VALORIZATION OF WASTE LAVENDER RESIDUE FROM THE ESSENTIAL OIL INDUSTRY FOR PRODUCTION OF ROSMARINIC ACID - A STUDY ON THE SOLID-LIQUID EXTRACTION

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ABSTRACT

The possibility for valorization of the waste lavender residue from the essential oil industry via solvent extraction was studied. The plant residue of Lavandula angustifolia, from which the lavender oil is extracted through steam distillation, contains Key Biologically Active Components (KBAC) such as: rosmarinic acid, caffeic acid, luteolin. The feasibility of the solvent extraction for their isolation was assessed by comparison of the kinetics and equilibrium of extraction of KBAC from spent and raw plant material (collected from the same batch before the steam distillation) using different solvent compositions. The parameters of the extraction process were experimentally and numerically optimized. To determine the most efficient solvent, two pure and two mixed solvents were tested: pure water, 99.9 % ethanol and their mixtures – (40 % and 60 % ethanol). Using 40 % ethanol as extraction solvent resulted in maximum recovery of KBAC. A mathematical model for the solid-liquid extraction from lavender materials was developed. The values of the model parameters were determined using the Regular regime method. A four-parameter empirical model for prediction of the effective diffusivity, D_{eff}, was also applied. The model adequacy was experimentally verified. Based on the theoretical and experimental results KBAC recovery the following extraction conditions were recommended: extraction time – 30 min, temperature - 30 °C, liquid-solid ratio - 0,01 m^3 kg^{-1} and 40 % ethanol as an extraction solvent.

Keywords: solid-liquid extraction, kinetics, lavender, modeling, rosmarinic acid, essential oil.

INTRODUCTION

The global essential oils market demand was estimated at 247.08 kilotons in 2020 and is expected to grow at a compound annual growth rate of 7.5 % from 2020 to 2027 [1]. The essential oils have gained their importance in therapeutic, cosmetic, aromatic, fragrant and spiritual uses [2, 3]. Their production generates enormous amount of residual biomass. These waste residues contain natural antioxidants which have attracted attention due to their beneficial effects to human health [4]. Their solid state allows straightforward removal of the contained bioactive substances from the matrix using an appropriate solvent. After target compounds isolation the residues were utilized for energy production [5]. There are some investigations aiming at valorization of waste residue from the essential oil industry but more complex investigations in this field are necessary [6].

Recently Bulgaria has overtaken France to become the world leader in lavender oil production with approximately 51681 tons of lavender fresh flowers produced during 2019. *Lavandula angustifolia* is the most widely cultivated species. During the production of lavender essential oil by steam distillation, the lavender volatile organic compounds are collected in the essential oils [7, 8]. Therefore, non-volatile organic components are expected to remain in the waste lavender

residue (WLR). This is an incentive for investigating the possibility for valorization of the waste lavender residue from the Bulgarian essential oil industry by solid-liquid extraction in the present study.

The KBAC are commonly isolated from the plant material by solid-liquid extraction [9]. Solid-liquid extraction is widely used for production of ingredients for the pharmaceutical, cosmetics, tobacco, and food industries and also applied for environmental purposes [10]. Selection of the most appropriate solvent for extraction is required to maximize the degree of extraction and minimize the operational costs.

Different aspects of KBAC solvent extraction from WLR and raw material (RM) have been object of research. Major attention has been paid to the use of water-ethanol mixtures as commercial solvents due to the ethanol safety and low price, as well as due to their higher capacities than water or ethanol alone. Concentrations of ethanol from 0 to 99.9 % (v/v) were investigated, and highest extraction degrees of KBAC were observed within the range from 30 % to 60 % ethanol [11, 12]. Temperature of 40 °C and liquid-solid ratio of 0.01 m^3 kg^{-1} were found favorable for the extraction rate [13 - 15].

Mathematical modeling is a powerful means for optimization of the equipment, simulation, design and control, allowing theoretical description of the process and evaluation of the mass transfer coefficients. A brief review and discussion of the various methods for mathematical modeling of solid-liquid extraction of plant raw materials is given by Simeonov et al. [10].

The extraction of valuable components from plant materials is most often limited by the mass transfer inside the pores of the solid phase. Each experimental kinetic curve represents in a hidden way all the factors influencing the diffusion rate - polydispersion, anisotropy, solid particles shape, and liquid phase concentration change. These factors are quantitatively evaluated by the effective diffusion coefficient ($D_{ef}f$) [16, 17]. The exact calculation of D_{eff} is of significant importance for the process engineering. A combination of the experimental and process analytical data is used for the calculation of D_{eff} using the Regular regime method [16, 17].

