INFLUENCE OF HYDRODYNAMIC PROPERTIES ON THE FOULING MECHANISMS OF MEMBRANES AND THEIR EFFICIENCY AND SELECTIVITY DECREASE

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ABSTRACT

This article discusses and analyses the latest concepts of depositions of colloidal, suspended, and organic substances on membranes. The existing models of concentration polarization in apparatuses of various design are described, the influence of generated deposits on decrease in efficiency and selectivity of membranes is estimated. It is demonstrated that the transient flow rate prevents concentrating of particles and organic molecules near membrane surface providing their detachment. However, despite favorable influence of hydrodynamic conditions on membrane operation, they are not sufficiently studied in order to control fouling which is also influenced by channel geometry and resistance, as well as adhesive and adsorptive properties of membrane material.

EXISTING CONCEPTS OF DEPOSITIONS OF SUSPENDED AND COLLOIDAL SUBSTANCES ON REVERSE OSMOSIS AND ULTRAFILTRATION MEMBRANES

Forecasting of decrease in membrane efficiency with time as a consequence of fouling is an urgent issue of operation of reverse osmosis plants.

The relevant procedures are based on the concepts of fouling mechanisms by various researchers. These concepts also specify the experimental researches. Review of published materials devoted to investigations into fouling of reverse osmosis membranes reveals that quite different mechanisms of this process are accepted by different researchers.

1. The theory of filtration with fouling forms the basis of models proposed in numerous works by Belfort, et al. (Altena, et al., 1983; Belfort, et al., 1979; Belfort and Marx, 1976; Belfort and Marx, 1978; Belfort, 1980; Belfort, et al., 1985; Green and Belfort, 1980; Reed and Belfort, 1982). This theory is used in several procedures forecasting decrease in membrane efficiency with time. This mechanism is based on the assumption that membrane fouling is governed by filtration features. Belfort believes that the filtration hypothesis is confirmed by experiments on microfiltration cells both upon dead-end filtration and under various velocities of tangential flow above membrane (Reed and Belfort, 1982), simulating the conditions in reverse osmosis apparatuses.

2. (Belfort, et al., 1985) developed filtration theory with consideration for calculated paths of particles moving in the flow as a function of their weights and velocities. As mentioned in the articles by Belfort, et al., 1985, the filtration theory frequently forecasts higher decrease in membrane efficiency than actual values. Hence, the filtration mechanism assuming deposition of all particles contained in initial treated water on membrane was improved by calculation of forces acting on a particle in the flow. The calculations were performed for laminar flow with parabolic velocity distribution over the channel height. In addition to pressing forces by convective flow and reverse diffusion the particles near membrane surface are affected by uplift force resulting from the difference in velocities of various fluid layers above membrane.

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Taking into account the lift forces of particles, the paths of particle motion in flow were calculated in Belfort, et al., 1985 and it was shown that under certain conditions (particle weight and velocity) not all particles are deposited on membrane. These adjustments are considered in calculations of deposit amount which influences on decrease in membrane efficiency according to the law of filtration with fouling.

3. The theory of stability of colloidal solutions near membrane surface described by Brunnele (Brunnle, 1980) and developed in other works (Kaakinen and Moody, 1984) relates the concentration polarization near the surface of reverse osmosis membrane with particle coagulation. Particle coagulation near membrane surface occurs due to increase in slat concentration in near-membrane layer and stability loss of colloidal solution.

4. The theory of gel formation or gel polarization (Nakao, et al., 1979) also describes coagulation or gel formation of high molecular solution near membrane surface as a consequence of concentration polarization. According to this theory gel is formed upon achievement of maximum allowable concentration of gel formation near membrane surface. The theory of gel formation was developed similarly to the theories of formation poorly water soluble deposits.

5. The theory of formation of colloidal deposits using adsorption mechanisms was describe by (Jackson and Landolt, 1973) with regard to colloidal solutions of iron hydroxide. According to the proposed mechanism the deposit is formed in two stages: nucleation on membrane surface and deposit growth. At the stage of deposit growth the authors apply the theory of stability of colloidal solutions.

