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MATHEMATICAL MODEL FOR THE DISCONTINOUS SOLID - LIQUID EXTRACTION OF CAROTENOIDS (part I)

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ABSTRACT. The carotenoids form an important non-nitrogenated group of natural pigments giving the yellow, red or blue colour to the tissues in which they are found. The biochemical role of these pigments exerts a particular influence in the processes of photosynthesis, respiration and germination, in the protection against photodestruction and in oxygen transport to the tissues. Many carotenoids extracts are being used as additive agents in the staining of food and pharmaceutical products. The recovery of these products from the plant material is mainly achieved using solid-liquid extraction technique. In this paper the basic consideration take for development of the mathematical model for solid – liquid extraction are presented: the general design of the technological process, the mass transport equation of the solute, the overall behaviour of the solid layer in the presence of the wetting fluid. It is evaluated the mass balance for the process and the driving forces evolution, the non dimensional similitude groups for non steady-state extraction. The calculus of static retention for the wetting liquid are presented too.

INTRODUCTION

Carotenoids are non nitrogenated pigments giving the yellow, red or blue colour to the tissues in which they are found. Carotenoids are found in all organs of the plants, both chlorophyllic and nonchlorophyllic. In the superior plants they are found in the leaves, fruits, stalks, roots, seeds, petals and pollen. They are water insoluble substances, but are soluble in organic solvents, the carotenoid pigments presenting specific absorption spectra in visible and ultraviolet light, which are used for their identification and quantitative determination. They are sensitive to heat, light, acids and oxygen. The biochemical role of the carotenoid pigments, although incompletely known, exerts a particular influence in animal life in the process of sight, growth, reproduction but also in plant life in the processes of photosynthesis, respiration, germination, in the protection against photodestruction, in oxygen transport to the tissues.

The carotenoids form an important group of natural pigments. Many carotenoid extracts are being used as additive agents in the food products due to the lack of toxicity, their chemical structure, their role as active biological precursors and to the possibility of transformation into other active biologic products [1]. The recovery of these substances from the plant material is mainly achieved using solid-liquid extraction technique [2].

THE MATHEMATICAL MODEL

The modelling of solid-liquid extraction should take into account the elementary processes interpenetrating and conditioning each other. These processes are important in the definition of the overall transfer and transport rate of the solute from the solid to the liquid mass, but also for more efficient separation process. The following fundamental aspects should be considered:

1. The general design of the technological process;
2. The mass transport equation of the solute;
3. The overall behaviour of the solid bed in presence of the wetting fluid.

The first of these fundamental aspects takes into account the nature of the design of technological process: discontinuous, semicontinuous or continuous. This aspect is found in the form and structure of the total or partial balance of the materials. In the case of the discontinuous extraction, the correlation relations can also be described in the forms presented below:

The overall property balance in the two phases can be written:

$$- dP_1 = dP_2$$

and explaining in relation with the value of the potential in each phase :

$$- d(M_1u_1) = d(M_2 u_2) \qquad (1).$$

Because in the case of the discontinuous process the amounts of materials involved in the contact do not changed:

$$- M_1du_1 = M_2du_2 \text{ , respectively } - M_1/M_2 = du_2/du_1 \text{ ;} \qquad (2),$$

this relation also offers the slope of the operation straight line.

Identifying the value of each differential equation with the corresponding expression, the following relations are obtained:

$$du_1 = - dP/M_1; \;\; du_2 = dP/M_2 \text{ ,} \qquad (3).$$

and then making a subtraction of the two relations member by member:

$$d(u_1\text{-}u_2) = - (1/M_1 + 1/M_2)dP, \qquad (4).$$

Accepting the hypothesis that the quantity of materials is not changed during the transfer process, the magnitude - $(1/M_1 + 1/M_2)$ is constant for a given situation and therefore, the letter C can designate it.

