Effect of ultrafiltration membranes properties and channel configuration on membrane fouling and performance

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Abstract. The work describes the existing views on colloidal, suspended and organic fouling in ultrafiltration (UF) membrane modules using for natural water treatment. The paper presents the results of the experimental research allowing for a quantitative determination of sorption and plugging rates, and for evaluation of their effect on membrane performance loss over time. Small colloidal particles pose a risk to UF unit due pore plugging; especially when membranes treat water with a very low content of suspended solids. This effect often cannot be detected during short-time pilot tests, but it can have a decisive influence on the operation of a membrane unit. Study of the filterability characteristic of water contaminants enables us to forecast the filtration type on UF membranes and to evaluate their performance losses. The paper also describes the effect of a feed channel structure – in particular, a presence of a feed spacer in spiral wound membrane modules – on channel hydraulic resistance growth. The technique of channel resistance estimation, depending on suspended particles concentration in the source water, is presented.

1 Effect of membrane surface properties on organic fouling

Membrane ultrafiltration technique is widely used nowadays for natural water treatment, but generally membrane facilities face thechallengeof their colloidal, organic and biological fouling and, as a result, the deterioration of membrane characteristics [1, 2].

The mechanism of organic fouling of reverse osmosis and ultra filtration membranes has been well studied[3 - 5]. According to [6], organic substances generate an adsorbed film on membrane surface, which has virtually no detrimental effect on membrane characteristics. However, experience shows that organic fouling does result in selectivity and performance loss over long time. This is, obviously, due to the fact that dissolved organic matter has very various properties and a complex picture of molecular-mass distribution. Organic molecules are adsorbed in the pores and on the surface of a membrane, changing its degree of hydrophilicity, i.e., "modifying" membrane surface. According to Fane [6], the concentration of high-molecular substance in the near membrane layer increases with time.

In [7] authors suggest a model based on the assumption that membrane flux decline during filtration of water containing natural organic compounds is accounted for by gel layer formation on the membrane surface, and by sorption occurring as a result of

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interaction of organic substances with one another and with the membrane material. This model can be described by equation:

$$J = \frac{\Delta P}{\mu(R_m + R_{ads1} + R_{ads2})}, \tag{1}$$

where R_m is membrane hydraulic resistance; R_{ads1} is resistance of the gel layer plus resistance induced by sorption of organic substances on the membrane surface; R_{ads2} is resistance caused by interaction of organic substances located on the membrane surface and in the solution.

The value R_{ads1}describes a change in membrane resistance during the initial period and grows over time to reach a certain equilibrium value R_{eq}. The value R_{ads2} increases during the entire filtration period, but its contribution to the total resistance is minor. The resistance R_{eq}, as shown by experiments described in [7] is directly proportionate to the amount of substances adsorbed on the membrane. The amount of adsorbed substances and, consequently, the value R_{eq}, are described by Langmuir and Freundlich equations:

$$R_{eq} = \frac{aC_m}{1 + bC_m}; \qquad R_{eq} = p \cdot (C_m)^q, \tag{2}$$

where a, b, p, q are adsorption isotherm coefficients, C_m – concentration of organic substance near membrane surface.

A more simplified outcome of the adsorption-induced fouling model is given in [8]:

$$R_{ads} = R_{ads}^{\max} \cdot (1 - e^{-pt}), \tag{3}$$

$$R_{ads}^{\max} = \frac{C_m}{const + C_m}. \tag{4}$$

Substances adsorbed by the surface of an UF membrane can change its properties: e.g., its surface charge or hydrophilicity. In a number of cases, membrane selectivity may increase due to pore constriction or surface charge change.

The intensity of organic matter adsorption on membrane surface has been studied by a number of authors [9, 10] using a circulation-mode experiment. In this method, a given volume of feed solution (natural water or a peat extract-based model solution) was circulated through a membrane module while the filtrate and concentrate were returned back to the feed solution. During the experiment the concentrations of organic compounds were measured using various methods (TOC determination [9],photoelectric colorimetry [10], gas-liquid chromatography [10] etc.). The decrease in the organic substance concentration in the circulating solutions observed during the experiment proves precipitation (or sorption) of organic compounds on the membrane surface. Multiple repetitions of the circulation-mode experiments made it possible to experimentally determine the laws of organic compound accumulation on membrane surface.

