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EXTRACTION PROCESS OF INTRACELLULAR SUBSTANCE

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Abstract. In this study the mathematical model of the extraction process from plant material is developed, taking into account the anatomical structure of plant material, namely the presence of cellular and intercellular spaces. The solution of the model enables to determine its kinetic coefficients D_c, D_t, process conditions, and predict the kinetics of the extraction process implementation in practice.

Keywords: extraction, intracellular substances, intercellular volume, diffusion.

1. Introduction

When the processes of extraction from solid organic substances are studied, it is traditionally accepted that they are characterized by a homogeneous porous medium where the diffusion of intracellular substance takes place [1, 2, 4, 5]. This diffusion process is characterized by one kinetic constant – diffusivity. This paper attempts to consider the most general form of influence of cellular organic material on the extraction kinetics. It is assumed that the process of internal diffusion is a two-stage extraction. The first stage is defined by the component transition from the cells into the intercellular space, overcoming resistance of barriers surrounding the cell. The second stage is the diffusion from the intercellular area to the boundaries of the solid body. This concept has been accepted for mathematical modelling.

2. Experimental

The substance which is contained in cells of organic raw material in many cases is extracted for needs of chemical-pharmaceutical or food industries. After penetration into the inner structure of the cell the extracting agent dissolves the necessary component and creates condition for its diffusion outside the cell space. In the most general case the structure of solid organic materials can be represented as a set of two spaces – cellular and intercellular, which are divided by cell membranes [3]. As a rule extraction process is preceded by drying of organic materials, resulting in removal of moisture from internal volume of the body. Consequently, this volume, which is free from water, will be filled with an extractant.

3. Results and Discussion

The structure of cell membranes is rather complicated but it probably represents the main resistance to the diffusion of the intracellular substance from cells into intercellular volume. Thus the transfer of the component to be extracted consists of the following stages:

- substance diffusion through pore barriers of the cell membrane into intercellular volume;
- diffusion in intercellular volume towards the outer surface of the particle;
- mass transfer from the particle surface to the main mass of the liquid.

The following assumptions were made at working out of the theory:

1) The resistance of the cell membrane is high enough to establish the concentration C_c in cell volume constant independent of coordinates inside the cell; this concentration depends only on time and on the position of the cell.

2) The mixing of solid and liquid phases is sufficiently intensive so that the stage of mass transfer from the particle surface to the main mass of liquid does not limit the rate of extraction.

3) The concentration in the main mass of liquid is sufficiently low in comparison with the inside concentration of cells.

4) The particle that consists of many cells has the spherical form. Its size is some mean value that is experimentally determined.

Together with these assumptions we simultaneously suppose that intercellular volume is a part of the transport area where substance sources (cells) act. Mathematical

extraction model is supposed to answer the question how the concentrations (inside the cell, in intercellular volume, and in the main mass of liquid) change with time?

The simplest model is based on the concept that the main diffusion resistance is concentrated in the cell membrane. The domain of C_c definition is the free volume in the cell V_c. In intercellular volume the concentration is slightly higher than the concentration in the main mass of the solution. The mathematical formulation of this problem is defined as follows:

$$\begin{cases} -V_c \dfrac{dC_c}{dt} = D_c F_c \dfrac{C_c - C_1}{\delta_c} & (1) \\ WC_1 = V_c N_p (C_{co} - C_c) & (2) \end{cases}$$

This system consists of kinetic equation (1) and equation of material balance (2). The solution of these equations is:

$$\frac{C_c}{C_{co}} = \frac{\beta + e^{-k_c(1+\beta)t}}{1+\beta} \tag{3}$$

$$\frac{C_1}{C_{co}} = \frac{\beta}{1+\beta}(1 - e^{-k_c(1+\beta)t}) \tag{4}$$

where $\beta = \dfrac{V_c N_p}{W}; k_c = \dfrac{D_c F_c}{V_c \delta_c} = \dfrac{D_c}{\delta_c R_{ekv}}$; N_p - quantity of cells in particle; D_c - diffusivity in the cell membrane.

Considering the results (3), (4) we can see that these equations contain only one kinetic constant k_c and do not contain the particle dimension l. Under this circumstance the number of extraction processes that can be explained by (3), (4) is restrictive.

$$\text{If } \beta << 1;\ \frac{C_1}{C_o} = \beta(1 - e^{-k_c t}) \tag{5}$$

This result can be obtained the other way, namely by integration of Eq. (1), assuming that $C_1 = 0$, and the further usage of balance Eq. (2). This way we will use in the future, taking into account that many extraction processes actually take place at small values of β.

More realistic model takes into consideration resistance to the diffusion movement of target substance in the intercellular volume and size of solid phase particle. Changing of the target component concentration in the volume of the cell with time is expressed by the kinetic equation:

$$\frac{dC_c}{dt} = -k_c(C_c - C) \tag{6}$$

Changing of the target component concentration in the intercellular environment with time is expressed by the kinetic equation:

$$\frac{dC}{dt} = k_c(C_c - C) - k_m(C - C_1) \tag{7}$$

where $k_m = \dfrac{D_m}{lR_{npb}}$.