The general kinetic equation of the property transfer $dP = k\ A\ \Delta U\ d\tau$ becomes under these conditions:

$$\frac{d\,(u_1 - u_2)}{u_1 - u_2} = -k\ C\ A\ d\ \tau \qquad (5).$$

In the hypothesis of the constant values for k, A, M_1, M_2 in time, the relation can be integrated by the separation of the variables

$$\int_{u_{1i-2i}}^{u_{1f-2f}} \frac{d\,(u_1 - u_2)}{u_1 - u_2} = k\ C\ A \int_0^{\tau} d\ \tau \qquad (6).$$

Designating the differences of the driving force in the initial and final moments by Δu_i and Δu_f, respectively $\Delta u_i = u_{1i} - u_{2i}$ and $\Delta u_f = u_{1f} - u_{2f}$; the integration of the relation generates the expression :

$$\ln\frac{\Delta u_f}{\Delta u_i} = -k\,C\,A\,\tau \quad \text{or} \quad \Delta u_f = \Delta u_i e^{-kCA\tau} \qquad (7).$$

The equation of the property balance $dP = - C^{-1}\,du$ in the above mentioned conditions can be integrated between the limits of the driving force differences for the limit of the process time :

$$P = -\frac{1}{C}\int_{\Delta u_i}^{\Delta u_f} d\,u \quad \text{or} \quad P = \frac{1}{C}\left(\Delta u_i - \Delta u_f\right) \qquad (8),$$

and the elimination of C between the relations (7) and (8) leads to the expression:

$$P = k\,A\,\frac{\left(\Delta u_i - \Delta u_f\right)}{\ln\frac{\Delta u_i}{\Delta u_f}}\tau \qquad (9).$$

In the above relations M1 and M2 are the property carrying entities, in this case concentration, [M] = [kg], [3].

The main steps of the mass transfer between the solid particles and the dissolving fluid which should be considered in the drawing up of the mathematical model of the solid-fluid extraction are :

- liquid diffusion in the solid porous granule;
- penetration of the cell membranes;
- solute dissolution in the intracellular solvent
- diffusion of the solute towards the solvent block surrounding the solid particle.

The so called extraction of the solute described by means of the above presented steps and influenced by usual parameters for the control of the transfer and transport processes: temperature, concentration, stirring degree, nature of the materials, is also technologically dependent on other practical aspects: size of the solid granules, the design of the raw material layer, physical properties of the solvent, the texture of the solid.

In the case of the solid-liquid extraction a normal phenomenon of drawning of the solid bed by the wetting fluid occurs. For an a complete recovery of the solute and for the economy of the process surges the need to remove the fluid remaining in the spaces between the particles. The fluid is retained between the granules of the solid material by the adhesion forces, by inclusion or absorption. When the fluid is drained from the solid packed by gravitational flow, the draining rate is the highest at the beginning of the process, (the maximum level difference between the upper level of the fluid and the level of the draining orifice), then it decreases in time, until the draining of the fluid ceases. In the solid packed remains a quantity of fluid adhering to the solid, this quantity being called residual saturation or static retention.

The variation of the saturation with the height of the solid packed was determined experimentally [4]. The draining height h_d is defined as the portion of the solid bed in which the sudden variation of the residual saturation from the saturation limit to drowning ($\varepsilon_r = 1$) takes place. In the lower part of the solid bed the saturation is always close to drowning because of the combined effects of wetting and gravity.

The values of the magnitudes intervening in the calculation of the quantity of fluid retained can be determined with the equations [5]:

- medium residual saturation:

$$\varepsilon_m = \frac{(H - h_d)}{H}\varepsilon_{r0} + \frac{h_d}{H} \quad (10).$$

- drainage height:

$$h_d = \frac{0.275/g}{\left(K/g\right)^{0,5}\left(\rho_l/\sigma\right)} \quad (11).$$

Permeability K for the layer can be calculated with Kozeny's relation:

$$K = \frac{1}{150}\frac{d_p^2\varepsilon^2 g}{(1-\varepsilon)^2} \quad (12).$$

The final residual saturation is:

$$\varepsilon_{r0} = 0,075 \quad \text{for} \quad \frac{K\ \rho_l}{\sigma} \le 0,02 \quad (13).$$

$$\varepsilon_{ro} = \frac{0,0018}{\left(K\ \rho_l/\sigma\right)} \quad \text{for} \quad \frac{K\ \rho_l}{\sigma} \ge 0,02 \quad (14).$$

Besides the fluid retention, the arrangement of the granules in a fixed bad leads to the modification of the specific magnitudes on which the transport and/or transfer is dependent.

An important aspect of solid-fluid contact is the diffusion within the porous granular material, another less studied aspect is the dependence on the operation parameters of the diffusion coefficient [6,7].

