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MEMBRANE PROCESSES OF SEPARATION OF SOLUTIONS IN A PULSATING FLOW

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The influence of the pulsations of the pressure gradient on baromembrane processes is considered. Formulas for calculation of the optimum pulsation frequency are given.

Problems on the limitedness of raw-material resources and on environmental contamination have become increasingly more pressing at present. Therefore, one of the most important scientific and technical problems faced by modern industry is the creation, development, and introduction of new high-efficiency and environmentally safe energy- and resource-conserving technologies. Such requirements are met to a large extent by membrane processes. A highly important place among them is occupied by baromembrane processes which include the processes of reverse osmosis, ultrafiltration, and microfiltration that are similar in their physical essence and instrument implementation. Alongside the traditional methods and in combination with them, these methods, as the most promising ones, are widely used for cleaning, separation, and concentration of solutions and gas mixtures of different kinds, since the number of specific technological problems solved with these methods has steadily grown [1].

However, as experience shows, the capacity of membrane devices for separation of a given solution largely depends not only on the use of one type of membrane or another and the structural features of filtering elements but also on the conditions of the process.

Most of the membrane units manufactured for the indicated purposes at present represent devices of the flow type in which the liquid components to be separated move on a closed-circuit basis in a channel (membrane element) formed by osmotic (semipermeable) membranes under the action of the pressure gradient produced at the ends of the channel. Due to the constant outflow of the low-molecular-weight fractions of the solution (solvent) through the osmotic membranes, the concentration of other fractions (dissolved substances) on the membrane surface gradually increases. This phenomenon has been called concentration polarization and is one of the main reasons why the capacity of membrane devices drops. Furthermore, it is noteworthy that, in ultrafiltration, concentration polarization can frequently lead to the formation of an impermeable gel layer on the membrane surface. Unlike the concentration-polarization layer, this layer exhibits a much higher resistance to the processes of mass transfer, comparable to the resistance of the membrane itself. Finally, separation of solutions virtually ceases on this portion of the membrane.

The membrane element and the processes in it are presented diagrammatically in Fig. 1. The element consists of a porous structure 1 determining the geometric shape of the membrane element; membrane 2 is fixed on the inside of the porous structure. In the diagram, the directions of flows are denoted by arrows. The formed concentration-polarization layer 3, becoming, as has been noted, the gel layer 4 in ultrafiltration, is also shown.

There are a number of methods allowing partial reduction in the influence of concentration polarization. This is attained, for example, by increasing the velocity of liquid flow in the intermembrane space, increasing the temperature of the solution to be separated, turbulizing the flow with vortex generators of different kinds, placed in the intermembrane space, introducing a certain number of solid particles or spheres up to 0.5 mm in diameter from a material with a density similar to that of the solution into the flow, etc. The above methods necessitate additional energy expenditure to circulate the solution in the circuit of the unit and have a limited field of application, as a rule. In particular, it is not necessarily acceptable or possible to increase the temperature, whereas the employment of vortex generators leads to an increase in the distance between the membranes, which decreases their working surface and, moreover, makes the structure of the membrane elements themselves much more complicated [1, 2].

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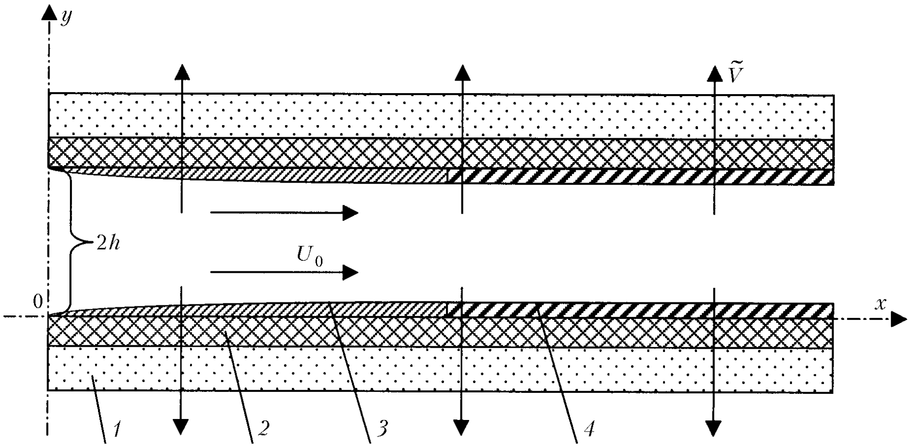

Fig. 1. Diagram of the membrane element: 1) porous base of the membrane; 2) membrane proper; 3) concentration-polarization layer; 4) gel layer.