This study aims to prove the viability of the solid-liquid extraction with hydro-alcoholic solvents for WLR valorization. The objective was approached by investigating the KBAC extraction kinetics from WLR and comparing it to that from RM. Target KBAC of lavender were rosmarinic acid, caffeic acid and luteolin which are representatives of the polyphenolic acids and flavonoids. A preliminary step was the experimental determination of a most efficient extracting agent (solvent), which is beneficial to the process economy. The optimal operating parameters of solid-liquid extraction were obtained based on the experimental and mathematical modelling data.

EXPERIMENTAL

Materials and chemicals

The waste lavender residue and raw plant material from one and the same batch were obtained from Galen-N Ltd. (Zelenikovo, Bulgaria). *Lavandula angustifolia* was grown in the region of Chirpan, Bulgaria, and collected in July 2020. The waste lavender residue (WLR) is the exhausted plant material after the essential oil extraction via steam distillation. The raw material (RM) was collected prior to the process of steam distillation. The plant material comprised of all stems, leaves and flowers. The material was dried at ambient temperature in a dry, well ventilated place and avoiding direct sun light. Sufficient amounts from both samples were milled and stored in airtight containers until utilization.

The solvents used were ethanol (p.a. 99.9 %, Valerus Ltd.), methyl alcohol, anhydrous and acetonitrile (ChromaAR HPLC Super Gradient - from Macron fine chemicals), water (ChromaAR HPLC - from Macron fine chemicals). Luteolin (97 %) was obtained from Alfa Aesar, rosmarinic acid (> 97 %) and caffeic acid (> 98 %,) from Sigma Aldrich.

Extraction design and operating conditions

Kinetic experiments of periodic extraction of lavender in a batch reactor were conducted. A diagram of the experimental installation is presented in Fig. 1. The extractions were performed in a stirred vessel 1. The angular velocity of the mixer was measured by the rev-counter 7 and regulated by the electronic regulator 6. The agitation rate of n = 4 s^{-1} was selected to ensure limiting internal diffusion [10]. At these conditions the process is limited by intraparticle diffusion (the external diffusion resistance is eliminated). Operating

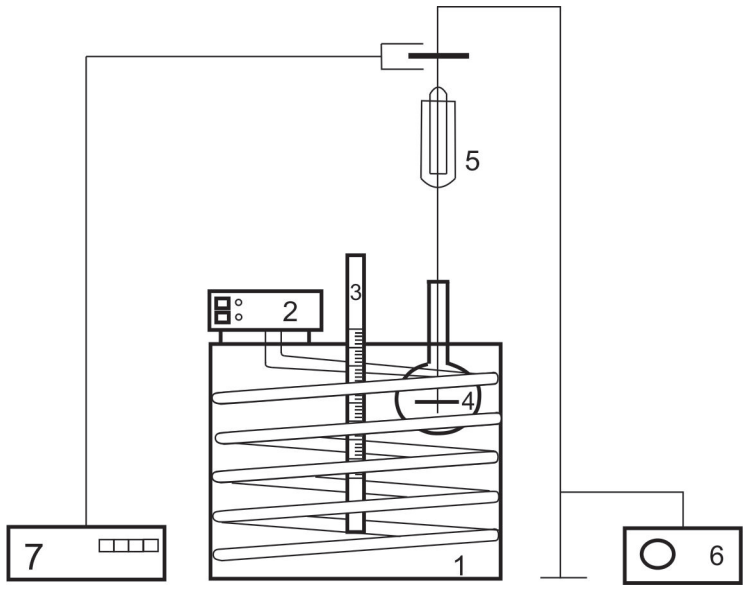

Fig. 1. Experimental set-up: 1- stirred vessel; 2 - heat controller; 3 - thermometer; 4 - extractor; 5 - hydraulic seal; 6 - electronic regulator; 7 - rev-counter.

temperature of 30°C was maintained by means of the thermometer 3 and heat controller 2.

A number of experimental series at liquid/solid ratio $\xi = 0.01\ m^3\ kg^{-1}$, temperature 30°C and different solvent compositions were carried out. After the extraction or at a certain time during the extraction samples were taken and sequentially filtered through filter paper and micro filter (0.2 μm RC) to separate the solids from the liquid phase.

