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A new approach in the production of cellulose membranes

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ABSTRACT

The research is related to the development of a method for modifying cellulose fiber to improve the operational characteristics of membranes. Epichlorohydrin and monoethanolamine were used as modifiers to plasticize the structure of the cellulose membrane. The consumption of modifiers, the temperature and duration of cellulose fiber modification, as well as the drying conditions of the resulting membranes on their properties were investigated. It has been shown that selected modifiers can act as plasticizers depending on the processing temperature. It was established that the resulting membranes are characterized by low productivity, but are capable of effectively reducing water color. It has been experimentally shown that the use of a modifier with a consumption of 15% allows to ensure the selectivity of color removal during filtration of a sodium humate solution at a level of more than 98%.

Keywords: membrane, cellulose, modification, epichlorohydrin, monoethanolamine.

INTRODUCTION

Over the past century, water consumption has been increasing year by year and water scarcity has become one of the major problems in the 21st century (He et al., 2021, Wang et al., 2024). Desalination and water reuse have developed rapidly over the past few decades to address the problem of water scarcity (Gude, 2017, Shemer et al., 2023). To increase the availability of fresh water, various strategies have been developed, which include the use of water treatment technologies by combining different methods and techniques (Padder & Bashir, 2023). Over the past decades, new materials have been developed for the implementation of traditional water treatment and purification technologies, including adsorption (Shkliarenko et al., 2023), coagulation and flocculation (Trus et al., 2022), oxidation (Radovenchyk et al., 2021), as well as membrane methods (Wang et al., 2024).

Among the mentioned methods, membrane water purification technologies are considered to be the most effective in removing physical, chemical, and biological types of pollutants. Membranes are made of different materials, which determine their efficiency, durability and resistance to contamination. Membranes based on polysulfone and polyethersulfone are characterized by high thermal and chemical resistance, and can withstand mechanical loads. However, they are sensitive to organic contaminants and require constant cleaning (Fiorentin-Ferrari et al., 2021, Deepthi et al., 2025). Fluoropolymers can also be the basis for the production of membranes and can be represented by polyvinylidene fluoride and its copolymers, polytetrafluoroethylene, etc. (Li et al., 2022). Fluoropolymer materials also have high thermal and chemical stability and long service life, but they are more expensive and have lower permeability.

Highly selective reverse osmosis membranes can also be made from fully-aromatic polyamide or semi-aromatic polyamide (Freger et al., 2021). They provide excellent retention of salts, bacteria and viruses. The biggest disadvantages in the operation of polyamide membranes are their sensitivity to chlorine, which is why it is necessary to apply water pretreatment, and their susceptibility to biofouling (Zhao et al., 2021, Meng et al., 2023). Cellulose acetate membranes are less expensive and have better biocompatibility, but they are quite sensitive to pH and temperature changes. In addition, they can be damaged by bacteria and microorganisms, which affects the mechanical strength of the membranes and their efficiency (Vatanpour et al., 2022).

Thus, it can be seen that membranes are made mainly from polymeric materials. Polymers can be classified according to their source of origin:

- synthetic polymers are the result of petroleum refining;
- natural polymers are obtained from plant and animal materials.

In view of the constant depletion of world oil reserves, it is necessary to develop methods of obtaining membrane materials based on renewable natural polymers. The environmental component of this approach is obvious. Research on the properties of membranes from natural polymers, such as cellulose, starch, chitin, alginate, etc. has been conducted for more than two decades (Mansoori et al., 2020). However, research is ongoing to improve the strength and selectivity of membrane materials based on plant components. For this purpose, cellulose is of the greatest interest, as it is a high molecular weight polysaccharide that is part of the cell wall of any plant biomass. Biomass is widely distributed in every corner of the planet; therefore, it is an accessible and at the same time renewable source of biopolymers. Many methods for producing membranes from cellulose fiber have been developed, but the issue of mechanical strength and selectivity still remains open. One of the methods for producing membranes from cellulose fiber is the use of modifiers based on the polymerization product of a mixture of epichlorohydrin and triethanolamine. In general, such a combination of components is not new and the main stages of obtaining membranes are:

- reaction between epichlorohydrin and triethanolamine with the formation of a polymerization product;
- addition of the polymerization product to the cellulose suspension with intensive stirring;
- formation of the membrane.

