UDC 628.168
DOI: 10.15587/1729-4061.2016.86187

EXPLORING THE PROPERTIES OF ULTRAFILTRATION MEMBRANES WITH A DYNAMIC LAYER AND BACTERICIDAL INOCULATION FOR THE PURIFICATION OF NATURAL WATERS

N. Nechitaylo
PhD, Associate Professor*
E-mail: n_np@mail.ru
E. Nagornaya
PhD, Associate Professor*
E-mail: ek_n@i.ua
E. Nesterova
PhD, Associate Professor*
E-mail: helena2010_10@mail.ru
*Department of Water Supply, Water Disposal and Hydraulics
State Higher Education Establishment «Pridneprovsk State Academy of Civil Engineering and Architecture»
Chernishevskogo str., 24-A, Dnepr, Ukraine, 49600

Проведено дослідження створення динамічного шару на поверхні ультрафільтраційної мембрани для вилучення забруднень з природних вод. Без попереднього хлорування в одну щабель обробки вдалося досягти рівня нормативних вимог. Встановлено, що мембрани піддаються біологічному обростанню, яке знижує експлуатаційні характеристики. Для виключення біологічного обростання запропонована методика модифікації поверхні мембран біоцидним щепленням

Ключові слова: ультрафільтрація, очищення природних вод, модифікація мембран, біоцидне щеплення

Проведены исследования создания динамического слоя на ультрафильтрационных мембранах для извлечения загрязнений из природных вод. Без предварительного хлорирования в одну ступень обработки удалось достичь уровня нормативных требований. Установлено, что мембраны подвергаются биологическому обрастанию, которое снижает эксплуатационные характеристики. Для исключения биологического обрастания предложена методика модификации поверхности мембран биоцидной прививкой

Ключевые слова: ультрафильтрация, очистка природных вод, модификация мембран, биоцидная прививка

1. Introduction

Application of membrane technologies for the preparation of drinking water from the natural sources is more and widely spread due to its high reliability as well as a reduction in the cost of membrane elements. For the surface fresh-water sources, it is the most expedient to use the method of ultrafiltration as its basic purpose is the removal of organic matter, suspensions, as well as viruses, bacteria and algae. This is predetermined by a mechanism of filtration through the pores of membrane – the so-called “sieve” mechanism.

However, this method [1–5] cannot be applied independently since, due to high contamination of natural sources of water supply with organic matter, a required degree of purification cannot be provided.

To solve this problem, it is proposed to use the modification of the surface of ready membranes without changing technological process of production. Modification should give new properties to the membrane, such as:

– bacteria static character or susceptibility to the low level of biofouling;

– simplicity of regeneration of the filtration layer;

– an increase in the degree of detention of contaminants.

2. Literature review and problem statement

To increase effect of detention of contamination, chemical methods are applied, such as preliminary coagulation and oxidation [6], introduction of powder-like activated carbon [2, 4], etc. Another essential shortcoming is a capability for the biological fouling of the ultrafiltration membrane.

Biological fouling of the surface of membrane with biofilms is referred to by authors of paper [7] as the Achilles' heel of the membrane methods of treatment. Microorganisms, which form a part of biofilm, use biodegradable admixtures from the feed water and they remain able to breeding for a long time, even if they are eliminated by more than 99 % at the previous stages of treatment.

A high degree of relevance of the topic of control over biological fouling is confirmed by article [8]. The authors proposed a procedure for monitoring biofouling at the ultrafiltration membranes using ultrasonic reflectometer, strengthened by the action of silicon dioxide. This makes it possible to conduct biotesting for fouling in the process of operation without opening the cells; however, this method is applicable only for flat membranes.

As can be seen from Fig. 1, the surface of membrane is ideal medium for the development of microbiological contamination.

First, the surface of membrane has high roughness, favorable for attachment of microorganisms. Second, nutrient medium is extracted and concentrated on the surface of membrane, which predetermines fairly dynamic development of biofilms.

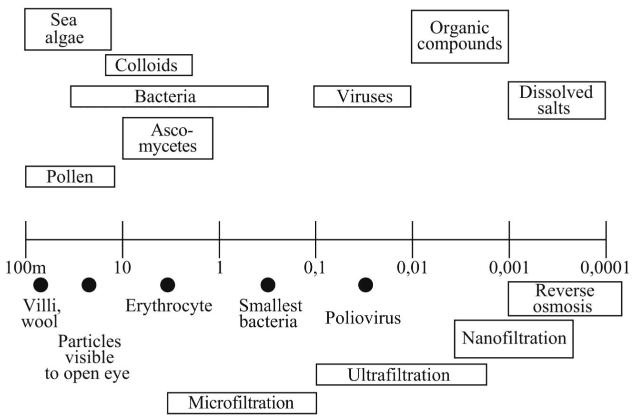

Fig. 1. Contaminants that are detained by the membrane methods of purification

Authors [9] noted that about 17 % of reduction in efficiency over the first 72 hours of operating is caused by the formation of biofilms at the surface of membrane. Paper [10] demonstrates a mathematical model of the effect of biofilms in the process of fouling. It is shown that biofilms exert considerable influence in the process of reduction in efficiency compared with the concentration polarization.

In [11], authors received a dependence of development of biofouling on the natural conditions, as well as the growth of chlorophyll in water reservoirs. Based on this, they demonstrated a dependence of the loss of efficiency in membranes of reverse osmosis because of external biological factors. The research, presented in this paper, is also relevant for other membrane methods.

