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Extraction simulation of porous media by CFD: recovery of trans-resveratrol from grape cane by pressurised low polarity water system

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Graphical abstract

Highlights

- A mathematical model consisting of heat, mass, momentum transfer with thermal degradation is developed for a semi-continuous pressurised low polarity water extraction.
- The model is able to predict extraction efficiency reflecting the changes in process conditions.
- The model produces valuable information about medium temperature, flow patterns and molecular and convective transfer of target solute.
- A good agreement between the experimental and predicted results was obtained.
- The developed model also contributes to design efforts in terms of solid and column properties like particle size, particle and bed porosity, column dimensions etc.

Abstract

A mathematical model of coupled momentum and mass transfer including thermal degradation of trans-resveratrol from grape cane powder was developed. The experimental results, which were used for model validation, were based on a solid-liquid extraction study which was previously conducted using a semi-continuous pressurized low-polarity water (PLPW) column extraction system. During extraction, the system is considered to work under isothermal and steady-state conditions regarding heat and momentum transfer. Verification of those assumptions is also obtained by the simulation of related time-dependent physics. The used mathematical models are based on macroscopic porous medium approach with volume averaged physical properties. The resulting equations were solved using Finite Element Method by COMSOL Multiphysics® version 5.3a. The model enables the prediction of the temperature distribution at pre-heating period, and concentration and degradation of trans-resveratrol in the column. The model can also simulate the changes in temperature and ratio of ethanol in the aqueous extraction solvent.

Keywords: finite element method, modelling, COMSOL, semi-continuous column

1. Introduction

In recent years consumers' perception leads the food industry to search natural sources for the production of value-added products. So this interest in bioactive/sanative compounds has encouraged researchers to find potential new sources. By-products of the agricultural industry are good sources of high-value phytochemicals and value-added industrial products like phenolic compounds, colouring and/or flavouring agents, antibiotics, anti-inflammatory agents etc. [1, 2]. In this extent, Rayne, Karacabey and Mazza [3] have previously discussed the potential of grape (*Vitis vinifera* L.) canes, a waste by-product of viticulture, being a natural and economic source of trans-resveratrol. Trans-resveratrol (a member of stilbenes) demonstrated a broad spectrum of biological effects including antioxidant capacity, cardioprotection, anticancer activity, anti-inflammatory effects, and estrogenic/antiestrogenic properties [4-7]. Thus, trans-resveratrol and its extraction potential from grape cane were extensively investigated [3, 8, 9].

The bioactive compounds in the agricultural wastes/by-products can be recovered using different extraction methods. The methodology depends on several parameters such as matrix being processed, selectivity, energy consumption, equipment cost and the value of the extract [10]. Among extraction techniques, column/solvent extraction is a widely applied one to gain target compounds from a solid matrix by the help of an appropriate solvent. For instance, Karacabey and Mazza [8] and Karacabey and Mazza [9] investigated the yield and antioxidant potential of grape cane extracts and optimized solid/liquid extraction process. However, there are some drawbacks like a high volume of solvent usage, low extraction performance, long processing time, poor product quality associated with using conventional extraction methods. To overcome these negative aspects of conventional extraction, there is an increasing demand to find more environmentally gentle and more effective extraction processes [11-13]. One of methods reported in literature is the use of pressurized low

polarity water (PLPW) extraction. It is also known as subcritical water extraction promising in extraction of polar and slightly non-polar compounds from biomaterials [14, 15].

The efficiency of PLPW is affected by several factors: temperature, time, solvent flow rate, particle shape and size, bed depth, and porosity as well as the presence of co-solvents as a modifier. In PLPW, pure water or its slight modifications with reagents are used as a solvent [14, 16, 17]. To achieve the high quality final product, process optimization and control practises should be followed. So the assessment of semi-continuous PLPW system is important to better understand the relation between process parameters and extraction performance, and to improve and/or to manipulate the process depending on the aims. However, process assessment, control and optimization are mostly based on experimental results and related statistical analysis rather than on predictive, engineering calculations [18, 19]. These studies are mostly based on the point of the kinematic view. Although it is simple for adoption to any food processing system, there are some limitations for their use, e.g., a requirement of new experimental data for each case; limited outcomes, ignoring lots of parameters etc. To overcome these drawbacks, new modelling approaches may be used. Mathematical models including momentum, heat and mass transfer phenomena are helpful to better understand the extraction system. Moreover, a multiphase porous media model of PLPW system can help to describe complex mechanisms of the extraction process and to explain system reactions against the change of process conditions (such as temperature, solvent concentration and flow rate) and material properties (effective diffusivity, permeability, viscosity, particle size, porosity of column and porosity of solid matrix etc.). But unfortunately, to the best of our knowledge, there is no study in the literature on CFD modelling of PLPW extraction technique.

Therefore, the objectives of this study are (1) to develop a mechanistic model for porous domains that includes heat, mass and momentum transfer with thermal degradation of bioactive compounds during a semi-continuous PLPW extraction process for extraction of trans-resveratrol from grape

cane, (2) to assess model responses against different process conditions (temperature, solvent composition and solvent velocity).