HPLC method for KBAC analysis

The content of KBAC in the obtained liquid extracts was determined by means of high-performance liquid chromatography (HPLC). Considerable number of works related to processing or application of natural extracts containing KBAC such as rosmarinic acid, caffeic acid, luteolin, carnosol, etc. relied on HPLC analysis for their quantification [12, 13, 18 - 23]. The method used in the present work was adapted from the literature [12, 13]. A ternary Hewlett Packard (HP), Series II 1090 liquid chromatography system was used, equipped with an UV-Vis diode array detector. The separation is carried out in an Agilent C18 column (15 mm x 4.6 mm, 5 μm particle size). The analysis conditions were 30°C, 0.7 mL min^{-1} flow rate, and 5 μL injection volume. The mixture of solvent A (75 mL acetonitrile + 420 mL water + 4.25 mL acetic acid) and solvent B (methanol) as a mobile phase was used. To achieve a sufficient separation, a method with 105 min duration and variable solvents gradient according to the following conditions: (1) 0–90 min, B: 0–100 %; (2) 90–103 min, B: 100–100 %; (3) 103–104 min, B:100–0 %; (4) 104–105 min, B: 0–0%, was applied. Two detection wavelengths were preset – 330 nm for rosmarinic and caffeic acid and 360 nm for luteolin. The peaks of target compounds in the chromatograms of the obtained extracts were identified by comparison of the retention times with those of their standards. Typical chromatograms of samples from hydroalcoholic extracts from lavender at 330 nm detection wavelength are shown in Fig. 2.

The HPLC method was calibrated with respect to KBAC by analyzing series of standard solutions, using six levels of concentration which covered the concentration range 0 - 2 g $L^{-1}$for all compounds. The coefficients of linear correlation for all calibration lines were over 0.996.

Plant material particle size characterization

Size and shape of the powder plant materials in this work were determined with a Camsizer XT system (Retsch Technology) with a dynamic measurement range of 1 μm to 3 mm in the X-Jet module for air pressure sample dispersion to avoid agglomeration of fine particles. The dispersion pressure was adjusted to

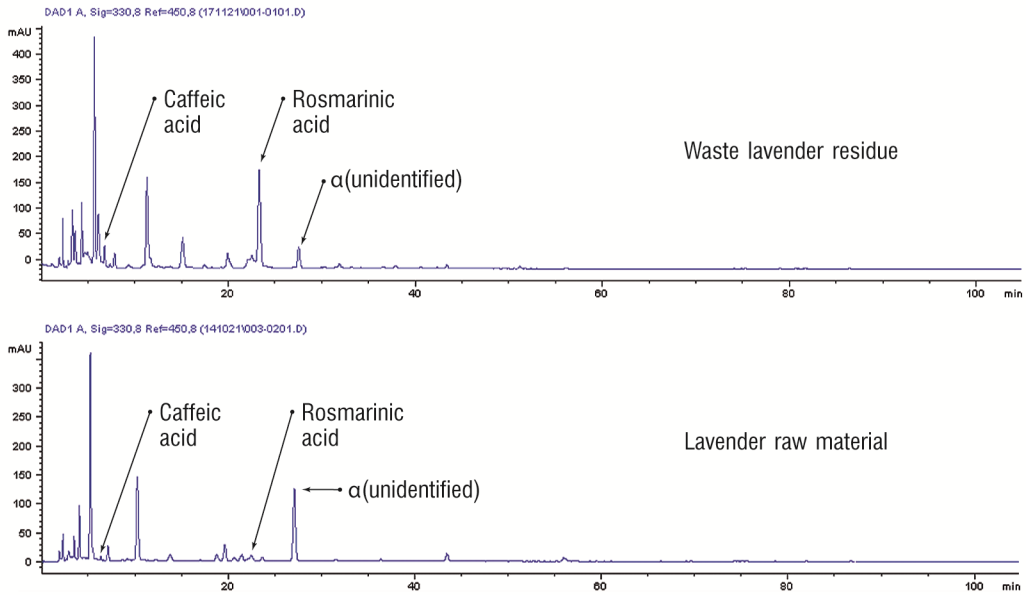

Fig. 2. Typical chromatograms at 330 nm detection wavelenght for extracts from WLR and lavender RM. Both samples were taken from extraction kinetics experiments at the 20th min.

50 kPa for analysis of the dried and milled lavender. The measurement is based on optical particle evaluation.

