PREPARATION AND CHARACTERIZATION OF POLYACRYLONITRILE MEMBRANES WITH ANTIBACTERIAL PROPERTIES

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A common problem in separation, fractionation and water treatment is the development of methods for modifying industrial PAN membranes to prevent biological contamination, including the formation of biofilm on the surface of the membrane, and prolong their use. We describe the method of formation of polyacrylonitrile membranes with antibacterial properties by addition into the casting polymer solution of antibacterial polymeric compounds: polyhexamethyleneguanidine chloride, oligourethanesemicarbazide with terminal cationic pyridinium chloride groups, and the polyvinylpyrrolidone-iodine complex. We investigated the effect of the addition of antibacterial compounds to the casting solution on the physicochemical, transport and antibacterial properties of the obtained membranes. We show that increasing the concentration of the bactericidal additives in the casting solution to 3% (wt.) leads to a change in the investigated physicochemical characteristics, water flux and membrane rejection of polyethyleneglycol and low molecular weight electrolyte type 2-1 ($CaCl_2$). We found that membranes prepared from the polymer solution with 3% (wt.) of antimicrobial substances are characterized by high antibacterial activity up to 50 days.

Keywords: *polyacrylonitrile membranes, antibacterial properties, antibacterial compounds*

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1. Introduction

Most of the asymmetric membranes are membranes obtained by phase inversion, the basis of which is the deposition of a polymer soluted due to immersion in the environment of the precipitator, which allows obtaining membranes with a wide range of macroporous structure and separation characteristics [1]. To study the aspects of phase inversion of polyacrylonitrile (PAN) membranes, in particular, the addition of functional modifying agents, it is necessary to determine the optimal parameters of the process. Thus, to obtain membranes with optimal water flux, it is crucial to experimentally select quantitative ratios of PAN and solvent, as well as to investigate the effect of the introduction of modifying agents on the flux and membrane performance characteristics [2].

Besides, a common problem in the processes of operation of membrane installations is the bio-fouling of the polymer membrane, which causes its destruction, reduced permeability due to blockage of pores and secondary contamination of water by the products of metabolism of microorganisms. Described modification of the membranes with biocidal substances, prevents bio-

contamination of the membrane and providing membrane new properties [3]. To create a highly selective ultrafiltration PAN membrane, it is necessary to use substances that will provide hydrophilicity of its surface and promote the formation of a fine porous structure. A promising compound for providing such properties is a polyvinylpyrrolidone-iodine complex, known for its hydrophilicity and biocompatibility [4]. Depending on its molecular weight, this complex is used as a pore-forming agent or hydrophilic additive in a casting solution to prepare membranes. It is relevant to study the effect of the polyvinylpyrrolidone-iodine complex on the functional properties of PAN membranes, and especially the expected occurrence of bactericidal properties in membranes [5].

For modification of membranes use bactericidal agents containing groups of quaternary ammonium, quaternary pyridines, guanidine, and others [6]. Modification of hydrophobic membranes by guanidine-containing substances allows, on the one hand, to hydrophilize their surface (in particular, the surface of pores) and, on the other, to give membranes specific separating characteristics due to the formation of bactericidal functional groups on their surface. Therefore, the creation of polymeric materials with antibacterial action has recently received considerable attention [7].

Treatment of membranes with high molecular weight surfactants (SAS) contributes to the significant change in their separation characteristics and enables them to hydrophilize their surface. The use of charged oligomer compounds (COC) as fillers in the process of membrane formation facilitates the manifestation in these membranes of the advantages of individual ingredients and many cases the production of membranes with higher productivity, selectivity and resistance to pollutants. The presence of ionogenic groups in the structure of the membrane determines their use as charged, charge-selective, ion-exchange membranes and membranes with additional functions. Also, COC is characterized by the presence of a hydrophilic oligooxypropylene component of the three-branched branched structure, containing three pyridinium chloride groups – $N^+C_5H_5Cl^-$ [8], the quaternary nitrogen of which should have membrane antibacterial properties.

The purpose of this work was to obtain and investigate the modified PAN membranes by introducing into the casting solution of functional modifying agents (oligourethanesemicarbazide based on branched trifunctional oligopropyltriol with MM 3000 with terminal cationic pyridinium chloride groups $-N^+C_5H_5(Cl^-)$ (COC), polyvinylpyrrolidone-iodine ($PVP-I_3$) complex, polyhexamethyleneguanidine chloride (PGMG) with molecular weight (MM) (5,000).