This approach is characterized by a high consumption of modifiers (up to 50%) at a low filtration capacity of the resulting membrane (Trembus and Hondovska, 2024). However, there is an overconsumption of modifiers, since the polymerization products are not completely adsorbed on the cellulose fiber, but remain in the aqueous environment. The problem can be solved by sequentially modifying the cellulose fiber first with epichlorohydrin and then with triethanolamine, followed by polymerization of the product directly on the cellulose fiber.

Therefore, the purpose of the work is to obtain and study the properties of membranes based on cellulose fiber modified with epichlorohydrin and monoethanolamine , and to establish the optimal parameters for forming and drying membranes.

MATERIALS AND METHODS

Softwood bleached sulphate cellulose was used as the starting material. Solutions of monoethanolamine and epichlorohydrin of analytical grade (purchased from Khimlaborreaktiv (Ukraine) were used as modifiers. The UPM-20 ultrafiltration membrane (based on aromatic polysulfanol with an average pore size of 20 nm) was used as a comparison sample in studies of filtration properties.

The cellulose was cut to 1×1 cm and soaked in a desiccator with distilled water for 20 min to swell. Then the fibrous mass was transferred to a laboratory hydrapulper, after which it was refining for three hours to reach grinding degree of 92 ± 2 °SR. Modification of the prepared cellulose was carried out at a mass concentration of 4%. The consumption of modifying substances was 5–15% of the mass of cellulose fiber. The ratio of monoethanolamine:epichlorohydrin was 1:1. The time of modification was 2–6 hours, and the temperature was 20–60 °C. Cellulose suspension was transferred into a heat-resistant beaker and the calculated amount of epichlorohydrin was added. After complete mixing, monoethanolamine was added to the reaction mixture. The mixture was kept for the specified period of time and temperature with constant stirring. After the modification process was completed, the suspension was diluted with water to achieve a fiber

concentration of 0.4% and membrane samples were formed. The membrane forming technology was studied using a laboratory hand sheet forming equipment LA-1 and a Buchner funnel using synthetic fabrics. Membrane samples were prepared with a mass of 80 g/m^2. The obtained membranes were dried in various ways: at ambient air temperature, in a drying cylinder and in the chamber of a laboratory hand sheet forming equipment. The diameter of the membrane was 5.9 cm.

The effectiveness of the membrane formation and drying technology was determined visually, and the filtration capacity was also determined. The filtration rate of distilled water and humate solution was determined, which was compared with the filtration rate of the same liquids through the UPM-20 ultrafiltration membrane (composite membrane - a layer of polyamide is applied to the polysulfonamide base). The filtration kinetics was studied at different pressure values during filtration. The research was performed on laboratory equipment including a filter cell, a water storage tank, a pump, and a permeate collection tank.

The test was carried out at temperatures of 13–25 °C (±3). After reaching the working pressure, the time during which portions of the permeate were taken was recorded. At the end of the test time, the experiment was stopped and the volume of water that passed through the membrane was recorded. The experiment was carried out three times. Membrane productivity was calculated according to the formula:

$$Q = \frac{V}{S \times t} \quad (1)$$

where: V – the volume of distilled water that passed through the membrane, m^3; S – the area of the membrane, m^2; t – the test time, hours.

The color of sodium humate and permeate solutions was studied using a photocolorimeter. The initial color of the sodium humate solution with a concentration of 100 mg/l was 1178 degrees. The color was determined at a wavelength of 400 nm. Quartz cuvettes (l=5 cm) were used in the studies.

Selectivity by color was calculated using the formula:

$$S = \left(1 - \frac{C_2}{C_1}\right) \times 100\% \quad (2)$$

where: C_1 – the color of the initial solution, degrees;
C_2 – the color of the permeate, degrees.

RESULTS AND DISCUSSION

The sequential modification of cellulose with epichlorohydrin and monoethanolamine occurs according to the scheme presented in Figure 1. Epichlorohydrin reacts with the hydroxyl groups of cellulose with the opening of the α-oxide cycle. The subsequent addition of monoethanolamine results in the formation of a high molecular weight polymeric compound. Modified cellulose was used to produce membranes.