As a particle diameter, d_{Sa}, the calculated Sauter mean diameter is adopted:

$$d_{\mathrm{Sa}} = \frac{1}{M_{-1,3}} = \frac{1}{\int_{x_{min}}^{x_{max}} x q_3(x) dx} \quad (1)$$

where x_{min} is the particle size below which there are no particles in a given size distribution, x_{max} is the particle size above which there are no particles in a given size distribution, $q_3(x)$ is the volume (mass) distribution density, $M_{-1,3}$ is the complete first moment of a $q_3(x)$ – sample distribution.

KINETIC STUDY AND MODELLING

Diffusion model

The extraction from solid materials is described by the nonstationary diffusion equation. In porous solids, for the three "classical" shapes of the solid phase (i.e. unlimited plate, infinite cylinder and sphere), the equation for symmetrical mass transfer has the following form:

$$\frac{\partial C_2(x,\tau)}{\partial \tau} = \frac{1}{X^t}\frac{\partial}{\partial X}\left[X^t D_{eff} \frac{\partial C_2(x,\tau)}{\partial X} \right] \quad (2)$$

This is a second order partial differential equation. At a constant value of the effective diffusion coefficient $D_{eff} = const$ it can be rearranged in the form:

$$\frac{\partial C_2}{\partial \tau} = D_{eff}\left(\frac{\partial^2 C_2}{\partial x^2} + \frac{t}{x}\frac{\partial C_2}{\partial x} \right) \quad (3)$$

The main equation is solved with the boundary and initial conditions presented below. The boundary condition, which assumes equality of the mass flow from the solid phase to the surface towards the mass flow in the fluid phase, is represented with Eq. (4).

$$-D_{eff}\left(\frac{\partial C_2}{\partial x} \right)_{x=x} = k\left(\frac{C_{2_{x=x}}}{m} - C_1 \right) \quad (4)$$

The boundary condition which shows a lack of mass flow in the center of the model particle is represented with Eq. (5):

$$\left(\frac{\partial C_2}{\partial x} \right)_{x=0} = 0 \quad (5)$$

The initial conditions at time zero is written as:

$$C_{2,\tau=0} = C_0 \quad (6)$$

The general analytical solution has the form:

$$\frac{C_0 - \overline{C_2}}{C_0 - C_m} = \frac{1}{1+\beta} - \sum_{n=1}^{\infty} \frac{4.(\upsilon+1)}{\mu_n^2 + 4(\upsilon+1)^2.\beta(1+\beta)} . \exp^{-\mu_n^2 \frac{D_{eff}\tau}{R^2}} \quad (7)$$

where C_0 is the initial concentration in the solid phase; $C_m = C_{1i}$ by periodical processes; C_{1i} -initial concentration in the liquid phase; $\overline{C}_2$ - average concentration in the solid phase; D_{eff} - effective diffusion coefficient in the pores of the solid phase; R - size of the solid particles; τ - time;

$$\beta = \frac{C_{1eq}}{C_0 - C_{1eq}} \ ;$$

C_{1eq} - equilibrium concentration in the liquid phase; μ_i - roots of the characteristic equation; v - shape factor for the solid phase; m - distribution coefficient, $m \approx 1$ because of the low concentration range (well known fact in literature for the investigated type of plant materials). The values of model coefficients were determined by means of the Regular regime method.

Regular regime method

This method is based on a comparison between the experimental data obtained under conditions of non-steady state mass transfer from the solid into the liquid phase, $\overline{C}_1 = f(\tau)$, with the analytical solutions (Eq. 2) under the same conditions. Adopted is the boundary case of $Bi = \infty$ and $\beta \to 0$ [24],

where $Bi = \frac{kR}{D_{eff}}$ and k is the local mass transfer coefficient, m s^{-1}. It is known that at the beginning of this regime $D_{eff} = const$ and from equation (7) for cylindrical shape of the solid phase with $\tau = 0, C_2 = C_0 = const, C_{1i} = 0$ one can obtain Eq. (8):

$$\frac{\overline{C_2}}{C_0} = \sum_1^{\infty} \frac{4}{\mu_n^2} e^{-\mu_n^2 Fo} \ , \qquad (8)$$

In Eq. (7) $Fo = \frac{D_{eff}}{R^2}$ is the Fourier number. With the increase of Fo > 0.198 (and respectively τ) the convergence of Eq. (8) increases and can practically be limited to its first term.

