ABSTRACT

Experimental kinetics has been obtained by extraction from leaves of Nicotiana tabacum L. at periodic conditions in a stirred vessel. The influence of the liquid-solid ratio and the kind of the solvent have been determined. A four parameters model for calculating the values of $D_{eff}$ has been found using non-linear regression of the experimental results. The diffusion model have been solved using variable $D_{eff}$. There is a very good coincidence between the numerical and experimental data.

Keywords: solid-liquid extraction, kinetics, effective diffusion coefficient, modeling.

INTRODUCTION

The solid-liquid extraction is a process whose products are widely used in pharmaceutics, cosmetics and food industries. The process description is very difficult because of the influence of a large number of parameters: variable in the time solid phase pore structure, irregular particle shape, large particle size distribution. The kinetic coefficients vary during the extraction [1]. There are two different ways to analyse these factors – analytical and numerical. Each experimental kinetic curve includes in a hidden way all factors that influence the diffusion process velocity. Quantitatively, these factors are reported by the effective diffusion coefficient. A lot of studies of $D_{eff}$ show that its value can decrease or stay constant during the solid-liquid extraction process. By $D_{eff} = \text{const}$ it can be obtained by solving the one-dimensional Fick’s law for the three “classical” shapes of solid phase – plate, sphere and cylinder [2 - 5]. However $D_{eff}$ is usually variable during the process. Different ways of describing this can be found in the literature – $D_{eff}$ as an exponential function of the extractable concentration in the solid phase or solid concentration and changing internal porosity of the solid material during the process [5].

There are currently plenty of investigations on the possibility of theoretical description of solid-liquid extraction and $D_{eff}$ estimation especially. They describe the difficulties by obtaining the analytical and numerical solutions, and especially their adequacy by designing the extraction process in production scale [6, 7]. There are experimental methods and those combining experimentally received data and analytical decisions of the process. For the calculation of $D_{eff}$, the method of Standard function and Regular regime are used [3, 8]. The use of empirical models is an alternative. They are with very limited possible application since they do not show the physical meaning of the complicated nonstationary diffusion process in solid phase and do not summarise certain class of phenomena [9, 10].

MATERIALS AND METHODS

Plant material

The experiments have been carried with important for the industry vegetable raw material - tobacco leaves (Nicotiana tabacum L.) for obtaining extracted compounds.

Extraction design

The kinetic experiments were performed in a stirred vessel. The raw material with the suitable size was put in a reactor and poured on with 96 % ethanol solution.
or water. The reactor was sunk in 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. After the extraction samples were 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 in stirred vessel. The process temperature was 20°C. In order to eliminate the external mass transfer resistance the velocity of the stirrer was maintained at n = 5 s\(^{-1}\). The experiments were performed with two different liquid-solid ratios (\(\xi = 0.03 \text{ m}^3/\text{kg}, \xi = 0.04 \text{ m}^3/\text{kg}\)). 96% ethanol and pure water is used 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 point of the kinetic curve was established based on the average value of three independent experiments.

Analytical method for the extract analysis

Weight analysis for extracted compounds determination

For quantitative determination of extracted compounds is used a weighing method with precision 10\(^{-3}\) g. The extracts are dried at temperature \(t = 70^\circ\text{C}\).

Kinetic study and modeling

When a convective transfer in the solid phase pores is missing, the mass transfer is described by the eq. (1):

\[
\frac{\partial C_2}{\partial \tau} = \frac{1}{X'} \frac{\partial}{\partial x} \left[ X' D_{\text{eff}} \frac{\partial C_2}{\partial x} \right]
\]

(1)

For \(D_{\text{eff}} = \text{const}\) it can be obtained by solving the one-dimensional Fick’s law for the three “classical” shapes of solid phase – plate, sphere and cylinder – eq. (2)

\[
\frac{\partial C_2}{\partial \tau} = D_{\text{eff}} \left( \frac{\partial^2 C_2}{\partial x^2} + \frac{t}{x} \frac{\partial C_2}{\partial x} \right)
\]

(2)

with boundary conditions:

\[
-D_{\text{eff}} \left( \frac{\partial C_2}{\partial x} \right)_{x=x} = k \left( \frac{C_2}{m} - C_1 \right)
\]

(3)

