

## Investigation of the mechanism and kinetics of extraction from plant materials

E. Simeonov<sup>1\*</sup>, Z. Yaneva<sup>2</sup>, C. Chilev<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, University of Chemical Technology and Metallurgy, 8 Kl. Ohridski Blvd., 1756 Sofia, Bulgaria,

<sup>2</sup>Chemistry Unit, Department of Pharmacology, Animal Physiology and Physiological Chemistry, Trakia University, Students Campus, 6000 Stara Zagora, Bulgaria

Received July 11, 2016; Revised January 24, 2017

A comprehensive systematic study on the mechanism of solid-liquid extraction of valuable components from plant materials was conducted. Experimental series of extraction of flavonoids from red geranium roots - *Geranium Sanguineum* L. (extractant 70% C<sub>2</sub>H<sub>5</sub>OH), and of tobacco concrete from tobacco leaves - *Nicotiana tabacum* L. (extractant H<sub>2</sub>O), were done. Parametric investigations of the effect of: solid phase size ( $R = 0.2 \times 10^{-3} \div 1.2 \times 10^{-3}$  m), effective diffusion coefficient ( $D_{eff} = 10^{-10} \div 10^{-12}$  m<sup>2</sup>s<sup>-1</sup>), partial mass transfer coefficient ( $k = 10^{-5} \div 10^{-7}$  ms<sup>-1</sup>), temperature ( $T = 20 \div 60$  °C) and liquid/solid ratio ( $\xi = 0.01 \div 0.03$  m<sup>3</sup>kg<sup>-1</sup>), on the changes in the solid/liquid concentration were done. Significant correlation between the experimental data and the model values is established.

**Key words:** Solid-liquid extraction, Numerical solution, Kinetics, Effective diffusion coefficient, Partial mass transfer coefficient, Modeling, Plant materials

### INTRODUCTION

Solid-liquid extraction is a process, the products of which are widely used in pharmaceuticals, cosmetics and food industries, and also applied for environmental purposes. The description and calculation of the process faces serious difficulties both from methodological and mathematical points of view. The latter provoked numerous scientific studies focused on the process kinetics [1-7], the diffusivities [8-12], the extraction yields [6,9], or the process design [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. Yet, the process description is very difficult because of the influence of a large number of parameters: variable in time solid phase pore structure, irregular particle shape, large particles size distribution, etc. The initial concentration of the active substance may also differ for the same raw material as a function of the crop area, storage conditions, operational temperature during the processing, and liquid/solid ratio. The kinetic coefficients also vary during the extraction process. To set up an experimental installation one needs to be acquainted with the diffusion type and the factors that are of main importance for the process. For that purpose, there are two different approaches, the first one is an analytical solution based on some simplifications for the three classic shapes of the solid phase. The

second approach is a numerical solution combined with experimental data to obtain the necessary kinetic parameters applying the method of standard function or characteristic function [15].

The process of extraction of useful components from plant raw materials has been almost ever limited by the mass transfer inside the solid phase pores. Each experimental kinetic curve (dependence) includes indirectly all factors that influence the diffusion process velocity, as solid polydispersion and anisotropy, solid particles form, change in liquid phase concentration.

Such a kinetic curve can be represented by an equation of the type:

$$C_1 = A - B \cdot e^{(-H \cdot \tau)}, \quad (1)$$

where  $A$ ,  $B$  and  $H$  are constants determined numerically on the basis of the experimental data that have specific physical meaning, compared with the analytical solution of the process of solid phase extraction [10,14]. Quantitatively, these factors are reported by the effective diffusion coefficient ( $D_{eff}$ ). The exact calculation of  $D_{eff}$  is of significant importance for the engineering solution of the process. In practice, there are experimental methods and such combining experimentally obtained data with analytical solutions. Chilev *et al.* (2014) suggested a new empirical model for the calculation of  $D_{eff}$  that was valid for a wide range of plant materials from which useful components were extracted with hydroalcoholic solutions [16].

The aim of the present study is to determine the mechanism and method of calculation and description of an extraction process by classical diffusion models, based on experimentally obtained

\* To whom all correspondence should be sent:  
E-mail: evgeni@uctm.edu

data. Furthermore, it establishes the effect of a number of parameters, characterizing a real system, on the extraction kinetics, in order to obtain more accurate modeling and control of the process.

## EXPERIMENTAL

### *Plant materials*

Experiments were carried out with two plant materials important to practice. The roots from *Geranium Sanguineum* L. were used as a solid phase for the extraction of flavonoids, and tobacco leaves (*Nicotiana tabacum* L.) - for obtaining tobacco concrete (extractable substances).

### *Extraction design*

The kinetic experiments were performed in a stirred vessel. The ground raw material with suitable size was placed in the reactor and poured on with 70% C<sub>2</sub>H<sub>5</sub>OH/H<sub>2</sub>O or pure H<sub>2</sub>O. The reactor was immersed in a water bath and the temperature was maintained constant, controlled by a thermometer. The mixture was continuously stirred. To ensure limiting internal diffusion the angular velocity of the mixer was regulated. After extraction, the samples were taken and filtered through pleated filter to separate the solid from the liquid phase.

### *Experimental conditions*

#### *System I: Geranium Sanguineum L. - 70% C<sub>2</sub>H<sub>5</sub>OH*

The kinetic study was carried out by periodical extraction from the roots of *Geranium Sanguineum* L. in a stirred vessel. The process temperature was  $T = 20^{\circ}\text{C}$ . To eliminate the external mass transfer resistance the agitation rate was maintained at  $n = 5 \text{ s}^{-1}$ . The experiments were performed with three sizes of the solid phase particles ( $R = 0.2 - 0.4 \text{ mm}$ ,  $R = 0.4 - 0.8 \text{ mm}$  and  $R = 0.8 - 1.25 \text{ mm}$ ), at a liquid/solid ratio  $\xi = 0.02 \text{ m}^3 \text{ kg}^{-1}$  and 70% C<sub>2</sub>H<sub>5</sub>OH/H<sub>2</sub>O solution as a solvent. The extracts were filtered with paper folded filter (Boeco Germany, Grade 6). The concentration of valuable compounds in the liquid phase ( $C_1$ ) after the extraction was measured. Each experimental point of the kinetic curve was determined based on the average value of three independent experiments.

#### *System II: Nicotiana tabacum L. - water*

The experimental results were obtained in a batch reactor at the following conditions: extraction temperature –  $T = 20^{\circ}\text{C}$  and agitation rate –  $n = 7 \text{ s}^{-1}$ , which ensured internal diffusion as a rate limiting stage (the external resistance was eliminated). The extraction experiments were conducted at three

liquid/solid values:  $\zeta = 0.01 \text{ m}^3 \text{ kg}^{-1}$ ,  $\xi = 0.02 \text{ m}^3 \text{ kg}^{-1}$  and  $\xi = 0.03 \text{ m}^3 \text{ kg}^{-1}$ . The initial concentration of the extractable substance (tobacco concrete) was experimentally determined -  $C_o = 607.97 \text{ kg m}^{-3}$ .