$$\frac{\bar{C}_2}{C_0} = B_1 e^{-\mu \frac{D_{eff}\tau}{R^2}} \qquad (9)$$

For the investigated system Bi→∞; B=0.69; μ=2.4 [10, 24, 25] and Eq. (9) becomes:

$$\lg \frac{C_2}{C_0} = \lg B_1 - 0{,}434 \mu_1^2 \frac{D_{eff}\tau}{R^2} \qquad (10)$$

or

$$D_{eff} = \frac{R^2}{0.434 \mu^2 \tau} \lg \frac{C_0 B_1}{C_2} \qquad (11)$$

RESULTS AND DISCUSSION

The main factors predetermining the viability of a solvent extraction process are temperature, solid-to-liquid ratio, extraction solvent, and time of extraction. In this study the temperature and solid-to-liquid ratio were selected based on sufficient data for their impact on the extraction of the same KBAC from plant materials. The optimal composition of the used as extraction solvents water-ethanol mixtures was determined experimentally. The optimal time of extraction for the specific milled plant material was evaluated through experimental and numerical investigation of the extraction kinetics.

WLR and RM particle size characterization

Fig.3 shows the cumulative particle size distributions (Q_3) and the volume distribution density (q_3) of lavender powder from WLR and RM. The mean Sauter diameters of the WLR and RM are 218 ±26 and 292±14 μm respectively, whereas the mean diameters of 50% ($d_{50.3}$) of the particles are smaller than 563±106 and 692±7μm. The Q_3 curves represent the percentage by volume of particles with a mean diameter equal to or smaller than a certain value in the range from 2 to 3000 μm in accordance with the limits of the measurement method. The q_3 curves show the volume distribution density. The curves shown in Fig. 4 are mean curves calculated as an average from minimum of 3 measurements for each fraction. Additionally, the q_3 distributions are smoothed with an adjacent averaging method with 20 points per window. The standard deviations given are calculated from the average (minimum of 3 measurements) for each plant material.

The widely spread distributions as well as the broad size-class measurement interval (0 to 3000 μm) necessary to cover all particle size classes and the significant difference between the two types of mean diameters adopted (d_{Sa} and $d_{50.3}$) indicates that the solid phase contains various sized particles proving to be challenging for particle size and shape analysis.