The variation of the quantity of property representing the amount of solute extracted in time is given by the mathematical equation:

$\frac{P - P_f}{P_0 - P_f} = e^{-\frac{kA\ \tau}{M}}$ which can be written in the criteria form:

$$\frac{P - P_f}{P_0 - P_f} = e^{-B_i F_0 G} \quad (15).$$

The quantity of property accumulated or extracted in time ΔP is calculated by the integration of the equation:

$$\Delta P = \int_0^\tau P dP = \int_0^\tau k(P_f - P_0) e^{-B_i F_0 G} = \frac{k(P_f - P_0)}{B_i F_0 G}\left[1 - e^{-B_i F_0 G}\right] \quad (16).$$

The analytical expression of the non steady-state diffusion becomes of the order II Fick's law diffusion equation. Depending on the mathematical method chosen for solving this equation, the final solution will have different forms and numerical coefficients, the differences between the solutions representing the accuracy of the calculus which, of course, is in direct relation with the chosen solving method. The solution of the non steady-state diffusion has great importance in the experimental determination of the diffusion coefficient, the most important physical parameter both as value and as physical significance for the mass transfer processes.

It should be pointed out that the experimental determination of the diffusion coefficients is a delicate operation involving specific equipment, long working times and a large amount of calculus [7].

CONCLUSIONS

The multitude of the mathematical models shows the phenomenon's complexity on a micro- and macro-scale; the calculus relations cannot detect this aspect in totality. Usually, the nature of the raw material is a decisive factor in the option selection of one or another model. This is due to the behaviour of the system: solvent-solute-solid matrix, i.e., the technological parameter called effective diffusion coefficient. The determination of effective diffusion coefficient is compulsory for a correct description of the extraction process. Being a material constant and dependent on the operational conditions, its determination is made by experimental measurements or by calculation, starting from data also obtained experimentally, too. The advantage of the determination by calculation is the accessible direct measurement of certain process parameters: concentrations, time or quantities.

Although apparently simple, the solid-liquid extraction operation is difficult enough to be caught in exact calculation relations, the accuracy of the estimations depending on the accuracy of the determination of the effective diffusion coefficient.

Notations

P = quantities of transported properties;
u = potential of properties, for mass transfer concentration, kg/kg;
k = overall transfer coefficient, kg/(m^2kg/kg);

A = transfer area, m^2;
$Bi_d = \beta * l / D_{ef} * \rho$; Biot number for diffusion;
$Fo_d = D_{ef} * \tau / l^2$; Fourier number for diffusion;
G = geometrical simplex of similitude;
H = height of the granular raw material, m;
g = gravitational acceleration, m/s^2;
d_p = particle diameter, m;
l = characteristic length, m;
β = partial mass coefficient, kg/m^2s;
ρ = density of fluid, kg/m^3;
σ = interfacial strength, N/m;
τ = time, s;
ε = free space into solid, m^3/m^3;
D_{ef} = effective coefficient of diffusion, s/m^2;
M = quantities of raw material, respectively solvent, kg;
1,2 = index for raw material, respectively solvent.

REFERENCES

1. Tamas V., Neamtu G.; *Pigmenti carotenoidici si metaboliti*; Ed. Ceres, Bucuresti, 1986.
2. Misca B.R.H., Literat L; *Hippophae fructus Oil Separation*, Selected Topics on Chemical Reaction Engeniering, 2-9 oct. 1994, Harmonia, Slovakia, p. 89 – 90.
3. Misca B-R.H.; *Teza de doctorat*; Cluj – Napoca, 1998.
4. Preiss J., Bord W.L.; *Liquid Retention in Packing Column*; Ind. Eng. Chem., 46, (1954), p. 1164 – 1171.
5. Dobre T., Floarea O.;.*Separarea compusilor chimici din produsele naturale*; Editura Matrix Rom, Bucuresti, 1997.
6. Misca B.R.H., Literat L,Ozunu A.; *Stabilirea etapei determinante de viteza la extractia din medii poroase prin analiza dimensionala generala*, Sesiunea jubiliara “50 de ani de la infiintarea Facultatii de Chimie Industriala si Ingineria Mediului din Timisoara”, 29 - 30, oct,1988.
7. Misca B.R.H.,Ozunu A,Dragan S.; *Determinarea coeficientului de difuziune in medii poroase*, Comunicare Simpozion “75 de ani de invatamint chimic romanesc la Alma Mater Napocensis” 20 - 21 mai, 1994, Cluj-Napoca.