

DEPTH FILTRATION MODEL FOR STANDARD PORE BLOCKING IN ULTRA- AND MICROFILTRATION MEMBRANES

Polyakov Yu.S.

USPolyResearch, USA; ypolyakov@uspolyresearch.com

Standard blocking of the pores of ultrafiltration (UF) and microfiltration (MF) membranes is one of the common processes in membrane technology [1-4]. If the size of a suspended particle is less than the diameter of a membrane pore, it may enter the pore and get deposited on its walls or pass through it and come out at the opposite end of the pore. As most of the natural and industrial suspensions are polydisperse and most of the commercial membranes are characterized by rather wide lognormal pore-size distributions, some of the suspended particles are too small to be sieved by the pore entrance and the selectivity of the membranes is usually less than 100%. The process of standard blocking occurs to a larger or smaller extent in most UF/MF membranes at the start-up stage of their operation and should be taken into account in designing the membrane equipment. Although the permeation rate during the standard blocking rapidly decreases with time due to the deposition of particles on the pore walls and narrowing of its flow cross-section (pore constriction), its value for the first several dozens of minutes of their operation may remain much higher than the permeation rate during the process of the following cake filtration, in which the pore rejects the particles and the permeation rate is controlled by the cake resistance [2, 5]. This makes the idea of using standard blocking in commercial membrane plants, such as submerged membrane bioreactors or other types of outside-in hollow fiber filters, look very attractive. This process can be used in designing a membrane filter that can provide the fractional separation of suspended particles, in which the larger particles are collected on the pressure side of the membrane and the smaller ones are deposited on the walls of its pores and/or pass through the membrane pores to the permeate. This process also takes place in affinity membrane filtration [6]. To design these standard-blocking applications, it is necessary to have a reliable theory that can simultaneously predict the variation of membrane permeation rate and selectivity with time. This theory will also be helpful in studying the UF/MF applications for medicine, biology, pharmaceuticals, and the food processing industry [2].

In the present paper, the macroscopic approach of the theory of depth filtration based on the concept of the filter (deposition) coefficient will be used to describe the standard blocking of pores in UF/MF membranes with allowance for the spatially nonuniform deposition of particles on the pore walls and pore constriction and predict the variation of permeate flux, profile of the number of deposited particles, and permeate concentration with time.

Consider a membrane with round cylindrical pores of the same radius r_0 and length l through which an incompressible isothermal suspension with low concentration (volume fraction) c_0 of spherical particles of the same radius a is filtered (Fig. 1). As in the classical approaches [2, 3], we assume that the diffusion of particles inside pores can be ignored, the liquid viscosity inside the pores remains constant, and the liquid inside the

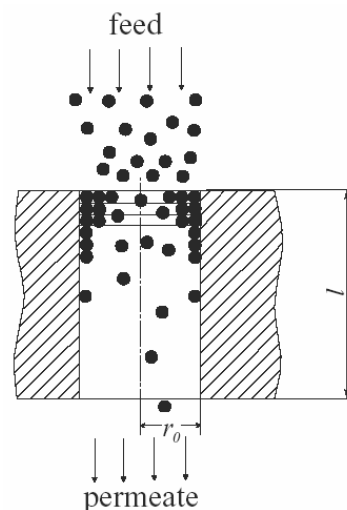


Fig. 1. Schematic diagram of UF and MF membrane standard blocking.

pores is perfectly mixed over their cross sections. As in the theory of depth filtration [7-8], we assume that particles can be collected by the walls of pores and the rate of this process is determined by the deposition (filter) coefficient, particle-collecting surface area inside the pore, and the local concentration of particles in it. As the concentration of suspended particles decreases with pore depth due to the deposition of particles on the inlet portion of the pore, the number of deposited particles should decrease along the pore (Fig. 1).

Let us divide the length of the pore into a sequence of circular sections with lengths equal to the diameter of the particle (Fig. 1). We assume that the particles can be caught by the pore wall itself or by the surface of the layer of particles deposited on the pore wall and that every circular section represents a short cylindrical pore the flow in which can be described by the Poiseuille formula. In this case, the liquid flow rate at the pore outlet can be defined by the formula:

$$w(t) = \pi P \left(8\mu \sum_{n=1}^N \frac{2a}{[r(\sigma_n)]^4} \right)^{-1}, \quad (1)$$

where P is the transmembrane pressure; r , the pore radius; μ , the dynamic viscosity; w , the flow rate of liquid through the pore, σ_n is the time-dependent volume fraction of particles deposited inside circular section n .