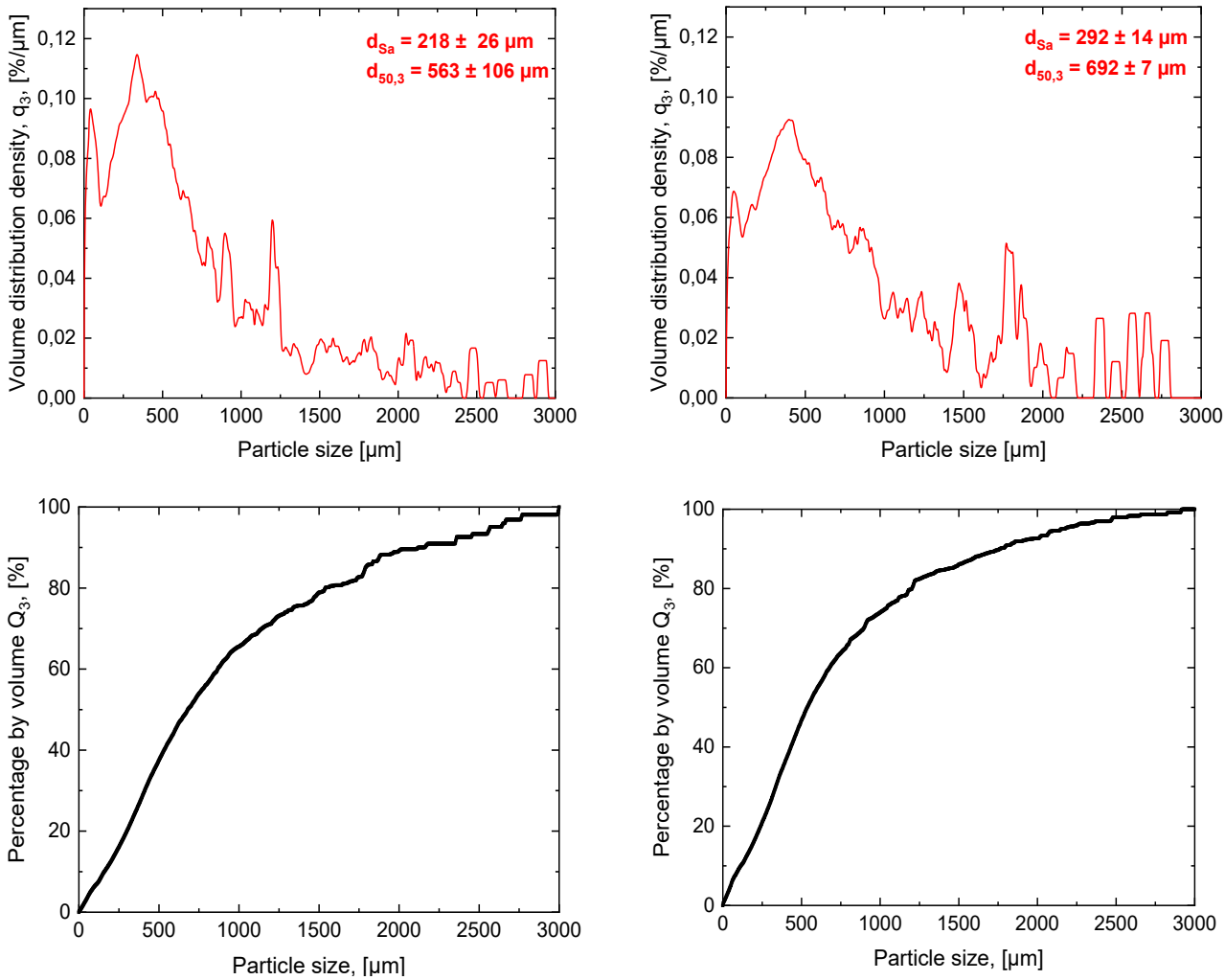

Fig. 3. Left - WLR, right – FRM; Up - q_3 volume distribution density, down - Q_3 percentage by volume.

Solvent selection

In this work, two pure and two mixed solvents were tested, respectively: pure water, 99.9 vol. % ethanol and mixtures between them - 40 vol. % and 70 vol. % ethanol. Hydro-alcoholic solvents were selected for extraction because the solvent polarity can be adjusted varying the ethanol concentration, these solvents are well known for their efficiency in the extraction of bioactive substances from plant materials, and for their safety in food and pharmaceutical applications. Thus, the extraction equilibrium with the four solvents of 0 vol. %, 40 vol. % and 60 vol. % and 99.9 vol. % ethanol were experimentally investigated. The results for the equilibrium concentrations of KBAC in the obtained extracts from WLR are shown in Fig. 4.

Obviously, with all solvents rosmarinic acid is the dominating KBAC amongst the three target compounds. Maximum amounts of KBAC in 40 % ethanol were found. This result is in agreement with the findings in earlier studies dealing with extraction of these components from rosemary [26, 27]. The measured equilibrium concentrations of the studied KBAC in the extracts from lavender RM were marginal as also can be seen from Fig. 2. Interestingly, the extracts from both plant materials have similar compositions of phytochemicals absorbing at 330 nm, with exception of rosmarinic acid and the unidentified compound α (Fig. 2). Rosmarinic acid is present in high concentrations in extracts from WLR while the peak for α is less intensive. Vice-versa, in extracts from RM, the peak for α is as intensive as the peak for rosmarinic acid in WLR extracts, while the peak for rosmarinic acid is marginal.

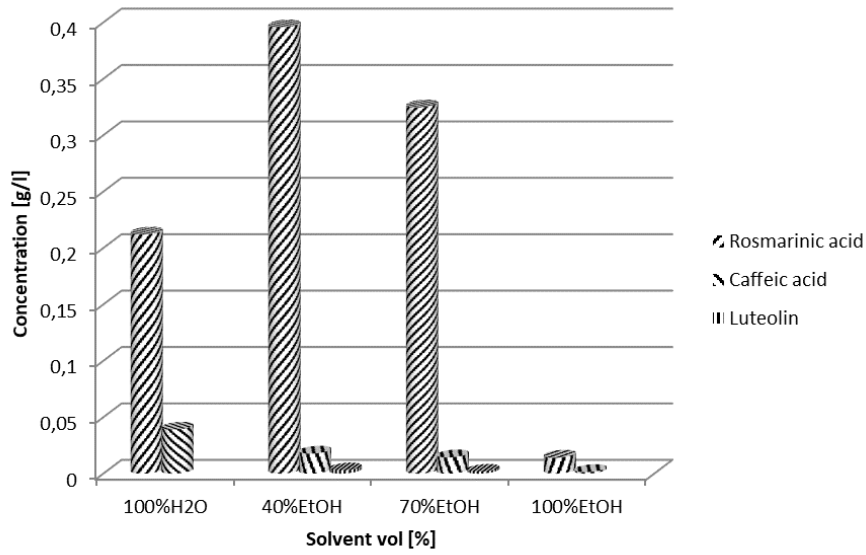

Fig. 4. Equilibrium concentrations of KBAC in extracts from WLR with different solvent compositions.

