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SOME KINETIC REGULARITIES OF INTRACELLULAR SUBSTANCE EXTRACTING

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Abstract. Adequacy of mathematical model of the extraction process of cellular structure solid bodies (plant material) has been proved taking into account its anatomical structure, namely the presence of cellular and intercellular environment. Diffusion coefficients through the cellular membrane D_c and in intercellular environment D_m have been determined. Experimental verification of the accumulation of intracellular substances in intercellular environment during the extraction process flow has been made.

Keywords: extraction, intracellular substance, intercellular environment, diffusion.

1. Introduction

After constructing the mathematical model of the extraction process from the plant material taking into account the anatomical structure, namely the presence of cellular and intercellular environment, after obtaining its solution, which has described the extraction process flow in the analytical form [1], it becomes necessary to use the developed theoretical base for determining kinetic constants and to estimate the adequacy of the proposed model in comparison with the real extraction process of cellular structure solid bodies. The obtained results should allow to calculate in practice the most important technological parameters (time of process, the extractant concentration, phase ratio, the size of solid phase particles, which undergo to joint extraction, *etc*.) of the real extraction process under industrial conditions. For this purpose it is necessary to study experimentally the kinetics of the extraction of cellular structure solid body and to record analytical dependences of the mass transfer coefficient k upon the size d of extracted solid particle.

2. Experimental

Marshmallow root (*radix Althaeae officinalis*) was used as the subject of studying. Raw material was grinded by the laboratory mill by the cut method to sizes $3{\cdot}10^{-3}$; $4{\cdot}10^{-3}$; $6{\cdot}10^{-3}$; $8{\cdot}10^{-3}$; $10{\cdot}10^{-3}$ m. The solid phase particle size was determined by a sieve test. Kinetics of the extraction was studied in the apparatus with a mixer at the temperature of 293 K. Desalted water was used as an extractant. Phase ratio was 1:30 (solid body:liquid). Obtained values of the kinetics of marshmallow root extraction are resulted in Table 1.

By substituting of experimental kinetics data of marshmallow root extraction of different sizes in Eq. (1) [1], in log-log coordinates, we can calculate values, (see Table 1, second line), by adding of which we build series of kinetic curves (Fig. 1). On their basis we can find valu-

Table 1

Kinetics extraction of grinded to several size marshmallow root

d, m	t, s	300	600	900	1800	2700	3900	5100	6600	10800
$4{\cdot}10^{-3}$	C_1, kg/m^{-3}	1.90	2.60	3.20	4.33	5.08	5.75	6.00	6.20	6.20
	$\ln(1-(C_1/C_{1p}))$	-0.36	-0.54	-0.83	-1.19	-1.71	-2.62	-3.40	-	-
$5{\cdot}10^{-3}$	C_1, kg/m^{-3}	1.70	2.20	2.60	3.90	4.50	5.20	5.70	5.93	6.20
	$\ln(1-(C_1/C_{1p}))$	-0.32	-0.44	-0.54	-0.99	-1.29	-1.82	-2.51	-3.13	-
$6{\cdot}10^{-3}$	C_1, kg/m^{-3}	1.30	1.80	2.10	3.00	3.60	4.40	4.80	5.30	5.90
	$\ln(1-(C_1/C_{1p}))$	-0.23	-0.34	-0.41	-0.66	-0.87	-1.24	-1.48	-1.92	-3.02
$7{\cdot}10^{-3}$	C_1, kg/m^{-3}	1.23	1.48	1.89	2.61	3.25	3.75	4.25	4.70	5.52
	$\ln(1-(C_1/C_{1p}))$	-0.22	-0.27	-0.36	-0.55	-0.74	-0.93	-1.15	-1.42	-2.21

es of parameter k, as the slope tangent of straight section of the curve and preexponential multiplier A, as the distance which cuts the direct prolongation of straight section of each of obtained curves on the ordinate axis.

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

Parameter $A = \left(\frac{1}{r+1}\right)$ is called as outwashing coefficient, because it characterizes the quantity of open or ruined cells in the grinding process for extracted materials.

