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Purification of water from heavy metal ions by a dynamic membrane with a surface layer of cellulose acetate

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Purification of water from heavy metal ions by a dynamic membrane with a surface layer of cellulose acetate

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Abstract. To reduce the concentration of heavy metal ions in drinking, natural and wastewater to the established standards, a dynamic membrane with a surface layer of cellulose acetate particles on a nylon substrate was obtained. A dynamic membrane layer was formed from cellulose acetate particles with sizes from 42 to 130 nm. The cellulose acetate content was 14 % by weight, upon receipt from a 10 % solution of cellulose acetate in acetone. After applying a layer of cellulose acetate to the surface of a nylon substrate, a decrease in the specific productivity of the membranes is observed more than 10 times due to the formation of a dynamic layer on the surface and in the pores of the substrate. During the operation of the membrane for 1 hour, there is a decrease in the specific productivity of the membrane by 1.5 times and an increase in the working pressure from 0.35 to 0.41 MPa by 1.2 times. A high selectivity of the dynamic nylon-ACd membrane with respect to iron ions 96%, copper 93% and chromium 93% was established with a specific productivity of 300 $dm^3/m^2 \cdot h$ and a pressure of 0.4 MPa. After purification of tap water with a dynamic membrane, the concentration of heavy metal ions does not exceed the MPC for water bodies for drinking water.

1. Introduction
Heavy metal ions have a negative effect on all living organisms, especially hydrobionts. So the maximum permissible concentration (MPC) of heavy metal ions for fishery waters is an order of magnitude lower than for drinking water and centralized water supply. The negative effects of heavy metal ions are based on their bioaccumulation and high toxicity. The main sources of heavy metal ions for natural waters are metal processing, galvanic, foundry, mining and chemical industries. Also often in centralized water supply systems, the concentration of heavy metal ions, especially iron, manganese, are at a high level.

For the purification of waters from heavy metal ions, precipitation, adsorption, ion exchange, distillation, and membrane methods are often used. The use of membranes in various fields of industry is part of the scientific and technological progress of modern production, and occupy a leading position in the national programs of developed countries. The distinctive properties of membrane processes for the separation of water mixtures are the simplicity of the hardware device, high efficiency, reliability, low energy consumption, minimization of mass characteristics, ergonomics. Of the membrane methods, they are most effective in the removal of heavy metal ions: reverse osmosis, ion-exchange membranes, nanofiltration, primation.

Polymeric membranes are widely used in wastewater treatment and in water treatment processes, however, they have several disadvantages: low permeability, low resistance in alkaline and acidic environments, insufficient mechanical strength, gradual and irreversible loss of ion selectivity during operation, reduced productivity due to phenomena of concentration polarization [1, 2]. Therefore, to improve the basic parameters of membranes, such as specific productivity, strength and retention ability, they modify the membranes by treatment with physical and chemical methods or obtain composite membranes consisting of several layers with certain properties. Among composite membranes dynamic membranes stand out. The advantage of such membranes lies in the possibility of replacing the contaminated dynamic layer with a new layer. Also, using particles of different dimensions, functional materials or several dynamic layers as a dynamic layer, it becomes possible to obtain different types of membranes: ultrafiltration, nanofiltration, and ion exchange.

2. Methods

This paper describes a method for producing and characterizing a dynamic nylon-cellulose acetate membrane "nylon-ACd" with a surface layer of cellulose acetate for water treatment and water treatment.

A microfiltration polymer membrane made of nylon with an average pore size of 0.45 μm was used as the initial substrate, on the surface of which a new layer of cellulose acetate was applied. The dynamic membrane layer was formed during the filtration process from the cellulose acetate particles present in the filtered suspension with particle sizes from 42 to 130 nm. To obtain a dynamic layer on a substrate with a diameter of 47 mm, a suspension of 15 cm^3 was consumed, which was obtained from a 0.5 % solution of cellulose acetate and distilled water. After that, the membrane was dried at a temperature of 30 °C in a thermostat for 1 hour. The mass content of cellulose acetate in the membrane was determined by the gravimetric method using an analytical balance.

The particle size of the dispersed phase of the suspension of cellulose acetate was determined by dynamic light scattering (DLS), and the ζ potential of the particles of the dispersed phase was determined by the PALS method. The phase shift of the scattered light was detected in the method using an Nano Brook Omni analyzer. A graph of the particle size distribution of 0.5 % and 5 % suspension of cellulose acetate in an aqueous solution of acetone is presented in figure 1.