While forecasting decrease in efficiency of reverse osmosis membranes due to fouling the most widely applied is the theory of filtration with fouling described below.

MODELS OF CONCENTRATION POLARIZATION

In the most cases while analyzing concentration polarization the initial solution in the apparatus channels is assumed to be well agitated in turbulent flow. According to the Nernst film model, on membrane surface there exists thin near-membrane layer where concentration of dissolved substance is higher than in the main flow of initial solution (Fig. 1). This process is described by the well-known mass balance equations:

\[
V \cdot C_p + V \cdot C + D \frac{dc}{dx} = 0
\]  

(1)

where \( V \) is the volumetric water flow rate passing via membrane, \( \text{cm}^3/(\text{cm}^2 \cdot \text{s}) \); \( C \) is the concentration of dissolved substance, \( \text{g/cm}^3 \); \( C_p \) is the concentration of dissolve substance in permeate, \( \text{g/cm}^3 \); \( D \) is the diffusion coefficient, \( \text{cm}^2/\text{s} \).

The boundary conditions of Eq. (1) are as follows:

at \( x = 0 \) (near membrane surface) \( C = C_w \);

at \( x = \delta \) (at the distance \( \delta \) from membrane surface) \( C = C_b \) (concentration in the flow).

Solution of Eq. (1) for these boundary conditions is as follows:

\[
c_w/ c_b = \frac{\exp \left( \frac{V}{D} \right)}{R_i + \left( 1 - R_i \right) \exp \left( \frac{V}{D} \right)}
\]  

(2)

where \( R_i \) is the membrane selectivity, \( R_i = (1 - C_p/C_w) \).

For high selectivity values Eq. (2) is as follows:

\[
c_w/ c_b = \exp \left( \frac{V}{k_o} \right)
\]  

(3)

where \( k_o \) is the coefficient of mass transfer, \( k_o = D/\delta \).

Sherwood in 1965 presented Eq. (3) as follows:

\[
c_w/ c_b = \exp \left( \frac{\nu \cdot S_c}{J_D \cdot U_h} \right)^{2/3}
\]  

(4)

where \( S_c = V \cdot D \) is the Schmidt number; \( \nu \) is the kinematic viscosity of fluid, \( \text{cm}^2/\text{s} \); \( U_h \) is the velocity flow rate (in tangential direction) above membrane, \( \text{cm/s} \); \( J_D \) is the Chilton-Colebrook factor,

\[
J_D = \frac{4}{V_d} \cdot S_c^{2/3}
\]
For the case of turbulent flow in tubular membranes, $J_D \approx \frac{f}{2}$, where $f$ is the friction factor, Eq. (4) is as follows:

$$c_w/c_b = \exp \left\{ \frac{2\nu \cdot S_c}{f \cdot U_b} \right\}$$

(5)

In 1966 Brian proposed the following equation for average concentration polarization in tubular membranes:

$$c_w/c_b = 1.333 \exp \left\{ \frac{2\nu \cdot S_c}{0.75f \cdot U_b} \right\}$$

(6)

It follows from Eqs. (5) and (6) that the main factors influencing on concentration polarization are membrane efficiency in terms of filtrate and velocity of tangential flow in channel above membrane. The friction factor $f$ can be increased by various approaches thus decreasing $C_w/C_b$.

For instance, in the channels formed by flat membranes (in rollers) separating screens are used in order to increase friction factor. In channels of tubular membranes the flow turbulence is achieved by spherical particles (0.7 mm in diameter), suspended in the flow, which at existing level of concentration polarization makes it possible to provide lower velocities of transient flow (1 cm/s) and significantly reduce power consumption (up to 15%) for circulation mode (Potts, et al. 1981).