Figure 2 shows photos of membrane samples obtained on a laboratory hand sheet forming equipment. This membrane formation process is accompanied by significant fiber losses, resulting in samples that do not meet the calculated mass. Fiber losses depend quite strongly on the content of modifying substances in the fibrous suspension. In the case of increasing the content of monoethenolamine and epichlorohydrin from 5 to 15%, the turbidity of the under-screen water visually decreases. In general, fiber losses were 35–20%. Moreover, the higher the consumption of modifiers, the lower the fiber losses. It is obvious that the modifier acts

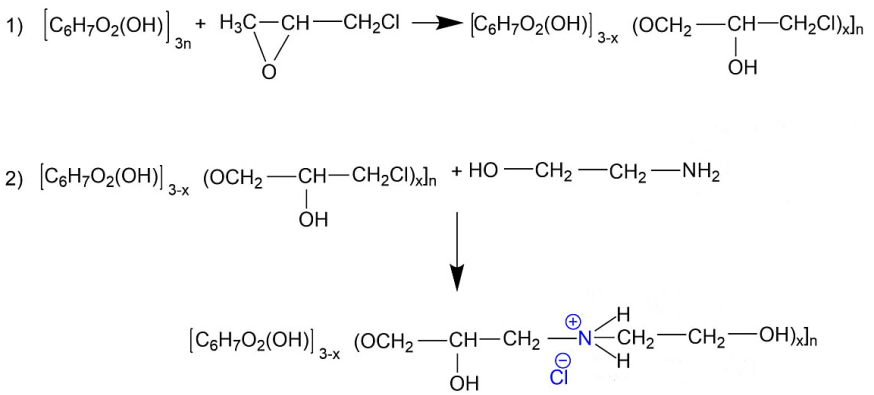

Figure 1. Cellulose fiber modification scheme

Figure 2. Visual appearance of cellulose membrane samples obtained on a laboratory hand sheet forming equipment (from left to right): with modifier consumption of 5, 10 and 15%

as a binding agent. It was also found that with an increase in the modifier consumption from 5 to 15%, the thickness of the membrane samples increases from 6.4 μm to 9.6 μm.

In this case, to achieve the required mass of membrane samples, it is necessary to increase the fiber consumption by 35, 27 and 20% with a modifier consumption of 5, 10 and 15%, respectively.

When forming membranes on a Buchner funnel, the efficiency of mass retention was significantly increased, as a result of which the obtained membranes correspond to the specified mass of 1 m^2. Figure 3 shows that in all cases membrane samples with a uniform distribution of fibers in the thickness of the sheet were obtained. All samples are characterized by the same thickness at the level of 11 μm. All membrane samples were subsequently obtained in this manner.

The results of the study of the influence of drying conditions on the structure of membranes are presented in Figure 4. The visual appearance of the membrane samples indicates that the drying temperature significantly affects the structure of the resulting membranes. It is obvious that the increased drying temperature contributes to significant plasticization of the modifier on the surface of the cellulose fiber, as a result of which the finished samples acquire significant rigidity. The results show that the lower the drying temperature, the more elastic the resulting membrane sample. Membrane samples dried at room temperature are characterized by high plasticity and elasticity. Membrane samples for

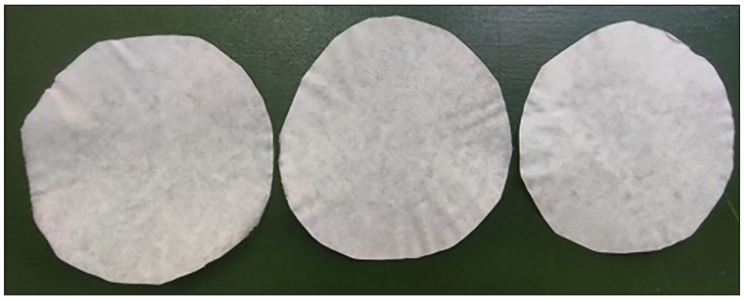

Figure 3. Visual appearance of cellulose membrane samples obtained on a Buchner funnel (from left to right): with modifier consumption of 5, 10 and 15%.

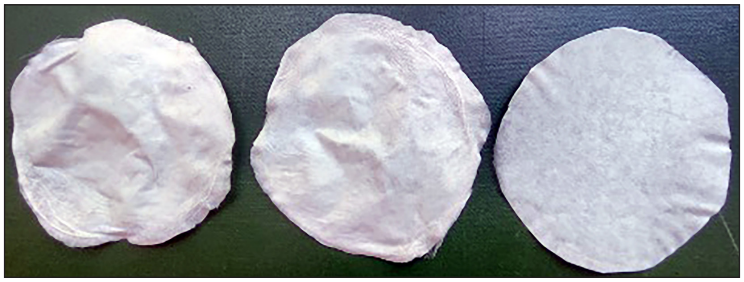

Figure 4. Visual appearance of cellulose membrane samples obtained by different drying methods (from left to right): in the drying part of the laboratory hand sheet forming equipment (120 °C), on the drying cylinder (90 °C), at ambient air temperature (28 °C)

further studies were dried at ambient temperature. The filtration properties of the obtained membranes from modified cellulose fiber were studied in laboratory conditions and the obtained values of productivity and selectivity were compared with the data for the UPM-20 membrane.