The system of Eqs. (6) and (7) with the equation of the material balance form the mathematical model of extracting from solid cellular structure, taking into account the diffusion resistance of the cell membrane, intercellular environment, and the size of extracted particle of solid phase:

$$\begin{cases} \dfrac{dC_c}{dt} = -k_c(C_c - C) \\ \dfrac{dC}{dt} = k_c(C_c - C) - k_m(C - C_1) \\ V\varepsilon C_{co} = V\varepsilon C_c + V(1-\varepsilon)C + WC_1 \\ t = 0; C = 0, C_c = C_{co}, C_1 = 0 \end{cases} \tag{8}$$

Linear system (8) is solved by Euler's method relative to:

C_c – given that : $t = 0, C = 0, C_c = C_{co}$; the solution looks like:

$$C_c = C_{co} e^{-k_c t} \tag{9}$$

C – given that: $t = 0, C = 0$; the solution looks like:

$$C = C_{co} \frac{k_c}{(k_m - k_c)}[e^{-k_c t} - e^{-k_m t}] \tag{10}$$

Eq. (10) describes the change of concentration of intracellular substance in an intercellular volume taking into account diffusion resistance of cell membrane and intercellular volume. Based on this equation we can find the time for which the maximal value of intracellular concentration of substances in the intercellular volume is achieved. To do this, we need to find the extremum condition. By means of differentiating the Eq. (10) by time:

$$\frac{dC}{dt} = C_{co} \frac{k_c}{(k_m - k_c)}[k_m e^{-k_m t} - k_c e^{-k_c t}] \tag{11}$$

and comparing the obtained result to zero we will find the time of achieving maximum concentration of the target component in the intercellular volume:

$$t_{\max} = \frac{\ln r}{(r-1)} \tag{12}$$

where $r = k_m / k_c$.

After the substitution of value (12) in (10) we get an expression for determining the maximum intracellular concentration of substances in the intercellular volume:

$$C_{\max} = C_{co}\frac{1}{(1-r)}[\exp(-r\frac{\ln r}{(r-1)}) - \exp(-\frac{\ln r}{(r-1)})] \quad (13)$$

The analysis of the obtained Eq. (13) allows to assert that kinetics of extracting of solids of cellular structure particles substantially depends on r, that is on correlation:

$$r = \frac{k_m}{k_c} = \frac{D_M \delta_c R_{екв}}{D_c l R_M} \quad (14)$$

namely on correlation of values of the coefficient of diffusion through a cell membrane D_c and coefficient of diffusion in an intercellular environment D_m or coefficient of mass transfer as well as size of solid phase particle l. Graphic dependences obtained by scanning functions (13) by computer (Fig. 1) show that the larger the correlation (14), *i.e.* smaller diffusion coefficient through cell membranes D_c and size of solid phase particle l, the higher the maximum on the curve, and the closer it is to the origin of coordinates, or the sooner the maximum concentration of target component in the intercellular environment is reached.

Finally, the solution of (8) relative to C_1 given that in equilibrium: $C_{co} = C_c = C = C_{1p}$,

looks like:

$$C_1 = C_{1p}\left(1 - \frac{1}{r+1}exp[-(k_m - k_c)]t\right) \quad (15)$$

Eq. (15) can be presented in the following form:

$$(1 - \frac{C_1}{C_{1p}}) = \frac{1}{1+r}\exp(-Kt) \quad (16)$$

where $$K = k_m - k_c = \frac{D_m \delta_c - D_c l}{\delta_c l} \quad (17)$$

Thus, the diffusive process is characterized by two kinetic constants: D_m and D_c, as well as by the size of the solid phase particle l. Under such conditions the process is limited by the exit of the component from cells, and kinetics depends on the size of particles of organic raw material. With the increase of the number l kinetics increasingly depends on the size of particles.

The increase of the concentration C_1 in the main mass of the liquid is determined by balance equation:

$$V\varepsilon C_{co} = V\varepsilon C_c + V(1-\varepsilon)C + WC_1$$
$$C_1 = \beta[\varepsilon(C_{co} - C_c) - (1-\varepsilon)C] \quad (18)$$

where $\beta = \frac{V}{W}$; $V\varepsilon$ – volume occupied by cells; ε – porosity.

This solution (17) is essentially different from the well known relation:

$$t \sim \frac{R^2}{D}$$

which can be obtained from [1, 2, 5]:

$$\frac{M}{M_o} = 1 - \sum_{n=1}^{\infty}\frac{6}{\pi^2 n^2}exp(-\pi^2 n^2 \frac{Dt}{R^2}) \quad (19)$$