2. Materials and Methods

2.1. Membranes

Polyacrylonitrile with MM 40 000 (manufactured by OJSC Naftan, Polymer Plant, Belarus), N, N-dimethylforamide (DMF) and dimethyl sulfoxide (DMSO) was used to prepare the membranes.

2.2. Substances for membrane modification

The bactericidal components used oligourethansemicarbazide based on branched trifunctional oligopropylentriol with MM 3,000 with terminal cationic pyridinium chloride groups $-N^+C_5H_5(Cl^-)$ (COC), polyhexamethyleneguanidine chloride

(PGMG) with MM 5 000 (STC "Ukrvodbezpeka", Ukraine), polyvinylpyrrolidone-iodine (PVP-I_3) complex (Sigma, USA). Polyethylene glycol (PEG) with a MM of 35 000 (Fluka, USA) and a low molecular weight electrolyte ($CaCl_2$) (Fluka, USA) was used to determine the membrane rejection.

2.3. Membranes preparation and modification

The PAN membranes were prepared by phase inversion method in the following sequence:

The casting solutions at 60°C consisted of 14 wt.% solutions of PAN in DMF and 14 wt.% solution PAN in DMSO was prepared and filtered under vacuum. To these solutions quantity of antibacterial components (complex PVP-I_3, PGMG, COC) were added. Solutions were cast at room temperature on a glass plate with a casting knife Elcometer 3570 (Micrometric Aluminum Film Applicators Elcometer) to control the thickness of 0.25 mm of the films with a preceding dry phase inversion in the atmosphere during the 90s. Then the films were immersed in a demineralized water coagulation bath at 22±2°C. After immersion, the membranes were kept in the coagulation bath for at least one night to complete the formation process. In order to remove the remaining solvent, additives out of the membrane structure, the membranes were rinsed with demineralized water and wet stored until tested.

2.4. Study of the transport properties

To study transport properties, an Amicon 8200 standard stirred cylindrical cell (Millipore Corporation, United States) was used. The volume flow rate of water through the membrane (J_v, L/(m^2·h) was calculated by the formula:

$$J_v = \Delta V/(S \cdot \Delta\tau),$$

where ΔV is the volume of the filtrate passed through the membrane with area S in time $\Delta\tau$.

The retention coefficient of poly(ethylene glycol) (PEG 35 000) by the membrane (R, %) was calculated by the formula:

$$R = (1 - C_f/C_{in}) \times 100\%,$$

where C_f is the substance concentration in the filtrate, g/dm^3, and C_{in} is the initial concentration of the substance.

2.5. Study of the Functional Properties of the Membranes

The hydrophilicity of the membranes was studied by measuring the contact angles by the sessile drop method.

The surface charge (ξ potential of the membranes) was measured using an electrokinetic analyzer (EKA, Anton Paar GmbH) with respect to a 1×10^{-3} M KCl solution.

The retention ratio of low molecular weight electrolyte type 2-1 ($CaCl_2$) with concentrations of $0.1 \cdot 10^{-2}$, $0.5 \cdot 10^{-2}$, $1.0 \cdot 10^{-2}$ mol/l was determined using a PAZ-3 flame photometer. The leaching of PGMG-chloride from the formed PAN membranes was determined by its content in water using a photo electro colorimeter FEK-056 with a wavelength $\lambda = 540$ nm in cuvettes with a layer thickness of 50 mm. We determine the difference in optical density of the solution with PGMG-chloride in combination with the eosin-H dye in the test water and the solution without eosin-H (as a control solution). We determined the concentration of PGMG in the precipitation bath and permeated.

2.6. Study of the Antibacterial Properties of the Membranes

The antibacterial activity against the *Escherichia coli* HB 101 strain and *Staphylococcus aureus* CCM 209 were determined. In the experiments, an overnight culture of bacteria grown on nutrient agar (Difso, United States) was used to subsequently prepare a cell suspension in a physiological NaCl solution with a concentration of 1 $\times 10^6$ cell/mL. The suspension was spectrophotometrically standardized using a DEN 1 densitometer to determine the number of cells in McFarland units (Biosan, Latvia). After dilution to a final concentration of 1 $\times$ 10^3 cells/L, the test culture suspension with a volume of 100 mL was passed through the studied membrane to a dry residue. After filtration, the membrane was incubated on an Endo differential diagnostic culture medium (Fluka, United States) at a temperature of 37°C for 24 h. The antibacterial activity was determined as the percentage of colony-forming units (CFUs) that have grown on the studied membrane compared to an unmodified membrane used as a reference sample. The intensity of growth of the *Escherichia coli* HB 101 and *Staphylococcus aureus* CCM 209 test culture was estimated using a four-point scale: from "+" (the presence of single colonies) to "++++" (a confluent growth of bacteria on the membrane surface).