The effect of pressure on membrane productivity was investigated on membranes made of modified cellulose fiber, which were obtained with different modifier consumption and at different modification temperatures. Distilled water was used to evaluate the productivity of the membranes. The results are presented in Figure 5.

As can be seen, the productivity of cellulose membranes decreases with increasing temperature of cellulose fiber modification. The content of the modifier does not affect the performance as much as the temperature. The use of a modifier with a consumption of 5 and 10% allows obtaining membranes with a slightly higher productivity, if compared with the UPM-20 membrane. Obviously, this is due to the fact that the size of the pores in the structure of the membranes obtained is slightly higher than in the comparative sample. However, cellulose membranes with a modifier consumption of 15% are slightly inferior to the UPM-20 membrane in terms of productivity. In this case, it can be concluded that a structure with smaller pores is formed than in the comparison membrane.

The filtration capacity of different membranes was also investigated using model solutions of sodium humate. The initial concentration was 100 mg/dm^3. The results of the membrane tests, namely the volume of the selected permeate depending on the duration of filtration, are presented in Table 1.

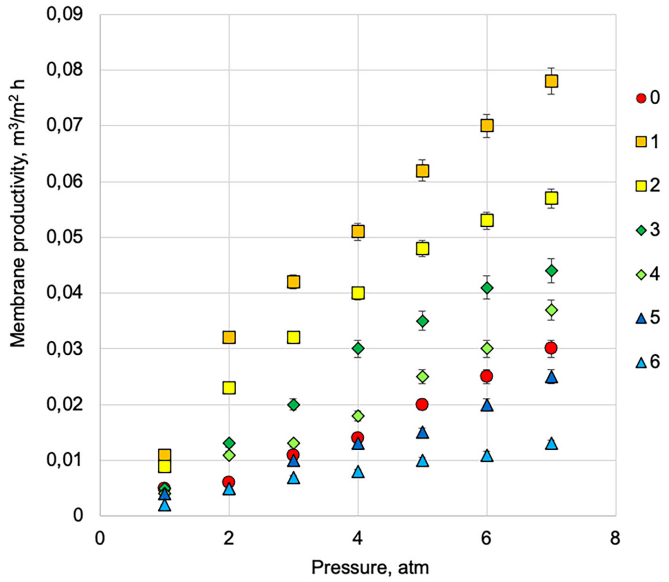

Figure 5. The effect of pressure on the productivity of membranes made of modified cellulose fiber obtained with different modifier consumption/at different modification temperatures: 1 – 5%/20 °C; 2 – 5%/40 °C; 3 – 5%/60 °C; 4 – 15%/20 °C; 5 – 15%/40 °C; 6 – 15%/60 °C in comparison with UPM-20 membrane (0)

Table 1. Membrane filtration capacity depending on filtration time at a constant pressure of 3 atm (sodium humate solution with a concentration of 100 mg/dm^3)

Sample No.	Filtration time, min	Permeate volume, ml			
		UPM-20 membrane	Cellulose membrane with a modifier content of 5%	Cellulose membrane with a modifier content of 10%	Cellulose membrane with a modifier content of 15%
1	10	23	6,5	4,8	3,8
2	20	22	6,0	4,6	3,6
3	30	21	5,6	4,4	3,6
4	40	20	5,5	4,4	3,6
5	50	17	5,4	4,3	3,4
6	60	15	5,3	4,2	3,4
7	70	13	5,2	4,0	3,4

Based on the results obtained, it can be concluded that increasing the filtration time leads to a decrease in the amount of water (permeate) passing through the membrane in all experiments performed. This is due to the fact that as a result of passing the sodium humate solution through the membrane under pressure, the density and maximum pore size decrease, which leads to a decrease in membrane productivity. The results show that increasing the modifier content leads to a decrease in the filtration rate. This is apparently due to the reduction in the pore size of the cellulose membranes as a result of the modification.