2. Modelling of transport phenomena

2.1. Model Description

A schematic diagram of the extraction cell, porous and liquid (non-porous) domains, used transfer and simplifications are presented in Figure 1. For further technical details about the cell and extraction procedure can be found in Cacace and Mazza [13] and Karacabey, Mazza, Bayındırlı and Artık [20]. For the simplification and to reduce computational requirements, two-dimensional axisymmetric geometry of a three-dimensional extraction column was considered for simulation where axial symmetry boundary was defined along the z-axis.

Three domains existed in the model (see Figure 1) which are;

- 1) The liquid domain where non-porous material was found at the inlet and outlet of the cell since there were frits at both endings to develop a uniform flow throughout the extraction cell,
- 2) Frits (including glass wool) and pipe walls where frits were used to disperse the flowing solvent homogeneously and,
- 3) The porous domain where grape cane powder (stagnant) was loaded and the solvent was flowing through and the porous medium was fully saturated.

In the developed model fluid flow (solvent solution), mass transfer with diffusion in particles forming porous domain and solvent, mass transfer by convection and heat transfer are considered.

Momentum conservation was developed from the Navier-Stokes equation and for the porous domain, Brinkman's equation (Darcy's extension of Navier-Stokes equation) was used.

2.2. Assumptions

Karacabey, Mazza, Bayındırlı and Artık [20] assumed that temperature distribution in the extraction cell was homogenous and kept constant at a set value. To verify the validity of the assumption, the time-dependent change of temperature was firstly investigated by a series of simulation. In these simulations liquid solvent was stagnant, so the only mechanism of heat transport was conduction (for results see section 3.5.). As a result, pre-extraction temperature profile of the system was obtained. Then, the temperature in the extraction cell was assumed to be constant and homogenous during extraction procedure following pre-heating step. As a macroscopic approach to porous materials, all phases were assumed to be continuous and local thermal equilibrium was valid which means temperatures of solid and liquid phases in the porous domain were equal [21].

Following pre-heating, the extraction was started by pumping the solvent at a specified flow rate. The desired pressure in the extraction cell was adjusted using a back pressure regulator (Upchurch Scientific, Oak Harbor, WA, USA) operating at a pressure level of 5.2 MPa. So the outlet pressure was 5.2 MPa. In the proposed model, the effect of frits on the flow field was neglected, since the flow passed through the cell against gravitational force. That is why the flow field at the entrance of the porous domain was found sufficiently homogenous. Moreover, the effect of frits on pressure was pretty small compared to the backpressure regulator. The Mach number (calculated to be between ≈ 0.005 - 0.03 for 0.5 - 3 ml/min) was well below 0.2 - 0.3 . Therefore, compressibility effects were small and the extraction solvent can be assumed to be incompressible. The flow was laminar at the tube inlet and outlet since Reynold's number was smaller than 2100 [22], and flow characteristics were Darcy for porous media (porous media Reynold's number by Ergun were between 0.03 - 0.2 for 0.5 - 3 ml/min at 105 - 160°C) [23, 24]. As a common approach in the literature, the fluid flow was simulated at steady state to decrease computational load. Thus there was no need to re-compute it during mass transfer simulation [25-27].

Regarding mass transfer, the phenolic molecules were transferred throughout the extraction solvent with diffusion and bulk flow. However, through the solid spheres forming porous medium, the only

mechanism regulating mass transfer was assumed to be diffusion. So the concentration was continuous between boundaries of grape cane particles and liquid solvent. As a particle size of the solid matrix, an averaged particle diameter was used [20]. Moreover, the Péclet number can be related to the efficiency of different mass transfer mechanisms and it is defined as a ratio of convective flux to molecular flux. Depending on the Péclet number, total flux is composed of sum of these both mechanisms ($Pe \approx 1.0$) or dominated by one of them ($Pe \ll 1.0$ molecular flux or $Pe \gg 1.0$ convective flux) [28, 29]. Different versions of the Péclet number for different systems can easily be found in the literature, however in column studies, Eq. 1 was suggested by Fetter [30].

$$Pe = \frac{ud}{D_d} \quad (\text{Eq. 1})$$

where u is velocity (m/s), d is average particle diameter (m) and D_d is molecular diffusivity in water (m^2/s). It was previously noted that molecular diffusivity of different compounds is about $1 \times 10^{-9} \text{ m}^2/\text{s}$ in water or liquids [31-33]. According to the Péclet number (calculated as $Pe \approx 1.83-10.93$ for 0.5-3 ml/min), mass transfer is dominantly held by advection in PLPW system thus effect of molecular diffusion for trans-resveratrol (tR) in extraction solvent was neglected [28].

To sum up, the assumptions were listed below.