The antibacterial activity of the modified membranes with antibacterial agents depending on operating time was examined by immersing the samples of each of the membranes separately into distilled water and holding them in water for 1 to 60 days. After that, a suspension of the *Escherichia coli* HB 101 test culture and *Staphylococcus aureus* CCM 209 were passed through the membranes as described above, and the antibacterial activity was determined from the number of CFUs related to the reference sample; that is, the number of CFUs was compared to that on the unmodified membrane. The intensity of growth of the test culture was estimated using the above four-point scale.

3. Results and Discussion

3.1. *Formation of PAN membranes*

Due to all the conditions of formation of PAN membranes and the results obtained in the previous studies (Fig. 1 – Fig. 3), the native PAN membranes were prepared with casting solution of PAN: DMF (or DMSO) = 14:86, evaporation time 60 seconds, coagulation bath 22°C distilled water.

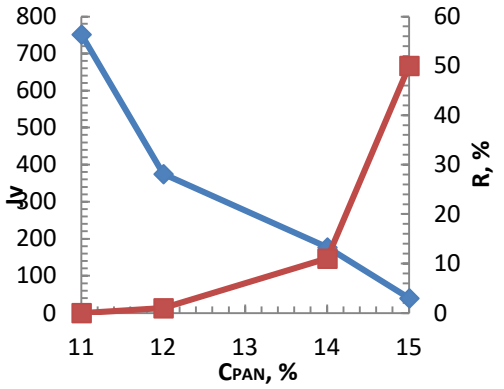


Fig. 1. *Water flux (Jv) and retention coefficient of PEG 35 000 vs. concentration of PAN in casting solution.*

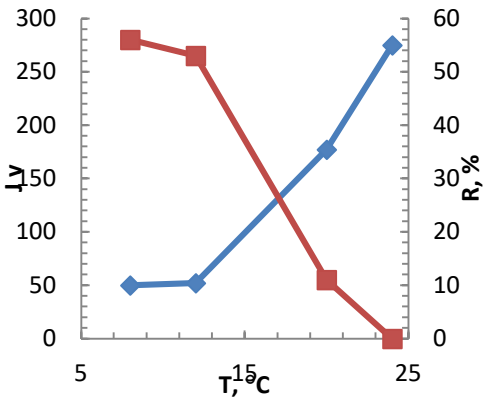


Fig. 2. *Water flux (Jv) and retention coefficient of PEG 35 000 vs. temperature of the coagulation bath (T, °C).*

The developed casting method produced PAN membranes with a *cut-off* of 150 000 (Fig.4) and used them as a basis for creating bulk-modified membranes with functional properties.

The structural characteristics of the obtained ultrafiltration PAN membranes by the method of scanning electron microscopy (SEM) were studied in a JEOL JSM-35C (Fig. 5). The microphotography clearly shows a dense surface layer and sections of macropores and micropores, indicating the creation of asymmetric morphology of the PAN membranes. The Molecular-retention curve, constructed according to the retention coefficients obtained by membranes of different PEG fractions from their aqueous solutions, set the values of the *cut-off* of the membranes (Fig. 4).

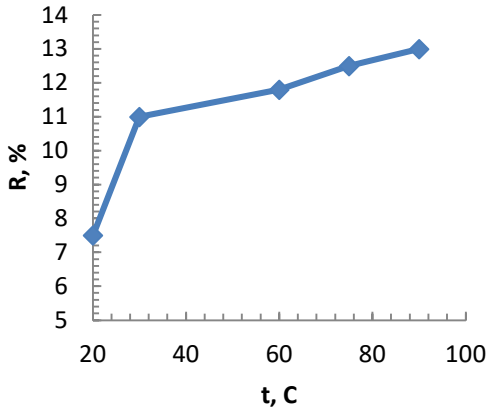


Fig. 3. *Retention coefficient of PEG 35 000 (R, %) vs. evaporation time of solution (τ, c).*