### *Analytical methods for the extraction analysis Spectrophotometric analysis for the determination of total flavonoids for system I - Geranium Sanguineum L. - 70% C<sub>2</sub>H<sub>5</sub>OH*

The content of total flavonoids was determined by a colorimetric method with catechin. A calibration curve was obtained following the procedure: in a 10 ml volumetric flask 4 ml distilled water, 0.3 cm<sup>3</sup> NaNO<sub>2</sub> and 1 cm<sup>3</sup> of previously prepared 100 mg dm<sup>-3</sup> catechin solution were added; the solution mixture was well shaken. After 5 min 0.3 cm<sup>3</sup> AlCl<sub>3</sub> and 2 cm<sup>3</sup> of NaOH were added and the solution was made up to 10 cm<sup>3</sup> with distilled water. Four more solutions with different catechin concentrations were prepared following the above cited procedure. The absorbances were measured on a UV/VIS spectrophotometer (BOECO – Germany S-22), at a wavelength of 510 nm vs a blank sample [17].

### *Weight analysis for the determination of extractable substances for system II - Nicotiana tabacum L. - water*

A weighing method with precision of 10<sup>-3</sup> g was applied for the quantitative determination of tobacco concrete. The extracts were evaporated in a drying oven at  $T = 70^{\circ}\text{C}$ .

### *Kinetics study and modeling*

In the absence of convective transport, the extraction from solid materials is described by the nonstationary diffusion equation ( $\frac{\partial C_2}{\partial x} \neq const$  and  $\frac{\partial C_2}{\partial \tau} \neq 0$ ). In porous solids, for the three "classical" shapes (unlimited plate, infinite cylinder and sphere) of the solid phase, the summary equation for symmetrical mass transfer has the following form [18]:

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

At  $D_{eff} = const.$  it can be rearranged by solving the one-dimensional Fick's law for the three "classical" shapes of the solid phase – plate, sphere and cylinder:

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

with the following boundary conditions:

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

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

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

$$\beta(C_0 - \bar{C}_2) = C_1 - C_m \quad (7)$$

The general analytical solution has the form:

$$\frac{C_0 - \bar{C}_2}{C_0 - C_m} = \frac{1}{1 + \beta} - \sum_{n=1}^{\infty} \frac{4 \cdot (\nu + 1)}{\mu_n^2 + 4(\nu + 1)^2 \cdot \beta(1 + \beta)} \cdot \exp^{-\mu_n^2 \frac{D_{eff} \tau}{R^2}} \quad (8)$$

where  $C_0$  is the initial concentration in the solid phase;  $C_m = C_{li}$  by periodical processes;  $C_{li}$  - initial concentration in the liquid phase;  $\bar{C}_2$  - average concentration in the solid phase;  $D_{eff}$  - effective diffusion coefficient in the pores of the solid phase;  $R$  - size of the solid particles;  $\tau$  - time;  $\beta = \frac{C_{1eq}}{C_0 - C_{1eq}}$ ;  $C_{1eq}$  - equilibrium concentration in the liquid phase;  $\mu_i$  - roots of the characteristic equation;  $\nu$  - 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 plant material).

The boundary condition of the third kind – eqn. (4), which assumes equality of the mass flow from the solid phase to the surface towards the mass flow in the fluid phase, can be presented as follows:

$$-\left. \frac{\partial \bar{C}_2}{\partial \psi} \right|_{\psi=R} = Bi (\bar{C}_{2,\psi=R} - \bar{C}_1) \quad , \quad (9)$$

where  $R$  is a characteristic particle size,  $\psi = x/t$  - relative coordinate, and  $Bi = kR/D_{eff}$  - Biot number.

The value of the partial mass transfer coefficient  $k$  depends on the hydrodynamic conditions of the porous particle wrapping, and it is a major kinetic indicator of the stage of the extraction process, which involves mass transfer from the solid surface

through the boundary layer to the core of the fluid flow. The value of  $Bi$  determines the mode of the diffusion extraction.

At high wrapping velocity  $k \rightarrow \infty$ ,  $Bi \rightarrow \infty$  ( $Bi > 30 \div 40$ ), the mode is internal diffusion, and the extraction rate is limited by solid phase diffusion. The opposite results correspond to lower values of the mass transfer coefficient  $k$ . At  $k \rightarrow 0$ ,  $C_2 \rightarrow const.$  and  $Bi < 1$  the mode is external diffusion, and the process rate is limited by external diffusion – mass transfer from the solid surface.

In the boundary conditions, the concentration  $C_l$  of the extractable component in the liquid phase is introduced. This concentration is approximately constant when the amount of the extractant is much greater than the amount of the extractable component. Such a ratio between the phases is some times artificially created in experimental conditions to facilitate the processing of the experimental data.

## RESULTS AND DISCUSSION

### Numerical solutions and analysis

The model described above can be used for extraction processes with various types of plant materials with different type of the internal structure and different size of the solid phase fractions, as well as when applying various extractants for the same raw material, etc. Practically, to use this model it is necessary to clarify the influence of the individual parameters on the type and accuracy of the solution and to present subsequent comparison with the experimental results for different liquid/solid systems.

Initially, a numerical study on the impact of various factors on the overall solution of the model was conducted. The programming environment MatLab 8.0 was used. The function „pdepe”, which solves initial-boundary value problems for systems of parabolic and elliptic partial differential equations (PDEs) in the one space variable  $x$  and time  $\tau$  with variable coefficients, was selected.

The coefficients may depend on  $x$ ,  $\tau$ ,  $C$  and  $\frac{\partial C}{\partial x}$ .

This function can be used for different types of symmetry - slab, cylindrical, or spherical.

The plant material may have different shapes and sizes. Usually they represent bits of herb leaves, flowers or roots. Therefore, the geometry of the system is a plate or a sphere. Thus, the numerical experiments were conducted for both types of system geometry. The solution of the differential eqn. (8) gives the distribution of

concentration in the solid phase over time. By the boundary condition eqn. (4), however, the concentration profiles in the liquid phase could be determined, and they can be compared with the experimental data. Therefore, the effect of individual factors on the distribution of concentration first in the solid phase and then in the liquid phase was initially examined. During the numerical experiments the following values of the variables, which were not changed in the course of the calculation procedure, were used:  $C_{2,0} = 317 \text{ kg m}^{-3}$ ,  $C_{1,0} = 0 \text{ kg m}^{-3}$  and  $C_{eq} = 5.8 \text{ kg m}^{-3}$ .