- The porous matrix was rigid during extraction.
- Thermal equilibrium throughout the porous domain (for assumption verification) and isothermal/steady-state conditions (for extraction simulations) were considered for temperature [20].
- Liquid transport was affected by pressure gradient and gravitational effects.
- Flowing fluid was incompressible (calculated as $Ma \approx 0.005-0.03$), the flow was laminar/Darcy where it was appropriate and flow pattern was stationary.
- Molecular diffusion has no effect on the mass transfer, however advection dominates the diffusive movement of extracted molecules.

- Soret and Dufour effects were neglected because they have cooperatively small effects on heat and mass transfer [34].
- Any reaction, e.g. evaporation of solvent which was avoided by a back pressure regulator providing the pressure level specified for this system, contributing to heat and flow issues did not exist.
- Viscous heat dissipation and pressure work can be neglected.

2.3. Governing Equations

2.3.1. Momentum equation

Stationary bulk flow of the used solvent in extraction tube is defined with Navier-Stokes equation [35],

$$\nabla \cdot \mathbf{u} = 0 \quad (\text{Eq. 2})$$

$$\rho_s(\mathbf{u} \cdot \nabla \mathbf{u}) = -\nabla p + \mu_s \nabla^2 \mathbf{u} + \rho_s \mathbf{g} \quad (\text{Eq. 3})$$

where $\mathbf{u}$ was velocity of fluid (m/s), p was pressure (Pa), μ_s was dynamic viscosity (Pa.s), ρ_s is density (kg/m³), $\mathbf{g}$ is gravitational acceleration in the direction of z-axis (see Figure 1) (m/s²) and t is time (s).

Viscosity (μ_s) and density (ρ_s) of the extraction solution is calculated using Eq. 4 as a function of volume fractions of water and ethanol in the mixture.

$$\mu_s = \mu_w v_w + \mu_e v_e \quad (\text{Eq. 4})$$

$$\rho_s = \rho_w v_w + \rho_e v_e \quad (\text{Eq. 5})$$

$$v_w + v_e = 1 \quad (\text{Eq. 6})$$

where v_w and v_e was volume fractions of water and ethanol, respectively.

Flow characteristics in the porous media is described by Eq. 7 (Brinkman's equation) [36].

$$\frac{\rho}{\varepsilon_b} \left(\mathbf{u} \cdot \nabla \frac{\mathbf{u}}{\varepsilon_b} \right) = -\nabla p + \frac{\mu}{\varepsilon_b} \nabla^2 \mathbf{u} + \frac{2}{3\varepsilon_b} \mu \nabla (\nabla \cdot \mathbf{u}) + \rho_s \mathbf{g} - \frac{\mu}{K} \mathbf{u} \quad (\text{Eq. 7})$$

where ε_b was porosity of the extraction bed and K was permeability of porous media (m^2). The ε_b is the ratio of the total volume of grape cane powder calculated using true density and total volume of extraction cell where the powder is loaded. When the fluid density is assumed to be constant, the $\nabla \cdot \mathbf{u}$ term can be omitted (Eq. 8) [35].

$$\frac{\rho}{\varepsilon_b} \left(\mathbf{u} \cdot \nabla \frac{\mathbf{u}}{\varepsilon_b} \right) = -\nabla p + \frac{\mu}{\varepsilon_b} \nabla^2 \mathbf{u} + \rho \mathbf{g} - \frac{\mu}{K} \mathbf{u} \quad (\text{Eq. 8})$$

2.3.2. Heat equation

The conservation of energy in the domain is described using Eq. 9 [35],

$$\rho_{eff} c_{p,eff} \left(\frac{\partial T}{\partial t} + \mathbf{u} \cdot \nabla T \right) = -k_{eff} \nabla^2 T \quad (\text{Eq. 9})$$

where $c_{p,eff}$ is specific heat capacity (kJ/kg.K), k_{eff} is thermal conductivity (W/m.K) and ρ_{eff} is density (kg/m^3) of porous extraction domain (effective values for solvent and powder). These effective properties were calculated using volume averaging technique. In this extent, the following mathematical expressions were used for calculation of thermal conductivity and heat capacity of solvent (Eq. 10-11), effective density, effective mass transfer coefficient, and effective heat capacity of extraction domain (Eq. 12-14), respectively.

$$k_s = k_w v_w + k_e v_e \quad (\text{Eq. 10})$$

$$c_{p,s} = c_{p,w} v_w + c_{p,e} v_e \quad (\text{Eq. 11})$$

$$\rho_{eff} = \varepsilon_b \rho_s + (1 - \varepsilon_b) \rho_b \quad (\text{Eq. 12})$$

$$k_{eff} = \varepsilon_b k_s + (1 - \varepsilon_b) k_b \quad (\text{Eq. 13})$$

$$c_{p,eff} = \varepsilon_b c_{p,s} + (1 - \varepsilon_b) c_{p,b} \quad (\text{Eq. 14})$$

where c_p is specific heat capacity (kJ/kg.K), k is thermal conductivity (W/m.K), ρ is density (kg/m^3) and the subscripts s , w , e and b correspond to solvent, water, ethanol and extraction bed (grape cane powder).