A simple, reliable, and efficient method (easily realizable technically) for controlling concentration polarization is the organization of a pulsating liquid flow in the intermembrane space, caused by the imposition of a harmonic component on the constant pressure difference. A simplified diagram of the setup on which such an operating regime can be reproduced is shown in Fig. 2. The setup operates as follows: the starting solution from tank 2 arrives at pump 1, which feeds it to the membrane module 4. After the separation of the filtrate, which is collected in tank 3, the major portion of the solution is recycled to the tank 2 for further separation. The required pulsation frequency of the pressure gradient is set with the electromagnetic valve 5, periodically partially covering pipeline 6 in front of the membrane module 4.

Experimental data on the ultrafiltration of grape juice that were obtained on a laboratory setup with the use of a pulsating regime have been given in [3]. The results of these experiments have shown that the imposition of pressure-gradient pulsations substantially improves the capacity of the setup as compared to the case of separation without pulsations (approximately 1.35–1.40 times). Furthermore, it is also clear from them that there is a pulsation frequency at which the capacity attains its maximum. Analogous results are available in [4, 5]. In [5], an experiment on filtration with the use of pulsations of a sucrose solution by the reverse-osmosis method has been presented.

However, theoretical conclusions of any value on determination of the optimum pulsation frequency enabling one to maximize the reduction in the phenomenon of concentration polarization have been absent until the present time. In this work, we consider the solution of this problem. We write the formulation of the problem for plane-chamber membrane devices. They include apparatuses consisting of plane (sheet-type) membranes laid on both sides of a porous material (drainage plate) or prepared directly on the surface of a porous plate. Let a liquid move in a plane symmetric channel of length L and height $2h$ under the action of a constant pressure difference on which small pulsations are imposed. The selectivity of the membranes will be considered to be ideal, and liquid flow in the channel will be considered to be steady-state. Then the system of equations describing this process and including the equations of motion, continuity, and convective diffusion has the form

$$\frac{\partial u}{\partial t} = -\frac{1}{\rho}\frac{\partial P}{\partial x} + \nu \frac{\partial^2 u}{\partial y^2} , \tag{1}$$

$$\frac{\partial P}{\partial y} = 0 , \tag{2}$$

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 , \tag{3}$$

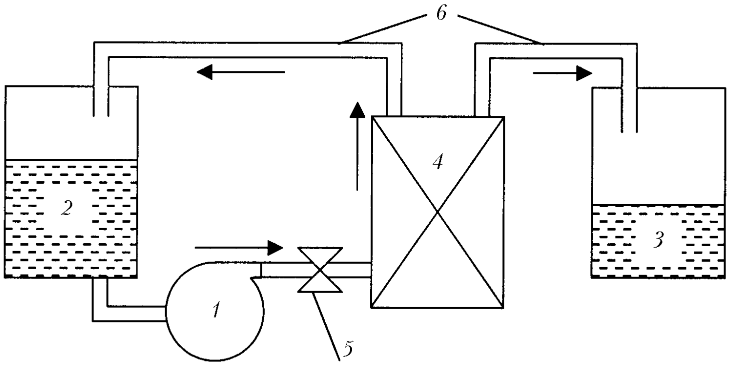

Fig. 2. Diagram of the setup: 1) pump; 2) tank for the starting solution; 3) tank for collection of the filtrate; 4) membrane module; 5) electromagnetic valve; 6) connecting pipelines.

$$\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial x} + v\frac{\partial C}{\partial y} = D\frac{\partial^2 C}{\partial y^2} \tag{4}$$

with boundary conditions

$$u\big|_{y=0} = 0\,, \quad v\big|_{y=0} = -\tilde{V}\,; \tag{5}$$

$$\left.\frac{\partial u}{\partial y}\right|_{y=h} = 0\,, \quad v\big|_{y=h} = 0\,; \tag{6}$$

$$C\big|_{x=0} = C_0\,, \quad C\big|_{t=0} = C_0\,, \quad \left.\frac{\partial C}{\partial y}\right|_{y=h} = 0\,; \tag{7}$$

$$\tilde{V}C_{\mathrm{w}} + D\left.\frac{\partial C}{\partial y}\right|_{y=0} = 0\,. \tag{8}$$

Since, from Eq. (2), it is evident that P is independent of y, for the pressure gradient, in accordance with the requirement of imposition of pulsations, we have

$$\frac{\partial P\,(x, t)}{\partial x} = \frac{\partial P\,(x)}{\partial x} - A\sin\omega t\,. \tag{9}$$

Formulation of the problem for a plane channel with one permeable surface is analogous to (1)–(9) but, instead of conditions (6), we must write

$$u\big|_{y=2h} = 0\,, \quad v\big|_{y=2h} = 0\,. \tag{10}$$

Devices of this type may include roll-type membrane elements that are widely used for cleaning of solutions by the reverse-osmosis method. Considerable portions with one permeable surface also exist in devices with two permeable surfaces [1].