Biocontamination may cause the following unfavorable factors of influence on the membrane systems [12–15]:

– reduction in the trans-membrane flow, in connection with the formation of biofilm, which decreases permeability of the surface of membrane;

– an increase in the pressure drop at the membrane, which requires increased pressure from the feeding side;

– membrane biodegradation, caused by the acid medium as a result of formation of by-products of vital activity of biofilm at the surface of membrane. For example, acetate cellulose membranes are the most receptive to biodegradation;

– an increase in permeability of the detained substances and reduction in water quality due to the accumulation of contamination in the biofilm at the surface of membrane, which increases a degree of concentration polarization;

– an increase in power consumption to force water through a membrane.

Thus, referring to data presented in papers [16, 17], it is possible to say with confidence that the accumulation of contamination due to growth in the biomass becomes fairly significant in 30–40 hours, and in 50 hours of operation of the installation, it is the main source of contamination. Accordingly, creation of a modified layer with bacteriostatic or biocidal properties will make it possible to considerably prolong the cycle between chemical washings of the membrane installations.

A method, by which this problem is solved now, is a periodic disinfection of membrane with the reverse washing by the solution of sodium hypochlorite. However, as can be seen from data on Fig. 2, an increase in the biomass starts in the first hours of operation and it means that there occurs the blocking of the pores of the membrane, which leads to the consequences, described above.

Articles [9, 18] examined introduction to the structure of membrane of the compounds, which decrease the immobilization of microorganisms on its surface. The authors proposed a solution on the immobilization of zinc ions to the polymer chains of membrane, which will make it possible to create a bactericidal layer [18].

Paper [19] explored a question of the antibacterial properties of ultrafiltration membrane, modified by graphene oxide with nanoparticles of silver. Putting on such a modifying layer makes it possible to give a stable antimicrobic effect to the membrane over the period of 3–4 days.

Testing a non-fouling membrane [20] demonstrated that the hybrid material of fabric, modified with HNTs-CS and Ag, displayed good resistance to the fouling. Furthermore, an antibacterial test demonstrated that the membrane possesses good antibacterial activity and was resistant against E. coli bacterium and staphylococcus aureus at 94,0 % and 92,6 %, respectively.

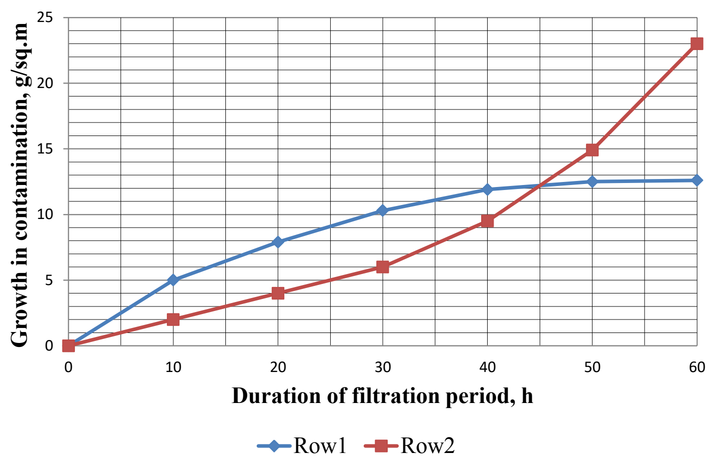

Fig. 2. Growth in contamination during purification of natural waters on the surface of membrane, row: 1 — increase in contamination on the surface of membrane, caused by organic and inorganic matter; 2 — increase in contamination on the surface of membrane due to the growth of biomass on its surface and attachment from the source

Traditionally, according to recommendations of manufacturers, a washing by the solution of sodium hypochlorite or by another oxidizing biocide is necessary to carry out once per 24 hours. This will make it possible to remove living biomass, as well as remove a part of the organic contamination. However, it should be noted that in the process of development microorganisms release polymers to attach to the surfaces, as well as proteins, polysaccharides and other products of vital activity. Biofilms are also immobilized on the surfaces of membrane near the pore space. This effect can be explained by the fact that pores are the places of the solvent outflow (pure water). Contaminated water or the concentrate that contains microbiological contamination and nourishing substratum (Fig. 1) are accumulated near the outflows in the maximum concentration.

The biofilms formed on the surface of membrane are one of strategies of survival of bacteria in the environment [21]. Thus, a basic structural component of biofilms are [22] exopolymers or polysaccharide strains. Exopolymers comprise approximately 85 % the entire mass of biofilm. As it is known, these biofilms are resistant to the disinfecting means [23]. Due to this reason, periodic washings by biocidal solutions do not prevent partial blocking of the pores of membranes.

Comparative study of the influence of biological fouling at the in-line coagulation with preliminary treatment by ozone, only with coagulation and without it, is represented in the paper *Fátima Rojasmembrane Serrano* [24]. A testing of these methods demonstrated that the best result is ensured only at the coagulation.

However, it is worthwhile noting that the proposed solutions can be used either at the stage of the creation of membranes under manufacturing conditions or they have insufficient effectiveness. The procedures proposed with the introduction of biocidal additives do not solve the problem of enhancing the effect of water purification.