2.3.3. Mass transfer equation

Transfer of the phenolic compounds in the bulk flow region is described using the Eq. 15 [35] as follows:

$$\varepsilon_b \frac{\partial c_i}{\partial t} + \mathbf{u} \cdot \nabla c_i = -D_i \nabla^2 c_i + R_i \quad (\text{Eq. 15})$$

where c_i is molar concentration of the dissolving species in extraction solvent (mol/m^3) and D_i is diffusion coefficient of species in that solvent (m^2/s), ε_b is the bed porosity, R_i is the degradation rate of tR for porous domain ($\text{mol/m}^3 \cdot \text{s}$) and D_i is assumed to be very small and negligible ($Pé < 1$). On the other hand, radial mass transfer in pellets is defined using the “Reactive Pellet Bed” module of COMSOL Multiphysics® as described in Eq. 16 [37].

$$4\pi N \left[r^2 r_{pe}^2 \varepsilon_{pe} \frac{\partial c_{pe}}{\partial t} = -D_{pe} \nabla \cdot (-r^2 \nabla c_{pe}) + r^2 r_{pe}^2 R_{pe} \right] \quad (\text{Eq. 16})$$

where c_{pe} is the concentration of tR per fluid volume inside the pore channel (mol/m^3), D_{pe} is the diffusion coefficient of tR in spherical pellets (m^2/s), R_{pe} is the degradation rate of ($\text{mol/m}^3 \cdot \text{s}$), r_{pe} is the radius (m) and ε_{pe} is the porosity of spherical particles, r is the non-dimensional coordinate and equal to r_{dim}/r_{pe} where r_{dim} is the spatial radial coordinate in the pellet (m), and N is the number of pellets per unit volume. N was calculated by using the solid fraction in the unit volume (from porosity) divided by a volume of a single pellet. The D_{pe} and R (degradation rate of tR corresponds to R_i and R_{pe} where appropriate) were calculated as functions of operation variables using experimental data from Karacabey, Mazza, Bayındırlı and Artık [20] and implemented as follows;

$$D_{pe} = \alpha - \beta T + \gamma v_e + \delta T^2 + \theta v_e^2 \quad (\text{Eq. 17})$$

$$R = -C k_0 e^{\left(\frac{-E_a}{R_g T}\right)} \quad (\text{Eq. 18})$$

where α , β , γ , δ and θ are coefficients of corresponding quadratic model of D_{pe} (6.1047×10^{-14} , 9.1163×10^{-15} , 1.4309×10^{-12} , 1.1469×10^{-16} and 2.7880×10^{-11} , respectively), C was tR concentration in

porous medium and corresponds to c_i and c_{pe} where appropriate, k_0 was $0.57 \text{ (s}^{-1}\text{)}$, E_a is activation energy (460.24 kJ/mole) and R_g is universal gas constant (8.314 J/mol.K).

2.4. Boundary and initial conditions

For preliminary heat transfer solutions which were held to figure out the validity of homogenous temperature distribution assumption, the initial temperature of the extraction domain was adjusted to room temperature ($\approx 25^\circ\text{C}$). The outer boundary temperature was at oven temperature depending on process conditions ($105, 120, 140$ or 160°C). Although it was not included in model geometry, heat transfer through cell wall was described by conduction using Eq. 19. For extraction simulations containing mass and momentum transfer simulations, temperature of the medium was constant and equal to set temperature of oven.

$$q_{wall} = -d_{wall}k_{wall}\nabla T \quad (\text{Eq. 19})$$

For fluid flow, the inlet velocities were adjusted to $0.5, 1, 2, 3 \text{ ml/min}$ depending on the case simulated. The outlet pressure was constant at 5.2 MPa . Velocity of fluid at boundaries (internal surface of the extraction cell and outer surface of the solid sphere particles) were zero, thus non-slip boundary conditions were attained where necessary.

For the mass transfer and chemical reactions, flux over the lateral boundaries and initial tR concentration of extraction solvent were adjusted to zero. For porous medium, the initial tR content was 4.06 mg/g dry weight of grape cane powder [8], and that corresponds to 7.93 mol/m^3 for porous medium (molecular weight of tR was 228.25 g/mol).