#### *Factors influencing the concentration change in the solid phase*

The parameters affecting the concentration distribution in the solid phase could be summarized as direct and indirect, or internal and external. The first group of parameters, on which the external diffusion mass transfer depends directly, includes the particle size  $R$  and the coefficient of effective diffusion  $D_{eff}$ . The latter is directly related to the structure of the solid phase. The second group includes factors associated with the external mass transfer of a substance: the partial diffusion coefficient in the boundary layer around the particle  $k$  and the concentration change in the liquid phase  $C_1$ .

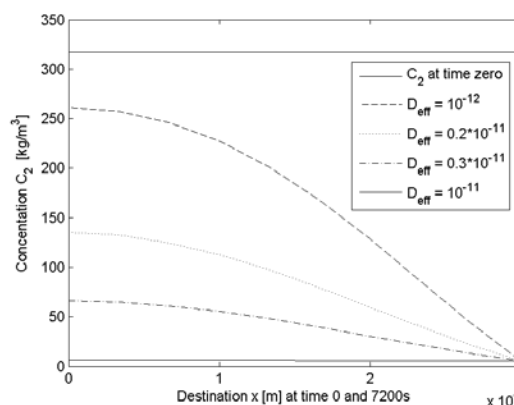
#### *Factors directly influencing the change of solid phase concentration*

##### *Effective diffusion coefficient ( $D_{eff}$ )*

The first parameter of this type is the effective diffusion coefficient. It is a complex function which depends on the pore diffusion coefficient and the structure of the solid phase – pore size distribution, pore curvature, etc. [14,15]. During the extraction process, the solid phase changes its structure regularly or irregularly, thus  $D_{eff}$  will generally depend on the spatial coordinates and time. To determine the effect of this parameter on the solution, numerical experiments at  $D_{eff} = const$  but changing in a different order, were conducted (Fig. 1).

The obtained solutions were for a plate. In this case, the system is symmetrical with the axis of symmetry passing through half the thickness of the plate. The numerical solutions were obtained for solid particle thickness  $R = 0.3 \times 10^{-3} \text{ m}$  and this spatial coordinate was divided into 10 parts (size of the integration step). Time changed from 0 to 7200 s, and the time interval was divided into 100 parts. The partial external diffusion coefficient was  $k = 10^{-5} \text{ m s}^{-1}$ . Figure 1 presents the change of the solid

phase concentration  $C_2$  depending on the spatial coordinate  $x$ , i.e. amending half the plate thickness from zero to  $R = 0.3 \times 10^{-3} \text{ m}$ . With respect to the time coordinate, the figure depicts the concentration profiles for the initial moment "zero" ( $C_2$  at time zero) and for the final moment (all other curves) at  $\tau = 7200 \text{ s}$ . Obviously, at  $\tau = 0 \text{ s}$  the concentration of the extractable component is  $C_2 = 317 \text{ kg m}^{-3}$  and it is regularly distributed in the solid phase volume. At  $\tau = 7200 \text{ s}$  for all values of  $D_{eff}$  the solution displayed the highest concentration in the particle center at  $x = 0$ , which decreased to the boundary value at  $x = R$ .



**Fig. 1.** Effect of  $D_{eff}$  on the change of solid phase concentration ( $C_2$ ).

The figure shows that the smaller value of  $D_{eff}$ , provokes the higher concentration in the center of the particle at the final time. At  $D_{eff} = 10^{-11} \text{ m}^2 \text{ s}^{-1}$ , the concentration in the core was practically equal to that at the plate surface  $C_2|_{x=0} \approx C_2|_{x=R}$ , i.e. the total quantity of the extractable component was extracted from the solid phase. Hence, the more intense the internal diffusion, the less amount of extractable component remained in the solid phase after specific time. According to Fig. 1, a relatively small modification of  $D_{eff}$ , with only one order of magnitude, resulted in large differences in the concentration profiles in the final point of time, i.e., a strong influence of the effective diffusion coefficient on the final solution was observed. It is known that at  $Bi \leq 1$  the process is limited by external mass transfer, for  $1 \leq Bi \leq 30 \div 40$  a combined mass transfer mechanism is observed, and at  $Bi \geq 30 \div 40$  the diffusion is internal [14,18]. In the case of the presented numerical experiments,  $Bi$  changed in the region 300 - 3000, i.e. the process was limited by internal diffusion.

Such study is essential when the target component is of high price, and it is necessary to be fully recovered from the solid phase. Thus, for a particular system at known  $D_{eff}$ , the final point of

time can be determined so that practically 100% of the extractable component can be extracted from the solid phase.

### Solid phase particles size

From practice, it is known that one of the stages during the preparation of the raw material for extraction is crushing or cutting of the solid phase, i.e. the particle size influences the overall process. To investigate this dependence, numerical experiments for different particle radius (in a spherical coordinate system) and different leaves thickness (for a plate) were conducted. The obtained results at  $D_{eff} = 10^{-11} \text{ m}^2 \text{ s}^{-1}$  are presented in Fig. 2. The other parameters are as in the numerical experiments for  $D_{eff}$  in the previous section. Figure 2 displays the solutions for spherical coordinate system at  $\tau = 0$  and  $\tau = 7200 \text{ s}$ .

Obviously, the larger the particles, the greater amount of the extractable component remained in them after 7200 s. At  $R = 1.4 \times 10^{-3} \text{ m}$ , the concentration in the particles center after 7200 s approximated the initial concentration. For small particles with  $R \leq 0.4 \times 10^{-3} \text{ m}$ , practically the entire quantity of the extractable component was extracted after 7200 s. Consequently, at a given intensity of the external diffusion, the greater the particle size, the greater amount of extractable components remained there after a certain period. In this case,  $Bi$  number varied between 200 and 1400, i.e. the rate limiting stage was internal diffusion. This study is essential when the target compound is of high price, and the optimization problem for choosing the time of extraction and particle size has to be solved, so that substantially the whole of the extractable component has to be extracted from the solid phase.

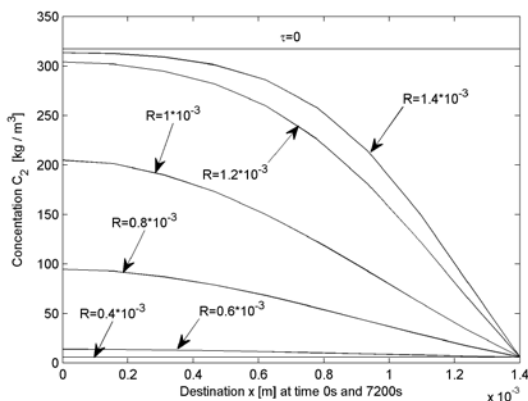


Fig. 2. Effect of the solid particles size ( $R$ ) on the change of solid phase concentration ( $C_2$ ).