Organic compounds adsorbed on the membrane surface form a thin film, which has virtually no effect on the membrane's performance or selectivity. After spreading over the entire membrane surface, the organic film stops growing and the rates of organic substance adsorption dramatically decrease. Experimental determination of organic substance adsorption rates enables us to measure the sorption capacity of the membrane surface.

Determination of the adsorption capacity of acetate UF membranes (UAM type, Russia) was performed for a mixture of humic acids (peat extract), simulating a natural organic matter (water colour). The preliminary finding was that the color of the prepared peat extract solution was directly proportional to the concentration of humic substances. The humic acid solution was prepared by dissolving peat extract in distilled water alkalized to pH = 10, and then was dosed into the feed water to obtain a specified concentration (color). The feed solution was circulated through a membrane module at high crossflow velocity for several hours without filtrate passage, to exclude fouling and pore plugging.

During the experiment, organic substances are absorbed by the membrane material and the color of the circulating solution continuously decreases (Fig. 1a). Based on the drop in the organic substance concentration in the circulating solution, one can calculate the amount of substance adsorbed on the membrane (Fig. 1b). The plot in Fig. 1b is used to determine the coefficient p in the adsorption equation (3) for an arbitrary time t. The sorption rate decreases as the membrane material becomes saturated with organic substances. Several series of experiments were conducted to determine the membrane sorption capacity in terms of humic acids. A freshly prepared peat extract solution was used for each series.

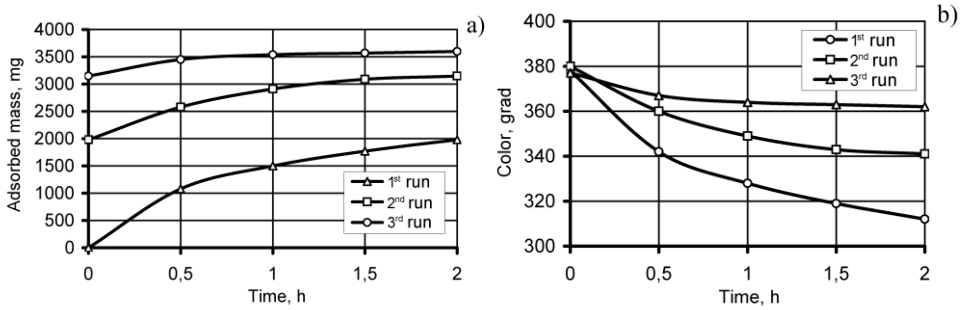

Fig. 1. Determination of humic substances adsorption on UAM acetate membranes: color in the circulating solution (a) andmass of adsorbed humic acids (b) by time (p = 0,46 h^{-1})

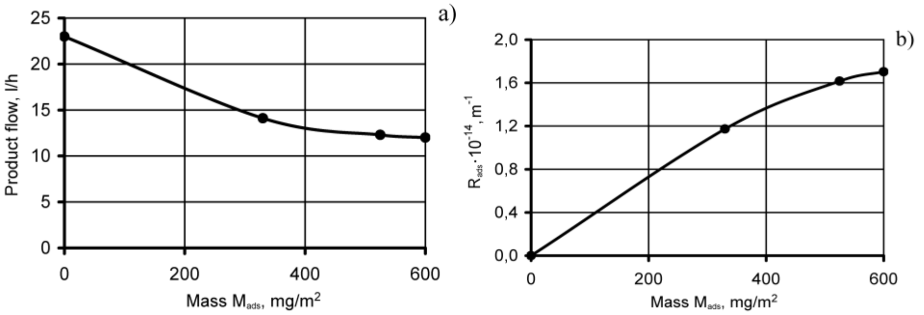

Fig.2. Influence of adsorbed humic substances on UF membrane characteristics: dependencies of membrane performance (a) and additional membrane resistance (b) on the mass of humic acids adsorbed on the membrane (k_{ads} = 0.917)

Membrane performance in clean water (Fig. 2a) was measured during the experiments to determine the value R_{ads}^{max} (Fig. 2b). Despite a relatively small amount of organic substances precipitating on the UF membrane (~ 600 mg/m^2), its performance decreased almost by two times (Fig. 2a), which proves that sorption occurs inside pores as well.

The dependencies in Fig 1b and 2a allow to predict the performance loss in UF membranes over time and to determine the amount of accumulated organic substances for treating water of a specified color.

