Obtaining and properties of a composite membrane with a surface layer of cellulose acetate

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Annotation. To reduce the concentration of dissolved salts in water treatment processes, a composite nanofiltration membrane with a surface layer of cellulose acetate on a polytetrafluoroethylene substrate was obtained. The cellulose acetate content was 17.6% by weight, upon receipt from a 10% solution of cellulose acetate in acetone. An increase in the membrane moisture capacity after modification from 0.6% to 68.5% was established, which is associated with an increase in the hydrophilicity of the membrane. The contact angle of the membrane with a drop of distilled water as a result of the deposition of cellulose acetate particles on the surface of the original membrane decreased from 130° to 53.8°. According to the results of scanning electron microscopy, it was found that the cellulose acetate particles are not located on the surface of the polytetrafluoroethylene substrate, but in the depth of its structure — in the pores, between the fibers, as a result, open pores overlap. After applying a layer of cellulose acetate to the surface of the membrane, the specific productivity of the membrane decreases by 10 times due to the accumulation of particles of cellulose acetate in the pores of the membrane. The maximum specific productivity of the modified membrane 412 dm³/m² h, is observed when passing distilled water. The retention capacity of the membrane in terms of total salinity in the separation of tap water with an initial salinity of 323 mg/dm³ was 75%.

1. Introduction

The use of membranes from the point of view of separation of water mixtures of various origin and composition is in daily demand and is widely used in industries such as chemical, petrochemical, food, electronic, gas, pharmaceutical, microbiological, nuclear, agriculture, medicine, water treatment for various purposes and others [1,2]. The use of membranes in various fields of industry is part of the scientific and technological progress of modern production. Membrane methods occupy a leading position in the national programs of developed countries [3].

Polytetrafluoroethylene, cellulose acetate, nylon-66, polyethersulfone, polyamide, polyethylene terephthalate, polysulfone, polyamline are used as materials for producing polymer membranes. These materials are characterized by different strength characteristics, resistance to aggressive environments and surface properties. Polymeric membranes are widely used in wastewater treatment, 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. Therefore, to improve the basic parameters of membranes, such as specific productivity, strength and retention ability, they modify membranes by treatment with physical and chemical methods or obtain composite membranes [4], consisting of several layers with certain required properties.
Physical methods for modifying membranes include, in particular, treatment with ultrasound, plasma, microwave radiation, thermal, radiation treatment in various media [5-8]. As a result of these processes, the specific productivity increases, the roughness and wettability of the surface layer of the membrane change. For example, in [9], polyethersulfone membranes were modified by plasma in argon with subsequent grafting of polyacrylic acid in the vapor phase. As a result of processing, the membrane becomes hydrophilic, modified membranes are less susceptible to fouling of the surface and pores than unmodified membranes, and the specific productivity of the membranes also increases. In addition, modified membranes are easier to regenerate.

To achieve high permeability and delaying ability of the reverse osmosis membrane, the authors of [10] achieved through the use of additives in the process of membrane polymerization. The membrane was obtained from cellulose acetate, using N-methylpyrrolidone and acetone as solvents, tetrahydrofuran was added as a pore-forming agent. The result is a cellulose acetate membrane with a dense surface layer on the surface and a porous support layer in the middle. The membrane showed high specific permeability and retention compared to the commercial reverse osmosis membrane of Hydration Technologies Inc.

In the next work [11], the authors obtained and studied the physicochemical properties of thin-film composite membranes consisting of a substrate and a surface layer. As the surface layer, polymeric materials from polyamide, cellulose acetate, polyacrylonitrile and polyetherimide were used, which were deposited on a polypethersulfone substrate by means of interfacial polymerization. The obtained membranes, the authors studied the contact angles of wetting, the degree of swelling, mechanical strength. The authors also obtained data from scanning electron microscopy of the surface layer of composite membranes. The obtained thin-film composite membranes were tested by the authors during the pervaporation of metal hydroxide solutions and showed high efficiency compared to existing membranes of this type.