It is necessary to develop a method, which makes it possible to comprehensively solve the problems of improving effectiveness of performance of membrane devices in terms of effectiveness of cleaning and simultaneous reduction of the influence of factors of biological fouling on the productivity of membrane devices directly at the facilities of water treatment. This solution will make it possible to adapt the devices to solve any tasks of water purification.

3. The aim and tasks of the study

The purpose of the conducted research was theoretical and experimental substantiation of modification of the surface of ultrafiltration membranes for improving efficiency of the process of natural waters purification.

To achieve the set goals, the following tasks were to be solved:

– development of a mathematical model for the formation of dynamic layer and blockage of ineffective pores when putting on a modifying layer;

– development of procedure for the laboratory tests of the compositions of a modifying additive and a biocidal inoculation;

– conducting semi-industrial tests for determining operational characteristics of the modified ultrafiltration membranes with a bactericidal layer.

4. Materials and methods of research

4. 1. Mathematical simulation of change in the diameter of pores when putting on a modifying dynamic layer

To enlarge the spectrum of the extracted contaminants, we proposed a technology for the modification of the membrane surface by putting on a dynamic layer with a partial blockage of non-effective pores (that is, pores that have large size in comparison to the extracted particles), as well as the creation of a dynamic surface layer, which overlaps the pores according to "bridge" principle with the introduction of biocides to the modified layer. This phenomenon is illustrated in Fig. 3.

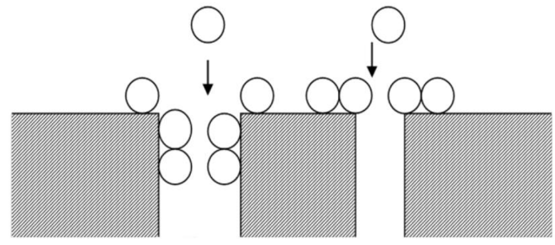

Fig. 3. Scheme of blocking the pores by different mechanisms: r — equivalent radius of the particle of contaminants; R — equivalent radius of the pore of membrane

Mathematical simulation of the change in the single size of the pore of complex shape is represented in article [25].

To describe the process of changing a diameter of the pores of ultrafiltration membrane during putting on a membrane-creating additive, we accepted the following assumption – a quantity of pores on the surface during modification does not change – only the size of a pore changes.

Volumetric flow through a membrane can be written down in the form of the following differential equation

$$JC = D\frac{dc}{dy} + JC_p, \quad (1)$$

where J is the theoretical specific permeability of membrane; D is the diffusion coefficient of the dissolved substance in the solvent, due to osmotic force; C is the concentration of the dissolved substance in the near-membrane zone; C_p is the concentration of the dissolved substance, which passed through the membrane.

For the formation of a dynamic layer, we assume the concentration of the dissolved substances in the incoming flow as constant C_1=const.

Concentration of the dissolved substance in the near-membrane zone C=const.

Distribution of the filtering openings is even by the length of filtering channel and the formation of effective filtering openings takes place by the mechanism of blocking the pores.

A change in pressure by the length of channel dp/dx and a change in the concentration of the dissolved substance dc/dx allows us to assume that Ddc/dx=const.

An ideal case is when a membrane-creating additive blocks ineffective pores and does not pass through the membrane C_p=0, that is, it is intercepted by 100 %.

Accordingly, the balance of masses can be written down in the following form

$$JC = D\frac{dc}{dy}, \quad (2)$$

in this case, $C_p=C_0$, that is, concentration of the membrane-creating additive in the starting solution.

$$JC - D\frac{dc}{dy} = 0. \quad (3)$$

Using a Poiseuille equation, permeability of the membrane is determined

$$J = \frac{\varepsilon \cdot r^2 \cdot \Delta P}{8 \cdot \mu \cdot \Delta l}, \quad (4)$$

where Δl is the thickness of the effective layer of membrane; ε is the porosity of membrane.

Differential conversion of equation (4) by the function of time will allow us to determine productivity of the system at any moment of time

$$\frac{dJ}{dt}=\frac{d}{dt}\left(\frac{\varepsilon\cdot r^2\cdot\Delta P}{8\cdot\mu\cdot\Delta l}\right), \tag{5}$$

$$\frac{dJ}{dt}=\frac{d\left(r^2\right)}{dt}\frac{\varepsilon\cdot\Delta P}{8\cdot\mu\cdot\Delta l}, \tag{6}$$

$$\frac{dJ}{dt}=2\cdot r\cdot\frac{d}{dt}\frac{\varepsilon\cdot\Delta P}{8\cdot\mu\cdot\Delta l}. \tag{7}$$

With the pore mechanism of sediment formation, there occurs a decrease in the radius of a pore, therefore,

$$r=r_0-\delta\cdot t, \tag{8}$$

where δ is the speed of sediment formation in a pore.

After substituting this expression in formula (7), we obtain

$$\frac{dJ}{dt}=2\cdot\left(r_0-\delta\cdot t\right)\cdot\frac{d\left(r_0-\delta\cdot t\right)}{dt}\frac{\varepsilon\cdot\Delta P}{8\cdot\mu\cdot\Delta l}, \tag{9}$$

therefore

$$\frac{dJ}{dt}=2\cdot\left(r_0-\delta\cdot t\right)\cdot\frac{dr}{dt}\frac{\varepsilon\cdot\Delta P}{8\cdot\mu\cdot\Delta l}. \tag{10}$$

Consequent conversions allow us to obtain the following form

$$dJ=\frac{\varepsilon\cdot\Delta P}{8\cdot\mu\cdot\Delta l}\cdot\left(r_0-\delta\cdot t\right)\cdot\left(-\delta\right)dt. \tag{11}$$

When putting on a membrane-creating additive, we assume the following conditions:

– pressure gradient ΔP=const over the entire process;

– thickness of effective pore layer is constant;

– porosity does not change, that is, there is no full blocking of effective pores due to the fact that we selected a porous mechanism of the process;

– viscosity in the near-membrane zone and supplied liquid is also constant.