The whole pore length l is divided into $N = \lfloor l/(2a) \rfloor$ circular sections. The value of coordinate z for section n is given by the expression:

$$z_n = a(2n-1), \text{ where } n = 1..N.$$

As the number of these “thin” circular sections is usually rather large, the sum given by (1) can be replaced to within a negligibly small error by the integral:

$$w(t) = \pi P \left(8\mu \int_0^l \frac{dz_1}{[r(\sigma)]^4} \right)^{-1}, \quad (2)$$

where σ is a function of time.

As in the phenomenological theory of depth filtration, the material balance equation will take the form [7-8]:

$$\frac{\partial(\varepsilon c)}{\partial t} + \frac{\partial}{\partial z}(cu) = -\frac{\partial \sigma}{\partial t}. \quad (3)$$

Eq. (3) is written for a unit volume of the membrane, which is treated as a porous medium. Here, c , the volume fraction of suspended particles, ε is the current porosity of the membrane, ε_0 is the initial membrane porosity, $(cu) = \frac{cw}{S}$ is the flux of particles through the cross section area $S = \frac{\pi r_0^2}{\varepsilon_0}$ of a unit membrane volume, $u = \frac{w}{S}$ is the flow (permeate) velocity.

Here, we assume that the value of w is the same throughout the pore at a fixed moment of time. In other words, the effect of the difference between the flow rate at the pore inlet and outlet is ignored because the change of permeate flow rate in the time of several seconds needed for the liquid to pass through the whole pore length usually does not exceed several percent.

In this case, the expression for the rate of deposition takes the form:

$$A(\sigma) w dt c = \frac{\pi r_0^2 l}{\varepsilon_0} d\sigma. \quad (4)$$

Here, $A(\sigma)$ accounts for the fraction of suspended particles deposited on a specific segment of the pore length.

Eq. (4) is written using the assumption that the volume of deposited particles is proportional to the produced permeate volume and the particle concentration.

Rearranging Eq. (4) yields the equation:

$$\frac{d\sigma}{dt} = \lambda(\sigma) u c, \quad (5)$$

where $\lambda = \frac{A(\sigma)}{l}$ is the traditional filter coefficient used in the theory of depth filtration [7-8].

The effect of the porosity of the layer of deposited particles is implicitly accounted for by the factor λ .

The initial and boundary conditions to the above equations can be written as

$$c = c_0, \quad \text{when } t \geq 0, z = 0; \quad (6)$$

$$c = 0, \sigma = 0, \quad \text{when } t = 0, z > 0. \quad (7)$$

The narrowing of a pore due to the collection of particles by its wall causes a decrease in the volume occupied by the suspension inside the membrane. In the case of cylindrical pores, the current membrane porosity ε is defined as

$$\varepsilon = \frac{\pi r^2 l}{\pi r_0^2 l} \varepsilon_0 = \frac{r^2}{r_0^2} \varepsilon_0. \quad (8)$$

Let us find the radius r as a function of σ for the case of cylindrical pores. The balance equation for this case is written as

$$-2\pi r l dr = \frac{\pi r_0^2 l}{\varepsilon_0} d\sigma. \quad (9)$$

Integrating the left- and right-hand sides of Eq. (9) in view of initial condition (7) yields the expression:

$$\frac{r}{r_0} = \sqrt{1 - \frac{\sigma}{\varepsilon_0}}. \quad (10)$$

Using the above expression, we obtain

$$\varepsilon = \varepsilon_0 [F(\sigma)]^2, \quad (11)$$

where $F(\sigma) = \sqrt{1 - \frac{\sigma}{\varepsilon_0}}$.

The filter coefficient can be written as the initial filter coefficient λ_0 multiplied by some function $B(\sigma)$ that accounts for the reduction of the filter coefficient with increasing σ :

$$\lambda(\sigma) = \lambda_0 B(\sigma). \quad (12)$$

We introduce the initial linear permeate velocity u_0 defined as

$$u_0 = \frac{w_0}{S}. \quad (13)$$

In this case, Eqs. (3) and (5) can be rewritten as

$$\frac{\partial(\varepsilon_0 [F(\sigma)]^2 c)}{\partial t} + u_0 \frac{\partial}{\partial z} \left(c \left\{ \frac{1}{l} \int_0^l \frac{dz_1}{[F(\sigma)]^4} \right\}^{-1} \right) = -\frac{\partial \sigma}{\partial t}, \quad (14)$$

$$\frac{d\sigma}{dt} = \lambda_0 u_0 B(\sigma) \left\{ \frac{1}{l} \int_0^l \frac{dz_1}{[F(\sigma)]^4} \right\}^{-1} c. \quad (15)$$