Cellulose acetate is an inexpensive and readily available material widely used in direct osmosis membranes. However, the effectiveness of pure cellulose acetate membranes is not high enough to separate salt solutions. In [12], the authors described a method for producing highly effective composite membranes for reverse osmosis consisting of cellulose acetate modified with polyvinyl alcohol and polydopamine. To obtain a membrane, polyvinyl alcohol was first crosslinked from the cellulose acetate membrane, then polydopamine was deposited on the surface. The modified membrane showed an increase in hydrophilicity, high retention ability and specific productivity for NaCl solution.

2. Methods

This paper describes the method of obtaining and the results of a study of the surface properties of composite polytetrafluoroethylene-cellulose acetate membranes (PTFE-AC)

A microfiltration polymer membrane of PTFE 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. To obtain a composite layer, a 10% solution of cellulose acetate in acetone was used. The surface layer was obtained by forming on the surface of the porous base a semipermeable layer of dissolved cellulose acetate present in the acetone aerosol. After that, the membrane was dried at a temperature of 28°C in a thermostat for 1 h, while the acetone evaporated, and the cellulose acetate layer remained on the surface of the substrate. The mass content of cellulose acetate in the membrane was determined by the gravimetric method using an analytical balance.

The moisture content of the membranes was determined by the gravimetric method, by wetting the membranes with distilled water and determining the moisture using an “A & MD” moisture analyzer.

The particle size of the dispersed phase of emulsions and suspensions was determined by dynamic light scattering (DLS), and the ζ potential of the particles of the dispersed phase was determined by the PALS method, and the phase shift of the scattered light was detected using a “Nano Brook Omni” analyzer. The particle sizes of the dispersed phase of cellulose acetate in a 10 % acetone solution are distributed in the range from 499 to 5761 nm, the value of the ζ potential is –0.9 mV.
The change in the surface structure of the membranes was recorded using a scanning electron microscope LEO-1430 VP (Carl Zeiss). Samples were glued onto aluminum plates, the surface of the membranes was sprayed with gold, by cathodic deposition in argon, and viewed in high vacuum.

The contact angle of the surface with distilled water before and after applying a layer of cellulose acetate was also determined at the membranes using the dropping method using a “Kruss DSA 20E” analyzer.

As the main indicators of the membrane separation process, we considered the specific productivity and retention capacity of the membranes in terms of total mineralization, which was calculated as the ratio of the total mineralization of water before and after membrane separation. In the process of membrane separation, a working pressure of 0.2 MPa was applied, the temperature of the liquid was 23°C. For membrane separation, tap water with a total salinity of 323 mg/dm³ was used.

3. Results and discussion

After applying cellulose acetate from a 10% solution in acetone to the substrate of a microfiltration polymer membrane made of PTFE, PTFE-AC composite membranes were obtained with cellulose acetate contents from 17.6 wt.%, the results are presented in Table 1.

| Membrane   | The initial mass of the membrane, g | The content of cellulose acetate, g | The content of cellulose acetate, wt.% |
|------------|------------------------------------|-----------------------------------|-------------------------------------|
| PTFE-AC    | 0.0893                              | 0.0157                            | 17.6                                |

As a result of the modification, the membrane mass increased by 17.6%. Next, we studied the change in the moisture capacity of the membranes as a result of applying a surface layer of cellulose acetate, the results are presented in Table 2.

| Membrane   | The content of cellulose acetate, wt.% | Moisture content, % |
|------------|---------------------------------------|---------------------|
| PTFE       | —                                     | 0.9                 |
| PTFE-AC    | 17.6                                  | 68.5                |

The moisture capacity of the initial PTFE membrane is low less than 1%, after applying a layer of cellulose acetate, an increase in moisture capacity of up to 69% is observed. Also, after applying a layer of cellulose acetate, the hydrophilicity of the composite membrane increases. This is confirmed by the results of measuring the contact angle of a drop of distilled water on the surface of the original and modified membranes. So, the contact angle of the surface of the initial PTFE membrane with distilled water is 130.3°, and the modified PTFE-AC membrane is 53.8°, which indicates an increase in the hydrophilicity of the composite membrane.