Despite the fact that in the previous experiment, membranes with a modifier content of 5 and 10% showed better performance values compared to the UPM-20 membrane, in the case of filtering a sodium humate solution, the pattern changed. All samples of the obtained membranes showed slightly worse results in terms of permeate volume. It is obvious that sodium humate is retained not only by the surface of the membranes, but also diffuses into the internal pores and clogs them, reducing the permeability. For all obtained membrane samples, the filtrate volume decreases over the same time with increasing modifier content. Moreover, the difference between the volume of the filtrate for the membrane with a modifier content of 15% is half as much as for a membrane with a modifier content of 5%.

The next stage of the research was the determination of the color of the samples of the selected permeate on a photoelectric colorimeter at a wavelength of 400 nm. Table 2 presents the values of the residual color of the permeate for different types of membranes, and Figure 6 presents the calculated values of selectivity by color.

Membrane samples characterized by the highest content of modifier are characterized by the best ability to reduce the color of the sodium humate solution. In terms of color reduction, the membrane with a modifier content of 15%

Table 2. Permeate color depending on the time of filtration of sodium humate solution with an initial color of 1178 degrees

Sample No.	Filtration time, min	Color, degrees			
		UPM-20 membrane	Cellulose membrane with a modifier content of 5%	Cellulose membrane with a modifier content of 10%	Cellulose membrane with a modifier content of 15%
1	10	179	196	133	93
2	20	173	194	128	91
3	30	161	186	120	90
4	40	154	180	115	90
5	50	142	173	109	89
6	60	139	165	108	85
7	70	139	163	107	85

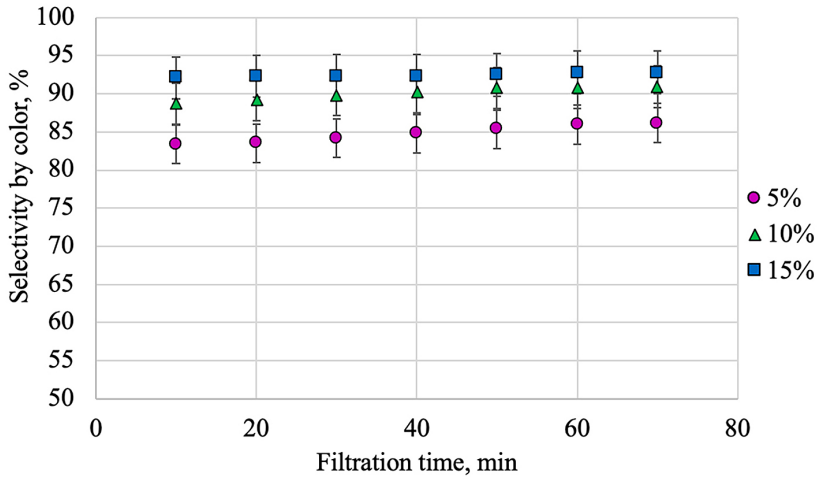

Figure 6. Effect of filtration time on color selectivity during filtration of sodium humate solution on obtained cellulose membranes with different modifier contents

provides slightly worse removal of sodium humates compared to UPM-20. But increasing the content of the modifier to 10 and 15% ensures obtaining membranes with better filtering capacity compared to the comparison sample. The lowest values of residual color correspond to the filtrate obtained by passing a sodium humate solution with a concentration of 100 mg/l through a membrane with a modifier content of 15%, and thus provide the best efficiency, which reaches 98%.

Thus, it has been shown that by modifying cellulose fiber with solutions of epichlorohydrin and monoethanolamine, membranes with a high ability to reduce the color of water can be obtained. However, it is necessary and important to further optimize technological parameters in order to obtain membranes with high permeability.

CONCLUSIONS

A method for producing membranes has been developed, which consists in modifying cellulose fiber with solutions of epichlorohydrin and monoethanolamine, followed by obtaining membrane samples from a diluted suspension of the modified fiber. The influence of forming and drying conditions on the properties of membranes was studied. It has been shown that the modifier acts as a binding agent to strengthen the cellulose fiber in the membrane structure. It has been shown that increasing the modifier consumption has a significant impact on the performance of membranes and their ability to retain sodium humates. Despite the fact that membrane performance decreases with increasing modifier content, the efficiency of sodium humate removal increases. The results obtained will form the basis of further research to determine the structural features of membranes and optimize the parameters of their use for various needs.

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