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MATHEMATICAL MODEL OF MASS TRANSFER FROM LAMINA OF THE LEAF INTO EXTRACTANT

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Abstract. A mathematical model of mass transfer from lamina (plant leaf) into the extractant is constructed considering its anatomical organization in particular the existence of cellular and intercellular space. Its solution allows to predict kinetics of the extraction process of the whole leaves at its implementation in practice.

Keywords: mathematical model, extraction, mass return, cellular substance, intercellular space, diffusion.

1. Introduction

The peculiarities of target components elimination from a raw material of cellular structure are connected with a cell wall, which locates on the way to target component and with variety of physiological state of the cell wall. Wall boundary layer of protoplasm makes impact on properties of the cell wall as a membrane, which separates the solution inside the cell (enchylema) from the solution of the intercellular space. While protoplasm is alive, the cell wall is semi permeable membrane, which holds compounds soluble in enchylema. In this case only penetration of extragent inside the cell is possible. And only after the certain interval of time in extragent environment due to *denaturation of proteins* the cell wall loses its character of semi-permeable membrane and begins to infiltrate the target component on either side. Herewith the compound diffusion rate through the membrane is limited by the concentration gradient and characteristic of membrane itself. After removal of the target component from the cell, its diffusion is limited by the intercellular space openings and by length of diffusion pathway of the target component to the outside surface. Furthermore, additional resistance results from the frequent collision of particles with the surface of intercellular space. This whole multiaspect complex of the diffusion phenomena occurring inside the plant material parts is termed as *internal diffusion* and characterized by internal diffusion coefficient D. This value is much less than free molecular diffusion D^*.

Therefore, the internal diffusion coefficient D is a complicated value and is the function of the diffusion coefficient through the cellular membrane D_c and diffusion coefficient in intercellular space D_m.

$$D = f(D_c; D_m)$$

Surface of leaf (lamina) is streamlined on both sides with the flow of extragent under identical conditions, in other words under stable, on the average hydrodynamic circumstances. The result is that the extracting target component drops into the extract from the surfacial layer of the leaf, and new portions of the target component moving from the interior layers substitute its place.

2. Experimental

The model is based on the principle that the target component in the leaf (lamina) thickness is transferred due to the molecular diffusion from the cell volume into the intercellular space generally formed by the colloid solution which fills "skeleton", diffuses through the intercellular space to the leaf surface, and from the leaf surface into the principal flow of the extragent due to the convective mass transfer.

Concentrations of the target component near epy phase boundary of both solid part and liquid are in equilibrium. Since high excess of extragent is used, epy concentration of epy target component in it is practically constant during whole extraction time. Molecular transfer in the leaf follows the difference equation of transient diffusion, which is given by the following expression in case of one-directional transport:

$$\frac{\partial C}{\partial t} = -D \frac{\partial^2 C}{\partial x^2} \qquad (1)$$

where D – averaged diffusion coefficient (mass transfer coefficient) of the component in thickness of the leaf, filled with extragent, m^2/s; C – concentration of the target component in the leaf, kg/m^3; t – time from the beginning of the process, s; x – spatial coordinate, perpendicular to the surface of the leaf (zero of coordinate system is placed inside the leaf (lamina).
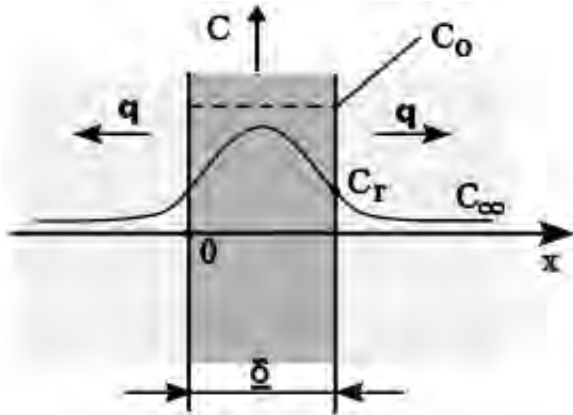

Fig. 1. A schematic drawing of the mass transfer from lamina:
C_0 – concentration in lamina (in the internal cell volume) at reference time; C_r – concentration on the edge;
C_∞ – concentration in the solution flow; q – mass flow from the surface; d – thickness of lamina (leaf)

In order to receive solution of the Eq. (1) for a particular process, it is necessary to complement it by uniqueness conditions, which include starting and boundary conditions:

Starting and final conditions, by which distribution of the concentration in the leaf (by thickness) is determined:

$$C(x) = C_0 \qquad \text{as} \qquad t = 0;$$
$$C(x) \to C^*(y_\infty) \quad \text{as} \qquad t \to \infty \qquad (2)$$

where $C^*(y_\infty)$ –concentration of target component in the leaf, equitable with concentration of liquid.