### Factors indirectly influencing the change of solid phase concentration

#### Partial mass transfer coefficient

This parameter is related to the external mass transfer through the boundary layer of the particle. Numerical experiments for various  $k$  values,  $D_{eff} = 10^{-11} \text{ m}^2 \text{ s}^{-1}$  and slab symmetry –  $R = 0.8 \times 10^{-3} \text{ m}$ , were conducted. The other parameters were as in the previous numerical experiments for  $D_{eff}$ . Figure 3 presents the numerical solutions for the initial and final time moments.

Obviously, for  $k \geq 10^{-6} \text{ m s}^{-1}$ , the latter parameter actually did not influence the concentration change in the solid phase, as these values of  $k$  correspond to  $Bi > 80$ , which means rapid diffusion through the external boundary layer. Thus, the process was limited by internal diffusion, and the external mass transfer did not influence the derived solution. For  $k \approx 10^{-7} \text{ m s}^{-1}$  and  $Bi \approx 8$  the external diffusion affected the overall process rate, i.e. the latter depended on both external and internal diffusion. In this case,  $k$  influenced the concentration distribution in the solid phase, which was confirmed by the numerical experiments presented in Fig. 3.

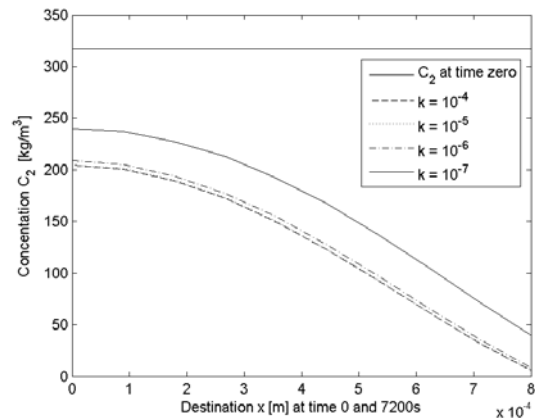
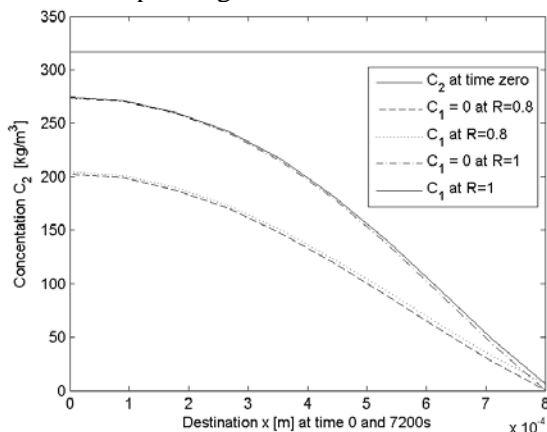


Fig. 3. Effect of  $k$  on the change of solid phase concentration ( $C_2$ ).

#### Liquid/Solid ratio

The second parameter that indirectly affects the solution is the liquid/solid ratio  $\zeta$ . It is directly related to the concentration in the liquid phase  $C_1$ . The concentrations in both phases are interconnected by the boundary condition eqn. (4). Since the concentration in the liquid phase is generally lower than that in the solid and it changes in a narrow range, very little influence of this parameter on the solution could be expected (i.e. the distribution of the concentration in the solid phase). Thus, numerical experiments at  $D_{eff} = 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ,  $k = 10^{-5} \text{ m s}^{-1}$  and at two values of the particle sizes  $R = 0.8 \times 10^{-3}$  and  $1 \times 10^{-3} \text{ m}$  were carried out. The values of the other parameters were the same

as those of the numerical experiments for  $D_{eff}$  in Section 3.2.1. To ascertain the impact of  $C_1$  on  $C_2$ , numerical solutions were obtained in which the boundary condition was set sequentially  $C_1 = 0$  (at liquid/solid ratio infinity) for the entire time interval and  $C_1 \neq const.$ , i.e. likewise  $C_1$  changes over time depending on the solution.



**Fig. 4.** Effect of the liquid/solid ratio ( $\xi$ ) on the solid phase concentration ( $C_2$ ).

According to Fig. 4 for both selected particle diameters, the difference between the solutions at constant and variable  $C_1$  was very small, i.e. the influence of this parameter on the distribution of concentration in the solid phase was very weak, as already mentioned.

In conclusion, the concentration profiles in the solid phase were mainly influenced by the effective diffusion coefficient and particle size. Depending on their values for a given system, an optimum solution with regard to the necessary extraction time and the recovery rate of the target component has to be found. The influence of the other parameters was much slighter, and it probably manifests in mixed modes (with both external and internal diffusion control), which practically do not occur for extraction processes from raw plant materials.

#### Factors influencing the change of liquid phase concentration

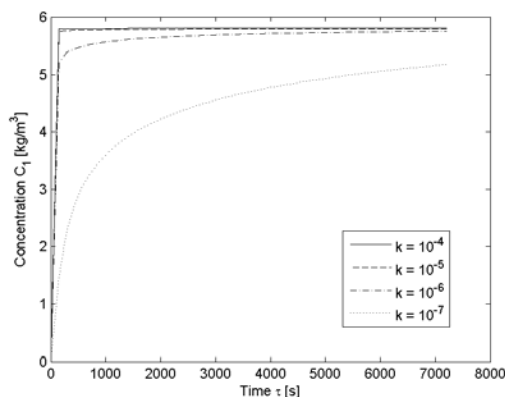
Liquid phase concentration depends on the following three factors:

1. Mass transfer to the interior of the liquid phase;
2. Intensity of mass transfer through the boundary layer around the particle;
3. Concentration on the solid phase surface  $C_2|_{x=R}$ .

The first factor is related to the mechanism of mass transfer of the extractable component in the liquid phase (molecular and convective diffusion). Typically, using suitable techniques (e.g., vigorous stirring) with a rather high accuracy the operation of the extractors approaches the ideal mixing regime. Thus, the concentration of the extractable component in the liquid phase at a given time is instantaneously equalized for the entire phase volume. Therefore, the impact of this parameter was eliminated.

#### Intensity of mass transfer through the boundary layer around the particle

The intensity of mass transfer through the boundary layer around the particle depends on the partial mass transfer coefficient,  $k$ . This coefficient depends mainly on the nature of the solvent and the extractable component and is in the order of  $10^{-4}$  -  $10^{-6}$   $m\ s^{-1}$ . Rarely, for highly viscous extractable agents and for mass transfer of organic macromolecules or complexes, it may be reduced to  $10^{-7}$   $m\ s^{-1}$ . By the *Biot* number, calculated on the basis of the values of  $k$  and  $D_{eff}$ , the rate limiting mass transfer mechanism – internal or external diffusion, could be determined. For extraction from plant materials,  $D_{eff}$  is usually of the order of  $10^{-11}$   $m^2\ s^{-1}$ , while  $k \approx 10^{-5}$   $m\ s^{-1}$ . The latter implies a limitation of the diffusion process in the solid phase pores, which is confirmed by numerous experimental results [10,14,18]. The effect of the mass transfer coefficient through the boundary layer around the solid particle on the liquid phase concentration was investigated. Numerical experiments (Fig. 5) were conducted for various  $k$  values at the following conditions:  $D_{eff} = 10^{-11}$   $m^2\ s^{-1}$ ,  $R = 0.8$  m, phase equilibrium constant  $m = 1$ . The other parameters: initial solid/liquid concentration, etc., were the same as those in the previous numerical experiments. *Bi* number changed in the range 8 – 8000.