The above equations can be written in dimensionless form as

$$\frac{\partial \left([F(\sigma)]^2 c \right)}{\partial \tau} + \frac{1}{c_0} \frac{\partial}{\partial Z} (cU(\tau)) = -\frac{1}{\varepsilon_0} \frac{\partial \sigma}{\partial \tau}, \quad (16)$$

$$\frac{\partial \sigma}{\partial \tau} = \frac{N_\lambda \varepsilon_0}{c_0} B(\sigma) U(\tau) c, \quad (17)$$

where

$$\tau = \frac{c_0 w_0}{\pi l r_0^2} t, \quad Z = \frac{z}{l}, \quad N_\lambda = \lambda_0 l, \quad U(\tau) = \left\{ \int_0^1 \frac{dZ_1}{[F(\sigma)]^4} \right\}^{-1}. \quad (18)$$

The initial and boundary conditions in dimensionless form are written as

$$c = c_0, \quad \text{when } \tau \geq 0, Z = 0; \quad (19)$$

$$c = 0, \sigma = 0, \quad \text{when } \tau = 0, Z > 0. \quad (20)$$

It can be shown that the first term in Eq. (16) is negligibly small (in most cases its contribution does not exceed 1%) as compared to the other terms in this equation. Consequently, Eq. (16) can be approximated by the equation:

$$\frac{1}{c_0} \frac{\partial}{\partial Z} (cU) = -\frac{1}{\varepsilon_0} \frac{\partial \sigma}{\partial \tau}. \quad (21)$$

Introduction of a new function $\Phi = cU(\tau) \frac{\varepsilon_0}{c_0}$ transforms Eqs. (21) and (17) to

$$\frac{\partial \Phi}{\partial Z} = -\frac{\partial \sigma}{\partial \tau}, \quad (22)$$

$$\frac{d\sigma}{d\tau} = N_\lambda B(\sigma) \Phi. \quad (23)$$

The boundary condition given by Eq. (19) takes the form:

$$\Phi = \varepsilon_0 U(\tau), \quad \text{when } \tau \geq 0, Z = 0. \quad (24)$$

Equation (22) can be replaced by the classical material balance equation used in depth filtration theory (in most cases the error does not exceed 1%) [7]:

$$\frac{\partial \Phi}{\partial \tau} + \frac{\partial \Phi}{\partial Z} = -\frac{\partial \sigma}{\partial \tau}. \quad (25)$$

As a result, we come to the problem given by (25), (23), (19), and (20), which is mathematically equivalent to two uncoupled ordinary differential equations [7]:

$$\frac{\partial \sigma}{\partial Z} = -N_\lambda B(\sigma) \sigma, \quad (26)$$

$$Z = 0, \quad \sigma = \sigma_0. \quad (27)$$

$$\frac{d\sigma_0}{d\tau} = \varepsilon_0 U(\tau) N_\lambda B(\sigma_0), \quad (28)$$

$$\sigma_0 = 0, \quad \tau = 0. \quad (29)$$

The system given by (26)-(29) can be solved for different functions $B(\sigma)$, which account for the mechanism of particle capture by the pore wall.

The simplest function corresponds to the case in which the increase in the number of deposited particles causes a decrease in the deposition rate because of the narrowing of the surface area available for the deposition of particles. The surface area on which particles can deposit at the initial moment is equal to $2\pi r_0 l$. Later, the surface area available for the deposition is defined by $2\pi r l$. Consequently, the desired function is given by the expression:

$$B(\sigma) = \frac{r}{r_0} = F(r). \quad (30)$$

Another function corresponds to the case in which only one layer of particles can deposit on the pore wall, the so-called case of Langmuir adsorption [8]. Here, the desired function is written as

$$B(\sigma) = 1 - \frac{\sigma}{\sigma_{\max}}, \quad (31)$$

where σ_{\max} is the value corresponding to the completed single layer.

Other possible functions can be taken from Ref. [7].

In the present paper, our consideration will be restricted to the study of the simplest function given by Eq. (30).

