Solid-liquid Extraction of Tannins from *Geranium Sanguineum L.* – Experimental Kinetics and Modelling

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This paper is concerned with the investigation and the modelling of a solid-liquid extraction process and the importance of the influencing factors (solid phase, particle size and liquid-solid ratio). The studied system is a plant material (*Geranium Sanguineum – L.)* and a solvent mixture – 70 % ethanol in water. From the results, it is clear that the valuable compounds' extraction rate is much more influenced by the solid particle size than the liquid-solid ratio. The process is described by a mathematical model which allows the determination of the effective diffusion coefficient (D_{eff}) for the investigated solid-liquid system. Its values are compared with the D_{eff} obtained by the methods of regular regime and the standard function. Very good correspondence is found.

Key words:
solid-liquid extraction, kinetics, diffusion coefficient, modeling, plant material, *Geranium-Sanguineum*

Introduction

Geranium sanguineum[1] is a perennial herbaceous plant in the family *Geraniaceae* with a branching out main stem and well-developed root system. On a mass scale, the roots are used for healing and when cut they are light pink in the beginning and become red later. The roots' composition mainly consists of tannins – non-hydrolising (catechin tannins) and hydrolising (gallates), about 0.36 % flavonoids – 0.16 % of which is hyperozid and a sum of kaempherol, quarcetin, miricitin, quercitirin and anthocyans – pelargonidin and malvin. The extracts from this part of the plant contain each group of the phenol compounds in different quantities or a combination of them in different ratios.

The solid-liquid extraction is a process whose products are widely used in pharmaceuticals, cosmetics, tobacco, and food industries and has also its application with environmental purposes. This provoked numerous scientific studies in this field focused on the process kinetics,[2–5] the diffusivity, the yield of extraction[6] and the process design.[7]

Mathematical modeling is a powerful tool for equipment optimization, simulation, design and control, allowing theoretical description of the process and evaluation of the mass transfer coefficients.[8–12] The possibility to extract maximum valuable compounds in short time is of significant interest for practice. The extraction rate is one of the technological criteria applied to evaluate the efficiency of extraction apparatus. The process description is very difficult due to the number of indefinable parameters influencing the process: solid phase pore structure (varies during extraction), irregular particle shape, large particle size distribution. The initial concentration of the valuable substances may also differ for the same plant raw material as a function of the crop area and storage condition. The process temperature, the solvent – solid ratio and the size of the solid phase particles are the technological parameters of the extraction process. The kinetic coefficients vary during the extraction as well.

In order to set up an experimental installation, the diffusion type and the factors that are of main importance for the process have to be known. There are three different approaches for that purpose: analytical solution for the three classical shapes of the solid phase, numerical solutions based on simplifications and experimental data description applying the method of standard or characteristic functions.[7]

The extraction of valuable components from plant raw material is ever limited by the mass transfer inside the pores of the solid phase. Each experimental kinetic curve (dependence) represents in a hidden way all the factors influencing the diffusion process velocity like polydispersion, anisotropy, solid particles form, liquid phase concentration change. These factors are given quantitatively by the effective diffusion coefficient.[11] The exact calculation of D_{eff} is important for the process engineering. The combination of the experimental and process analytical data is used for the calculation of

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D_{eff} using the methods of Standard function and Regular regime.[13,14]

The aim of this work is first to evaluate the importance of the technological parameters solid-liquid ratio (ζ) and solid particle size (δ) for the extraction rate, and second to create a mathematical model of the process which allows the determination of D_{eff} for a real liquid-solid system.

Materials and methods

Plant material preparation

The roots from *Geranium Sanguineum L.* were used as a solid phase. They were grinded and separated in three fractions: δ = 0.2–0.4 mm, δ = 0.4–0.8 mm and δ = 0.8–1.25 mm.

Extraction design

The kinetic experiments were performed in a stirred vessel. The ground raw material with the suitable size was put in a reactor and poured on with 70 % ethanol solution. The reactor was sunk in a water bath and the temperature was maintained constant and controlled by a thermometer. The mixture was continuously stirred. To ensure limiting internal diffusion, the angular velocity of the mixer was regulated. The extraction samples were then taken and filtrated through plaited filter to separate the solid from the liquid phase.