Boundary conditions on body surface, whereof the target component is excreted, are deduced from the conditions of noncumulation of component within the phase boundary. This means that the component quantity, which is delivered from the volume of the solid body to the surface of the phase boundary, must be equal to the component quantity, which is removed from the surface of the phase boundary into the flow of the liquid because of mass transfer.

Flow of the component in leaf thickness close to the phase boundary, caused by mass conduction, is characterized by the analogue of the Fick's first law:

$$q = D\left(\frac{\partial C}{\partial x}\right)_{x=d}; \quad 0 \le x \le d \qquad (3)$$

Mass quantity, which escapes from the solid body, may be presented by the equation of mass transfer. Then the flow from the surface of the solid body into liquid phase:

$$q = b\left(y_p - y_\infty\right)$$

where b – coefficient of mass transfer, m/s;

In such a case, boundary conditions are written as:

$$-D\frac{\partial C}{\partial x} = b\left(y_p - y_\infty\right) \text{ as } x = +d$$

$$D\frac{\partial C}{\partial x} = b\left(y_p - y_\infty\right) \qquad \text{as} \qquad x = -d \qquad (4)$$

where y_p – concentration of the component in liquid close to the phase boundary, kg/m^3; y_∞ – concentration of the component in the flow of liquid, kg/m^3; d – half of thickness of the leaf, m.

To get the solution, our task should be transformed into dimensionless form, taking into account peculiarities of the balance at mass transfer.

Under low concentrations, the phase equilibrium is characterized by the linear equation:

$$y = mC \qquad (5)$$

where m – constant of phase equilibrium.

By using the Eq. (5), let us exclude the values "y" from boundary conditions replacing them by equivalent values "C".

From equilibrium at phase boundary, we have:

$$y_p = mC_r \qquad (6)$$

Let us transform the equation of mass transfer at phase boundary, multiplying it by m/m:

$$b\left(y_p - y_\infty\right)\frac{m}{m} = bm\left(\frac{y_p}{m} - \frac{y_\infty}{m}\right) = bm(C_r - C_\infty) \qquad (7)$$

Let us introduce the value of redundant concentration:

$$q = C - C_\infty \qquad (8)$$

Considering that, concentration of extract is low, so $C_\infty = const$, then $\partial q = \partial C$ and thus we can rewrite expression (8) as:

$$\frac{\partial q}{\partial t} = D\frac{\partial^2 q}{\partial x^2} \qquad (9)$$

Boundary conditions:

$$-D\frac{\partial q}{\partial x} = aq \text{ at } x = +d$$

$$D\frac{\partial q}{\partial x} = aq \text{ at } x = -d \qquad (10)$$

where $a = mb$

Starting and final time conditions will be as follows:

$$q = q_0 = C_0 - C_\infty \qquad \text{at} \quad t = 0$$
$$q \to 0 \quad \text{at} \quad t \to \infty \qquad (11)$$

Solution of the Eq. (9) under boundary (10) and starting conditions (11) takes the form [1]:

$$q = q_0 \sum_{n=1}^{\infty} \frac{4(J+1)Bi^2}{m_n^2(Bi^2 - 2JBi + m_n^2)} e^{\left(-m_n^2 \frac{Dt}{R^2}\right)} \quad (12)$$

where $J = -0.5$ for lamina; m_i – radicals of characteristic equation $m = (2n-1)\frac{p}{2}$; $Bi = \frac{ad}{D}$ – modified Bio criterion of mass transfer (it includes constant of phase equilibrium m). The Eq. (9) has a set of solutions (radicals), which can be found by one of approximate numerical techniques, for instance by a dichotomy method. Radicals m_n belong to intervals, divisible by p: m_1 – within the interval $(0, p)$; $m_2 - (p, 2p)$; $m_3 - (2p, 3p)$ and so on. For extreme case:

1) at $Bi \to \infty$

$$m_1 = p/2, m_2 = 3p/2, ..., m_n = (2n-1)p/2 \quad (13)$$

2) at $Bi \to 0$ $\quad m_1 = 0, m_2 = p, ..., m_n = (n-1)p$

Beginning with a certain time point, the Eq. (12) is limited by alpha and at $Bi \to \infty$ constant $B_1 = 8/\pi$; $\mu_1 = \pi/2$ for infinite lamina [1].

Introducing the system of dimensionless values:

$$t = \frac{D_m t}{R^2}; c = \frac{D_c R^2}{D_m R_c^2}; R_c^2 = \frac{V_c d_c}{F_c} \quad (14)$$

where R_c – size of plant cell, m; R – size of extracted lamina of the leaf, m.

Solution of the Eq. (9) under boundary (10) and starting conditions (11) taking into account the system (14) takes the form:

$$q = q_0 \sum_{n=1}^{\infty} B_n e^{\left(-m_n^2 ct\right)} \quad (15)$$

where $B_n = \frac{8}{(2n-1)^2 p^2}$.

Under those circumstances the process is limited by extraction of the component from the cell, kinetics depends upon the particle size of the extracted material:

$$ct = \frac{D_c R^2}{D R_c^2} \cdot \frac{Dt}{R^2} = \frac{D_c F_c t}{V_c d_c} = \frac{D_c t}{R_{eq} d_c} = k_c t \quad (16)$$

where k_c – coefficient of mass transfer through the cell membrane, m/s; δ_c - thickness of the cell membrane, m; V_c – internal volume of cell, m^3; F_c – area of the cell surface, m^2; $R_{eq} = \frac{V_c}{F_c}$ – equivalent radius of the cell, m.

It follows from the Eq. (15) that increasing χ kinetics progressively depends upon the particle size. Nevertheless diffusion of the target component through the cell membrane D_c appears to be the determinative issue, however the resistance of intercellular space affects essentially kinetics, the resistance is determined by the coefficient of diffusion in intercellular space D_m. Phenomenon of achievement the specific maxima of the target component in intercellular space have been discussed in details in Ref. [2]. In the present article we make an effort to concretize the problem, namely to apply the theory of diffusion of the target component through the cell membrane into intercellular space, then in intercellular space to the phase boundary, for the case of leaf extraction as the model of infinite lamina. Described model is valid for an unlimited leaf with the constant thickness and constant coefficient of mass conduction. According to the additivity rule, the overall resistance of mass transfer is determined as:

$$k = \frac{1}{\frac{d_c}{D_c} + \frac{R}{D_M} + \frac{s}{D} + \frac{1}{b_1}} \quad (17)$$

where s – thickness of diffusion boundary layer; β_1 – coefficient of convective diffusion.

3. Results and Discussion

In Fig. 2 kinetics of extraction of ribwort leaf fragmented to $1 \cdot 10^{-3}$, $3 \cdot 10^{-3}$, $5 \cdot 10^{-3}$ and $1 \cdot 10^{-2}$ m with deionized water at temperature 293 K is presented. As it seen from Fig. 2, the size of extracted particles of the leaf has an essential impact on the duration of equilibrium achieving time. With increasing the size, the equilibrium achieving time increases.

Obtained experimental curves of the kinetics of ribwort leaf extraction fragmented to specified sizes are well characterized by the Eq. (15). Taking the logarithm of (15), we obtain the Eq. (18):

$$\ln \frac{q}{q_o} = \ln B - ct \quad (18)$$

The Eq. (18) in coordinates: $\ln \frac{q}{q_o} = f(t)$ describes the line, which allows to determine the value χ as the slope of straight-line section. According to the experiment with increasing the size of the leaf lamina, the absolute value of the coefficient χ decreases (Fig. 3). The dependence of the value χ on the size of the extracted lamina is characterized by the Eq. (19) (Fig. 3):