**Fig. 5.** Effect of  $k$  on the change of  $C_1$ .

Figure 5 displays the concentration profiles in the liquid phase, obtained by the numerical solution of the model for the time period 0 – 7200 s. Obviously, at  $k = 10^{-4}$  and  $10^{-5} \text{ m s}^{-1}$  and  $Bi = 8000$  and 800, respectively, the curves practically interflowed. These values corresponded to rapid mass transfer through the boundary layer around the particle, and demonstrated that further increase of  $Bi$  by  $k$  would be senseless and would not alter the rate of concentration change in the liquid phase. The effect of  $k$  became apparent at values  $k < 10^{-6} \text{ m s}^{-1}$ , i.e.  $Bi < 80$ . Then the mass transfer through the boundary layer around the particle was hindered, as for  $Bi = 80$  ( $k = 10^{-7} \text{ m s}^{-1}$ ) the rate of  $C_1$  increase was significantly reduced.

#### Phase equilibrium constant

The equilibrium state of extraction represents the dependence of the equilibrium concentration in the liquid phase on the solid phase concentration for a given temperature and at various liquid/solid ratios. Usually, it is a straight line of the type:  $C_1^* = m \cdot C_2$ , where  $m$  is the phase equilibrium constant. The values of this constant could be larger or smaller than unity. The equilibrium type affects the entire extraction process. The equilibrium constant is included in the boundary condition presented by eqn. (4), thus influencing the solution of the task. The effect of this parameter on the liquid phase concentration change was numerically investigated. The numerical experiments were conducted for  $m = 0.5, 1, 2$  and 3, corresponding to equilibrium line slopes:  $25^\circ 65'$ ,  $45^\circ$ ,  $63^\circ 43'$  and  $71^\circ 57'$ , respectively. The values of the other parameters were as follows:  $k = 10^{-6} \text{ m s}^{-1}$ ,  $D_{eff} = 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ,  $R = 0.3 \times 10^{-3} \text{ m}$  and  $Bi = 30$ . Figure 6 presents the strong influence of this parameter on the type of the obtained solutions. The equilibrium constant affected the nature of the curvature of the obtained solutions, and hence the accuracy of the calculation.

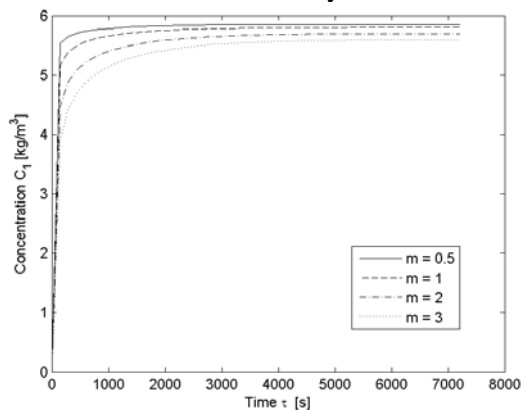


Fig. 6. . Effect of  $m$  on the change of  $C_1$ .

#### Effective diffusion coefficient in the solid phase pores

Since the concentration on the grain surface,  $C_2|_{x=R}$ , depends on the one hand on the effective diffusion coefficient of the extractable component  $D_{eff}$ , and on the other on the partial external mass transfer coefficient  $k$  in the boundary layer around the particle, the complex influence of both parameters was tested.  $D_{eff}$  and  $k$  participate in the calculation of  $Bi$ . Since  $C_1$  is lower than the solid phase concentration  $C_2$  (increased driving force) and if the mass transfer through the boundary layer is very intensive (at  $k = 10^{-4}, 10^{-5} \text{ m s}^{-1}$ ), the concentration  $C_2|_{x=R}$  ceases to depend on  $D_{eff}$  and depends only on  $k$ . The change in the value of  $D_{eff}$ , in this case, influenced the distribution of the extractable component inside the particle (as depicted in Fig. 1), but did not influence the boundary concentration  $C_2|_{x=R}$ , which was approximately equal to  $C_1$ . Figure 7 presents the change of boundary concentration with time for  $k = 10^{-4}$  and  $10^{-7} \text{ m s}^{-1}$ ,  $D_{eff} = 10^{-9}$  and  $10^{-11} \text{ m}^2 \text{ s}^{-1}$ , respectively, and  $R = 0.3 \times 10^{-3} \text{ m}$ . The corresponding values of  $Bi$  are 30, 3000 and 0.03, 3, respectively.

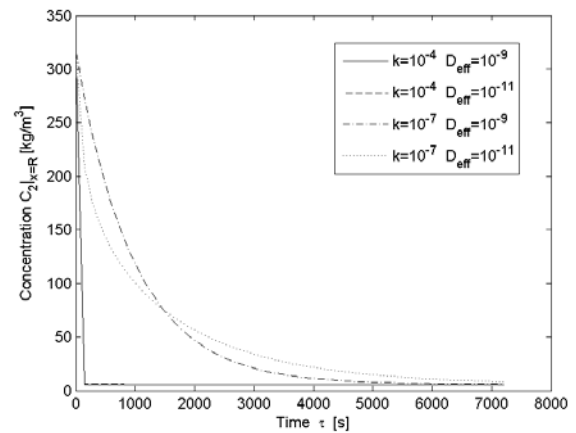


Fig. 7. Effect of  $k$  and  $D_{eff}$  on the concentration  $C_2|_{x=R}$ .