2.5. Model solution and validation

The partial differential equations describing heat, mass and momentum transfer in extraction process were solved using finite elements method with COMSOL Multiphysics® (5.3a, Burlington, USA). The model parameters are presented in Table 1. The 2D axisymmetric geometry was created and meshed in COMSOL software. Mesh sensitivity was performed by a number of series of mesh

refinement until mesh density no longer has an impact on the simulation results [38]. For mesh sensitivity, nine simulations were conducted with changing number of elements between 1588 and 215698. Mean absolute error (%) between results were calculated and it was 0.61% between the minimum and maximum mesh densities (Figure 2). This error is far below the acceptable deviation of the analytical laboratory measurements (5%) and within the analytical uncertainty of HPLC devices [39]. It means that so small amount of variation may not be determined even in the experimental measurements. Therefore, the lowest mesh density was preferred to decrease computation time. The model was validated using the experimental data presented by Karacabey, Mazza, Bayındırlı and Artık [20] for tR concentration at the extraction cell outlet. In order to evaluate the goodness-of-fit between experimental data and predictions of the mathematical model, the standard error of estimate (SEE) was calculated using Eq. 20.

$$SEE = \sqrt{\frac{1}{n} \sum_{i=1}^n (c_P - c_E)^2} \quad (\text{Eq. 20})$$

where n is the total number of samples, c_P and c_E are predicted and measured concentrations, respectively.

2.3. Extraction procedure and experimental setup

In brief, the system consists of a LC pump, temperature-controlled oven, a cylindrical extraction cell, a back pressure regulator, a cooling unit, a fraction collector, and fittings and tubing at required numbers and length, respectively. The flow rate (ml/min), inlet and outlet temperatures of extraction cell, oven temperature were controlled and monitored. The tR was extracted from dried grape cane powders. Experimental studies have been conducted in the Pacific Agri-Food Canada Research Center, Summerland, Canada. The results have been extensively evaluated to find the effects of process parameters being controlled in the PLPW system, and the detailed analysis has been reported by Karacabey, Mazza, Bayındırlı and Artık [20].

3. Results and Discussion

3.3. Model Validation

The mathematical model was developed to predict the performance of *tR* extraction of the PLPW system as described by Karacabey, Mazza, Bayındırlı and Artık [20]. The predicted results were compared against the experimental data from the same reference study. In Figure 3A-3H, the comparison between experimental and simulation data shows the viability of model predictions. According to the findings, *SEE* values ranged approximately between 3.25×10^{-2} and 1.30×10^{-1} which are quite acceptable since there are up to 27% average deviations available in the literature for different extraction systems [40, 41]. The good agreement with experimental data was especially observed from simulations at different temperatures and ethanol concentrations. However, simulations at different flow rates deviated from experimental ones. Possible reasons for the deviation was further argued in the following section (Section 3.4.).

3.4. Effect of process parameters on efficiency

3.4.1. Velocity

The *tR* was extracted from grape cane powder by using pressurized solvent extraction method. Extracts were fractionated and analysed by an HPLC to determine the resveratrol concentrations. At the beginning of the process, a slow rise in the concentration of *tR* was observed. That was followed by a rapid increase up to maxima where the extract fraction reached the highest *tR* concentration. The remaining period was the gradual decrease in *tR* content of extract fractions. This trend was observed for all trials carried at different conditions, only with changes in slopes (Figure 3A – 3H). Briefly, the extraction trend composed of three stages, (1) rinsing free resveratrol and solvent penetration into solid matrix, (2) compound diffusion throughout the solid matrix and (3) final extraction stage being a gradual decrease in concentration [20]. This trend is common for internal diffusion-controlled mass transfer processes. Internal diffusion phenomena in extraction process is the movement of solvent into solid matrix wetting the solid, dissolution of target compounds, molecular transfer of these compounds (diffusional transfer) to solid surface, mass transfer

throughout the thin solvent film on the solid surface. Molecular and/or convective transfer of solute into bulk fluid followed the internal diffusion. At the last stage, diffusional, convective or both of them depends on the movement of fluid. If the solvent velocity is high enough, convective mass transfer is the main mechanism for transfer of target compounds and it is faster than internal diffusion [28, 29]. Thus, extraction rate is controlled by internal diffusion as in the current study. For this type of mass transfer taking place during extraction, flow rate may adversely affect the concentration of target compounds (Figure 3A – 3H) [42]. A possible reason for this phenomena was explained by Bocquet, Romero, Sanchez and Rios [40] for extraction of caffeine. As the velocity of solvent increases, extraction efficiency increases as a result of a higher concentration gradient [41, 43], but up to a threshold. Over the threshold, the resistance for local mass transfer becomes negligible (not contributing the mass transfer) and any further increment in the solvent velocity decreases extraction efficiency. At higher flow rates, time of interaction between solvent and solid matrix surface also decreases and this limits solute transfer to the unit volume of solvent and reduces process efficacy (Figure 3A – 3H) [44].

Deviation from the experimental data under the effect of flow rate change can be related to the quite complex mass transfer mechanisms of natural materials. According to mass transfer phenomena, there are three mechanisms. They may separately or together control the mass transfer taking place in natural materials, and the mechanistic models are based on assumptions depending on these mechanisms. According to Shotipruk, Kiatsongserm, Pavasant, Goto and Sasaki [42], those were briefly summarized as;

- (1) Diffusion through a stagnant liquid film around the solid plant particles,
- (2) Diffusional transport through the containing matrix by diffusion through the bulk material or down its pores,
- (3) Removal by partitioning into the flowing solvent.