By virtue of the linearity of the equations, the pulsating liquid flow in the intermembrane space can be considered as a set of two motions: the motion caused by the constant component of the pressure difference and the oscillating motion due to the harmonic component; in this case we have $\partial P(x)/\partial x >> A$. This enables us to analyze the processes in the channel caused by each individual motion. Thus, we can assume that the outflow of a part of the liquid (solvent) through the osmotic membrane is determined just by the constant component of the pressure difference. Consequently, the transmembrane velocity characterizing it remains constant for a fairly long time interval (as compared to the pulsation period), i.e., $\tilde{V}$ = const. Since the value of the transmembrane flow is low as compared to the value of the main flow directed along the channel axis, the first flow has been disregarded, as a rule, in description of the pulsating motion of solutions [3]. It is precisely this flow, however, that is mainly responsible for the occurrence of the phenomenon of concentration polarization (the above phenomenon is not observed in the absence of this flow). This means that for a more accurate determination of the velocity profile we cannot disregard this factor (the second condition from (5)). On the basis of what has been said above, we can obtain expressions for the thickness of the concentration-polarization layer and for the concentration of dissolved substances on the membrane surface directly from the system of equations (1)–(4) with boundary conditions (5)–(8), setting the pulsation frequency ω equal to zero. Then the process becomes steady-state and the system of equations (1)–(4) describing it is simplified, since the terms containing time derivatives drop out and the pressure gradient of (9) loses its dependence on time. A solution (based on the semiintegral approach) of this system for the case in question has been proposed in [6, 7]. Therefore, without resorting to the calculations available there, we write the final formulas to compute the quantities of interest, which have been represented in [6, 7] in dimensionless form:

$$\Delta = \frac{\ln \theta_w}{\mathrm{Pe}\, V}, \tag{11}$$

for the thickness of the concentration-polarization layer and

$$\theta_w - \ln \theta_w - \frac{1}{2} \ln^2 \theta_w = 1 + \frac{V\xi\, \mathrm{Pe}^2 V^2}{3\,(1 - V\xi)}, \tag{12}$$

for the concentration of dissolved substances on the membrane surface, where $\mathrm{Pe} = U_0 h/D$ is the diffusion Péclet number, $\Delta = \tilde{\Delta}/h$, $\theta_w = C_w/C_0$, $V = \tilde{V}/U_0$, and $\xi = x/h$ (throughout the text, the quantities having dimensions and notation symbols identical to those of the corresponding dimensional quantities have a ~ sign above).

According to [8], for a plane channel with one permeable surface the thickness of the polarization-concentration layer will also be determined by expression (11), whereas for the concentration of dissolved substances on the membrane surface we have

$$\theta_w - \ln \theta_w - \frac{1}{2} \ln^2 \theta_w = 1 + \frac{V\xi\, \mathrm{Pe}^2 V^2}{3\left(1 - \frac{1}{2} V\xi\right)}. \tag{13}$$

Thus, the main contribution to the formation of the concentration-polarization layer is made by the constant component of the pressure gradient. The pulsating component in turn causes a shear viscous wave to form at the membrane surface [9, 10]. This results in a periodic transfer of solution layers at the membrane surface from the region with a higher concentration to the region with a low concentration and conversely. Thus, the action of convective diffusion aimed at destroying the concentration-polarization layer will be more intense. The layer thickness to which vibrations of the liquid layer penetrate depend on the frequency and the kinematic viscosity of the solution to be separated. This relationship has been determined in a number of works, for example, in [9, 10], and has the form

$$\tilde{\delta} \sim \sqrt{\frac{\nu}{\omega}}. \tag{14}$$

It is correctly assumed that the influence of the pulsations will be the largest when the thickness of the concentration-polarization layer and the penetration depth of the shear viscous wave are quantities of the same order of magnitude, i.e.,

$$\Delta \sim \delta\,, \qquad (15)$$

where $\delta = \tilde{\delta}/h$.