As described in [3, 11] the membrane material affects the organic adsorption rate and adhesion of colloidal and suspended particles. Experiments showed that acetate membranes are less subject to organic and colloidal fouling [12]. Long-term developments were targeted at creating new types of membranes with modified surfaces that could "reject" a number of foulants contained in water (bacteria, colloids, and organics) and, thanks to this, could ensure a long service life of a membrane with minimum fouling and efficient removal of foulants during hydraulic flushing. However recent research has demonstrated that membrane organic fouling is not only determined by membrane polymer properties, but rather on the whole of the surface chemistry determining the amount and strength of the possible foulant–membrane interactions [3, 5].

2 The impact of fouling on feed channel resistance increase in spiral wound membrane module

Like in deep bed filtration wherein suspended and colloidal substances are deposited in the pores of the filter bed forming "arches" in the mouths of pore channels, a similar picture can be observed at places where feed spacer nodes contact the membrane surface in spiral wound elements. At high velocities, the "arches" are destroyed by hydrodynamic forces.

The amount of suspended solids trapped in the bed due to particle adhesion to the bed surface and carried out can be described by standard equations for deep-bed filtration [13]. Similar to filtering through a granulated bed, one can use experimentally obtained dependencies for spiral wound module cross flow resistance calculations.

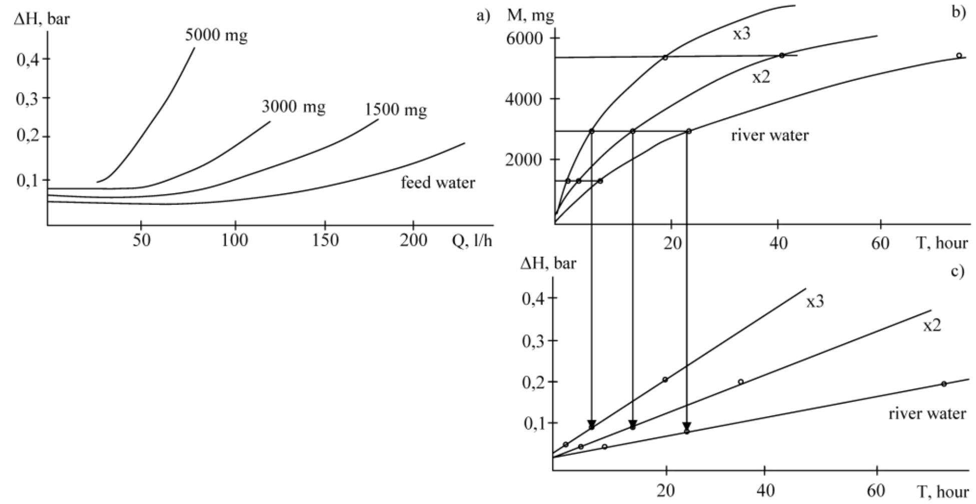

Fig.3. Example of resistance increase over time in an 1812-type spiral wound membrane module

Fig. 3 shows an example of feed channel resistance determination in an 1812-type spiral wound element. Fig. 3a presents the results of determination of head loss from cross flow velocity for different quantities of cake accumulated in membrane module. Based on the determination of fouling rates, the cake amount on a membrane was forecasted depending on the period of module operation with feed water of a specified composition (Fig 3b). The forecast shown in Fig. 3c is for river water and for river water concentrated by 2 and 3 times. Based on the data in Fig. 3b, each cake quantity can be correlated with the resistance in fouled membrane module and depends on water quality, time and cross flow flux.

3 The impact of pore plugging on UF membranes performance

As we know, membrane performance loss over time can be explained by cake growth and membrane resistance increase due to partial pore plugging. The pore plugging effect, unfortunately, is not taken into account by the majority of models describing the membrane filtration process. Nevertheless, this process is of a very significant importance, since small particles (smaller than membrane pore sizes) present in water turn out to be deleterious for membrane units. It is the presence of small particles in water and the risk of their penetration into the membrane body that explains the need for pre-coagulation and binding of small particles into larger agglomerates, which underlies the operating specifications related to Norit, Inge and other membrane units.

Small particles are especially dangerous during operation in a dead-end filtration mode at high operating pressures, when small particles may thoroughly plug the pores and be difficult to remove during backflushing. Probably, it is this fact that explains an often unsuccessful experience of surface water treatment in a dead-end filtration mode with coagulation in direct flow. Inefficient coagulation often results in up to 12% of water consumption for UF membranes backwash.