This fact underscores the potential of WLR from the essential oil industry as a feedstock for the production of rosmarinic acid.

Extraction kinetics

Experiments for studying the extraction kinetics were performed with 40 vol. % ethanol as a solvent, which has been selected as an optimal solvent based on the equilibrium study. Rosmarinic was chosen as modelling compound representative for all KBAC in the extracts. Extraction kinetics was found to follow similar trends with respect to caffeic acid and luteolin.

Determination of the effective diffusion coefficient

The model described above can be used for extraction processes with various types of plant materials with different internal structure and size of the solid phase particles, as well as when applying various extraction solvents and the same plant material. Practically, to use this model one needs to obtain the value of the effective diffusion coefficient (D_{eff}) [28]. It is a complex function of the pore diffusion coefficient and the structure of the solid phase - pore size distribution, tortuosity, etc. [29, 30]. During the extraction process, the solid phase changes its structure regularly or irregularly, thus D_{eff} generally depend on the spatial coordinates and time. This parameter can be obtained by means of the regular regime method (RRM) (Eq.11).

In order to use D_{eff} in the numerical scheme for solving the mathematical model, values for D_{eff} for any time point must be known. When using RRM, only discrete values of D_{eff} for experimental time points can be determined. Therefore, the discrete values of D_{eff} obtained via RRM were regressed with an appropriate function. A four-parameter model for the effective diffusivity was suggested [31]:

$$D_{eff} = ae^{b\tau} + ce^{d\tau} \quad (12)$$

On the legend of Fig. 5 with D_{eff} *RRM* are indicated the discrete values of D_{eff} obtained by RRM, and with D_{eff} *Appx* (continuous curve) the approximated values of D_{eff}. The parameters *a, b, c* and *d* in Eq.11 were determined non-linear regression. A very good coincidence between D_{eff} *RRM* (with mean square error of $R^2 = 0.9906$) and calculated results was observed.

Numerical solution

The model presented above was solved numerically using MatLAB software. „pdepe", solves initial-boundary value problems for systems of parabolic and

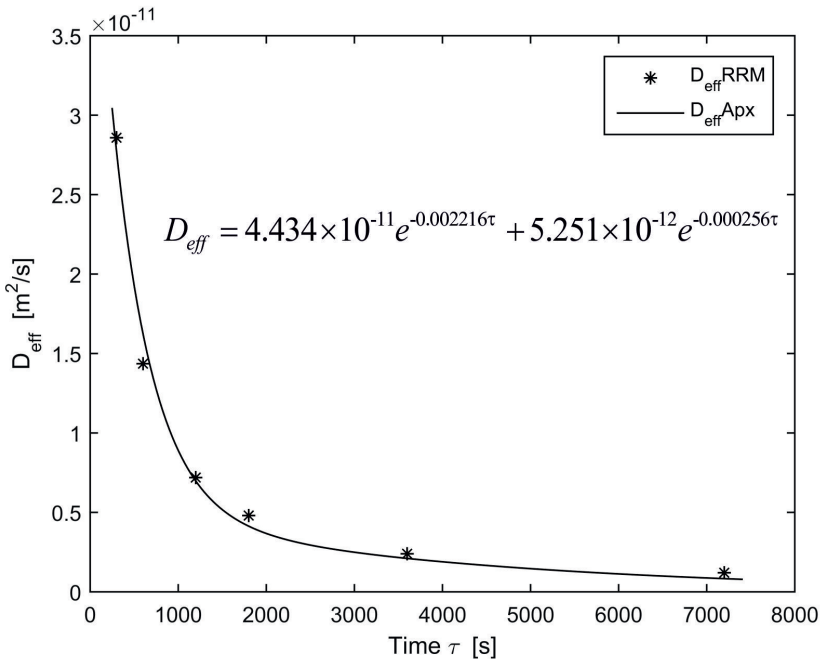

Fig. 5. Determination of D_{eff} of rosmarinic acid.

elliptic PDEs with variable coefficients in one space variable *x* and time *t*. Coefficients can depend on x,t, C and $\frac{\partial C}{\partial x}$.

This function can be used for different types of symmetry - slab, cylindrical, or spherical. The mean Sauter diameters of 218±26 and 292±14 μm, for WLR and RM respectively, were used in the model.

The mathematical model was verified through comparison with the experimental data for rosmarinic acid extraction from WLR and RM, illustrated in Fig. 6.