3. Results and Discussion

Analyzing Fig. 1 we can clearly distinguish two lines which characterize two periods of extraction. First (I) up to 300 s, the fast dissolving and outwashing of target substances from ruined cells and the second period (II) of extraction – the slow diffusion of target substances from the entire cell. The relative number of target substances, extracted during the first period, indicates the number of damaged cells and determined the numerical value of outwashing coefficient A.

More detailed analysis of obtained mass transfer coefficients k depending on the grinding degree d allows to claim that this dependence is logarithmic in nature (Fig. 2) and is described by analytical equation:

$$k = -0.000809\ln d - 0.00385 \qquad (2)$$

Parameter A is determined by the dependence (Fig. 2):

$$A = 0.91\text{-}10.5d \qquad (3)$$

Overall kinetic equation of marshmallow root extraction:

$$C_1 = 0.62\cdot(1 - (0.91 - 10.5d)\exp -(-0.000809\ln d - 0.00385)\,t) \qquad (4)$$

Eq. (2) has the practical usage of obtained results in this case. By substituting the average diameter of plant cells in it, we receive a mass transfer coefficient value through cell membranes k_c. Using its value and formula (5) [1] we find the order of the diffusion coefficient through cell membranes, providing that the cell membrane has the shape of a ball.

$$k_c = \frac{D_c F_c}{V_c d_c} = \frac{6D_c}{d_c d_c} \qquad (5)$$

The average diameter of plant cells according to the literature data [3] $d_c = 5\cdot10^{-5}$ m, and thickness of cell membranes $\delta_c = 2\cdot10^{-6}$ m.

$k_c = -0.000809\ln(5\cdot10^{-5}) - 0.00385 = 4.16\cdot10^{-3}$ 1/s

Then :

$$D_c = \frac{k_c d_c d_c}{6} = \frac{4.16\cdot10^{-3}\cdot2\cdot10^{-6}\cdot5\cdot10^{-5}}{6} = 6.9\cdot10^{-14}\,\text{m}^2/\text{s}, \qquad (6)$$

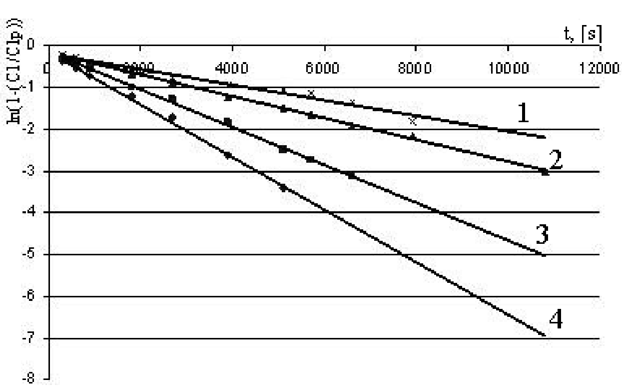

Fig. 1. Logarithmic dependence of the kinetics of target substances extraction from the marshmallow root of different sizes: $7\cdot10^{-3}$ m (1); $6\cdot10^{-3}$ m (2); $5\cdot10^{-3}$ m (3) and $4\cdot10^{-3}$ m (4)

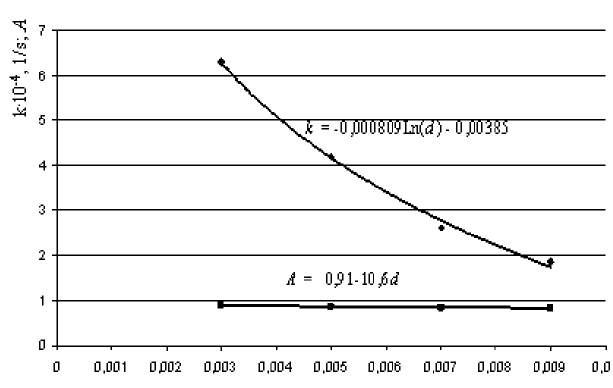

Fig. 2. Dependence of mass transfer coefficients k and coefficient A upon size d in the process of target substances extracting from the marshmallow root