The first one is generally assumed to be negligible and the remaining last two of them are the main mechanisms controlling mass transfers in extraction mediums. If the proposed model does not reflect all of the mechanisms taking place during extraction, predictions can deviate from experimental values. In such cases, more experimental data are required to further explain the extraction mechanism and to build more accurate models.

3.4.2. Temperature

The distribution of *tR* concentration in extraction column was shown in Figure 4A – 4F, where extraction temperature and time were the model input variables. In those figures, the reduction in *tR* concentration firstly started at the inlet region of the extraction column and progressed to the outlet. The concentration of *tR* was deposited into the directions perpendicular to the axial solvent flow and outlet region of the extraction column. This was related to convective transport of resveratrol molecules with axial solvent flow from the inlet to outlet. Moreover, molecular diffusion of *tR* molecules throughout the spherical cane powders firstly started at the region close to the inlet. When extraction solvent moved to the outlet region, its *tR* concentration increased gradually. As a result, transfer rate of *tR* from the solid phase to the solvent decreased due to lower concentration gradient. However, for the later stage of extraction, more *tR* molecules were extracted from solid particles around the outlet. This is due to the *tR* depletion of solid-phase around the inlet. Additionally, convective transport of *tR* molecules was slower at the position being close to the internal side surface of the column than that observed at the positions close to the cylindrical axis (Figure 4A – 4C).

The accumulation of *tR* was decreased and all *tR* molecules were washed out with solvent with time progress. This phenomenon was faster at higher temperature levels (Figure 4A – 4F). For example, almost a uniform distribution of *tR* concentration throughout the extraction column was observed with extraction time, when set temperature value was 105°C (Figure 4A – 4C). However, a significant difference was seen at temperature of 140°C with time progress (Figure 4D – 4F). This is related to

the improved transport of target molecules by diffusion and convection. Both mechanisms are accelerated with temperature elevation due to the changes in physical properties of solid and solvent mediums like viscosity, density, solubility, mass transfer coefficient, diffusion coefficient etc. [15, 45]. So *tR* distribution was not uniform in extraction column at high temperature, and accumulation close to outer surface and outlet region was obvious. Acceleration of mass transport due to higher temperature can also be seen in Figure 5. Under the same processing conditions (1 ml/min flow rate and 7.4% ethanol solution), *tR* concentration of the collected solvent from cell outlet increased with temperature rise. It is obvious that the model's response to the temperature rise was weak, especially at the highest temperature level. Thus, the positive effect of temperature on mass transfer was not limitless and it disappeared while reaching a threshold temperature [40]. A similar case was observed for velocity, as well. Another reason for the fade effect of temperature on extraction efficiency can be due to thermal degradation of *tR*. High temperatures of extraction may cause possible concurrent degradation of phenolic compounds which were previously mobilized at lower temperature or even the decomposition of residual phenolics remaining in the plant matrix [45]. From average degradation rates in porous domain presented in Figure 5, degradation of *tR* accompanies to reaction of outlet concentration to temperature change. The higher temperature was applied to system, more *tR* was degraded.

3.4.3. Ethanol concentration

Two different solvent mixtures (7.4% and 15%) were used to show the effect of ethanol as a co-solvent in water on the performance of the PLPW extraction system. The *tR* concentration was increased to almost two-fold (Figure 3A – 3H) with the increment of ethanol concentration. The developed mechanistic model also explained the effect of ethanol concentration and good agreement with experimental data was observed (Figure 3A – 3H). This improvement in extraction yield of *tR* is related to the change of solvent characteristics, especially solvent polarity depending on solvent composition [8, 46]. When the polarity of solvent and solute is similar, better extraction yield

is achieved. A lower solubility of a compound in water is associated with the energy required to overcome the attraction between the water molecules. As a result, solubility of non-polar compounds in water is limited. Since the energy required to break the configuration of water molecules becomes dominant for these covalent molecules [47, 48]. In the PLPW system, an increase in temperature is one of the tools to reduce the polarity of water. However, a decrease in polarity of water with elevated temperatures (even at boiling point or higher) was not enough for the best solubility of *tR* in the current study. Thus, the use of modest quantities of modifier became necessary to adjust the solvent polarity. Accompanying changes in other physical properties of extraction solvent with an increase in ethanol ratio also helped for the extraction of *tR*. High prediction performance of the developed mechanistic models is related to the parameters those included. These parameters (density, dynamic viscosity and diffusivity of the target compound in Table 1) were defined as dependent on the ethanol concentration. In other words, all those related parameters affecting extraction performance considered the change of solvent composition and resulted in changes in extraction performance. This is also a sign of the requirement of complex mechanistic models considering process parameters as well as physical properties.