Experimental conditions

The kinetic study was carried out by periodical extraction from roots of *Geranium Sanquineum – L.* in a stirred vessel. The process temperature was 20°C. This process temperature was chosen due to our previous experiments in this field investigating the influence of δ, ζ and T/°C on the extraction rate. In this work are shown the results at the highest extraction rate conditions.

In order to eliminate the external mass transfer resistance, the speed of the stirrer was maintained at 5 s^{-1}. In our previous experiments we determine the minimum agitation speed by which the concentration of extracted components in the liquid phase is constant, i. e. the external diffusion resistance is eliminated. This is a requirement of the standard function (D_{eff}) application (presence of an internal diffusion regime, i.e. Bi > 30).

The experiments were performed with three sizes of the solid phase particles (δ = 0.2–0.4 mm, δ = 0.4–0.8 mm and δ = 0.8–1.25 mm) and at three different liquid-solid ratios (ζ = 0.01 $m^3\ kg^{-1}$, ζ = 0.02 $m^3\ kg^{-1}$ and ζ = 0.03 $m^3\ kg^{-1}$). 70 % ethanol is used as a solvent. The extracts were filtered with paper folded filter (Boeco Germany, Grade 6). The concentration of valuable compounds (tannins) in the liquid phase (γ_1) after the extraction was measured. Each point of the kinetic curve was established based on the average value of three independent experiments.

Analytical method for the extract analysis

The concentration of tannins in the extracts (liquid phase) was measured by the modified Loewental method.[15,16] It is based on the titration with $KMnO_4$. 2 mL of the filtrated extract were added to 750 mL distilled water. 25 mL of indicator indigocarmin-sulphonic acid were added to the sample. Standard solution of $KMnO_4$ (0.02 mol L^{-1} = 0.1 N, Titrisol®, Merck) was used for the titration. The concentration of the extracted valuable compounds is calculated by the volume of $KMnO_4$ used for the oxidation process.

Statistical methods

The concordance between the experimental data and the calculated values was established by the root mean squared deviation (RMSD) by the following equation:[16]

$$RMSD = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(experimental - calculated)^2} \quad (1)$$

The average absolute deviation was expressed as follows:

$$\overline{dev}\,(\%) = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{experimental - calculated}{experimental}\right|\cdot 100 \quad (2)$$

Kinetic study, diffusion coefficients and modelling

The proposed methods consist of analysis of the kinetic behavior during a periodical solid-liquid extraction considering the following diffusion model:

$$\frac{\partial\gamma_2(x,\tau)}{\partial\tau} = D_e\left[\frac{\partial^2\gamma_2}{\partial X^2} + \frac{t}{X}\frac{\partial\gamma_2}{\partial X}\right] \quad (3)$$

where γ_2 – concentration in the solid phase.

There are two methods for determination of D_{eff} based on the combination between analytical solutions of (3) and experimentally obtained $\gamma_2 = f(\tau)$ for the boundary case $Bi \to \infty; \beta \to 0$.[13]

Method using the standard function

This method is based on the comparison between the analytical solution and the standard function. Eq. (3) in combination with boundary conditions gives the following results for the three classical forms of the solid phase:[13]

$$\frac{\gamma_0-\bar{\gamma}_2}{\gamma_0-\gamma_m}=\frac{1}{1+\beta}- -\sum_{n=1}^{\infty}\frac{4\cdot(\nu+1)}{\mu_n^2+4(\nu+1)^2\cdot\beta(1+\beta)}\cdot e^{-\mu_n^2\frac{D_{eff}\tau}{R^2}} \tag{4}$$

where γ_0 – initial concentration in the solid phase; $\gamma_m=\gamma_{1i}$ by periodical processes, γ_{1i} – initial concentration in the liquid phase, $\bar{\gamma}_2$ – average concentration in the solid phase; D_{eff} – effective diffusion coefficient in pores of the solid phase; R – size of the solid particle; τ – time, $\beta=\dfrac{\gamma_{1eq}}{\gamma_0-\gamma_{1eq}}$, γ_{1eq} – equilibrium concentration in the liquid phase; μ_i – roots of the characteristic equation; ν = 1/2 for sphere shape of the solid phase.