It follows also from Eqs. (5) and (6) that large organic molecules are the most dangerous for concentrating in near-membrane layer, since they are characterized by inferior diffusion. In addition, their presence in water can increase viscosity. Both these factors increase the Schmidt number $S_c$.

Analysis of concentration polarization as a function of various factors for laminar flow was performed by Fischer (Potts, et al., 1981). Various channel types were considered (flow between two flat membranes and flow in tubular membrane channel). The results of analysis of concentration polarization for tubular membranes are summarized below.

The coordinates used for solution of the problem are illustrated in Fig. 2.

The velocity field is determined by the Navier–Stokes equation and the following equation in cylindrical coordinates:

- in radial direction (along the r axis):

$$u \frac{\partial v}{\partial \theta} + v \frac{\partial u}{\partial r} = -\frac{1}{\rho} \frac{\partial p}{\partial r} + \frac{\partial^2 v}{\partial \theta^2} + \frac{\partial^2 v}{\partial r^2} + \frac{1}{r} \frac{\partial v}{\partial \theta} - \frac{v}{r^2}$$

(7)

Stationary state in the flow is described as follows:

- in axial direction (along the x axis):

$$\frac{\partial u}{\partial x} + v \frac{\partial u}{\partial r} = \frac{1}{\rho} \frac{\partial p}{\partial x} + \nu \left[ \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial r^2} + \frac{1}{r} \frac{\partial u}{\partial r} \right]$$

(8)

$$\frac{\partial}{\partial x} \left( r \cdot u \right) + \frac{\partial}{\partial r} \left( r \cdot v \right) = 0$$

(9)

Boundary conditions for the equations describing the velocity field are as follows:

a) $u(x, h) = 0$ (there is no motion in axial direction near membrane surface);

b) membrane efficiency is constant, $v(h) = v_w$;

c) $v(0) = 0$

d) material balance under stationary conditions for indefinite fluid volume near membrane surface (salt does not pass via membranes):

e) symmetry:

$$\left( \frac{\partial c}{\partial r} \right)_{r=0} = 0$$

f) profile of initial concentrations $c(0, r) = c_o \text{ (constant)}$.

Approximate analytical solution of this set of differential equations is as follows:

![Fig. 2 Concentration polarization in tubular membranes upon turbulent flow.](image-url)
where \( I = \frac{\delta L}{4a^2} \); \( \bar{c} \) is the average concentration of dissolved substance; \( \delta = \frac{v_w}{u(0)}; L = \frac{x}{h}; \alpha = \frac{D}{v_w h} \).

Fischer et al. (Potts et al. 1981) used these results for description of concentration of dissolved substance as a function of length of tubular channel and concentration as a function of channel diameter.

Similar analysis was performed by Brian for the case of flow between parallel flat membranes (for roller and filter-presses).

EXISTING CONCEPTS OF FOULING INFLUENCE ON DECREASE EFFICIENCY AND SELECTIVITY OF MEMBRANES

In There are numerous concepts of fouling influence on membrane performances. Kimura, et al. (Bian, et al., 2000) believe that accumulation of deposit as a consequence of its high hydraulic resistance leads to decrease in membrane efficiency. With decrease in ion transfer rate via membrane the concentration polarization decreases and selectivity of apparatuses increases (Fig. 3).

Belfort, et al., mentioned that deterioration of membrane selectivity is related with hindered ion diffusion from membrane surface to solution as a consequence of existence of fine deposit layer. Such explanation of decrease in selectivity of membranes seems to be the most appropriate.

The works by Karelin, 1988 are based on the Merten model. According to their concepts deposit increases the layer height of concentration polarization by the thickness of deposit layer.

Decrease in membrane efficiency is probably caused not by increase in hydraulic resistance of deposit layer but by increase in concentration polarization and decrease in active pressure \((P-P_{osm})\).

In addition, increase in pressure drop upon passing of concentrated product via apparatus should be taken into account, it results in significant decrease in active pressure above membrane, thus decreasing its efficiency. The value of such drop can be very important, causing telescoping of roller elements.

