе екстракције из листа тимјана (*Thymus vulgaris* L.). Испитани су различити поступци екстракције са воденим раствором етанола: екстракција у апаратури по Сокслету, шаржна ултразвучна екстракција на лабораторијском нивоу као и шаржна екстракција са мешањем на полуиндустријском нивоу. Процеси екстракције са етанолом су поређени са процесом екстракције са наткритичним угљеник(IV)-оксидом на 10 МПа и 40 °С. Експериментални подаци су анализирани помоћу математичког модела заснованог на другом Фиковом закону у циљу одређивања и поређења коефицијената дифузије у периоду константне и опадајуће брзине екстракције. У периоду брзе екстракције, вредности коефицијената дифузије су биле један до три реда величине веће у односу на вредности коефицијената дифузије за период споре екстракције. Највећа вредност коефицијента дифузије била је одређена за период брзе екстракције код процеса наткритичне екстракције. Код процеса екстракција са етанолом, примена ултразвука, мешање и повећање температуре су позитивно утицали на брзину преноса масе у периоду испирања. С друге стране, највећи утицај на повећање брзине преноса масе у периоду споре екстракције имала је примена ултразвука.

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