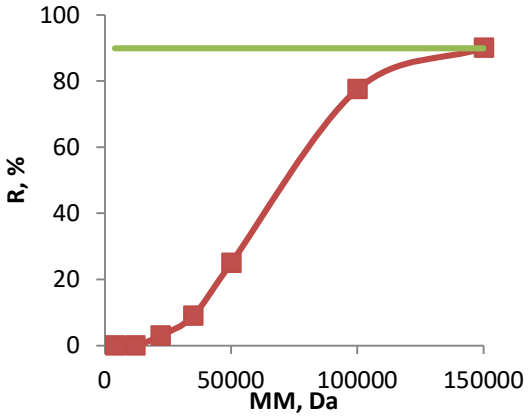
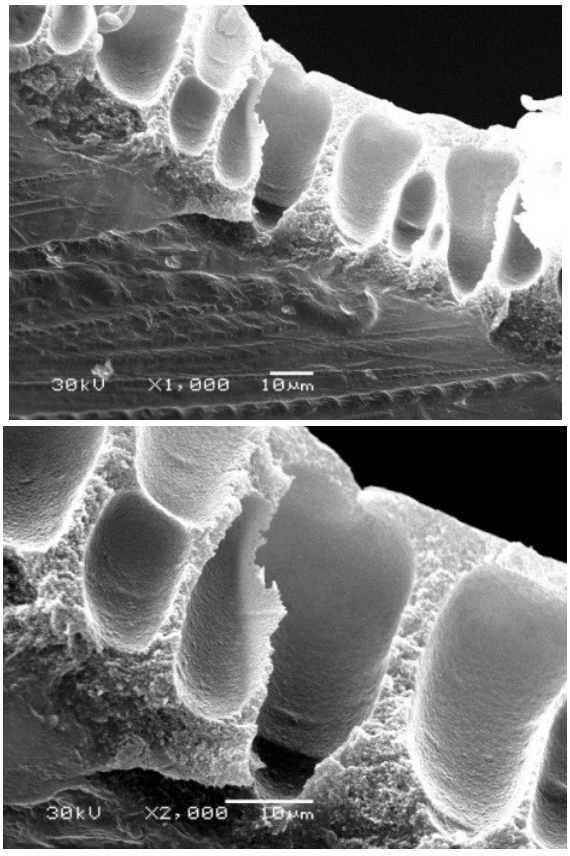


Fig. 4. *Separation curve of PAN membrane (cut-off).*

The obtained results of MM PEG clipping (Fig. 4) indicate that a wide pore size distribution characterizes the PAN membranes from a solution of 14% PAN in DMF without annealing, as evidenced by the range of molecular mass retention from the minimal MM calibrant to MM *cut-off* membranes – 150 kDa.



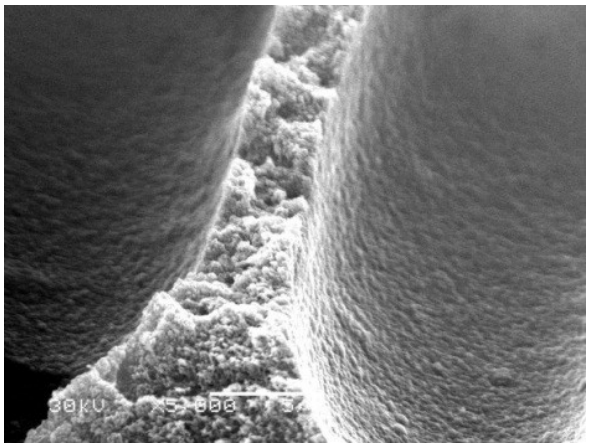


Fig. 5. *SEM micrographs of the surface and cross-section of the PAN membranes of the typical asymmetric structure.*

3.2. Obtaining PAN membranes modified by PVP-I_3 complex

The PVP-I_3 complex is very effective for surface disinfection, which has been confirmed by studies of human and animal infections [9]. The base of antiseptic properties of iodine is its ability to replace covalently bound hydrogen in the groups -OH, -NH, -SH and -CH in molecules in the cell wall of bacteria [10]. In the presence of polymers capable of binding iodine (iodophores) to functional groups containing oxygen, complexes form by a donor-acceptor mechanism. In pivilinylpyrrolidone-iodine (PVP + iodine), iodophor is polyvinyl-2-pyrrolidone (PVP) [11]. So, we expected that the modification of the PAN membranes with complex PVP-I_3 would contribute to their hydrophilization, respectively, to reduce the tendency of the membranes to contamination and change their bactericidal characteristics.