These assumptions and an understanding of the “sieve” mechanism of the work of ultrafiltration membranes enables us to assert that while putting on a dynamic layer for blocking “not effective” pores, the expansion of spectrum of the extracted contaminants is possible.

4. 2. Examination of the blocking of pores in flat membranes under laboratory conditions

To verify a theory of the formation of dynamic layer, we conducted tests on the flat membrane under a dead end mode.

When putting on a dynamic layer, polymeric compositions on the base of polyacrylamide are used most frequently, the compositions combining polyacrylamide and iron-containing or aluminum-containing reagent, as well as each reagent separately. However, the application of the indicated chemical substances does not solve a problem of the surface blocking due to the fouling of the surface of ultrafiltration membrane by biofilms.

To solve a problem of the biofilms formation, it is proposed to introduce biocidal additives to the dynamic layer of membrane. Imidazolines can be used ss a polymeric base or quaternary ammonium compounds as a biocidal base. They include guanidine polymeric biocides of the Akvaton-10 type. The basic acting substance of which is polyhexamethylene guanidine hydrochloride (PHMG-HC). PHMG-HC is a polymeric cation polyelectrolyte that has a wide biocidal spectrum of action to both gram-positive and gram-negative bacteria, viruses, as well as fungus. Due to its charge, it will create a surface layer. The second biocidal additive, which is used in the study, is benzalkonium chloride, which makes it possible to perform practically instantaneous decontamination of surfaces, as well as possesses prolonged action.

Requirements to the formed dynamic layer:

– prolonged character of action (not less than 5–6 days);

– universal action both to algae, fungus and to microorganisms;

– resistance to leaching;

– possibility of easy restoration of membrane to the original filtration characteristics;

– simple technique of putting on a biocidal layer, so as not to complicate the proposed procedure for the creation of a dynamic layer;

– standard biocides that are used in the technology of food production and drinking water.

A membrane has a negative charge of the surface; accordingly, the selection comes down to the polymeric biocides with the nonionogenic or preferably with the cationic properties. The selected biocides – benzalkonium chloride and polyhexamethylene guanidine – are in full agreement with the above presented requirements, they have a wide biocidal and algaecide spectrum of action.

Combination of guanidine and polyaluminium chlorine reagents makes it possible to create a dynamic layer with bactericidal properties. This is a very important property for the dynamic layer, since bacteriological films will not supposedly form at this combination. To verify this hypothesis, we designed a laboratory installation with a flat membrane (Fig. 4), through which the aqueous solution of polyguanidines, polyacrylates and aluminum polyoxychlorides was passed. When measuring, we took into account the factors that decrease accuracy of obtaining experimental data:

– a change in pressure above the surface of the filtering element;

– temperature deviation (a change by 1 °C may yield a measurement error about 3 %);

– presence in the water of petroleum products, dissolved gases and other hydrophobic particles that can block performance of membrane;

– aggressive substances that may destroy membrane and a dynamic layer;

– humic and fulvic acids with high adhesive capacity, which may lead to the formation of deposition layer at the surface of membrane.

In order to reduce influence of the deflecting factors at the formation of a dynamic layer at the surface of membrane, water is passed in advance through a hollow fiber filter with size of pores 0,02 μm. This allows us to completely exclude factors that cause the blocking of pores due to contaminants, which are contained in water, hydrophobic and colloidal particles. Thus we obtain a "clean" modified layer at the surface of membrane without additional components that contaminate water.

Thus, for the reverse osmosis there is a procedure for determining the so-called colloidal index – SDI, when flat membrane filters with the cell of 0,45 μm are used. This size of pores is selected due the fact that it characterizes transition of the particles from the truly dissolved state into the state of the suspended particles [4, 26].

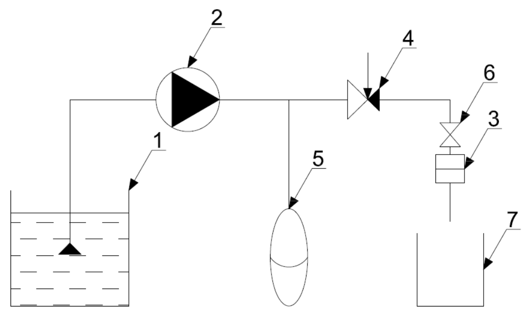

Fig. 4. Laboratory installation for the evaluation of modifying effect of different additives: 1 — reservoir for starting water; 2 — pump; 3 — holder with a flat membrane; 4 — reducer with the manometer; 5 — membrane tank; 6 — valve; 7 — measuring cylinder

The procedure of experiment consisted of the following: water after passing through the ultrafiltration membrane is poured into reservoir 1, from where, with the help of pump 2, it is fed to the system. To regulate pressure and obtain constant drop through membrane filter 3, pressure reducer 4 is set to the "after itself" mode on the line of supply, which ensures operating pressure of 10 mm H_2O, and hydraulic tank 5 to eliminate pressure fluctuation. Tap 6 is open. Water passes through membrane filter 3 and it enters beaker 7.