3.5. Verification of model assumptions

In the developed model two major assumptions were made regarding the system/operation settings. They were (1) the uniform temperature distribution in the extraction cell which was constant at set temperature of column oven and (2) exclusion of frits to decrease computational load. To verify the first assumption, a number of time-dependent simulations were performed to obtain temperature profile of the system. The extraction solvent was stagnant in these simulations representing the pre-heating section of process. The results of these simulations (temperature distribution in the cell) were presented in Figure 6. They were given for the line from the geometrical centre of the cell to the boundary (indicated with an arrow in Figure 6). Experimental extraction processes were carried out at four different temperature levels (105°C, 120°C, 140°C, and 160°C) by Karacabey, Mazza,

Bayındırlı and Artık [20]. At any level of oven temperature, internal temperature of extraction cell increased during the pre-heating period. Almost uniform temperature distribution was attained for each extraction trial in less than 10 minutes (Figure 6). Temperature difference between set value and minimum temperature level in the extraction column was less than 1°C . This corresponds to a difference smaller than 1% of set temperature, which is acceptably small for temperature distribution, especially when temperature levels higher than 100°C . For example, when the set value for oven was 105°C , the calculated minimum temperature in the extraction column was 104.02°C . It reached at that level in 7.83 minute of 10 minute pre-heating period. Similarly, its minimum level reached to 159.12°C for 8 minute of the pre-heating period at oven temperature of 160°C . Briefly, it can be concluded that the assumption of stationary state and isothermal conditions during extraction was valid for temperature of PLPW extraction system. Same assumptions were previously followed in different extraction studies [40, 41, 49]. Additionally, the pre-heating period of 10 min is long enough to attain the set temperature point before extraction process is started.

To verify the latter approximation, that is keeping the frit out of the geometry, velocity profile of the extraction medium should be evaluated. Because a frit is required to be assembled into the column system to achieve uniform flow pattern and to avoid fluctuations in heat and mass transfer taking place which are directly effective on process efficiency. Thus, the predicted velocity profile for extraction medium was given in Figure 7A – 7C. Velocity profile was almost same at different temperature levels indicating that temperature did not create any significant difference. This was due to the very limited change of the solvent viscosity between $105\text{-}160^{\circ}\text{C}$ [50]. Similarly, the effect of flow rate was also investigated on the velocity profile. An increase in flow rate caused distinct velocity profiles changes. Variation in velocity throughout cell radius (r-direction) increased with varying flow rate from 0.5 ml/min to 3 ml/min . This change was distinct at a high solvent flow rate. However, variation in solvent velocity was also diminished at the axial distance level of 3 mm from cell's entrance. It means that only 3 mm distance from the surface on the inlet side of the extraction column was enough to attain a uniform flow pattern (Figure 7A – 7C). This behaviour was related to

the friction of extraction solvent and also the orientation of flow direction which is against gravity. So after a short distance from the inlet, the velocity reaches to fully developed state considering the entry effects on the hydrodynamics of fluid flow. These outcomes were coincident with the assumption of a uniform velocity profile at the entrance of the extraction column.

4. Conclusion

In the present study, a mechanistic model was developed for a semi-continuous pressurized low polarity water (PLPW) extraction system. Macroscopic porous domain approach was followed during model development efforts and volume averaging technique was employed to calculate the domain where required. Momentum and mass transfer were considered in the proposed model and thermal degradation of trans-resveratrol (*tR*) was described by a kinetic model. Assumption related to thermal condition was also verified using a time-dependent heat transfer simulation. Predictions were validated against the experimental *tR* concentrations measured at system outlet. The model provides a deeper understanding of the process mechanisms and the effect of the systems parameter on results.

It was shown that the temperature of the extraction cell reached equilibrium within less than 10 minutes. So it was verified that extraction of *tR* took place at the constant set temperature. The model can react to changes in process conditions which are temperature, solvent flow rate and ethanol concentration of solvent. According to the model outputs, temperature and solvent flow rate were effective on extraction yield. However, their impacts were not limitless and fading out as their levels increased. These can be attributed to short contact/interaction time of solvent and particle, and negligible resistance of mass transfer after a threshold level. Elution of target compounds is faster with higher temperatures and velocities. However, due to thermal degradation of solute at higher temperatures, it may not be favourable after a certain level. All in all, more experimental data may be required to further improve model performance, particularly about flow rate effects.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Captions of Figures and Tables

Figure 1. Schematic illustration of 3D extraction cell and axisymmetric geometry with transport mechanisms in consideration.

Figure 2. Sensitivity of trans-resveratrol concentration against mesh density at the cell outlet where operating temperature, flow rate and ethanol concentration of solvent are 120°C, 1 ml/min and 7.4%, respectively.

Figure 3A

Figure 3B

Figure 3C

Figure 3D

Figure 3E

Figure 3F

Figure 3G

Figure 3H

Figure 3. Comparison of experimental data to model predictions for different levels of process parameters (temperature, ethanol concentration of extraction solvent and flow rate)

Figure 4. trans-Resveratrol concentration distribution in extraction column under constant solvent concentration of 7.4% (v/v, ethanol/water) and flow rate of 1 ml/min at temperature level of 105°C at 5th minute of extraction (A), 105°C at 20th minute of extraction (B), 105°C at 50th minute of extraction (C), 140°C at 5th minute of extraction (D), 140°C at 20th minute of extraction (E), and 140°C at 50th minute of extraction (F).

