

MATHEMATICAL MODELING OF POROUS ADSORPTION LAYERS USED IN A MEMBRANOUS GAS SEPARATION

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Abstract

The article considers the analysis of the membrane surface resistance influence on a mass transfer intensity. Objective of the analysis was to develop approaches for engineering calculation of the process. The article carries out analysis of modern approaches for description of different porous adsorption layers' structure and offers new models of porous adsorption layers used in a membranous gas separation modeling as well.

Keywords: Modeling; porous adsorption layers; porousness; substance flow; membranes; ultrafiltration.

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1.0 INTRODUCTION

The most sound and practically useful classification system of porous adsorption layers, offered for the first time in the work [1], then it achieved some progress in the works [2]. In accordance with this approach, it is sufficient to detail two characteristics to cover all the diversity of the adsorbents' porous layers structures. These characteristics include formation mechanisms of porous systems and general nature of the structure. According to the first characteristic, the most of the systems can be divided into two large groups. The work [4] conditionally specifies them as a system of growth and system of addition. On the principle of structure difference, the adsorption layers can be divided into porous layers with clearly ordered structure and chaotic structure layers.

The system of growth is usually characterized by a specific morphology, "structure morphology", often unique in any other process. The systems of growth

include coke, pumice stone, sponge, foam, active carbons, zeolites, Colmacel, etc. The well founded approach to the modeling of addition layers lies in their consideration as a mass accumulation of finished elements of any shape.

2.0 STATEMENT OF THE PROBLEM

Let's note key problems occurring during the modeling, and then let's set possible ways for their solution.

The main structural characteristic of the adsorption layer is its porousness or porosity ϵ . We should understand that the porousness is a macroscopic feature of the layer and can be determined only on very large sites of porous systems with a great number of elements.

The stochastic "component" of description in this case can be presented as follows, if take $(1 - \alpha)$, for

the addition systems there will be probability to fill the whole porous system by the elements. Therefore, ε has meaning of porous probability in the general system.

The advantageous of such approach for the addition systems is that the porousness value, interpreted as the probability, does not depend on the nature of components, and can be determined without indication of their specific geometrical dimensions. In a result, this significantly simplifies the experimental determination of this characteristic.

Let's consider the adsorption layers, defined above as the growth systems or cluster systems. A mathematical apparatus of fractal theory can be involved to describe a similar diffusion-restricted aggregate [5]. According to the fractal model, the adsorption layer can be presented in the form of integrated cluster. A growth of this cluster occurs by addition of particles joining to the cluster surface by a diffusion mechanism. At that, dynamics of the cluster is expressed in a movement of active area, i.e. field, where new particles join to the cluster.

Trajectories of the particles start out of the field engaged by the cluster and end at the moment of joining of the particle with the cluster. This process can be described as a random walk with the help of Smoluchowski equation of the next form:

$$\frac{dn_k(t)}{dt} = \frac{1}{2} \sum_{i+i+j=k} K_{ij} n_i(t) n_j(t) - n_k(t) \sum_{j=1}^{\infty} K_{jk} n_j(t) \quad (1)$$

where $n_k(t)$ is a density of k -fractional clusters.

A kernel of K_{ij} system of equations (1) considers a collision cross sections dependence of the clusters' dimensions and mobility.

As a surface of the cluster in the diffusion-restricted aggregate area has a very complex shape, there is almost zero probability that the diffusing particle joins the cluster inside the completely developed area. The maximum probability of joining of the particles to the clusters' "bulges" is $P_m = \max$. A joining probability of the particles achieved the cluster in the active area can be evaluated as $1 - P_m$. In a result we obtain the next kinetic equation for the cluster growth in a great number of particles N :

$$\frac{d\bar{r}_N}{dN} = P_m(N)a \quad (2)$$

where a is a typical size of the joining particle (adsorbent grain).

The cluster, modeling the adsorption layer, is characterized by two parameters: mean radius of the cluster \bar{r}_N and width of the active area ψ . The next relation follows in a great number of particles N of the fractal theory:

$$\bar{r}_N \sim N^\gamma - N^{1/D_F} \quad (3)$$

where D_F is a fractal dimensionality of the cluster structure, γ is a figure depending on the

characteristic length.