We can narrow Fo > 0.1 to the first term of (4):

$$\frac{\gamma_0-\bar{\gamma}_2}{\gamma_0-\gamma_m}=\frac{1}{1+\beta}- -\frac{4\cdot(\nu+1)}{\mu_1^2+4(\nu+1)^2\cdot\beta(1+\beta)}\cdot e^{-\mu_1^2\frac{D_{eff}\tau}{R^2}} \tag{5}$$

and by comparison of this equation with the standard function (6):

$$\overline{\overline{\Phi}}^*(\tau)=\frac{\gamma_0-\bar{\gamma}_2}{\gamma_0-\gamma_m}=A-B\exp(-H\tau) \tag{6}$$

where $Fo=\dfrac{D_{eff}\tau}{R}$

it is obvious that the coefficients A, B and H are respectively equal to:[14]

$$A=\frac{1}{1+\beta} \tag{7}$$

$$B=\frac{4\cdot(t+1)}{\mu_1^2+4(t+1)^2\cdot\beta(1+\beta)} \tag{8}$$

$$H=\frac{\mu_1^2D_{eff}}{R^2} \tag{9}$$

by $A\cong 1$ ($\beta=0$) the coefficient of the effective diffusion D_{eff} is:

$$D_{eff}=\frac{HR^2B}{2(t+1)} \tag{10}$$

where $t=2$ for sphere shape of the solid phase.

Method using regular regime

This method is based on a comparison between the experimentally obtained data by a non-constant mass transfer from the solid into the liquid phase with the analytical solutions by the same conditions of mass transfer.

It is known that at the beginning of this regime D_{eff} = const. and for eq. (3) for sphere shape of the solid phase by $\tau=0,\gamma_2=\gamma_0=const,\gamma_{1i}=0$ we can obtain:

$$\frac{\bar{\gamma}_2}{\gamma_0}=\sum_{n=1}^{\infty}\frac{6}{\pi^2n^2}e^{-\pi^2n^2\frac{D_{eff}\tau}{R^2}} \tag{11}$$

where γ_1 – concentration in liquid phase; γ_{1i} – initial concentration in liquid phase.

For Fo > 0.1 we can narrow (11) to its first term:

$$\frac{\bar{\gamma}_2}{\gamma_0}=B_1e^{-\mu\frac{D_{eff}\tau}{R^2}} \tag{12}$$

For the investigated system $Bi\rightarrow\infty;B_1=\pi/6;$ $\mu_1=\pi^{5,13}$ eq. (12) becomes:

$$\lg\frac{\gamma_2}{\gamma_0}=\lg B_1-0.434\mu_1^2\frac{D_{eff}\tau}{R^2} \tag{13}$$

where $Bi=\dfrac{kR}{D_{eff}}$, k – local coefficient of mass transfer, m s^{-1}.

Diffusion model

The extraction from the solid phase can be described with a mathematical model of the type:

$$\frac{\partial\gamma_2}{\partial\tau}=D_{eff}\left(\frac{\partial^2\gamma_2}{\partial x^2}+\frac{t}{x}\frac{\partial\gamma_2}{\partial x}\right) \tag{14}$$

with boundary conditions:

$$-D_{eff}\left(\frac{\partial\gamma_2}{\partial x}\right)_{x=x}=k\left(\frac{\gamma_{2x=x}}{m}-\gamma_1\right) \tag{15}$$

$$\left(\frac{\partial\gamma_2}{\partial x}\right)_{x=0}=0 \tag{16}$$

$$\gamma_{2_{\tau=0}} = \gamma_0 \tag{17}$$

where m – distribution coefficient, $m \approx 1$ because of the low concentration range (well known fact in literature for the investigated plant material).

Results and discussion

Kinetics

The influence of the particle size on the valuable compounds extraction at 20 °C and $\zeta = 0.02$ m^3 kg^{-1} is illustrated in Fig. 1. The concentration of extracted tannins was the highest during the extraction from the smallest particles ($\delta = 0.2$–0.4 mm) and the lowest in the case of the biggest particles ($\delta = 0.8$–1.25 mm). A fast kinetics for all three solid particle sizes for this system is observed.