Each 10 minutes we register the volume of water, which passed through the membrane, which makes it possible to determine reduction in the consumption at constant pressure. The membrane is washed in 1 hour and the experiment is repeated until the 2 times reduction in efficiency relative to the initial. Quantitative measurements are performed for the confirmation of the theory about blocking the pores with the use of a bactericidal additive. For this purpose, we conduct pre-treatment only in the presence of aluminum oxychloride in the water, and then the second stage is carried out with the use of two reagents in the ratio 10:1. A quantitative assessment makes it possible to determine if an "inoculation" from guanidines is formed at the surface of the membrane. The blocking of pores in this case must occur more rapidly and more effectively, which will manifest itself by the reduction in productivity.

Water without the additives is passed for 15 minutes at constant pressure with consequent measurement of consumption – thus the initial filtering properties are determined.

A modifying solution is prepared in parallel:

1) 4 g/l of the coagulant Polvak 68 by Al_2O_3 are added;

2) polyacrylamide are introduced to the solution for reaching the concentration of 0,1 g/l (polyacrylic solutions are prepared with the use of cationic, anionic and non-ionogenic polyacrylates);

3) the solution of polyhexamethylene guanidine is prepared for reaching the concentration of 0,1 g/l.

The membrane before the passage of the solution is wetted for 24 hours to achieve the effect of swelling.

Pure water is passed first through the membrane without the membrane-creating additives. A change in consumption is registered over 30 min. This period is selected based on recommendations of manufacturers for the duration of filtration cycle between hydraulic washings of membrane. The experiment is repeated 5 times with each of the mixtures. Graph (Fig. 5) displays the averaged indicators.

This experiment demonstrated a possibility of the surface modification of the membrane with the aid of all types of mixtures.

It is possible to draw the following conclusions based on this research:

– all solutions allow the modification of the filter surface;

– the fastest modification is accomplished with the help of the mixture Polvak 68 and cationic polyacrylamide;

– the slowest modification occurs with the help of the mixture Polvak 68 and the PHMG-HC solution.

This difference in the modifying capacity is not essential. However, a surface modification with the aid of PHMG-HC will make it possible to create a polymeric antibacterial film on the surface of membrane.

Next it is necessary to determine operational parameters of the system with a dynamic membrane, as well as obtain recommendations regarding the loads and filtration cycles.

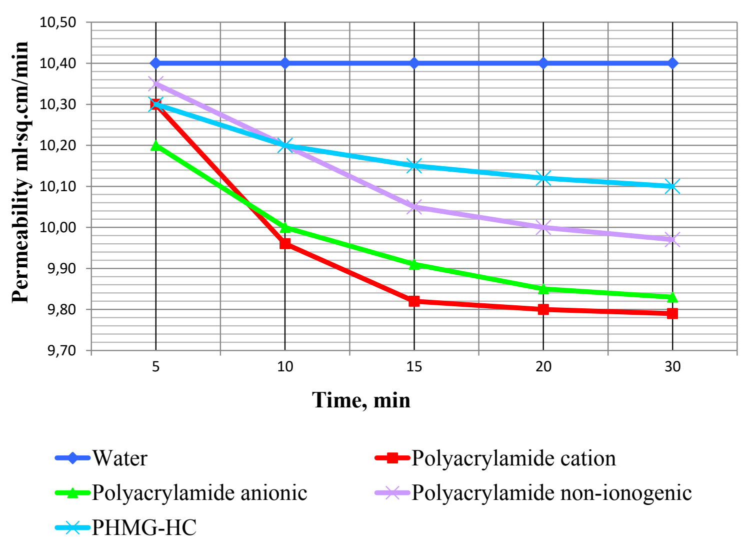

Fig. 5. Change in permeability of a flat membrane filter in the course of filtration with different additives

4. 3. Study of the operating characteristics of membranes with a bactericidal inoculation at the surface

In order to confirm theoretical studies, we designed an installation [27] with a semi-industrial membrane of PAN with the area of 5 m^2. For the initial tests, as a dynamic membrane-creating additive, we used the composition of Polvak 68 and the cationic type polyacrylamide. This composition was used due to the fact that at the stage of laboratory tests it ensured the most rapid and full result of the blocking the pores. As a result of putting on the additive, the retarding properties of membrane were changed, which made it possible to extract organic matter that specifies coloration to the indices at the level of 5–10 color degree and to decrease oxidability to less than 2 mgO_2/l. We also controlled the level of residual aluminum – its index after the treatment was less than 0,1 mg/l. These characteristics of the removal of contaminants were obtained at the starting coloration of water at 80–162 color degree and the oxidability index in the range of 8–16 mgO_2/l. Another important task of this research was to establish a possibility of water treatment in one step with the minimum preliminary cleaning by the filters with the rating of filtration 100 μm, as well as in the absence of chlorination. Such a level of extraction of contaminants makes it possible to perform chlorination for the disinfection of water without forming linked trihalomethanes. Microphotographs in Fig. 6, 7 display a change in the filtration layer before and after putting on a membrane-creating additive. As is clear from the above described facts and given results, this method proved to be effective for the water purification from the surface sources.