The summarized analytical decision is:

\[
\frac{C_0 - C_2}{C_0 - C_m} = \frac{1}{1 + \beta} \sum_{n=1}^{\infty} \frac{4(\nu + 1)}{\mu_n^2 + 4(\nu + 1)^2} \cdot (1 + \beta).
\]

(4)

where \(C_0\) – initial concentration in the solid phase; \(C_m = C_1\) for periodical processes, \(C_1\) – initial concentration in the liquid phase, \(C_2\) – average concentration in the solid phase; \(D_{\text{eff}}\) – effective diffusion coefficient in pores of the solid phase; \(R\) - size of the solid particle; \(\tau\) - time,

\[
\beta = \frac{C_{1\text{eq}}}{C_0 - C_{1\text{eq}}},
\]

\(C_{1\text{eq}}\) – equilibrium concentration in the liquid phase; \(\mu_i\) – roots of the characteristic equation; \(\nu = -1/2\) for plate shape of 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).

RESULTS AND DISCUSSION

The experimentally received data for the extraction kinetics for the investigated system solid-liquid can be described with an acceptable accuracy by the following equation (8)

\[
C_1 = A - B \exp^{-H\tau}
\]

(8)

The values of \(A\), \(B\) and \(H\) are estimated by nonlinear regression of experimental data and presented in Table 1 for different temperatures, solid-liquid ratios and different extraction solvents.

A numerical decision of the mathematical model with variable coefficient of the effective diffusion is found. The program medium MatLab 8.0.1 is used. A four parameters equation of the type (9) is proposed:
The coefficients in this exponential equation are determined by a non-linear regression of the experimental data. The $D_{\text{eff}}$ change for the certain working conditions is presented in Fig. 1 and Fig. 2.

The results show a very good correspondence between the experimentally received data for $D_{\text{eff}}$ calculated by the regular regime method [8] and those calculated by eq. (9). It shows that this function can be used successfully for modelling kinetics by extraction from plant material using water-alcoholic solutions as solvent system. In the Fig. 3 and Fig. 4 the decision of the numerical model with variable effective diffusion

$$D_{\text{eff}} = a.e^{b\tau} + c.e^{d\tau}$$ (9)

Table 1. Coefficients A, B and H in model equation (8).

<table>
<thead>
<tr>
<th>Working conditions</th>
<th>A</th>
<th>B</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t = 20 , ^\circ C; \xi = 0.03 , m^3/kg; solv - water$</td>
<td>8.464</td>
<td>8.458</td>
<td>0.04948</td>
</tr>
<tr>
<td>$t = 20 , ^\circ C; \xi = 0.04 , m^3/kg; solv - 96% Ethanol$</td>
<td>2.216</td>
<td>1.171</td>
<td>0.003734</td>
</tr>
</tbody>
</table>

Fig. 1. Values of $D_{\text{eff}}$ for $t = 20 \, ^\circ C; \xi = 0.03 \, m^3/kg$ and solvent water.

Fig. 2. Values of $D_{\text{eff}}$ for $t = 20 \, ^\circ C; \xi = 0.04 \, m^3/kg$ and solvent 96% ethanol.

Fig. 3. Mathematical modeling of experimental results by $t = 20 \, ^\circ C; \xi = 0.03 \, m^3/kg$ and solvent water.

Fig. 4. Mathematical modeling of experimental results by $t = 20 \, ^\circ C; \xi = 0.04 \, m^3/kg$ and solvent 96% ethanol.
coefficient is presented. There is a very good correspondence when modeling the experimental results.

The obtained model is empirical. It has no thermodynamical explanation. The base of its creation is the numerical analysis of the experimental data, their accurate description and simultaneous modeling of all studied process parameters.

CONCLUSIONS

The extraction kinetic from Nicotiana tabacum L was experimentally obtained. The effective diffusion coefficient was calculated by the method of regular regime. A simple nonlinear function for determining $D_{eff}$ for different extraction conditions was found. The model is compared with experimental values for $D_{eff}$ (regular regime method) and it was verified that the suggested mathematical description can be used for process modeling by extraction from plant materials.

For all cases of numerical modeling of experimental data, a very good correspondence between the experimental and model results is present. The carried out analysis and the proposed mathematical model can be used in extraction processes for different kinds of vegetable raw materials and variable technological parameters influencing the extraction process intensity.

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REFERENCES