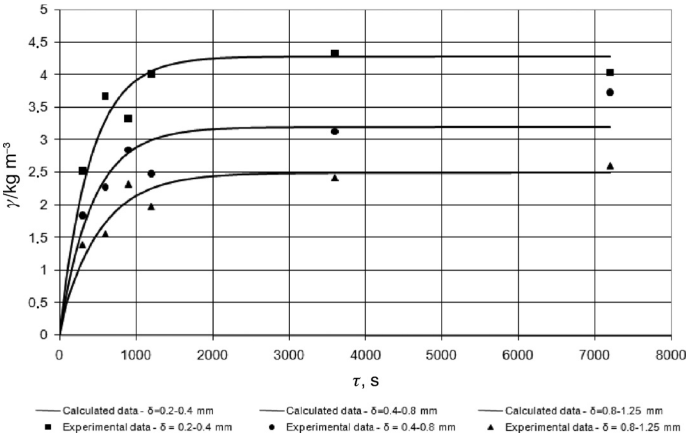

Fig. 1 – *Kinetics of extraction from Geranium Sanquineum – L. with 70 % ethanol by different sizes of solid phase particles and* $\zeta = 0.02$ *m*^{3} *kg*$^{-1}$

The experimental data by solid phase with particle size $\delta = 0.4$–0.8 mm and various liquid-solid ratios (ζ) are shown in Fig. 2.

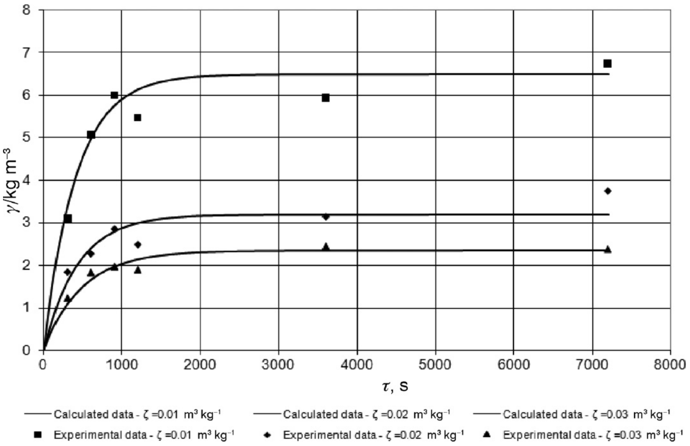

Fig. 2 – *Kinetics of extraction from Geranium Sanquineum – L. with 70 % ethanol by different liquid-solid ratios and* $\delta = 0.4$–0.8 *mm*

The experimentally obtained data for the extraction kinetic of the investigated system solid-liquid can be described with acceptable accuracy by the following eq. (18)

$$\gamma_1 = A - Be^{-H\tau} \tag{18}$$

The values of A, B and H are numerically estimated and presented in Table 1 for different solid-liquid ratios and solid phase particle size.

Table 1 – *Values of A, B and H for describing the kinetics*

ζ, m^3 kg^{-1}	0.02	0.02	0.02	0.01	0.03
δ, mm	0.2–0.4	0.4–0.8	0.8–1.25	0.4–0.8	0.4–0.8
A	5.61	4.26	3.64	7.80	3.00
B	5.59	4.00	3.55	7.70	2.87
H	0.0027	0.00155	0.00125	0.0026	0.0027
RMSD	0.143	0.079	0.097	0.413	0.165
dev%	2.33	1.79	3.31	5.44	5.77

The extraction rate η is calculated for the experimental conditions by the eq. (19)

$$\eta_i = \frac{\gamma_0 - \gamma_{2i}}{\gamma_0} \tag{19}$$

where γ_{2i} – concentration in the solid phase after extraction for experimental time τ.

Presenting the kinetics by the method of standard function

The standard function (6) is calculated based on the kinetic eq. (18) for $\delta = 0.4$–0.8 mm and $\zeta = 0.02$ m^3 kg^{-1}. In order to use this method for presenting the extraction kinetics it is necessary that the extraction process reaches equilibrium and an internal diffusion regime (Bi > 30)[14] is present.

The value of the initial concentration of valuable compounds in the solid phase (γ_0) is necessary for the calculations. It is determined with the following the methodology: a multiple extraction from the solid phase is done ($\tau \rightarrow \infty$) – it is assumed that all valuable compounds present in the solid phase are transferred into the liquid phase; the concentration of useful compounds measured in the liquid phase is restated as a concentration in the solid phase using the porosity of the solid phase (pores volume) and the solid-liquid ration by the extraction.

The coefficients of effective diffusion D_{eff} are estimated using the method of standard function by eq. (8) and the results are presented in Table 2.