The fractal theory gives a proper expression for the active area width as a mean distance between the cluster branches [6]:

$$\psi \sim \bar{r}_N^{(3-D_F+\chi)/2} \quad (4)$$

where χ is a figure of anisotropy of the adsorption layer.

A full depth of the layer can be used in the quality of characteristic length in the area of diffusion-restricted aggregate.

Now the next expression can be offered for estimation of the layer porousness:

$$\varepsilon = \frac{\bar{r}_N^{3-D_F+\chi}}{r^3} \quad (5)$$

The fractal dimensionality, for which it is necessary to develop a method of its experimental determination, is seen to be the most important characteristic of the cluster type adsorption layers [7]. However, at that, we can use known methods of experimental determination of the porousness, based on hydrodynamic investigations of a neutral (non-adsorbed in the layer) liquid flow.

2.1. Solution Of The Problem

Determination of the layer fractal dimensionality is carried out by the next formula. To our opinion, this approach to the layer structure modeling extremely reproduces its complex structure and allows adequately describe the main characteristics.

In a general case, a dissolved matter flow through J_C membrane is composed from the sum of two flows: the first, resulting from entrainment of the dissolved matter molecules with J_V dissolvent flow and proper diffusion flow J_D of the concentrated component through the membrane.

$$J_C = J_V + J_D \quad (6)$$

The component of this flow can be presented in the next form

$$J_V = \chi \bar{C}_S J \quad (7)$$

Where J is a full solution flow through the membrane, \bar{C}_S is a mean concentration of the dissolved matter molecules in the solution, χ is a percolation coefficient.

In a differential form, the last relation looks like:

$$\frac{dJ_V}{dt} = \chi \left(C_S \frac{dJ}{dt} + J \frac{dC_S}{dt} \right) + C_S J \frac{d\chi}{dt} \quad (8)$$

The percolation coefficient, for that matter, is a characteristic of membrane permeability and it relates to used in calculation of membranes concept of membrane reflection coefficient σ /1/ by the

relation:

$$\chi = 1 - \sigma \quad (9)$$

The diffusion flow of the dissolved matter through the membrane is determined by the next way:

$$J_D = -w\Delta\Pi \quad (10)$$

where w is the dissolved matter molecules mobility coefficient, $\Delta\Pi$ is an osmotic pressure difference.

The dissolved matter flow towards J_r dissolvent, during an ultrafiltration concentration, is very important characteristic, really determining an efficiency of the concentration process. It follows from (6), (7) and (9):

$$J_r = -\sigma J_v + \frac{J_D}{C_s} \quad (11)$$

The membrane quality can be estimated with the help of a diffusion permeability coefficient, calculated in a total volume no-flow condition:

$$\chi_D = -\frac{J_D H}{\Delta C_s} \quad (12)$$

where H is the membrane depth, ΔC_s is the dissolved matter concentrations difference before and after the membrane.

Using the mobility concept, the relation (12) will be in the next form:

$$\chi_D = w\Delta\Pi / \text{grad}C_s \approx wH\Delta\Pi / \Delta C_s = wHRT \quad (13)$$

where R is a gas constant; T is the process temperature. The next expression for the dissolved matter flow through the membrane depending on its full and diffusion permeability follows from (12):

$$J_c = \chi \bar{C}_s J + \chi_D \text{grad} \zeta \quad (14)$$

Using formula (6), we obtain:

$$J_c = \chi \bar{C}_s J + \chi_D \frac{\Delta\Pi}{HRT} \quad (15)$$

The permeability coefficient χ of the dissolved matter macromolecules through the membrane pores depends on the macromolecules configuration and deformability, curved pores.

The macromolecule is deformed the stronger, the more a transverse gradient of the flow rate at the entrance of the membrane pore. Let's estimate this gradient from the next considerations.