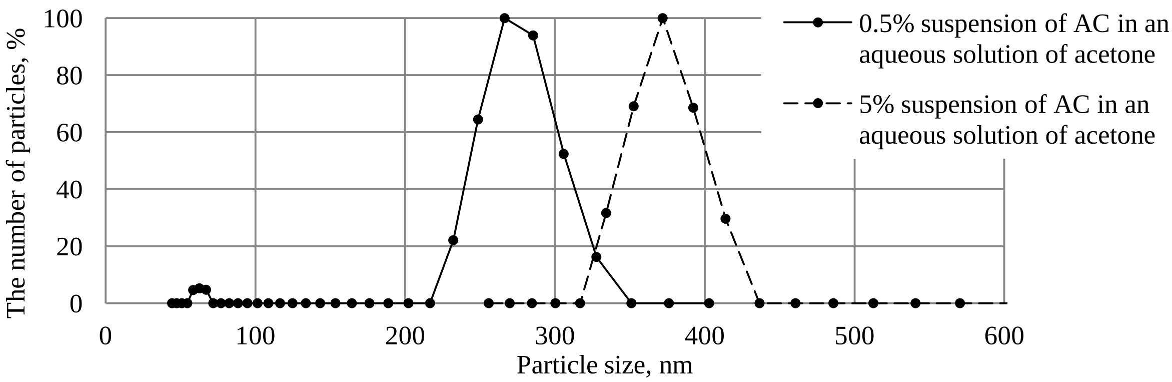

Figure 1. A graph of the particle size distribution of the dispersed phase of a suspension of cellulose acetate in an aqueous solution of acetone.

As the main indicators of the membrane separation process, we considered the specific productivity and selectivity of membranes with respect to heavy metal ions, which was calculated as the concentration of heavy metal ions in water before and after membrane separation.

In the process of membrane separation, a working pressure of 0.35 MPa was applied, the temperature of the liquid was 25 ° C.

For membrane separation, tap water with a specific electrical conductivity of 350 μS/cm and a gross iron concentration of 2.02 mg/dm^3 was used.

The concentration of the studied metal ions in the initial solution and the filtrate was measured by atomic absorption spectrometry (AAS) with electrothermal atomization “Quantum Z. ETA”. The spectrometer measures the concentration of chemical elements, the analytical resonance spectral lines of which lie in the spectral range of the device (190 - 850 nm), by atomic absorption analysis using electrothermal atomization.

3. Results and discussions

According to figure 1, the particle sizes of the dispersed phase of a 0.5% suspension of cellulose acetate are distributed in the range from 42 to 130 nm, and at a higher concentration of cellulose acetate, aggregation of particles is observed, particle sizes increase more than 3 times and range from 334 to 437 nm.

The results of the content of cellulose acetate in the surface layer of the membrane after applying a dynamic layer of particles, established by the gravimetric method, are presented in table 1.

Table 1. The mass content of cellulose acetate in a dynamic membrane.

Membrane	Initial Mass membranes, g	Cellulose acetate content, g	Cellulose acetate content,% (by weight)
nylon-ACd	0.0911	0.0132	14.4

As a result of applying particles of cellulose acetate particles dynamically from a 0.5% suspension onto a nylon substrate, dynamic nylon-ACd membranes with a cellulose acetate content of 14.4 % (mass) were obtained.

Next, we studied the parameters of the membrane separation process, one of the main of which is the specific productivity of the membranes.

The results of studies of the specific productivity of the membranes are presented in table. 2.

Table 2. Specific performance of dynamic membranes.

Membrane	The content of the modifying substance,% (by weight)	Specific capacity of membranes, dm^3/m^2 · h	
		for distilled water	by tap water
nylon	-	5026	4567
nylon-ACd	cellulose acetate-14.4	430	423
nylon-PS [3]	polystyrene -15.4	309	262

After applying a layer of cellulose acetate to the surface of a nylon substrate, a decrease in the specific productivity of the membranes is observed more than 10 times due to the formation of a dynamic layer on the surface and in the pores of the substrate. In the process of filtering tap water, the specific productivity of the original and modified membranes decreases. To compare the characteristics of the obtained membrane, data on the performance of a dynamic membrane with a surface layer of polystyrene (nylon-PS) are presented.

Table 3 and figure 2 show the process parameters of membrane filtration of tap water with a dynamic nylon-ACd membrane.

Table 3. Parameters of the process of membrane filtration of tap water with a dynamic membrane nylon-ACd.

№	Filtration time, sec.	Specific capacity of membranes, dm^3/m^2 · h	Electrical conductivity, μS / cm	Pressure, MPa

1	0	-	350	-
2	107	423	285	0.35
3	240	340	283	0.37
4	540	302	283	0.38
5	770	295	282	0.39
6	1080	292	281	0.39
7	1760	290	281	0.40
8	3600	287	280	0.41