Table 2 – *Values of D_{eff}, calculated by the method of standard function*

ζ, m^3 kg^{-1}	0.02	0.02	0.02	0.01	0.03
δ, mm	0.2–0.4	0.4–0.8	0.8–1.25	0.4–0.8	0.4–0.8
D_{eff}, m^2 s^{-1}	$1.04 \cdot 10^{-11}$	$2.11 \cdot 10^{-11}$	$5.18 \cdot 10^{-11}$	$3.60 \cdot 10^{-11}$	$3.70 \cdot 10^{-11}$

From a diffusion point of view, the smaller the particles the better the access of the liquid to the pores of the solid phase (not only to the meso but to some of the micro pores). The idea was to show the value of D_{eff} for reaching the desired extraction rate for all particle sizes and solid-liquid ratios. It is natural (proved by the presented experimental data) that the time for reaching the equilibrium (τ_{equ}) is shortest for an extraction from the smallest particles size. However, its correlation with D_{eff} is not unambiguous. Usually the value of D_{eff} grows rapidly at the beginning of the process by reaching a maximum, which does not correspond to τ_{equ}. This statement is based on many of our practical observations through studying the extraction kinetics from plant materials.

Often, after it reaches its maximum, the value of D_{eff} starts to decrease (diffusion resistance in the solid phase increases) due to the changes in the solid phase structure. The extraction is already present from not only the meso pores but some micro pores as well, and even some "closed" pores up to this point.

Presenting the kinetics by the method of regular regime

Using the method of regular regime, eq. (13) is graphically presented in Figs. 3 and 4 for the different experimental conditions. It is obvious that a regular regime of extraction is present from the very beginning of the process since the graphic is linear in the whole range of the semi-logarithmic coordinates. This is valid for the three particle sizes as well as for the three liquid-solid ratios. The received values for D_{eff} are listed in Table 3.

Using this method, Bi number can be estimated. For sphere solid phase particle (which we consider the solid phase) the relation between Bi number and μ_{i} is given by the following eq. (20)

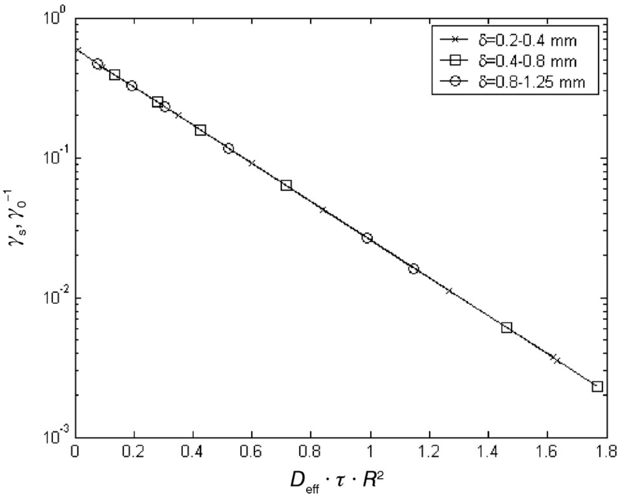

Fig. 3 – *Kinetic curve by existing regular regime by different sizes of solid phase particles and $\zeta = 0.02$ m^3 kg^{-1}*

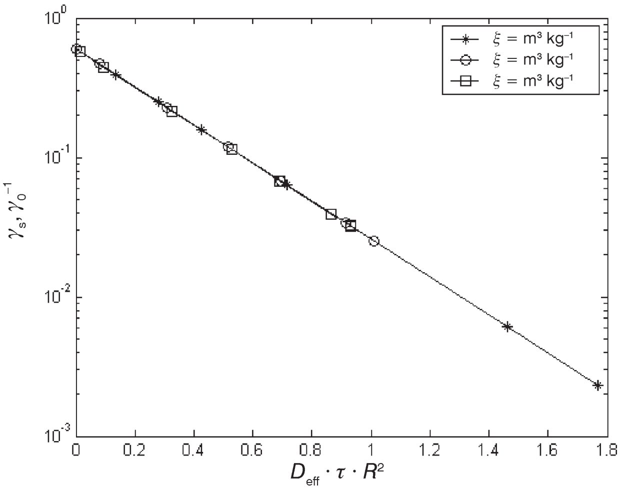

Fig. 4 – *Kinetic curve by existing regular regime by different liquid-solid ratios and $\delta = 0.4$–0.8 mm*

$$\cot g\mu_1 = \frac{1}{\mu_1} + \frac{1}{\dfrac{3\beta}{\mu_1} - \dfrac{\mu_1}{Bi}} \tag{20}$$