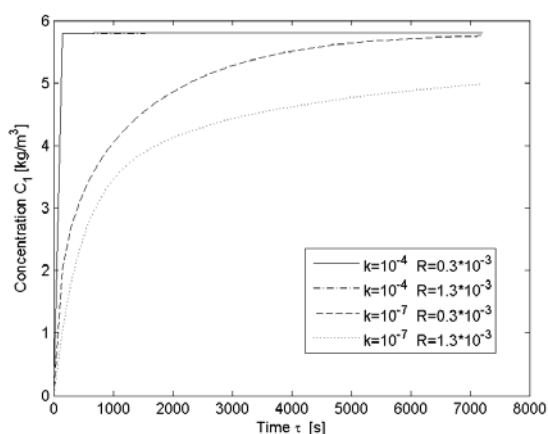
According to the data in Fig. 7 in the case of large values of  $k = 10^{-4} \text{ m s}^{-1}$ , i.e. rapid mass transfer through the external boundary layer, corresponding to  $Bi = 30$  and 3000 (mixed mass transfer mode),  $D_{eff}$  did not influence the type of the obtained curves. Hence, the change of  $C_2|_{x=R}$  depended only on  $k$ , rather than  $D_{eff}$ . For  $D_{eff} = 10^{-9}$  and  $10^{-11} \text{ m}^2 \text{ s}^{-1}$  the curves coincided (Fig. 7). For small values of  $k = 10^{-7} \text{ m s}^{-1}$ , i.e. hindered mass

transfer through the boundary layer, the curves for both  $D_{eff}$  values were well distinguished. In this case, the external and internal diffusion became commensurable ( $Bi = 0.03$  and  $3$ ). For  $k = 10^{-7} \text{ m s}^{-1}$  and  $D_{eff} = 10^{-9} \text{ m}^2 \text{ s}^{-1}$  ( $Bi = 0.03$ ) there was a pronounced external diffusion mode and  $D_{eff}$  started to affect the change of the liquid phase concentration. According to the figures, the impact of  $D_{eff}$  was less pronounced than that of  $k$ . Consequently, the dependence of the change of  $C_2$  on  $D_{eff}$  varied but only when the overall speed of the process was limited by external diffusion and this change was insignificant.  $D_{eff}$  did not affect  $C_2$  for the cases of limiting internal diffusion or mixed mass transfer mode.

#### Solid particles size

Almost similar results were obtained when the impact of particle size on the change of concentration in the liquid phase was investigated (Fig. 8).

The corresponding values of  $Bi$  for the four cases displayed in Fig. 8 were 3000, 13000 and 0.3, 3. Hence, at  $k = 10^{-4} \text{ m s}^{-1}$  the process was controlled by internal diffusion, and at  $k = 10^{-7} \text{ m s}^{-1}$  the mode was mixed. Obviously, the effect of solid particles size was more significant for low  $k$  values, i.e. mixed mass transfer mode -  $Bi \leq 3$ . At  $k \approx 10^{-4} \text{ m s}^{-1}$ , the curves coincided. In that case,  $C_1$  did not depend on the solid particles size.



**Fig. 8.** Effect of the solid particles size ( $R$ ) on the change of  $C_1$ .

It can be summarized that  $C_1$  was influenced mainly by the rate limiting diffusion mechanism related to  $Bi$ , which is in direct correlation with  $k$ . At  $k = 10^{-4} - 10^{-5} \text{ m s}^{-1}$  ( $Bi \geq 60 \div 70$ ), the diffusion is fast, thus  $C_1$  and  $C_2|_{x=R}$  did not depend

on  $D_{eff}$  and the solid particles size. At  $k = 10^{-6} - 10^{-7} \text{ m}^2 \text{ s}^{-1}$  ( $Bi \approx 30 \div 0.03$ ), slight dependence of the concentration profiles in the liquid phase on  $D_{eff}$  and on the solid particles size was established.

The equilibrium phase constant also affected the accuracy of the solution, although less than  $k$ , but again in the regions of mixed and external diffusion control of the process. The influence of this parameter in the case of internal diffusion was insignificant. For most extraction systems, the value of the equilibrium phase constant is approximately 1, but in some cases of multi component extraction of polymers, and when mixed extracting agents (containing both polar and non-polar molecules) are applied, this value can be variable.

Numerical studies aimed to establish the influence of the size of the integration step on the spatial coordinate and time were conducted. For this purpose, solutions were obtained by dividing the spatial coordinate and the time interval into 5, 10, 100, 200, 500 and 1000 parts. The resulting solutions were identical regardless of the step of integration in space or time. This indicated greater resistance of the solution and could be accepted as a criterion for reliable results.

#### Experimental validation

The experimental data for target compounds extraction at different process conditions are presented in Table 1.

The experimentally obtained data for the extraction kinetics of the investigated solid-liquid systems can be described with an acceptable accuracy by eqn. (1). The values of  $A$ ,  $B$  and  $H$  were estimated by nonlinear regression analysis of the experimental data and presented in Table 2 for different sizes of the solid phase - *System I Geranium Sanguineum L.* - 70%  $\text{C}_2\text{H}_5\text{OH}$  and different solid-liquid ratios - *System II Nicotiana tabacum L.* -  $\text{H}_2\text{O}$ .

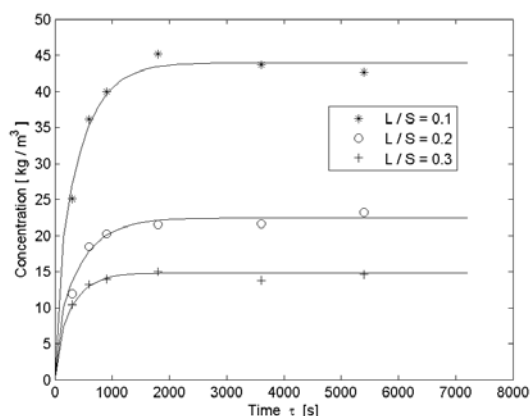
#### Effect of the liquid/solid ratio

To investigate the effect of the liquid/solid ratio on the process kinetics, extraction experiments with *Nicotiana Tabacum L.* were conducted. The experimental results are presented in Table 1. They were described with sufficient accuracy by eqn. (1). The values of the constants  $A$ ,  $B$  and  $H$  were determined by non-linear regression on the basis of the experimental data. The effective diffusion coefficient was calculated by the *Standard function method* [14-18]. Its values are presented in Table 2.



Numerical solutions of the model for the three liquid/solid ratios were obtained. Figure 9 displays the experimental data and the numerical solutions.

Obviously, satisfactory compliance between the experimental and model curves was achieved.



**Fig. 9.** Mathematical modeling of the experimental results for different liquid/solid ratios.

#### Effect of the particle size

To study the influence of the solid phase size on the process kinetics, extraction experiments of total flavonoids from *Geranium Sanguineum L.* were performed. The experimental data are presented in

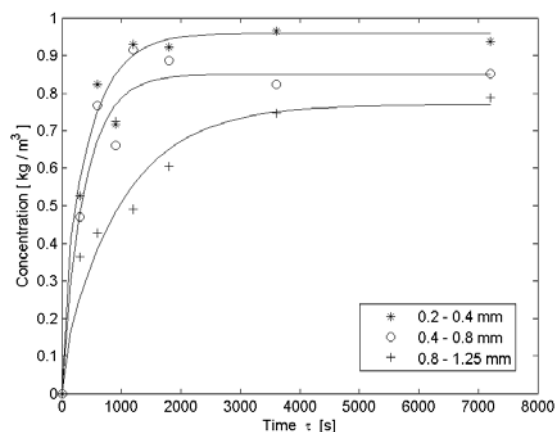
**Table 1.** Experimental data for extracted components concentration in the liquid phase  $C_1$  ( $\text{kg m}^{-3}$ ) under different process conditions