Figure 5. Trans-resveratrol concentration at the outlet of different cell at different temperatures (dashed lines) and average degradation of trans-resveratrol in the porous domain (shaded areas) where flow rate and ethanol concentration are 1 ml/min and 7.4%, respectively.

Figure 6. Temperature distribution in extraction column from coldest point (geometrical centre) to the boundary under constant outer temperature values of 105°C, 120°C, 140°C and 160°C at 1th, 5th and 8th min of pre-heating process.

Figure 7. Predictive velocity profile of extraction solvent and its change according to the axial distance from inlet surface of column for all levels of process parameters (temperature, ethanol concentration of extraction solvent and flow rate, levels not specified for clarity, for details please see [20]).

Table 1 Input parameters, symbols, values and corresponding units

Parameters	Symbols	Value	Unit	Source
Density				
Grape cane (bulk)	ρ_b	761.00	kg/m ³	Turrell et al. (1967)
Grape cane (true)	ρ_{pe}	1492.50	kg/m ³	Average of data from Plötze and Niemz (2011)
Water*	ρ_w	$999.7968 + 6.8317 \times 10^{-2}T - 1.0740 \times 10^{-2}T^2 + 8.2141 \times 10^{-4}T^{2.5} - 2.3031 \times 10^{-5}T^3$	kg/m ³	Popiel and Wojtkowiak (1998)
Ethanol	ρ_e	$-272.4867 + 6.2533T - 9.5162 \times 10^{-3}T^2$	kg/m ³	Calculated using data from Velisa (2011)
Specific heat capacity				
Grape cane powder	$C_{p,b}$	1192.40	J/kg.K	Turrell et al. (1967)
Water*	$C_{p,w}$	$4.2174 + 5.6182 \times 10^{-3}T + 1.2992 \times 10^{-3}T^{1.5} - 1.1535 \times 10^{-4}T^2 + 4.1496 \times 10^{-6}T^{2.5}$	J/kg.°C	Popiel and Wojtkowiak (1998)
Ethanol	$C_{p,e}$	$18.3420 + 9.5490 \times 10^{-2}T - 1.4756 \times 10^{-4}T^2$	J/kg.K	Calculated using data from Velisa (2011)
Thermal conductivity				
Grape cane powder	k_b	0.26	W/m.K	Calculated from Turrell et al. (1967)
Water*	k_w	$0.5650 + 2.6364 \times 10^{-3}T - 1.2517 \times 10^{-4}T^{1.5} - 1.1535 \times 10^{-6}T^2 + 9.4129 \times 10^{-4}T^{0.5}$	W/m.°C	Popiel and Wojtkowiak (1998)
Ethanol	k_e	$135.1408 - 1.6434T + 7.9757 \times 10^{-3}T^2 - 1.8296 \times 10^{-5}T^3 + 2.3233 \times 10^{-8}T^4 - 1.1156 \times 10^{-11}T^5$	W/m.K	Calculated using data from Velisa (2011)
Steel	k_{wall}	53	W/m.K	Gardner and Ng (2006)
Dynamic viscosity				
Water*	μ_w	$(557.8246 + 19.4088T + 0.1360T^2 - 3.1161 \times 10^{-4}T^3)^{-1}$	Pa.s	Popiel and Wojtkowiak (1998)
Ethanol	μ_e	$3.8217 \times 10^{-3} - 1.4854 \times 10^{-5}T + 1.4684 \times 10^{-8}T^2$	Pa.s	Calculated using data from Velisa (2011)
Porosity				
Bed	ε_b	0.24		Present study
Particle	ε_{pe}	0.49		Average of data from Plötze and Niemz (2011)
Degradation rate constant	k_0	0.57	s ⁻¹	Calculated using data from Karacabey et al. (2012)
Energy of activation	E_a	460.24	kJ/mol	Calculated using data from Karacabey et al. (2012)
Average particle radius	r_{pe}	1.28×10^{-4}	m	Karacabey et al. (2012)
Permeability	K	$\varepsilon_{bed}^3 / [\theta S_v^2 (1 - \varepsilon)^2]$	m ²	Scheidegger (1957)
Specific surface area of particles	S_v	$A_s/V_p = [\pi(2r_{pe})^2] / [\pi(2r_{pe})^3/6] = 3/r_{pe}$	m ⁻¹	Ergun (1952)
Wall thickness	d_{wall}	6.1×10^{-3}	m	Karacabey et al. (2012)
Inlet velocity	q_{in}	0.5, 1, 2, 3	ml/min	Karacabey et al. (2012)
Environment temperature	T_{env}	105, 120, 140, 160	°C	Karacabey et al. (2012)
Ethanol concentration	v_e	7.4, 15	v/v, %	Karacabey et al. (2012)

* Temperatures were used in °C where indicated.

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