Selecting, as Δ, the maximum value of this quantity (it will be attained for $\xi = L/h$) and returning to dimensional quantities for the convenience of employment of final formulas in practical calculations, after the corresponding substitution, we can calculate from (15) the optimum frequency of the process:

$$\omega_{\text{opt}} \sim \frac{\nu \tilde{V}^2}{D^2}\left[\ln^2 \frac{C_{\text{w}}}{C_0}\right]^{-1}, \qquad (16)$$

$$\frac{C_{\text{w}}}{C_0} - \ln \frac{C_{\text{w}}}{C_0} - \frac{1}{2}\ln^2 \frac{C_{\text{w}}}{C_0} = 1 + \frac{\tilde{V}^3 hL}{3U_0 D^2 \left(1 - \dfrac{\tilde{V}L}{U_0 h}\right)}\,. \qquad (17)$$

It is clear that formula (16) will also hold for the plane channel with one permeable surface. In this case, instead of (17), we must determine the concentration of dissolved substances on the membrane surface in accordance with (13) from the equation

$$\frac{C_{\text{w}}}{C_0} - \ln \frac{C_{\text{w}}}{C_0} - \frac{1}{2}\ln^2 \frac{C_{\text{w}}}{C_0} = 1 + \frac{\tilde{V}^3 hL}{3U_0 D^2 \left(1 - \dfrac{\tilde{V}L}{2U_0 h}\right)}\,. \qquad (18)$$

Relations (16)–(18) yield that the optimum frequency of pressure pulsations in the plane channel depends on both certain physical properties of the solution to be separated (diffusion coefficient of a dissolved substance and coefficient of kinematic viscosity of the solution) and the conditions of the process (velocity of the main flow and transmembrane velocity) and the geometric parameters of the selected membrane element (length and half-height of the channel). Substitution of the characteristic values of the above quantities into (16) and (17) enables us to evaluate ω_{opt}; according to this evaluation, we have $\omega \sim 10^0$–10^2 Hz. For the case where $\dfrac{C_{\text{w}}}{C_0} >> \ln \dfrac{C_{\text{w}}}{C_0}$ (this case is inherent in low rates of ultrafiltration and reverse osmosis) (dimensionless parameter $\text{Pe}V \sim 10^3$), the calculations are substantially simplified, and we can write (16) and (17) in the form of one formula:

$$\omega_{\text{opt}} \sim \frac{\nu \tilde{V}^2}{D^2}\left[\ln^2\left(1 + \frac{\tilde{V}^3 hL}{3D^2 U_0\,(1 - \tilde{V}L/U_0 h)}\right)\right]^{-1}. \qquad (19)$$

Another popular channel shape employed in membrane elements is a cylindrical shape (tubular and hollow-fiber membrane elements). The solution of an analogous problem for a cylindrical channel is available in [11] and also leads to formula (16). The concentration of dissolved substances on the membrane surface should be sought from the equation

$$\frac{C_{\text{w}}}{C_0} - \ln \frac{C_{\text{w}}}{C_0} - \frac{1}{2}\ln^2 \frac{C_{\text{w}}}{C_0} = 1 + \frac{\tilde{V}^3 RL}{4U_0 D^2 \left(1 - \dfrac{2\tilde{V}L}{U_0 R}\right)}\,, \qquad (20)$$

where R is the channel radius.

Thus, knowing the geometric parameters of the membrane elements and the physical properties of the liquid solutions or gas mixtures to be separated, we can find the optimum frequency of pulsations of the pressure gradient, at which the capacity of the setup is the highest.

Example. Let us determine the optimum frequency of the process for an aqueous solution of sucrose in the experimental setup described in [5]. The sucrose solution with a coefficient of kinematic viscosity of $\nu = 10^{-6}$ m^2/sec and a diffusion coefficient of $D = 0.45 \cdot 10^{-9}$ m^2/sec moves in the pulsating regime in a channel of length $L = 2.20$ m and radius $R = 3.23 \cdot 10^{-3}$ with an average velocity of $U_0 = 1.48 \cdot 10^{-1}$ m/sec. The value of the transmembrane velocity is $\tilde{V} = 2.22 \cdot 10^{-6}$ m/sec. Substituting these data into formula (20), we find $\frac{C_{\text{w}}}{C_0} - \ln \frac{C_{\text{w}}}{C_0} - \frac{1}{2} \ln^2 \frac{C_{\text{w}}}{C_0} \approx 1.53$. Hence by the iteration method we obtain $\ln^2 \frac{C_{\text{w}}}{C_0} \approx 1.70$. Substituting this value into (16), we compute the optimum frequency of the process $\omega_{\text{opt}} \approx 3$ Hz, which is in satisfactory agreement with the result of the experiment.

NOTATION

A, pulsation amplitude; C, concentration of a dissolved substance; C_0, concentration of a dissolved substance at the channel inlet; C_{w}, concentration of a dissolved substance on the membrane; D, diffusion coefficient of a dissolved substance; h, half-height; L, length; P, pressure in the channel; t, time; $\tilde{V}$, transmembrane velocity; U_0, average velocity of the flow at the channel inlet; u and v, components of the vector of velocity of the flow; ρ, density of the solution; ν, coefficient of kinematic viscosity of the solution; ω, pulsation frequency; ω_{opt}, optimum pulsation frequency. Subscripts: w, value of the quantity on the membrane surface; opt, optimum.

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