It can be easily shown that the solution to the system given by (26)-(29) is written as [7]

$$\sigma = \varepsilon_0 \left(1 - \tanh \left[\frac{N_\lambda Z}{2} + \operatorname{arctanh} \left(1 - \frac{N_\lambda}{2} \int_0^\tau U(\tau) d\tau \right) \right] \right)^2. \quad (32)$$

The expression for σ_0 at the pore inlet is given by

$$\sigma_0 = \frac{\varepsilon_0}{4} \left(4N_\lambda \int_0^\tau U(\tau) d\tau - \left\{ N_\lambda \int_0^\tau U(\tau) d\tau \right\}^2 \right). \quad (33)$$

According to Eq. (18), the equation for $U(\tau)$ takes the form:

$$U(\tau) = \left\{ \int_0^1 \frac{dZ_1}{[F(\sigma)]^4} \right\}^{-1} = \left\{ \int_0^1 \frac{dZ_1}{\tanh \left[\frac{N_\lambda Z_1}{2} + \operatorname{arctanh} \left(1 - \frac{N_\lambda}{2} \int_0^\tau U(\tau) d\tau \right) \right]^4} \right\}^{-1}. \quad (34)$$

The above integral can be evaluated analytically, for example, using *Mathematica* or *Maple*. However, the expression is too awkward to be listed here.

Introduction of a new variable $y = \int_0^\tau U(\tau) d\tau$ transforms Eq. (34) to

$$\frac{dy}{d\tau} = \left\{ \int_0^1 \frac{dZ_1}{\tanh \left[\frac{N_\lambda Z_1}{2} + \operatorname{arctanh} \left(1 - \frac{N_\lambda}{2} y \right) \right]^4} \right\}^{-1}, \quad (35)$$

which is subject to the initial condition:

$$y(0) = 0. \quad (36)$$

Once the above equation for y is numerically solved, we can determine the value of $U(\tau)$:

$$U(\tau) = \left\{ \int_0^1 \frac{dZ_1}{\tanh \left[\frac{N_\lambda Z_1}{2} + \operatorname{arctanh} \left(1 - \frac{N_\lambda}{2} y(\tau) \right) \right]^4} \right\}^{-1}. \quad (37)$$

The actual particle retention R_d of a membrane, which can be a function of time, will be defined as

$$R_d = 1 - \frac{c_l}{c_0}, \quad (38)$$

where c_l is the particle concentration at the pore outlet.

Let us find the expression for c_l .

According to Ref. [7], the problem given by Eqs. (25), (23), (19), and (20) is characterized by the identity:

$$\frac{\sigma}{\sigma_0} = \frac{\Phi}{\Phi_0}, \quad (39)$$

where σ_0 and Φ_0 are the values of σ and Φ at the pore inlet.

Using the definition of Φ , we obtain

$$\frac{\Phi}{\Phi_0} = \frac{c}{c_0}. \quad (40)$$

Consequently, the particle concentration c_l can be determined by the formula:

$$c_l = c_0 \frac{\sigma_l}{\sigma_0}, \quad (41)$$

where σ_l , which is the specific deposit at the pore outlet, and σ_0 can be calculated using Eqs. (32) and (33) with $U(\tau)$ given by Eq. (37), respectively.

The expression for the critical standard blocking time τ_{cr} , at which the critical value of the pore inlet radius is reached, can be easily obtained from Eqs. (10) and (33):

$$\rho_{cr} = \sqrt{1 - \frac{\sigma_0(\tau_{cr})}{\varepsilon_0}} = 1 - \frac{N_\lambda}{2} \int_0^{\tau_{cr}} U(\tau) d\tau. \quad (42)$$

The value of τ_{cr} can be found by numerical solution of Eq. (42).

1. P. Le-Clech, V. Chen, T. A. Fane, *J. Membr. Sci.* 284 (1–2) (2006) 17–53.
2. L.J. Zeman, A.L. Zydney, *Microfiltration and Ultrafiltration: Principles and Applications*, Marcel Dekker, New York, USA, 1996.
3. K.-J. Hwang, Ch.-Y. Liao, K.-L. Tung, *J. Membr. Sci.* (287) (1–2) (2007) 287–293.
4. S.V. Polyakov, E.D. Maksimov, V.S. Polyakov, *Theor. Found. Chem. Eng.* 29 (4) (1995) 329–332.
5. Yu.S. Polyakov, D.A. Kazenin, *Theor. Found. Chem. Eng.* 41 (1) (2007) 56–65.
6. E. Klein, *J. Membr. Sci.* 179 (1) (2000) 1–27.
7. C. Tien, *Granular Filtration of Aerosols and Hydrosols*, Butterworths Publishers, Boston, USA, 1989.
8. M. Elimelech, J. Gregory, X. Jia, R. Williams, *Particle Deposition and Aggregation: Measurement, Modelling, and Simulation*, Butterworth–Heinemann, Oxford, England, 1995.