The increase in pressure drop on apparatus is mainly determined by its design. When roller elements were opened and fouled membranes were visually examined, it was revealed that flow channels (gaps) between the fibers of feed spacer are fouled to a higher extent than the remaining membrane surface. This probably can be attributed to the fact that the contacting areas between feed spacer and membrane are fouled causing high longitudinal resistance against the flow (Riddle, 1992).

Therefore, the decrease in membrane efficiency is caused by increase in concentration polarization and decrease in acting pressure.

Hydraulic resistance of deposit probably does not influence on membrane efficiency. While dismantling apparatuses it can be seen that the deposit structure is very loose, its hydraulic resistance is negligible in comparison with resistance of membrane. Thus, calculations of hydraulic resistance of deposit and its
compressibility are practice. Moreover, impairment of performances upon operation is reflected mainly on decrease in selectivity rather than efficiency. Otherwise, that is, upon decrease in efficiency due to resistance of deposit, such significant decrease in selectivity would not be observed.

Therefore, the main reason of decrease in concentration polarization and main parameter of the model is the thickness of deposit layer. For the cases when concentration polarization is reduced to minimum the thickness of polarization layer is assumed to be equal to the thickness of deposit layer and concentration polarization can be calculated as follows:

$$\frac{C_w}{C_b} = \exp\left(\frac{\gamma V \beta}{R \left(1 - R\right) \exp\left(\frac{\gamma V \beta}{D}\right)}\right)$$

While developing the model of influence of deposit on membrane selectivity the Nernst film model was used. According to this model a thin boundary layer exists near membrane surface: stationary film with the thickness $\beta$. Salt transfer in this layer is limited by molecular mechanisms: diffusion determined by the molecular coefficient $D$. When deposit is formed on membrane surface the thickness of boundary layer increases by the height of deposit layer, hence, salt transfer over total thickness of deposit layer occurs only due to molecular mechanisms which significantly hinders salt transfer from membrane surface to the flow core in comparison with the mode without deposit (Fig. 4).

Herewith, probably, the density of deposit structure can also play its role in decrease in membrane selectivity. Turbulent pulsations are gradually attenuated, and the thickness of boundary layer near loose deposit can be lower than that of dense deposit of the same height.

In laminar flow concentrated boundary layer and velocity field are formed (Namguk, et al., 2000). Concentration profile in laminar flow is formed by combined action of longitudinal convection and diffusion. The velocity profile is developed already at the channel input.

When deposit layer exists on membrane surface the concentration gradient is established over the height of this stationary layer. The velocity profile already does not influence on transfer in deposit layer. Thus, at channel input the concentration polarization is determined by the thickness of deposit layer. Probably, in the channel end the concentration gradient will be determined by the velocity profile in channel and in the boundaries of deposit layer by the thickness of deposit layer (Fig. 5).

ANALYSIS OF FORMATION MECHANISMS OF COLLOIDAL DEPOSITS ON REVERSE OSMOSIS MEMBRANES

Visual examination of deposits on membranes extracted from roller element reveals that the deposits have very loose uncompressible structure despite high pressure in the channels. This invokes new approaches to the mechanism of deposit formation and influence of deposit on deterioration of membrane properties which cannot be a consequence of high hydraulic pressure of deposit layer.

First of all, it should be mentioned that the reverse osmosis transfer has nothing in common with microfiltration, which is frequently applied for simulation of deposit formation on reverse osmosis membranes. The resistance of microfilter is negligible, therefore, as a consequence of high pressure difference the particles, captured by the filter, are pressed to its surface. Reverse osmosis transfer is the transfer of water molecules via membrane wall

![Fig. 4](image1.png) Concentration profile near the surface of reverse osmosis membrane without and with deposit formation upon turbulent flow.