$\tau$ (s)	<i>Nicotiana Tabacum L.</i>			<i>Geranium Sanguineum L.</i>		
	$\xi = 0.01$ ( $\text{m}^3 \text{kg}^{-1}$ )	$\xi = 0.02$ ( $\text{m}^3 \text{kg}^{-1}$ )	$\xi = 0.03$ ( $\text{m}^3 \text{kg}^{-1}$ )	$R=(0.2-0.4)$ $\times 10^{-3}$ (mm)	$R=(0.4-0.8)$ $\times 10^{-3}$ (m)	$R=(0.8-1.25)$ $\times 10^{-3}$ (m)
300	25.14	11.93	10.38	0.527	0.470	0.364
600	36.15	18.45	13.26	0.823	0.767	0.428
900	39.99	20.28	13.94	0.717	0.661	0.725
1200	-	-	-	0.929	0.915	0.491
1800	45.16	21.5	15.00	0.922	0.887	0.604
3600	43.7	21.68	13.77	0.965	0.823	0.746
5400	42.64	23.19	14.60	-	-	-
7200	-	-	-	0.937	0.852	0.788

**Table 2.** Values of the coefficients A, B, and H from eqn. (1) and of  $D_{eff}$  calculated by the standard function method.

Parameter	A	B	H	$D_{eff} \times 10^{10}$ ( $\text{m}^2 \text{s}^{-1}$ )
For Liquid/Solid Ratios ( <i>Nicotiana Tabacum</i> )				
$\xi = 0.01$ ( $\text{m}^3 \text{kg}^{-1}$ )	43.7	43.1	0.003	0.30955
$\xi = 0.02$ ( $\text{m}^3 \text{kg}^{-1}$ )	22.2	22.1	0.0026	0.28064
$\xi = 0.03$ ( $\text{m}^3 \text{kg}^{-1}$ )	14.3	13.8	0.0045	0.47784
For particle size ( <i>Geranium Sanguineum</i> )				
$R = 0.4 \times 10^{-3}$ (m)	0.933	0.9272	0.002713	1.2097
$R = 0.8 \times 10^{-3}$ (m)	0.8406	0.8391	0.002824	5.0567
$R = 1.25 \times 10^{-3}$ (m)	0.7532	0.6815	0.001053	4.7499

Table 1. Solid particles with average sizes of  $0.4 \times 10^{-3}$ ,  $0.8 \times 10^{-3}$  and  $1.25 \times 10^{-3}$  m were used for the experiments. The values of the parameters from eqn. (1) and those of  $D_{eff}$  are presented in Table 2. Figure 10 illustrates the experimental data and the numerical model solutions for the three studied cases.

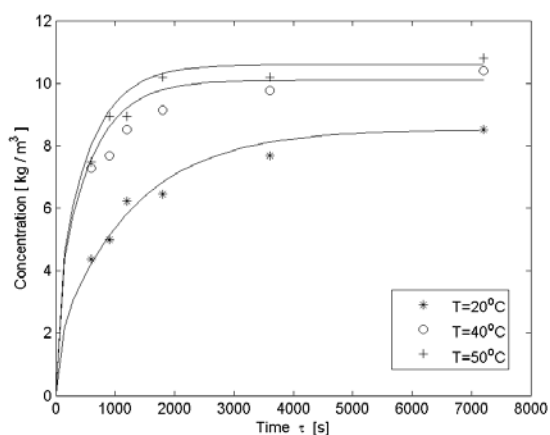


**Fig. 10.** Mathematical modeling of the experimental results for different particle sizes.

According to Fig. 10, when the particles size was reduced, the quantity of the extracted component increased and the kinetics of the process was intensified. Satisfactory correlation between the experimental and model data was observed.

#### Effect of temperature

To study the effect of temperature on the concentration profiles in the liquid phase, experimental data from a previous publication of the scientific team was used [16]. The obtained numerical solution for the examined system was compared to the experimental data.



**Fig. 11.** Mathematical modeling of the experimental results for different temperatures.

Figure 11 presents the experimental results and numerical solutions of tannins extraction from *Cotinus coggygia*. The processing temperature was  $T = 20, 40,$  and  $50^\circ\text{C}$ . The experiments were performed at liquid/solid ratio  $\zeta = 0.02 \text{ kg m}^{-3}$ , density of the solid phase  $\rho_{sol} = 961 \text{ kg m}^{-3}$ , characteristic solid particle size  $R = 1.5 \times 10^{-4} \text{ m}$ , and initial tannins concentration in the solid phase  $C_0 = 353.66 \text{ kg m}^{-3}$ . The values of the constants  $A, B$  and  $H$  and the coefficient  $D_{eff}$  (calculated by the standard functions method) were published previously [16]. A direct relationship between temperature and the quantity of the extracted tannins was observed. There is a good agreement between experimental and modeled results.

## CONCLUSIONS

A parametric study of the influence of various parameters on the concentration change in the solid and liquid phase, during the extraction of target components from plant materials, was conducted. The extraction kinetics of the systems *Geranium Sanguineum* L.–70%  $\text{C}_2\text{H}_5\text{OH}$  and *Nicotiana tabacum* L. –  $\text{H}_2\text{O}$  was experimentally investigated. The comparative analyses outlined that the effect of

the various tested parameters on the process kinetics was complex and its magnitude was determined by the mode of the diffusion control based on  $Bi$  number values. The experimental data showed that, in all cases of extraction from plant materials, the process was controlled by internal diffusion. Thus, the main parameters influencing the kinetics of the process were the effective diffusion coefficient and the size of the solid particles.

The decrease in the solid particles size at constant other parameters lead to a decrease of the  $Bi$  value. According to the conducted numerical experiments, the extraction process was intensified at smaller particle sizes. At particles sizes smaller than  $R = 0.4 \times 10^{-3} \text{ m}$ , practically the entire quantity of the target component was extracted after 7200s. The latter was confirmed by the experimental data for extraction of flavonoids from *Geranium Sanguineum* L. The effective diffusion coefficient depended predominantly on the temperature and the solid phase structure, as confirmed by both the performed numerical experiments and the experimental data for tannins extraction from *Cotinus coggygia* L. Therefore, by increasing the temperature the amount of the extracted material was increased. The liquid/solid ratio was directly related to the change of the liquid phase concentration  $C_1$ . The numerical experiments displayed slighter influence of this parameter on the numerical model solution. The liquid/solid ratio affected predominantly the driving force and therefore, the intensity of the diffusion process. The latter was confirmed by the experimental data of target compounds extraction from *Nicotiana tabacum* L.

The influence of the partial mass transfer coefficient through the external boundary layer and the equilibrium phase constant was investigated numerically. These two parameters affected the model solution only in the regions of mixed and external diffusion control ( $Bi < 30 \div 40$ ). For internal diffusion, the influence of both parameters was insignificant.