One of effective ways to reduce the plugging effect by small particles is transition from a dead-end filtration to a cross flow recirculation mode wherein high flux velocity over the membrane removes particles from its surface. Such mode is used both for water with a high suspended solid content and for treated water. E.g., at Moscow South-West WTP, UF facility is used for post-treatment of water that has already been subjected to coagulation, sedimentation and filtering, but UF units most of the time operate in a recirculation mode.

Simultaneously, as was already demonstrated in a number of works [14, 15], water subjected to coagulation and filtering treatment contains small particles – most dangerous in terms of membrane performance loss. In order to reduce the membrane pore plugging risk, it seems appropriate to use membranes with smaller pore sizes, but unfortunately they have reduced performance. Evidently, provided by low cost UF modules with capillary membranes, manufacturers considered that it is uneconomical to use membranes with the molecular cutoff below 100 kDa. The use of a recirculation mode (with cross flow velocities 0.2-1.0 m/s) results in a high energy consumption. Therefore, developers of UF technologies limited themselves to the dead-end filtration mode with a mandatory pre-coagulation of feed water.

Meanwhile, it is absolutely obvious that the use of membranes with smaller pore sizes (20-30 kDa) working in recirculation mode reduces the concentration polarization level and improves the quality of treated water in terms of organic content, reduces the risk of membrane plugging and formation of colloidal cake. The narrow spread of UF in water treatment practice can, probably, be explained by high capital and operational costs. The existing, widely implemented capillary membrane UF technology is a sort of compromise at the current stage of industrial development of the membrane technology. Cheapening of membrane modules and improvement of spiral wound membrane modules, less costly than capillary and tubular ones, will lead to a change in their application technology.

When UF unit operates in a dead-end filtration mode, one can observe a slow, run-to-run decline in membrane performance. An irreversible performance loss is caused by cake accumulation in dead areas of membrane module and plugging of part of the pores. Membrane performance decline during one filter run is shown in Fig. 4a, where the data were obtained during filtration of river water in a dead-end mode through an 1812-model spiral wound module using MGA-100 UF membranes (200 kDa) at pressure 2.0 bar.

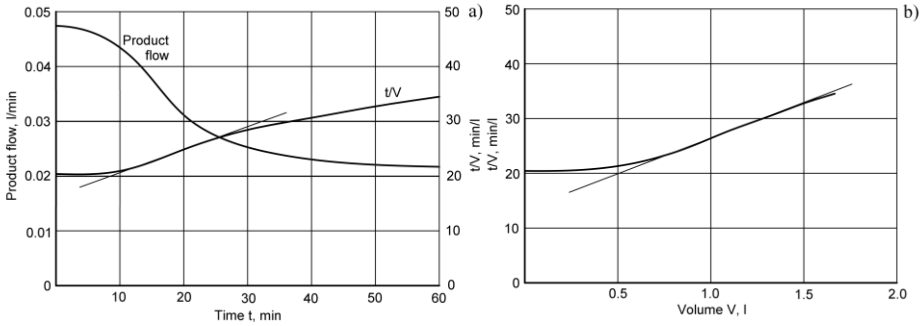

Fig.4. Dependency of performance loss in an 1812-type UF module during one filter run and processing of this dependency in the coordinates *V – t/V* and *t – t/V*

Since the process of membrane performance decline is described by an equation for an incompressible cake filtration, the plot of the value *t/V* (relation of the filtration time to the volume of filtered water, min/l) against the volume of filtered water *V* is presented as a straight line (Fig. 4b) [12].Due to its high resistance, the formed cake obviously entraps small particles which cause plugging. As can be seen from the plots in Fig. 4a, a sharp drop in UF membrane performance is preceded by a short straight section, a period when the membrane performance remains at the initial level, and the cake resistance is not high enough to cause a performance drop. On the plot in coordinates *t/V – t* (Fig. 4a) a sloped section is preceded by a section parallel to the X-axis. Evidently, during this period small particles seep through the membranes and plug the pores. Membrane plugging reveals with time and is noticed by performance loss after quite a long period.

In order to forecast membrane performance loss, it is necessary to determine the effect of membrane plugging on the performance rate, i.e., to reveal the dependency of performance on the volume of filtered water (for various types of feed water). If plugging occurs slowly as pores are clogged, then the process is described by a straight line in the coordinates *t/V – t*(where *t* is filtration time, *V* is volume) [12].