![Fig. 5](image2.png) Development of concentration polarization as a consequence of membrane fouling upon laminar flow: a) at the channel input; b) at the middle of the channel.
at certain pressure. The particles in water are not pressed against membrane, since at relatively low membrane efficiency high pressure on particles directed to membrane surface cannot exist. All pressure is consumed for overcoming of resistance of membrane and drain channel. Increase in the existing pressure leads to increase in membrane efficiency and, hence, increase in resistance of water passing via membrane and drain system. Thus, pressing of particles to membrane as a consequence if pressure drop is excluded.

Mechanism of particle adsorption on membrane surface is the most probable. At the same time participation of reverse osmosis transfer in formation of deposit layer should not neglected. Transfer via membrane causes motion of particles in flow to membrane. Hence, adsorption of particles (adhesion) to membrane surface increases due to constant transfer of particles to membrane surface. At the same time coagulation of particles approaching membrane surface with those already attached to the surface is possible.

The mechanism proposed by Brunnele, 1980 does not completely match actual processes. Coagulation occurs upon certain conditions, certain concentrations of coagulating particles are required. Meanwhile, as evidenced in practice, membrane fouling occurs even at extremely low concentrations of colloidal particles in water (for instance, iron: up to zero concentrations).

INFLUENCE OF HYDRODYNAMIC FORCES OF PARTICLE DETACHMENT ON INTENSITY OF DEPOSIT FORMATION OF SUSPENDED AND ORGANIC SUBSTANCES

The phenomenon of concentration polarization increases resistance of deposit layer due to accumulation of suspended particles on membrane surface. As already shown, numerous models describe decrease in membrane efficiency (both for ultrafiltration and reverse osmosis, as well as nanofiltration).

The model of filtration with fouling is the most widely known and the most successfully describes fouling upon slurry filtration in the mode of dead-end filtration via microfilters and ultrafilters. However, as mentioned elsewhere (Potts, et al., 1981), this model cannot describe fouling upon tangential mode of membrane apparatuses or upon constant recirculation of initial water. In such mode after initial deposit formation on membrane surface the deposit growth is terminated as a consequence of influence of tangential discharge: detachment of particles.

When surface waters are treated by means of membranes, the membranes are fouled with suspended and colloidal particles as well as organic substances (humic acids). Since the sizes of various colloidal particles and organic substances contained in water are different, their diffusion properties vary significantly. Thus, at the start of the process membranes are fouled with subsequent decrease in their efficiency. Upon treatment of surface water the deposit growth can be stopped after layer formation and growth at the start of the process, decrease in efficiency and, as a consequence, in concentration polarization. Thus, even in tangential mode the model of filtration with fouling can be applied for description of deposit formation.

As mentioned elsewhere (Potts, et al., 1981), upon ultrafiltration treatment the membrane fouling runs in accordance with the model of filtration with fouling and accumulation of high molecular impurities and colloidal/suspended particles on membrane surface. Deposit formation continues until membrane efficiency decreases so that concentration polarization drops and particles are detached from deposit surface, thus preventing further deposit growth.

When cleaning is performed in tangential mode at constant pressure the deposit formation can be conventionally subdivided into two stages:

- accumulation of undetachable deposit layer; and
- achievement of equilibrium between rates of deposit accumulation and particle detachment.

However, as mentioned by some researchers on the basis of experience, equilibrium is achieved upon significant decrease in membrane efficiency when facility should be deactivated and deposit should be dissolved by chemical washings.

In order to control (prevent) fouling various measures are applied:

1. Preliminary coagulation aiming at particle coarsening, decrease in resistance of deposit, improvement of reverse diffusion of particles (improvement of detachment). It should be mentioned that coagulation and binding of small sized particles reduces the chance of clogging, which is probably the most important factor of retention of membrane efficiency.

2. Increase in particle detachment rate by increase in velocity of transient flow.

3. Increase in efficiency of hydraulic (back) washings.
The models of reverse transport are being developed, that is, mechanism of decrease in membrane fouling by increase in velocity of transient flow.