Table 2

Kinetic constants of marshmallow root extraction

d, m	k, 1/s	ln$A$	A	Kinetic equation
$4\cdot10^{-3}$	6.35×10^{-4}	- 0.12	0.88	$C_1 = 0.62(1\text{-}0.88\exp(-6.35\cdot10^{-4})t)$
$5\cdot10^{-3}$	$4.20\cdot10^{-4}$	- 0.15	0.86	$C_1 = 0.62(1\text{-}0.86\exp(-4.20\cdot10^{-4})t)$
$6\cdot10^{-3}$	$2.63\cdot10^{-4}$	- 0.17	0.84	$C_1 = 0.62(1\text{-}0.84\exp(-2.63\cdot10^{-4})\,t)$
$7\cdot10^{-3}$	$1.86\cdot10^{-4}$	- 0.19	0.82	$C_1 = 0.62(1\text{-}0.82\exp(-1.86\cdot10^{-4})\,t)$

Mass transfer coefficient k is the total coefficient of mass transfer through the cell membrane k_c, and the coefficient of mass transfer in the extracellular environment $k_м$. Mass transfer coefficient $k_м$ is the average characteristic, which reflects the mass conduction of target component in the volume (extracellular environment) of solid body filled with extractant. In addition to the phenomenon of diffusion in the liquid environment it also considers the structure and size of capillaries, their sinuosity, the influence of surface forces, the change in viscosity extractant, *etc*.

Overall value k is the function of $k = f(k_c, k_м)$ for certain particles size of solid phase. Since k_c is a constant value, in connection with a fixed value of the average diameter of plant cells and thickness of its membranes, only $k_м$ can change the subject of extraction at the same time with the change of particle size of solid phase. During the real extraction, according to the experiment with increasing of particle size of solid phase, the absolute mass transfer coefficient k decreases.

The results of the kinetic study of the marshmallow root extraction is used for mathematical model [1], namely:

$$k = -(k_м - k_c) \tag{7}$$

Under these conditions for the particle size of $4 \cdot 10^{-3}$ m the mass transfer coefficient in the extracellular environment $k_м$ is determined by the following equation: $6.35 \cdot 10^{-4} = k_м - 4.16 \cdot 10^{-3}$

$$k_м = 4.79 \cdot 10^{-3}\ 1/\text{s} \tag{8}$$

Mass transfer coefficient in the extracellular environment $k_м$ for each fixed size d of the studied plant materials was determined in the same way.

Diffusion coefficient $D_м$ is not physical and chemical constant in the extracellular environment, but only its average estimation, it should be close to constant and not depend on the size.

To estimate the order of the diffusion coefficient in the extracellular environment $D_м$ by the decision of the mathematical model [1] it is necessary to determine the area of mass transfer. Taking into account the anatomic structure of the marshmallow root, and grinding cross cutting method we can take cylinder as the form of particles. Although the root surface is covered with epidermis which is low permeable for water, it is still partially destroyed in the process of crushing and apparently is conductive for the extract. Therefore the mass transfer area should be considered as a conditional cylinder surface. Then for mass transfer coefficient in the extracellular environment $k_м$ the following expression is valid:

$$k_м = \frac{D_M F_M e_M}{dV_M e_M} = \frac{2D_M p R^2\left(2 + \frac{2d}{R}\right)}{d^2 p R^2} = \frac{4D_M (R+d)}{d^2 R} \tag{9}$$

Hence:

$$D_M = \frac{k_M d^2 R}{4(R+d)} \tag{10}$$

Substituting the value of appropriate parameters in (10) within the studied marshmallow root sizes we can realize that diffusion coefficient in the extracellular environment $D_м$ is really close to a constant value and has the order:

$$D_M = \frac{4.79 \cdot 10^{-3} \cdot (4 \cdot 10^{-3})^2 \cdot 0.8 \cdot 10^{-3}}{4(0.8 \cdot 10^{-3} + 4 \cdot 10^{-3})} = 6.38 \cdot 10^{-9}\ \text{m}^2/\text{s}$$