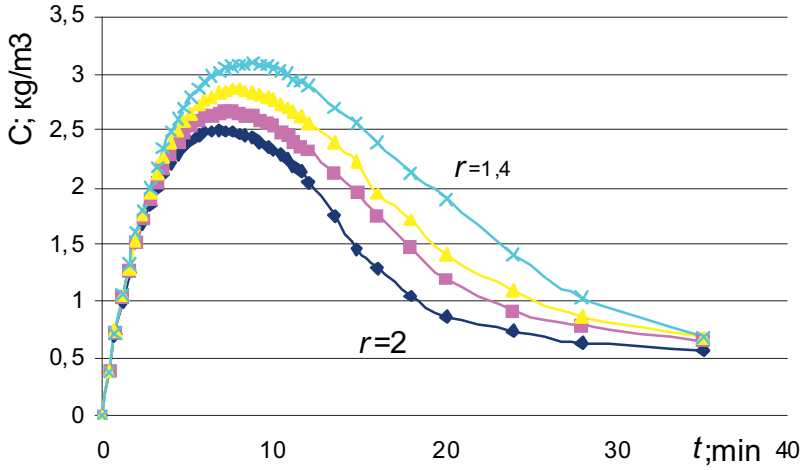

Fig. 1. Change of concentration of intracellular substance in intercellular volume with time

where $\frac{M}{M_o} = \frac{C_1}{\beta\varepsilon C_{co}} = \frac{C_1}{C_{1p}}$

If extraction is carried out by infusion or mixing the process is not sufficiently effective to neglect resistance to the diffusion boundary layer. Then the extractant is stationary on the surface of solid phase particles, and the model is supplemented by kinetic equation (20):

$$\frac{d(C_{1n} - C_1)}{dt} = k_M (C - C_{1n}) - k_3 (C_{1n} - C_1) \quad (20)$$

where $k_3 = \frac{D}{\partial}$; D – coefficient of molecular diffusion.

Thus, the mathematical formulation of the model will look like:

$$\begin{cases} \frac{dC_c}{dt} = k_C (C_c - C) \\ \frac{d(C - C_1)}{dt} = k_C (C_c - C) - k_M (C - C_1) \\ \frac{d(C_{1n} - C_1)}{dt} = k_M (C - C_{1n}) - k_3 (C_{1n} - C_1) \end{cases} \quad (21)$$

The solution of the system (21) relative to $(C_{1n}\text{-}C_1)$ is obtained by inserting Eq. (10) into (20):

$$\frac{d(C_{1n} - C_1)}{dt} + k_3 (C_{1n} - C_1) = \\ = C_{co} \frac{k_M k_C}{(k_M - k_C)} [\exp(-k_C t) - \exp(-k_M t)] \quad (22)$$

Using Euler's method, given $t = 0, (C_{1n} - C_1) = 0$ we obtain:

$$(C_{1n} - C_1) = C_{co} [a_1 \exp(-k_C t) + \\ + a_2 \exp(-k_M t) + a_3 \exp(-k_3 t)] \quad (23)$$

where $a_1 = \frac{k_C k_M}{(k_M - k_C)(k_3 - k_C)}$;

$$a_2 = \frac{k_C k_M}{(k_M - k_C)(k_3 - k_m)};$$

$$a_3 = \frac{k_C k_M}{(k_C - k_3)(k_M - k_3)};$$

In the conditions of equilibrium:

$$C_{co} = C_{1n} = C_c = C_{1p}$$

Eq. (23) will be rewritten:

$$C_1 = C_{1p} (1 - [a_1 \exp(-k_C t) + \\ + a_2 \exp(-k_M t) + a_3 \exp(-k_3 t)] \quad (24)$$

The obtained solution allows to predict the increase of concentration of target substances (intracellular substances) in the extract taking into account cell membrane resistance, intercellular volume resistance, and resistance to molecular diffusion of immobile layer of the extractant which is in a free volume among the extracted raw material.

4. Conclusions

The mathematical model of extraction from solid cellular structure is developed taking into account anatomical structure, namely the presence of cellular and intercellular environments. According to the solution of the mathematical model, diffusion process is characterized by two kinetic constants – diffusion coefficient in the intercellular environment D_m and coefficient of diffusion through a cell membranes D_c, and the size of the solid phase particle l. Under such conditions, the process is limited by the component output from the cells and kinetics significantly depends on the size l of organic material particles.

Nomenclature

C – concentration in intercellular volume; C_c – concentration in cells; C_{co} – initial concentration in cells; C_1 – concentration in the main mass of liquid; D_c – diffusivity in the cell membrane; D_m – diffusivity in intercellular volume; F_c – surface of the cell; N_p – quantity of cells in particle; l – size of the particle; $R_{екв}$ – linear cell characteristic; t – time; δ_c – thickness of membrane; ∂ – thickness of boundary laminar layer; V_c – volume of the cell; W – volume of main mass liquid; $V\varepsilon$ – volume occupied by cells; D – coefficient of molecular diffusion; ε – porosity of raw material.

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ПРОЦЕС ЕКСТРАГУВАННЯ ВНУТРІШНЬОКЛІТИННОЇ РЕЧОВИНИ

Анотація. *Побудовано математичну модель процесу екстрагування рослинної сировини, враховуючи її анатомічну будову, а саме наявність клітинного та міжклітинного простору. Рішення її дозволяє визначити кінетичні коефіцієнти D_c, D_m, режим процесу та прогнозувати кінетику при реалізації процесу екстрагування на практиці.*

Ключові слова: *екстракція, клітинна речовина, міжклітинний простір, дифузія.*