The results of the study of the membrane surface by scanning electron microscopy with a magnification of 7000 times are presented in figure 1.
Figure 1. Microphotographs of the membrane surface: a — initial PTFE membrane; b — a composite membrane of PTFE-AC with a surface layer of cellulose acetate (an increase of 7000 times).

Figure 1a shows the initial PTFE membrane, which consists of particles in the form of spheres interconnected by fibers, on the surface onto which particles of cellulose acetate are applied, which are present in the acetone aerosol. Figure 1b shows that the cellulose acetate particles are not located on the surface of the PTFE substrate, but in the depth of its structure — in the pores, between the fibers of PTFE, resulting in overlapping of open pores. After modifying the membranes, 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 3.

| Membrane  | The content of cellulose acetate, wt.% | Specific capacity of membranes, dm$^3$/m$^2$ h by tap water |
|-----------|--------------------------------------|---------------------------------------------------------|
| PTFE      | —                                    | 4936                                                   |
| PTFE-AC   | 17.6                                 | 412                                                    |

After applying a layer of cellulose acetate to the surface of a PTFE substrate, the specific productivity of the membranes decreases by a factor of 10 due to the intensive accumulation of particles of cellulose acetate in the pores of the membrane. The maximum performance of the original and modified membranes is observed when passing distilled water.

The retention capacity of the modified membranes was evaluated by the salinity of the original tap water and its permeate. The results are presented in Table 4.

| Membrane  | The content of cellulose acetate, wt.% | Total salinity, mg/dm$^3$ | Retention capacity, % |
|-----------|--------------------------------------|---------------------------|-----------------------|
| PTFE      | —                                    | 323±32                    | 1.5                   |
| PTFE-AC   | 17.6                                 | 318±32                    | 75.0                  |

According to Table 4, the total salinity of tap water is 323 mg/dm$^3$. After the separation of tap water through the initial membrane of PTFE, the mineralization decreases within the error of the measurement procedure. And after filtering the water through the composite membranes of PTFE-AC, in the permeate a decrease in total mineralization by 4 times is observed, the retarding ability of the modified membrane was 75%. The retention capacity of commercial nanofiltration membranes in
terms of total mineralization is on average 85-90%, for example, the retention capacity of the “EMO-N-350” membrane is 85%, and that of the “NF90-4040” membrane is 87.7-93.5% [13]. The retention capacity of the resulting membrane is slightly lower than that of commercial membranes, but at the same time, a lower pressure of 0.2 MPa is applied when filtering with a PTFE-AC membrane, and 0.6 MPa when filtering with an “EMO-N-350” membrane, with a membrane brand “NF90-4040” a pressure of 2 MPa was applied [13].

4. Conclusion
The composite nanofiltration membrane with a surface layer of PTFE-AC cellulose acetate is hydrophilic, according to the SEM results, it is seen that the cellulose acetate particles are located in the depth of its structure — in the pores, between the fibers of PTFE. It is established that the specific productivity of the composite membrane is reduced by a factor of 10, as a result of applying a layer of cellulose acetate. It has been determined that a composite membrane is capable of retaining dissolved salts from tap water. So the retention capacity of the membrane in terms of total mineralization was 75%, which is slightly lower than that of commercial nanofiltration membranes. This membrane is recommended to be used in water treatment processes, before the reverse osmosis process for preliminary removal of dissolved salts.

Acknowledgments
The work was supported by a grant from the President of the Russian Federation for state support of young Russian scientists – PhDs (MK-1107.2019.8) and with financial support from Kazan (Volga Region) Federal University.

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