After determining the kinetic coefficients k_c, k_m, it is possible to clarify the nature of the kinetic curves of accumulation (intracellular substances) of the target substance in the intercellular environment according to solutions of the mathematical model [1]. For this purpose time t_{max} of achieving the value of target substance maximum concentration in the extracellular environment can be written as follows for convenience of calculation:

$$t_{\max} = \frac{\ln r}{(k_M - k_c)};\ \text{where}\ r = \left(\frac{k_M}{k_C}\right) \tag{11}$$

Then the value of maximum concentration of target substance in the extracellular environment is written [1]:

$$C_{\max} = C_{co}\left(\frac{k_M}{k_C}\right)^{-\frac{k_M/k_C}{1-\left(k_M/k_C\right)}} = C_{co}(r)^{-\left(\frac{r}{1+r}\right)}. \tag{12}$$

The statement about achieving certain maximum value of target substance in the extracellular environment in the process of extracting is confirmed by the experimental data such as extracting of marshmallow root in the apparatus equipped with rotary-pulsation vehicle (RPV).

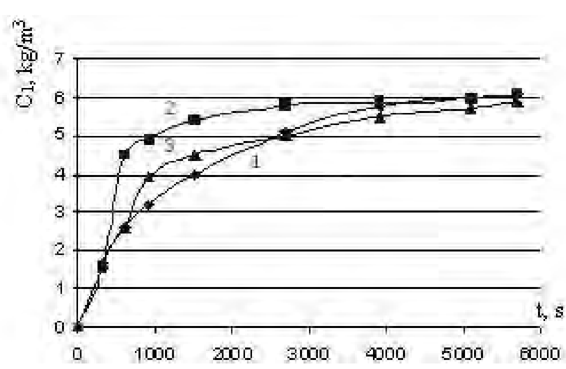

Fig. 3. Kinetic curves of marshmallow root extraction: without RPV (1); switching RPV at the 5th minute of the extraction process (2) and switching at the 10th minute (3)

Time of achieving the maximum value of polysaccharides concentration in the extracellular environment for marshmallow root with the medium size of $5 \cdot 10^{-3}$ m is calculated by the formula (11):

$$t_{max} = \frac{\ln \frac{4.58 \cdot 10^{-3}}{4.16 \cdot 10^{-3}}}{(4.58 - 4.16)10^{-3}} \approx 300 \text{ s.}$$

Extracting marshmallow root with the medium size of $5 \cdot 10^{-3}$ m in the apparatus equipped with rotary-pulsation vehicle, the maximum increase in extract polysaccharides concentration was observed with three minutes switching of rotary-pulsation vehicle at the fifth minute of extraction process, in other words when the estimated maximum polysaccharides concentration in the extracellular environment was achieved.

When switching RPV earlier or much later, such rapid increase in the extractant concentration was not observed (Fig. 3).

4. Conclusions

Adequacy of mathematical model of the extraction process of cellular structure solid bodies (plant material) was proved taking into account its anatomical structure, namely the presence of cellular and intercellular environment. Time of accumulation of intracellular substances in the intercellular environment in the course of extraction process was theoretically calculated and experimentally verified.

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; 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; e – porosity of raw material.

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ДЕЯКІ КІНЕТИЧНІ ЗАКОНОМІРНОСТІ ЕКСТРАГУВАННЯ ВНУТРІШНЬОКЛІТИННОЇ РЕЧОВИНИ

Анотація. *Доведено адекватність математичної моделі процесу екстрагування твердих тіл клітинної будови (рослинна сировина), враховуючи її анатомічну будову, а саме наявність клітинного та міжклітинного середовища. Визначено коефіцієнт дифузії через клітинну оболонку* D_c *та в міжклітинному середовищі* D_m*. Експериментально підтверджено накопичення внутрішньоклітинної речовини в міжклітинному середовищі в процесі перебігу екстракційного процесу*

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