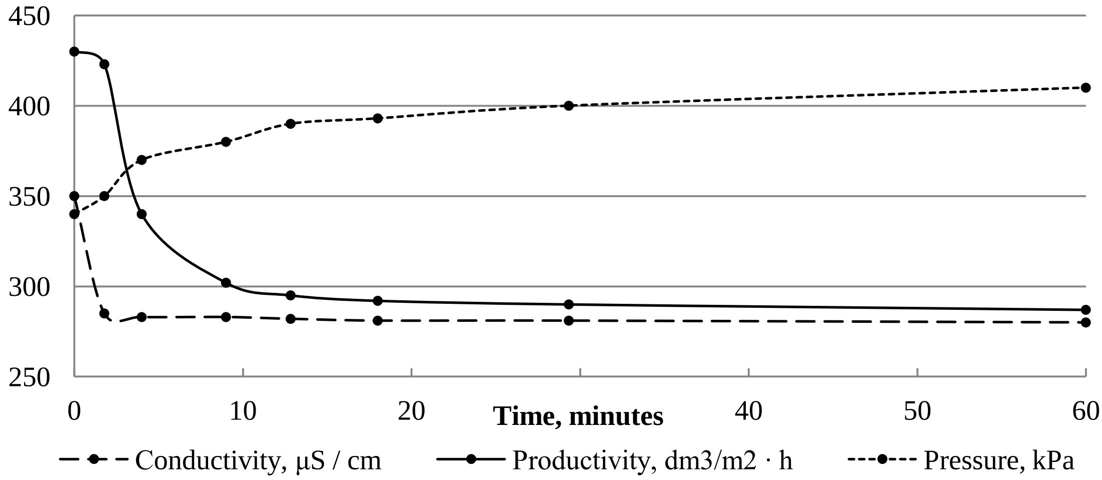

Figure 2. Parameters of a filtration process with a dynamic nylon-ACd membrane.

During the operation of the membrane for 1 hour, there is a decrease in the specific productivity of the membrane by 1.5 times and an increase in the working pressure from 0.35 to 0.41 MPa by 1.2 times. According to the graphs presented in figure 2, it can be seen that the specific productivity of the membrane decreases intensively during the first 10 minutes from 423 to 302 dm^3/m^2 1.4 h by 1.4 times, which is associated with the phenomenon of concentration polarization, which subsequently leads to the formation of a gel membrane over the surface layer and sedimentation. For the rest of the membrane separation process, the productivity is stabilized, during the 50 minutes of filtration there is a slight decrease in specific productivity by only 2.8 %. The working pressure of the membrane filtration process increases rapidly for the first 12 minutes by 11 % and subsequently increases by 5 % within 48 minutes. The electrical conductivity of the solution gradually decreases over the entire period of the membrane filtration process.

The selectivity of the dynamic membrane was evaluated by the removal of heavy metal ions from tap water.

Table 4. The selectivity of the dynamic membrane of nylon-ACD for heavy metal ions.

Index	Concentration of heavy metal ions mg/dm^3		Selectivity, %	Standard *, mg/dm^3	Standard **, mg/dm^3
	Original	Permeate			
Iron	2.0	0.084	95.8	0.3	0.1
Copper	0.21	0.015	92.8	0.1	0.001
Manganese	0.038	0.009	76.3	0.1	0.01
Chromium	0.027	0.002	92.6	0.5	0.02

* GN 2.1.5.689-98 Maximum Permissible Concentrations (MPC) of chemicals in the water of water bodies of domestic, drinking, and cultural and domestic water use;

** Water quality standards for fishery water bodies (approved by order of the Federal Agency for Fisheries of January 18, 2010 No. 20)

The selectivity of the dynamic membrane of nylon-ACd is high with respect to ions of iron, copper and chromium. On average, the retention capacity for heavy metal ions is 80 %. The concentration of iron and copper ions in the initial solution exceeds the maximum permissible concentration (MPC) of chemicals in the water of water bodies for drinking and water use, and when compared with water quality standards for water bodies of fishery importance, excesses were found for all certain metal ion concentrations. After water treatment, the concentration of heavy metal ions does not exceed the maximum permissible concentration for water bodies for drinking water, and there are excesses in the content of copper ions for water quality standards for water bodies of fishery value.

4. Conclusion

To purify water from heavy metal ions, a dynamic membrane with a surface layer of cellulose acetate with particle sizes from 42 to 130 nm was obtained. The specific productivity of a dynamic membrane for distilled and tap water is determined. The parameters of the process of membrane filtration of tap water depending on the filtration time are established. High selectivity of the dynamic membrane of nylon-ACd with respect to ions of iron, copper, chromium, more than 92 % was revealed. The concentration of heavy metal ions after purification does not exceed the maximum permissible concentration of chemicals in the water of water bodies for drinking water. It is recommended to use the membrane in the processes of water treatment and water purification from heavy metal ions.

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References

[1] Fazullin D D, Mavrin G V, Shaikhiev I G, Nizameev I R 2018 *Petroleum Chemistry* **58** 145- 51
[2] Chunxia Li et all 2019 *Desalination and water treatment* **130** 44-53
[3] Fazullin D D, Mavrin G V, Shaikhiev I G 2019 *Innovative approaches to solving modern problems of rational use of natural resources and environmental protection: collection of articles. doc. Int. scientific and technical conf. (Alushta)* Part 1 (Belgorod: Publishing House of BSTU) pp 330-6