A rate of the solution in the membrane pores is determined by the next relation:

$$u^* = \frac{r^2 \Delta P}{8qL\mu} \quad (16)$$

where r is the pore radius; ΔP is the membrane depth pressure difference; L is the membrane

depth; μ is the dissolvent dynamic viscosity. Here q is the curved pores coefficient related to the Carrman-Kozeny constant k expression:

$$k = Cq^2 \quad (17)$$

where C is an empiric coefficient, determined by the membrane structure (usually $C \sim 2-2.5$).

At the same time, the flow average rate in the distance from the porous layer can be estimated through the membrane mean surface porosity ε_s :

$$\bar{u} = u\varepsilon_s \quad (18)$$

Introducing a disturbed rotation radius R_F of a solvated particle (Figure 1), which is completely determined by physical-chemical characteristics of the considered system, we obtain the gradient rate required estimation on the macromolecule deformation specific scale:

$$\frac{du}{dr} \sim \frac{r^2 \Delta P (1 - \varepsilon_s)}{8qL\mu(R_F - r)} \quad (19)$$

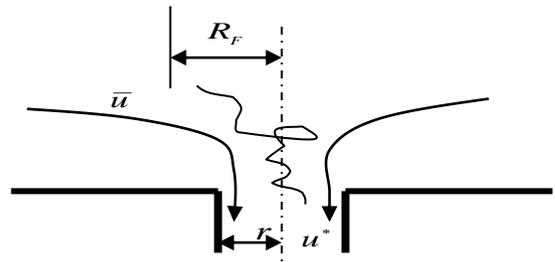


Figure 1 Scheme of the flow near the pores

The pressure difference, at which the gradient rate estimation will be the same order as the macromolecule backward relaxation time $1/\tau$ (i.e. the gradient critical value is realized) will pertain to the maximal membrane permeability by the detected component:

$$\Delta P_{cr} \approx \frac{8qL\mu(R_F - r)}{r^2(1 - \varepsilon_s)\tau} \quad (20)$$

2.2 Results Of The Calculation

The article considers the analysis of the membrane surface resistance influence on a mass transfer intensity. Objective of the analysis was to develop approaches for engineering calculation of the process.

Figure 2 schematically shows concentrations distribution of the matter filtrating through the membrane depth in the flow direction.

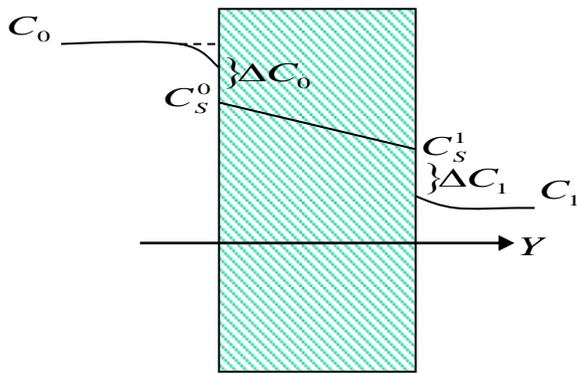


Figure 2 Concentrations distribution of the matter filtrating through the membrane.

Owing to the membrane surface layer characteristics, it is assumed that it can be provided by the diffusion resistance, which results in the surface jumps of a concentration of carried over the membrane admixture both from external and internal sides of the membrane (Figure 2).

Then, the admixture total flow through the membrane J in a near-equilibrium approach can be written as:

$$J_e = \beta_e (C^0 - KC_S^0) \tag{21}$$

where β_e is a mass-transfer coefficient from the membrane external side; K is the surface resistance coefficient, i.e. the equilibrium constant, establishing relation between concentration of the matter on the membrane surface and in the filtering mixture flow on the flow and membrane boundary.

A similar relation from the membrane internal surface can be written in the next form:

$$J_i = \beta_i \left(\frac{C_S^1}{K} - C^1 \right) \tag{22}$$

where β_i is a mass-transfer coefficient from the membrane internal side. The admixture flow inside the membrane is determined by the internal diffusion intensity:

$$J = D_i (C_S^0 - C_S^1) / h \tag{23}$$

where D_i is the internal diffusion coefficient, h is the membrane depth.