The numerical modeling of all experimental data displayed satisfactory compliance between the experimental and model results. The comparative analyses and the suggested mathematical model could be applied for the simulation and description of extraction processes from various plant materials at verified technological parameters influencing the process intensity.

## NOMENCLATURE

$A$  = coefficient defined by eqn. (1)  
 $B$  = coefficient defined by eqn. (1)  
 $Bi$  = Biot number ( $Bi = kR/D_{eff}$ )  
 $C_1$  = concentration in the liquid phase ( $\text{kg m}^{-3}$ )  
 $C_{1eq}$  = equilibrium concentration in the liquid phase ( $\text{kg m}^{-3}$ )  
 $C_2$  = concentration in the solid phase ( $\text{kg m}^{-3}$ )  
 $C_o$  = initial concentration in the solid phase ( $\text{kg m}^{-3}$ )  
 $\bar{C}_2$  = average concentration in the solid phase ( $\text{kg m}^{-3}$ )  
 $D_{eff}$  = effective diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ )  
 $H$  = coefficient defined by eqn. (1)  
 $k$  = external mass transfer coefficient ( $\text{m s}^{-1}$ )  
 $m$  = distribution coefficient  
 $n$  = agitation rate ( $\text{s}^{-1}$ )  
 $R$  = characteristic size of the solid particles (m)  
 $T$  = temperature ( $^{\circ}\text{C}$ )  
 $x$  = coordinate (m)

*Greek Letters*

$\delta$  = solid particles size (mm)  
 $\mu_i$  = roots of the characteristic equation  
 $v$  = shape factor  
 $\zeta$  = liquid/solid ratio ( $\text{m}^3 \text{kg}^{-1}$ )  
 $\rho_{sol}$  = density of the solid phase ( $\text{kg m}^{-3}$ )  
 $\tau$  = time (s)  
 $\psi$  = relative coordinate ( $\psi = x/t$ )

## REFERENCES

1. C.H. Chon, R. Yusoff, G.-C. Ngoh, *Chem. Eng. Res. Des.*, **92** (6), 1169 (2014).
2. M. Cisse, P. Bohuon, F. Sambe, C. Kane, M. Sakho, M. Domier, *J. Food Eng.*, **109** (1), 16 (2012).
3. A. Stoiza, T. Dobre, M. Stoescu, A. Sturzoiu, O.C. Parvulescu, *Food Bioprod. Process.*, **94**, 218 (2015).
4. R. Wongkittipong, L. Prat, S. Damroglerd, C. Gourdon, *Sep. Purif. Technol.*, **40** (2), 147 (2004).
5. J. D. Espinoza-Pérez, A. Vargasa, V.J. Robles-Olvera, G.C. Rodríguez-Jimenes, M.A. García-Alvarado, *J. Food Eng.*, **81** (1), 72 (2007).
6. A. Bucić-Kojić, M. Planinića, M. Tomasa, M. Bilića, D. Velica, *J. Food Eng.*, **81** (1), 236 (2007).
7. M. Pinelo, J. Sineiro, M. J. Núñez, *J. Food Eng.*, **77**, 57 (2006).
8. T.A. Nguena, P. Verbovena, N. Scheerlincka, S. Vandewalleb, B.M. Nicolăia, *J. Food Eng.*, **72**(1), 63 (2006).
9. I. Seikova, E. Simeonov, E. Ivanova, *J. Food Eng.*, **61**, 165 (2004).
10. E. Simeonov, I. Tsibranska, A. Minchev, *Chem. Eng. J.*, **73**, 255 (1999).
11. I. Seikova, E. Simeonov, *Sep. Sci. Technol.*, **38** (15), 3713 (2003).
12. M. Izadifar, O.D. Baik, *Sep. Purif. Technol.*, **63** (1), 53 (2008).
13. A. Senol, A. Aydin, *J. Food Eng.*, **75** (4), 565 (2006).
14. E. Simeonov, I. Seikova, I. Penchev, A. Minchev, *Ind. Eng. Chem. Res.*, **42** (7), 1433 (2003).
15. E. Simeonov, I. Seikova, I. Pentchev, A. Mintchev, *Ind. Eng. Chem. Res.*, **43**, 4903 (2004).
16. Ch. Chilev, V. Koleva, E. Simeonov, *Ind. Eng. Chem. Res.*, **53**, 6288 (2014).
17. D. Marinova, F. Ribarova, M. Atanasova, *J. Chem. Technol. Metall.*, **40** (3), 255 (2005).
18. G.A. Axelrood, W. Lisjanski, Extraction (Solid-liquid systems); USSR, *Chimia*: St. Peterburg, 115 (1974).

## ИЗСЛЕДВАНЕ НА МЕХАНИЗМА И КИНЕТИКАТА НА ЕКСТРАКЦИЯ ОТ РАСТИТЕЛНИ СУРОВИНИ

Е. Симеонов<sup>1\*</sup>, З. Янева<sup>2</sup>, Ч. Чилев<sup>1</sup>

<sup>1</sup>Катедра „Инженерна химия“, Химикотехнологичен и металургичен университет, бул. „Кл. Охридски“ 8, 1756 София, България

<sup>2</sup>Секция „Химия“, Катедра „Фармакология, физиология на животните и физиологична химия“, Ветеринарномедицински факултет, Тракийски университет, Студентски град, 6000 Стара Загора, България

Постъпила на 11 юли 2016 г., коригирана на 24 януари 2017 г.

(Резюме)

Проведено е цялостно систематично изследване на механизма на извличане на полезни компоненти при твърдотечна екстракция от растителни суровини. Извършени са серии от експерименти на екстракционно извличане на флавоноиди от корени на кръвен здравец - *Geranium Sanguineum* L. (екстрагент 70%  $\text{C}_2\text{H}_5\text{OH}$ ), и на тютюнев конкрет от тютюневи листа - *Nicotiana tabacum* L. (екстрагент  $\text{H}_2\text{O}$ ). За целта бе проведено параметрично изследване на влиянието на параметрите: размер на твърдата фаза ( $R = 0.2 \times 10^{-3} \div 1.2 \times 10^{-3}$  m), коефициентът на ефективна дифузия ( $D_{eff} = 10^{-10} \div 10^{-12}$   $\text{m}^2 \text{s}^{-1}$ ) частен коефициент на масопренасяне ( $k = 10^{-5} \div 10^{-7}$   $\text{ms}^{-1}$ ), температура ( $T = 20 \div 60$   $^{\circ}\text{C}$ ) и хидромодул ( $\zeta = 0.01 \div 0.03$   $\text{m}^3 \text{kg}^{-1}$ ), върху изменението на концентрацията в твърдата и течната фаза. Установена е много висока степен на корелация между експерименталните и моделни стойности.