Several operations are required in order to determine the time dependency of membrane performance loss due only to pore plugging.

1) First we determine the share of water volume passed through the membrane, which caused plugging. In the plot, this volume corresponds to the initial period of filtration (the plugging process) until cake layer is build up and can be introduced as a coefficient *k*:

$$V_f^n = k \cdot Q_f^{avg} \cdot T_f,$$

where Q_f^{avg} is the average performance during the filtration cycle, T_f is the filtration cycle time, V_f^n is the volume corresponding to the noticeable membrane performance loss occurs during the filtration cycle.

2) The entire unit operation period *T*, during which membrane productivity loss is observed, can be divided into several periods (*i* = 4 to 6) within which the average performance for such period can be determined as:

$$Q_{avg}^i = \frac{V_f^i}{T_i}$$

3) Within each period of time T_i the total volume of filtered water V_f^i and the average filtrate flow rate ${Q_{avg}}^i$ can be determined.

4) Then we determine the share of filtrate volume corresponding to plugged filtration for each volume V_f^i:

$$V_{f.n.}{}^{i} = k \cdot V_f^i,$$

and the time of filtration during which plugging occurs:

$$T_t^3 = \frac{V_{f.n.}^i}{Q_{avg}^i}$$

5) Knowing the value of the filtration time, the volume of filtered water and the performance rate for each period, we can plot the value *t/v* against the filtration time *t* and against volume *V*, which will allow us to forecast membrane performance loss during plugging.

In order to forecast performance loss in membranes due to pore plugging, one can determine the time dependency of performance using the cell for determination of the Modified Fouling Index – MFI [16]. To obtain the volume of water to examine, we can use first portions filtered through microfiltration membranes before cake formation begins. By plotting a chart in the coordinates t – t/V, we can determine the values of volume V_i^n and periods T_i^n by the slope angle.

After studying the operation of membranes with various types of feed water, one can draw the conclusion that particle size distribution plays a significant role. A specific problem is posed by small particles (<0.1 um): they are more difficult to remove from water. Besides that, cake formed by such foul ants has a significantly higher resistance than that of large particles. Small particles are especially dangerous when they plug the pores of UF membranes. The treatment practice often shows that the more thorough pre-treatment was applied to water, the greater influence small particles exert on membrane fouling.

Small particles can be found in inorganic colloidal foul ants. These are aluminosilicates (clay particles) 0.3 to 1 um in size, and colloidal particles of iron, aluminum; silicates. Components of organic colloidal particles include proteins, carbohydrates, fats, oils, and surfactants. Aromatic acids, like, e.g., humic acids, in most cases exist in the form of very small colloids (< 0.01 um), which often appear unstable and, depending on the pH value, cause membrane fouling.

The review [17] states that modern methods of water quality (degree of removal of colloidal and organic substances) evaluation based on water microfiltration and on study of experimentally obtained dependencies of cake resistance on the volume of filtered water often yield unexpected results. This can be explained by presence in coagulated and filtered water of particles, which cause plugging of micro filters used in tests and, as a result, loss of their performance, which is often greater than when they filter untreated water.

That is why for water treatment using ultra filtration, one should take into account the composition of the feed water, as well as the nature and sizes of particles contained therein in order to avoid the risk of plugging and premature loss of membrane performance.

4 Conclusions

1. Performance loss in UF membranes in water treatment units occurs due to sediment layer formation and linear gain of resistance, while performance drop in NF elements occurs due to increase in membrane module resistance and drop of operating pressure.

2. Research shows that organic compounds exert an insignificant effect on performance and selectivity of UF membranes, and the degree of characteristic degradation in the latter depends on the membrane material and the degree of its hydrophobicity.

3. The degree of performance loss in UF membranes is naturally dependent on the concentration of suspended solids in water being processed: the more numerous they are, the faster performance declines due to formation of a cake layer on the membrane surface. In addition, another phenomenon can be observed, especially in a transition flow mode: cake accumulation occurs in the nodes of the feed spacer causing an additional increase of the general hydraulic resistance.

4. During treatment of water with a very low content of suspended solids, membrane pores are plugged resulting in a major performance loss. This effect often cannot be detected during short-time pilot tests, but it can have a decisive influence on the operation of a membrane unit. Study of the filterability characteristic of water under treatment enables forecasting of the filtration type using ultra filtration membranes and enables evaluating the drop in their performance.

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