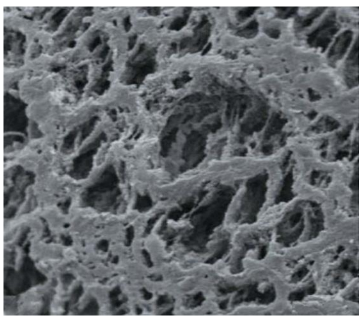

Fig. 6. Microphotograph of membrane fabric before putting on a dynamic layer (magnification ·1500)

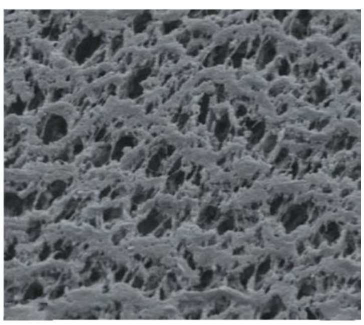

Fig. 7. Microphotograph of membrane fabric after modification (magnification ·1500)

However, it was established that in the absence of water pre-treatment with chlorination, at the surface of membrane a layer of the deposits of biological origin is actively developed. This can be explained by the fact that the extracted substances are either the biomass by themselves or they are nutrient medium, which is illustrated in Fig. 2.

To conducting the research, we used a semi-industrial installation, which was designed to test the method of the modification of membranes in the process of water purification. In the experiment, we used three membrane modules operating in parallel, each of which has active area of 5 m^2. The modification of two modules is performed according to a standard technique of treatment using aluminum oxychloride. The third membrane is treated with the help of aluminum oxychloride and a mixture of biocides. The changes, connected with the introduction of biocides, were made in the procedure of putting on a dynamic layer. Biocide, in contrast to the basic forming additive, was fed impulsively each 5 minutes. This makes it possible to form a layered piling of biocide due to the fact that the applied polymers have a charge. Biocide was fed into the system using a pump-dispenser. Biocides are introduced in the ratio 10:1:0,33 (aluminum polyoxychloride: PHMG-HC: benzalkonium chloride), all ratios are given by the acting substance.

5. Results of research into a change in the operating characteristics of dynamic ultrafiltration membrane with a biocidal inoculation and without it

Three modules are set to work in parallel. Duration of testing is seven days. Water from the river Dnepr is supplied to the modules. The first module undergoes a hydraulic washing only. The second module undergoes a hydraulic washing and washing with the help of sodium hypochlorite two times in a 24 hour period. The third module, exposed to additional modification, similar to the first one, is washed by hydraulic method. Hydraulic washings are performed each 30 minutes. Pressure before the membrane module is set at 0,1 MPa. Consumption is registered using rotameters. Filtration is conducted under a dead end mode. Average daily consumption for each type of modification and washing is calculated based on the obtained data. Obtained data are represented in the graph (Fig. 8).

The membrane, modified without a biocidal additive and not exposed to periodic washing with the help of sodium hypochlorite, demonstrated the worst result due to the biofouling. Biofouling starts to exert effect on the filtration capacity already in the first 24 hours of work. Subsequently, the graph illustrates a gradual loss of efficiency. At the third day, avalanche-like fall begins, due to the formation of biofilms, which is correlated with the research [28].

The membrane with a dynamic layer and periodic treatment by sodium hypochlorite of the dose in 20 mg/l by active chlorine demonstrated stable performance. In the first hours after the washing by hypochlorite, an increase in the productivity occurred, supposedly because of the elimination of the oxidizable organic matter from the surface of membrane.

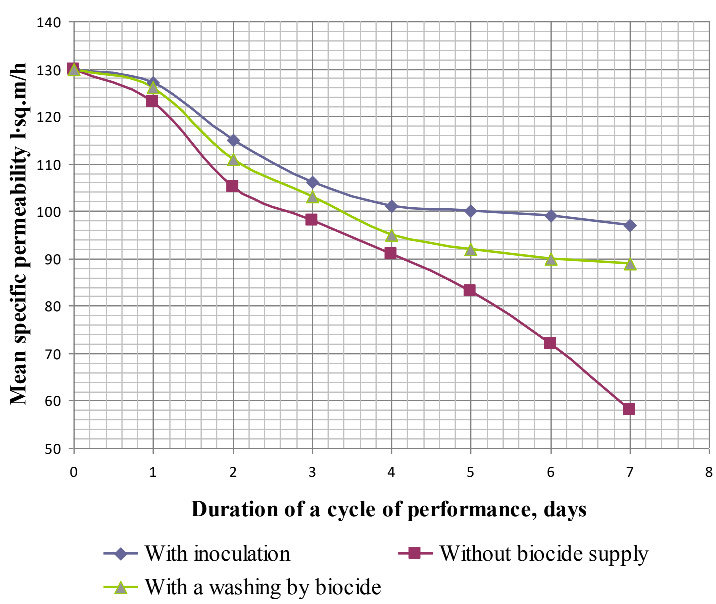

Fig. 8. Change in the permeability of membranes treated by different methods under the action of detained contaminants

The membrane with the modified dynamic layer and bactericidal inoculation demonstrated the most stable performance and a lower reduction in efficiency.

6. Discussion of results of research into the properties of ultrafiltration membranes with a dynamic layer and bactericidal inoculation for the purification of natural waters

Using a Poiseuille equation, we demonstrated a possibility of blocking the pores that have large size compared to the extracted contaminants. This theory is based on the "sieve" mechanism for the process of water purification and the possibility of blocking non-effective pores. This allowed us to predict a possibility of their blocking during the gel formation on the surface by forming a dynamic layer both inside the pores and on the surface of membrane.