If we ignore delay and accumulation of the matter in the membrane internal area, it will be possible to write the equilibrium condition of three mentioned flows as:

$$J_e = J_i = J \tag{24}$$

It follows from the relations (*):

$$C_S^1 = \frac{C^0 + C^1 Z}{K + Z/K} \tag{25}$$

$$C_S^0 = \frac{1}{K^2 + Z} \left[C^0 \left(K + \frac{\beta_i h}{D_i} \right) + C^1 K \left(Z - \frac{K \beta_i h}{D_i} \right) \right] \tag{26}$$

where Z factor can be considered as some integral parameter, which characterizes the membrane carrying capacity by the admixture:

$$Z = \frac{\beta_i}{\beta_e} + \frac{K \beta_i h}{D_i} \tag{27}$$

Then, an expression for the full admixture flow through the membrane has the next form:

$$J = \beta_i \frac{C^0 - K^2 C^1}{K^2 + Z} \tag{28}$$

Considering from thermodynamic considerations that $K \geq 1$ [8], we can make a conclusion that in some relations between concentrations of the admixture from the membrane external and internal sides, the membrane surface resistance can result in the flow "choking". Indeed, from $J = 0$ condition we obtain:

$$\left(\frac{C^0}{C^1} \right)_{san} = K^2 \tag{29}$$

It follows from the model analysis that influence of the membrane surface resistance can be reduced in fulfillment of the condition:

$$\beta_e \ll \frac{D_i}{hK} \tag{30}$$

Figures 3, 4 show some calculation results by the mentioned model, illustrating qualitative dependence of the specific flow through the membrane on the surface resistance coefficient.

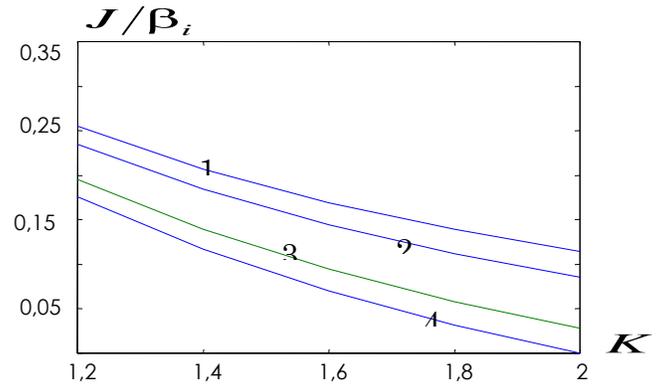


Figure 3 Dependence of the specific flow through the membrane on the surface resistance coefficient.

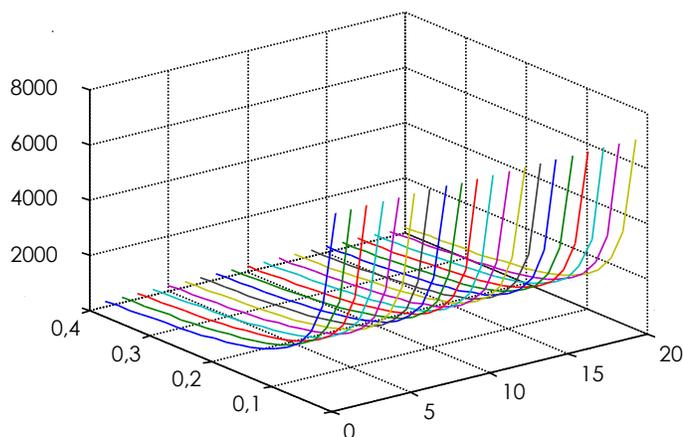


Figure 4 The Dependence of the dimensionless critical pressure drop $\overline{\Delta P_{cr}}$ from the geometric parameters of the membrane

$$\overline{\Delta P_{cr}} = \frac{\Delta P_{cr} \tau}{8\mu}; \quad A = \frac{L}{R_F}; \quad B = \frac{r}{R_F}$$

3.0 CONCLUSION

The ultrafiltration separation process is a closing technological stage of many processes. Application of the membranous technology on the closing technological stage provides reagentless methods, [9]

phase transfer rejection, energy saving and ecological cleanness. It is important to note simplicity of the implementation and opportunity to carry out processes in low temperatures.

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