Table 3 – *Values of D_{eff}, calculated by the method of regular regime*

ζ, m^3 kg^{-1}	0.02	0.02	0.02	0.01	0.03
δ, mm	0.2–0.4	0.4–0.8	0.8–1.25	0.4–0.8	0.4–0.8
D_{eff}, m^2 s^{-1}	$1.58 \cdot 10^{-11}$	$3.60 \cdot 10^{-11}$	$7.45 \cdot 10^{-11}$	$5.20 \cdot 10^{-11}$	$5.25 \cdot 10^{-11}$

The received values for Bi number are in the range 58 – 87 for the different experimental conditions and this is proof that an internal diffusion regime is present.

Diffusion model

The basic diffusion model for a solid-liquid extraction[13] was used with constant coefficient of effective diffusion received applying the methods of regular regime and standard function. The numerical solution is made with software MATLAB 7.9.0. The graphical interface *PDE tool* is used.

The solution of the diffusion model (14), (15), (16) and (17) for $\delta = 0.4 - 0.8$ mm and $\zeta = 0.02$ m^3 kg^{-1} is graphically presented in Fig. 5 and it is compared with the experimental data.

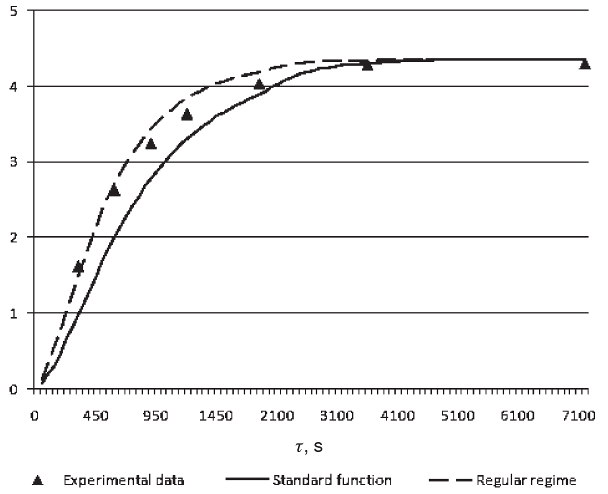

Fig. 5 – *Numerical solution of the diffusion model by using D_{eff} obtained by the methods of regular regime and standard function*

RMSD for the data received with D_{eff} obtained by the method of standard function compared with the experimental results is 0.38 and for data obtained with the regular regime RMSD is 0.168. This leads us to conclude that the method of the regular regime gives more accurate results than the method of the standard function. However, for the investigated system we can accept that both methods are suitable for describing the extraction process accurately enough.

Conclusions

In this work, the extraction kinetics, the influence of solid phase particle size and liquid-solid ratio on extraction rate are studied. Higher extraction rate for shorter time is observed for $\delta = 0.2 - 0.4$ mm compared to other solid phase size ($\eta = 0.98$ by $\tau = 1600$ s for $\delta = 0.2 - 0.4$ mm; $\eta = 0.98$ by $\tau = 2800$ s for $\delta = 0.4–0.8$ mm; $\eta = 0.98$ by $\tau = 5200$ s for $\delta = 0.8 - 1.25$ mm). A mathematical model of the process is created and solved using coefficient of effective diffusion received by the methods of standard function $D_{\text{eff}} = 2.11 \cdot 10^{-11}$ and regular regime $D_{\text{eff}} = 3.04 \cdot 10^{-11}$. There is a very good correspondence between the analytical and experimental data. The methods of the standard function and the regular regime are found to be very reliable for describing an extraction process from plant materials.

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List of symbols

A – coefficient, –
B – coefficient, –
Bi – Biot number, –
D_{eff} – effective diffusion coefficient, m^2 s^{-1}
Fo – Fourier number, –
H – coefficient, –
k – local coefficient of mass transfer, m s^{-1}
m – distribution coefficient, –
R – size of the solid particle, mm
T – temperature, °C
t – solid particle shape coefficient, –
x – distance, mm

Greek symbols

δ – solid particle size, mm
ζ – solid-liquid ratio, m^3 kg^{-1}
γ – tannin concentration, kg m^{-3}
μ – roots of the characteristic equation, –
η – extraction rate, –
τ – time, s
ν – solid phase shape coefficient, –

Indices

eq – equilibrium
0 – initial
1 – liquid phase
2 – solid phase

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