A coincidence between experimental (marker symbol) and model results (continuous curves) is

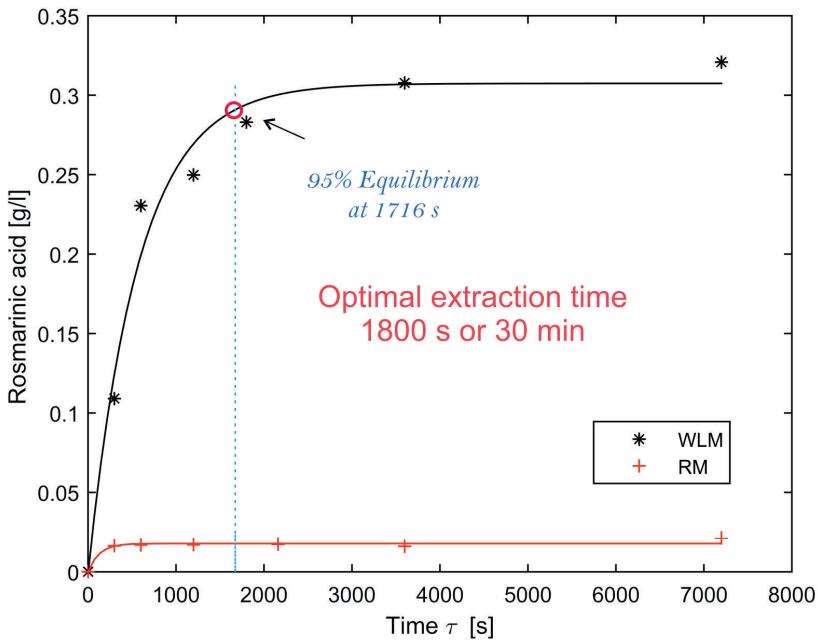

Fig. 6. Numerical solution.

obvious. A rapid yield increase in the beginning and slow solute recovery at the end has been observed [28 - 31]. In Fig. 6 is also evident an order of magnitude higher concentration of rosmarinic acid in extracts from WLR compared to RM. This may be explained with the changed structure of the WLR plant matrix following the steam distillation and the removal of the essential oil components. We speculate that rosmarinic acid is extracted from structures in the WLR plant material that were previously inaccessible for the extraction solvent. Besides, before the steam distillation, the non-polar molecules of the lavender essential oil are present in the solid matrix of RM and hinder the extraction of KBAC by the polar hydro-alcoholic solvents. The degree of extraction can be calculated by the following expression:

$$\eta = \frac{C_{1eq} - C_1}{C_{1eq}} \times 100\% \quad (13)$$

The numerical results showed that for the WLR a degree of extraction η = 95 % was reached at 1716 s after the beginning of the extraction. Consequently, the optimal time of 1800 s was derived for the specific plant materials.

CONCLUSIONS

The present investigation has confirmed possibility for valorization of the waste lavender residue from the essential oil industry via solid-liquid extraction of contained biologically active compounds. HPLC methods for detection and quantification of key biologically active compounds such as rosmarinic acid, caffeic acid and luteolin in the obtained liquid extracts were developed. The dried and milled plant materials for extraction were characterized in terms of their particle size distribution and mean geometrical dimensions. The extraction equilibrium and kinetics from waste lavender residue and lavender raw material were experimentally investigated. Ethanol-water mixtures with four different compositions ranging from pure water to absolute ethanol were tested for their ability to extract the target bioactive constituents from both the spent and the raw material. The solvent with ethanol-water ratio 40:60 (v/v) offered the highest extraction capacity.

A mathematical model for modeling of the solid-liquid extraction from the lavender plant materials was developed and solved numerically. The effective diffusion coefficient of rosmarinic acid in the solid phase was calculated by means of the method of regular regime. A simple exponential function to approximate D_{eff} was successfully used. A very good agreement between experimental results and model predictions was found.

A simplified qualitative explanation for the experimentally observed higher yield of the rosmarinic acid in the extract from the waste lavender residue compared to the one from the raw material was proposed.

Based on the results achieved, the optimal operating conditions for recovery of rosmarinic acid from waste lavender residue via solvent extraction were stated - extraction time 30 min; temperature 30 °C, solid to liquid ratio, 0.01 m^3 kg^{-1} and solvent composition 40 vol. % ethanol. The proposed methodology and mathematical model can be used for the design of the extraction process from different plant species and with variable operational parameters influencing the process efficiency.

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