The data received as a result of experiment demonstrated a possibility of applying this technology in the process of water purification. However, the development of biofilms at the surface of membrane proved to be one of the limitations. Biofilms caused the reduction in the filtration capacity. In order to reduce the influence of biofilms, we introduced biocidal inoculations to the membrane-creating layer. These inoculations allowed us to obtain a membrane with stable filtration properties and to decrease the influence of biomass on the process of membranes contamination, which is evidenced by the conducted experiment.

A shortcoming of this method is the fact that in comparison with the membranes without a dynamic layer, initial productivity of the modified membranes is reduced by 10–15 % or requires an increase in the operating pressure by 12 %.

The obtained technique makes it possible to adapt the finished membrane elements to specific operating conditions. Creating a dynamic layer with a biocidal inoculation will enable an increase in efficiency of the purification of water from the surface sources of water supply.

Membrane devices with a modified surface can be applied for single-stage purification instead of the standard technologies employed at the pumping-filtration stations in Ukraine.

7. Conclusions

The given studies allowed us to substantiate and estimate a possibility of the membrane surface modification in the process of purification of natural waters:

1. A mathematical substantiation of the membrane surface modification using the filtration equation of Poiseuille and mass transfer is proposed. This model enables the estimation of membranes performance efficiency when the pores are blocked.

2. The developed technique of the membrane surface modification made it possible to qualitatively estimate the possibility of conducting semi-industrial tests and to select modifying additives and bacteriological inoculations. Using as a modifying mixture the coagulant Polvak 68 and the PHMG-HC solution enables the creation of a polymeric antibacterial film at the surface of ultrafiltration membrane.

3. We carried out semi-industrial tests, in the process of which it was determined that the modified bactericidal layer improves operating characteristics of membranes. A general productivity of membrane increases. Duration of the filtration cycle when putting on a modifying layer is not less than seven days.

Results of the conducted studies may be applied for the design and operation of facilities for the preparation of water with different quality.

References

1. Lahoussine-Turcaud, V. Coagulation pretreatment for ultrafiltration of a surface water [Text] / V. Lahoussine-Turcaud, M. R. Wiesner, J.-Y. Bottero et. al. // Reaserch and Technology. American Water Works Association, 1990. – P. 82–87.
2. Alpatova, A. L. Ultrafiltratsionnaya ochistka prirodnyih vod ot guminovyih veschestv i tyazhelyih metallov [Text] / A. L. Alpatova. – Kyiv, 2001. – 137 p.
3. Zapol'skyy, A. K. Fizyko-khimichni osnovy ochyshchennya stichnykh vod [Text] / A. K. Zapol'skyy, N. A. Mishkova-Klymenko, I. M. Astrelin, M. T. Bryk, P. I. Hvozdyak, T. V. Knyaz'kovi; A. K. Zapol'skohyy (Ed.). – Kyiv: Libra, 2000. – 552 p.
4. Svittsov, A. A. Vvedenie v membrannuyu tehnologiyu [Text] / A. A. Svittsov. – Moscow: DeLi print, 2007. – 208 p.
5. Dyitnerskiy, Yu. I. Membrannyie protsessyi razdeleniya zhidkih smesey [Text] / Yu. I. Dyitnerskiy. – Moscow: Himiya, 1975. – 232 p.
6. Mulder, M. Vvedenie v membrannuyu tehnologiyu [Text] / M. Mulder; Yu. P. Yampolskyy (Ed.). – Moscow: Mir, 1999. – 513 p.
7. Flemming, H.-C. Biofouling – the Achille's heel of membrane processes [Text] / H.-C. Flemming, T. Griebe, G. Schaule at al. // Desalination. – 1997. – Vol. 113, Issue 2-3. – P. 215–225. doi: 10.1016/s0011-9164(97)00132-x
8. Sim, S. T. V. Monitoring membrane biofouling via ultrasonic time-domain reflectometry enhanced by silica dosing [Text] / S. T. V. Sim, S. R. Suwarno, T. H. Chong , W. B. Krantz, A. G. Fane // Journal of Membrane Science. – 2013. – Vol. 428. – P. 24–37. doi: 10.1016/j.memsci.2012.10.032
9. Dong, L. Fabrication and anti-biofouling properties of alumina and zeolite nanoparticle embedded ultrafiltration membranes [Text] / L. Dong, H. Yang, S. Liu, X. Wang, Y. F. Xie // Desalination. – 2015. – Vol. 365. – P. 70–78. doi: 10.1016/j.desal.2015.02.023
10. Bucs, S. S. Biofouling in forward osmosis systems: An experimental and numerical study [Text] / S. S. Bucs, R. Valladares Linares, J. S. Vrouwenvelder, C. Picioreanu // Water Research. – 2016. – Vol. 106. – P. 86–97. doi: 10.1016/j.watres.2016.09.031
11. Huang, S. Investigation of environmental influences on membrane biofouling in a Southern California desalination pilot plant [Text] / S. Huang, N. Voutchkov, S. C. Jiang // Desalination. – 2013. – Vol. 319. – P. 1–9. doi: 10.1016/j.desal.2013.03.016
12. Vrouwenvelder, J. S. Diagnosis of fouling problems of NF and RO membrane installations by a quick scan [Text] / J. S. Vrouwenvelder, D. Van der Kooij // Desalination. – 2002. – Vol. 153, Issue 1-3. – P. 121–124. doi: 10.1016/s0011-9164(02)01111-6