Three developed models are known: diffusion due to Brownian motion for low molecular organic substances, detachment diffusion for macromolecules, and migration model for colloids. These models of reverse transport demonstrate that stability of performances of membrane ultrafiltration facilities (efficiency in terms of filtrate) increases with increase in detachment rate and size of particles contained in water.

For colloidal particles and humic substances contained in surface water the Brownian diffusion model and the detachment model give different estimations of reverse transport of impurities from membrane surface into solution. With decrease in particle size and molecular weight of organic substances the coefficient of Brownian diffusion increases and the coefficient of detachment diffusion decreases. Efficient value of the diffusion coefficient is the sum of both diffusion coefficients.

Upon nanofiltration the concentration of high molecular substances in near-membrane layer increases. Large organic molecules with low diffusion coefficient foul membranes quicker and to a higher extent due to low solubility and higher concentration achieved in near-membrane layer (Cho, et al., 2000).

Decrease in membrane efficiency upon filtration of water containing organic compounds is stipulated by formation of gel layer on membrane surface and sorption occurring as a consequence of interaction of organic substances with membrane material (Cho, et al., 2000):

\[
J = \frac{\Delta P}{\mu\left(R_m + R_{ads1} + R_{ads2}\right)}
\]  

where \( R_{ads1} \) is the resistance of gel layer plus resistance stipulated by sorption of organic substances on membrane surface; \( R_{ads2} \) is the resistance stipulated by interaction of organic substances on membrane surface and in solution.

\( R_{ads1} \) increases with time to the equilibrium value \( R_{ads1}^{eq} \).

The main factors which influence on the dynamics of this process are concentration of organic substances in treated water and specific flow rate via membrane.

Upon extended filtration under constant pressure without back washing the formation of deposit layer is described by the following equation obtained from Eq. (14):

\[
\frac{P}{\mu J} = R_o + R_c = K \cdot \frac{V}{A} + \frac{P}{\mu J_o}
\]

where \( P \) is the pressure, \( Pa; J_o \) is the initial membrane filtration rate, \( m/s; R_o \) is the membrane resistance \( (m^{-1}); V \) is the permeate volume, \( m^3; A \) is the membrane surface area, \( m^2; K \) is the coefficient of specific resistance \( (K=\alpha C) \), where \( \alpha \) is the specific resistance of deposit, \( m/kg \); \( C \) is the concentration of impurities; \( R_c \) is the resistance of deposit \( (m^{-1}) \).

Fig. 6 illustrates \( \frac{PA}{\mu J} \) as a function of volume \( V \), described by direct line. Variation of slope angle of the plot with increase in velocity of tangential flow is attributed to detachment of particles from membrane surface, decrease in their concentration and specific resistance of the deposit (Bian, et al., 2000).

The influence of velocities of transient flow on concentration polarization and coefficient of mass transfer upon treatment of water containing soluble organic substances is illustrated in Fig. 7 and 8.
CONCLUSIONS
Deposition velocities of suspended substances depend on velocity of water transient flow via channel: the higher the velocity, the lower the amount of deposits on membranes. Mechanism of deposition on membrane is comprised mainly particle adhesion to membrane surface. Depending on the membrane properties (hydrophilicity, surface charge, and so on), the deposition velocities of suspended particles and organic compound can vary. Current projects are oriented at development of membranes with modified surface which repulses some inclusions. It should be mentioned that the channel geometry influences critically on the apparatus operation efficiency. Longitudinal hydraulic resistance of the channel increases with fouling. Decrease in membrane efficiency is directly related with increase in hydraulic resistance which is attributed to decrease in operating pressure.

As will be demonstrated in subsequent works devoted to testing of apparatuses of new design with decreased hydraulic resistance, the intensity of increase in hydraulic resistance, hence, of decrease in efficiency is significantly lower. This makes background to consider that operation of reverse osmosis and nanofiltration facilities is possible without pre-treatment due to improvements of channel design, selection of membrane material and hydrodynamic operation mode.

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