$$\chi = -0.0003 \ln R - 0.0013 \quad (19)$$

Substituting the average radius of the plant cell $25 \cdot 10^{-5}$ m [4] in the Eq. (19) we obtain the value of $\chi = 0.0018$.
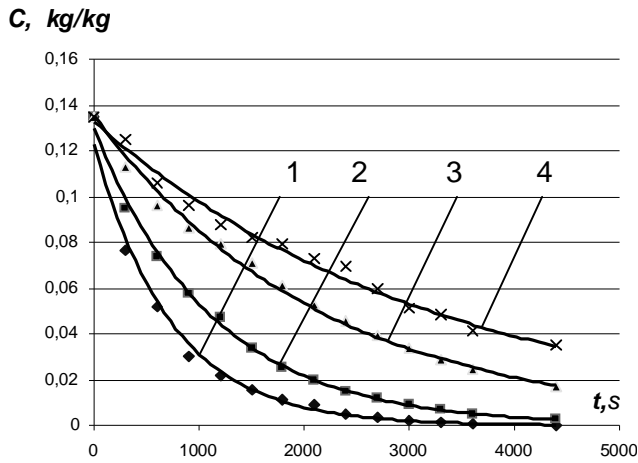
C, kg/kg

Fig. 2. Kinetics of extraction of ribwort leaf fragmented
to sizes (m): $1 \cdot 10^{-3}$ (1); $3 \cdot 10^{-3}$ (2); $5 \cdot 10^{-3}$ (3) and $1 \cdot 10^{-2}$ (4)
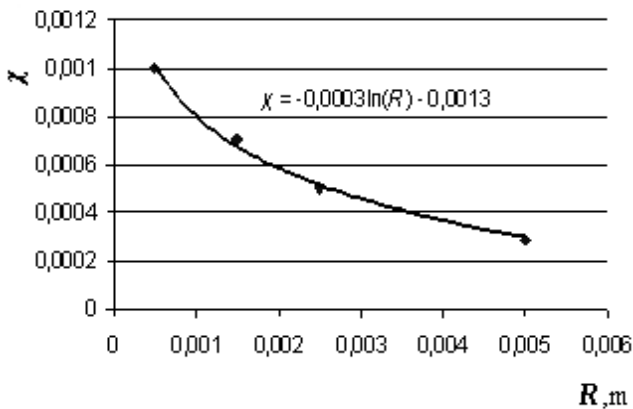

$$\chi = -0,0003 \ln(R) - 0,0013$$

Fig. 3. The dependence of χ on the size
of the extracted lamina of the leaf

On the other hand, taking into account the assumption (14) and under conditions that the size of lamina of the extracted leaf is equal to the size of the plant cell $R_c = R$, the ratio of the coefficient of diffusion through the cell membrane to the diffusion coefficient in the intercellular space is:

$$c = \frac{D_c R^2}{D_m R_c^2} = \frac{D_c}{D_m} = 0.0018 \qquad (20)$$

Coefficient of mass transfer through the cell membrane k_c and coefficient of the diffusion through the cell membrane D_c for leaves are described in Ref. [3] and equal to $15.32 \cdot 10^{-4}$ and $2.5 \cdot 10^{-14}$ m^2/s, respectively. Then coefficient of the diffusion in the intercellular space according to the Eq. (20) has the value of $D_m = 1.4 \cdot 10^{-11}$ m^2/s.

4. Conclusions

A mathematical model of mass transfer of lamina (plant leaf) in the extraction process is constructed considering its anatomical organization in particular existence of the cellular and intercellular space. Its solution allows to determine kinetics coefficients D_c and D_m, process conditions and to predict kinetics at implementation of the extraction in practice.

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МАТЕМАТИЧНА МОДЕЛЬ МАСОВІДДАЧІ ВІД ПЛАСТИНИ ЛИСТКА У ЕКСТРАГЕНТ

Анотація. Побудовано математичну модель масовіддачі від пластини листка у екстрагент враховуючи анатомічні особливості рослинної сировини, а саме наявність клітинного та міжклітинного середовища. Розв'язання такої задачі дало можливість прогнозувати кінетику процесу екстрагування неподрібненого листя при реалізації її на практиці.

Ключові слова: математична модель, екстракція, масовіддача, клітинна речовина, міжклітинне середовище, дифузія.