13. Kramer, J. F. The solution to reverse osmosis biofouling. In Proceedings of IDA World Congress on Desalination and Water Use [Text] / J. F. Kramer, D. A. Tracey. – Abu Dhabi, Saudi Arabia, 1995. – P. 33–44.
14. Abd El Aleem, F. A. Biofouling problems in membrane processes for water desalination and reuse in Saudi Arabia [Text] / F. A. Abd El Aleem, K. A. Al-Sugair, M. I. Alahmad // International Biodeterioration & Biodegradation. – 1998. – Vol. 41, Issue 1. – P. 19–23. doi: 10.1016/s0964-8305(98)80004-8
15. Ridgway, H. F. Microbial adhesion and biofouling of reverse osmosis membranes [Text] / H. F. Ridgway; B. S. Parekh (Ed.). – In Reverse Osmosis Technology: Application for High Pure Water Production; Marcel Dekker, 1988. – P. 429–481.
16. Shinenkova, N. A. Primenenie mikroultrafiltracii dlja ochistki vod poverhnostnyh istochnikov [Text] / N. A. Shinenkova, A. A. Povorov, L. V. Erohina // Seriya critical technologies. Membranes. – 2005. – Vol. 28, Issue 4. – P. 21–25.
17. Pervov, A. G. Vliyanie biologicheskogo zagryazneniya na rabotu obratnoosmoticheskih i ultrafiltratsionnyih membrannyih elementov [Text] / A. G. Pervov, A. P. Andrianov, E. A. Telitchenko // Seriya critical technologies. Membranes. – 2004. – Vol. 1, Issue 21. – P. 3–17.
18. Zhang, J. Fabrication of poly (ether sulfone) / poly (zinc acrylate) ultrafiltration membrane with anti-biofouling properties [Text] / J. Zhang, M. Zhang, K. Zhang // Journal of Membrane Science. – 2014. – Vol. 460. – P. 18–24. doi: 10.1016/j.memsci.2014.02.030
19. Li, J. Anti-bacterial properties of ultrafiltration membrane modified by graphene oxide with nano-silver particles [Text] / J. Li, X. Liu, J. Lu, Y. Wang, G. Li, F. Zhao // Journal of Colloid and Interface Science. – 2016. – Vol. 484. – P. 107–115. doi: 10.1016/j.jcis.2016.08.063
20. Chen, Y. Biofouling control of halloysite nanotubes-decorated polyethersulfone ultrafiltration membrane modified with chitosan-silver nanoparticles [Text] / Y. Chen, Y. Zhang, H. Zhang, J. Liu, C. Song // Chemical Engineering Journal. – 2013. – Vol. 228. – P. 12–20. doi: 10.1016/j.cej.2013.05.015
21. Ilina, T. S. Bioplenki kak sposob suschestvovaniya bakteriy v okruzhayuschey srede i organizme hozyaina: fenomen, geneticheskiy kontrol i sistemyi regulirovaniya ih razvitiya [Text] / T. S. Ilina, Yu. M. Romanova, A. L. Gintsburg // Genetika. – 2004. – Vol. 40, Issue 11. – P. 1445–1456.
22. Smirnova, T. A. Strukturno-funktsionalnaya harakteristika bakterialnyih bioplenok [Text] / T. A. Smirnova // Mikrobiologiya. – 2010. – Vol. 79, Issue 4. – P. 435–446.
23. Kulishov, S. A. Mikrobnyie bioplenki kak ob'ekt izucheniya v nauchno-issledovatelskoy rabote uchaschihsya [Text] / S. A. Kulishov, I. N. Lyikov // Molodoy uchenyiy. – 2016. – Vol. 4. – P. 240–245.
24. Rojas-Serrano, F. Comparative study of in-line coagulation and/or ozonization pre-treatment for drinking-water production with spiral-wound ultrafiltration membranes [Text] / F. Rojas-Serrano, J. I. Pérez, M. Á. Gómez // Chemical Engineering and Processing: Process Intensification. – 2016. – Vol. 105. – P. 21–29. doi: 10.1016/j.cep.2016.04.004
25. Nechitaylo, N. P. Chislennoe modelirovanie zakuporki poryi ultrafiltratsionnoy membranyi pri ee modifikatsii [Text] / N. P. Nechitaylo, N. N. Belyaev // Problemy vodosnabzheniya, vodootvedeniya i gidravliki. – 2015. – Vol. 25, Issue 324. – P. 169–175.
26. Dytnerskij, Y. I. Obratnyj osmos i ultrafiltracija [Text] / Y. I. Dytnerskij. – Moscow: Himia, 1978. – 351 p.
27. Nechitaylo, N. P. Nauchnoe obosnovanie obrazovaniya dinamicheskogo sloya na poverhnosti ultrafiltratsionnoy membranyi dlya ochistki prirodnyih vod s ispolzovaniem reagentov [Text] / N. P. Nechitaylo // Scientia, Tehnika. – 2016. – Vol. 2, Issue 2. – P. 26–28.
28. Pervov, A. G. Ultrafiltracija -tehnologija budushhego [Text] / A. G. Pervov, N. B. Motovilova, A. P. Andrianov // Vodosnabzhenie i sanitarnaya tehnika. – 2001. – Vol. 9. – P. 9–12.