3.3. Effect of polyvinylpyrrolidone-iodine complex adding on the characteristics of modified PAN membrane.

The effect of introducing a complex of polyvinylpyrrolidone-iodine into the casting solution PAN-DMFA during the formation of membranes confirmed that PAN membranes modified with complex PVP-I_3 as a charged pore-forming agent change characteristics in relation to the native membranes. (Tab.1).

Table 1. *Dependence of concentration of PVP-I_3 complex on properties of PAN membranes*

Membrane	Sample #	C PVP-I_3,%	J_v, l/(m^2×h)	R, %	ξ, mW*	Wetting angle, °
PAN	1	0	177	11	-11,2	86
PAN-PVP-I_3	2	1	176,35	10	-11,2	56
	3	1,5	182,85	9	-11,0	47
	4	2	192,93	7	-11,0	39
	5	2,5	200,06	4	-11,0	37
	6	3	201,98	3	-11,0	37

Adding complex PVP-I_3 up to 2.5% in the casting solution, there is an increase of water flux and a further rise of complex adding has a negligible effect on the performance. Changing the pore size of the selective working layer of membranes, as well as increasing water flux, contribute to reducing the retention of PEG 35 000. The introduction of the PVP-I_3 complex leads to significant hydrophilization of the membrane surface, confirming the measured boundary wetting angles of the obtained membranes

with water. The results of the ξ-potential measurement of the modified PAN surface show no changes in the electro-surface properties of the modified membranes compared to the unmodified membranes.

3.4. Obtaining PAN-membranes modified with guanidine-containing oligomer

Polyhexamethyleneguanidine (PGMG) salts exhibit significant bactericidal action against many microorganisms, so it was necessary to investigate their effect on the formation of antibacterial membranes [12]. Due to the polymeric nature of PGMG salts do not have inhalation toxicity, which, combined with the simplicity of synthesis and the availability of input materials, allows it to be used in areas of human activity where antimicrobial protection is required, in particular for water purification and disinfection. As the basis for the creation of modified bactericidal membranes used PAN membrane formed by the above method of phase inversion.

Effect of PGMG-chlorides adding on the characteristics of modified PAN membrane.

The bactericidal compound PGMG-chloride was introduced directly into the casting solution PAN-DMSO. Its concentration in the casting solution varied from 0.5 to 3.0 %. Therefore, the introduction of PGMG-chloride into the solution affects the properties of the modified membranes, compared with the native membrane (Table 2).

We found that the water flux of PAN-PGMG membranes decreases with increasing concentration of PGMG in casting solution 5 times and retention of PEG 35 000 increases to 22%. This effect indicates that the presence of PGMG-chloride in the casting solution leads to the formation of membranes with a fine porous structure.

Table 2. *Dependence of concentration of PGMG salts on properties of PAN membranes*

Membrane	Sample #	C $_{PGMG}$,%	J_v, l/(m^2×h)	R, %	ξ, mW*	Wetting angle,°
PAN	0	0	580	0	-11,2	86
PAN-PGMG	12	0,5	600	0	-9,0	58
	13	1,0	500	2	-5,1	58
	14	1,5	350	11	-1,0	55
	15	2,0	200	16	2,0	46
	16	2,5	120	20	5,0	33
	17	3,0	110	22	9,1	33

* Note: The ξ potential is measured for the KCl solution with concentration $1 \cdot 10^{-3}$ M

The results (Tab.2) of the measurement of the ξ-potential of the surface of modified PAN membranes PGMG-chloride show a change in the electro-surface properties of the modified membranes compared to the unmodified membranes. The added cationic PGMG chloride promotes surface recharge, i.e. the membrane acquires a positive charge. The introduction of PGMG into the structure of the obtained PAN membranes also contribute to the hydrophilization of their surface compared to the membrane without

oligomer, as evidenced by a significant decrease in the boundary wetting angles of the surface of the modified membranes with water. Consequently, guanidine-containing oligomers are capable of altering the surface properties of membranes due to the fixation in the structure of membranes of cationic ionogenic groups, which significantly affect the change of surface charge and its hydrophilicity.

PGMG-chloride is a water-soluble substance. It is necessary to control the concentration of PGMG-chloride in the precipitating bath during the formation of the membrane. We washed obtained PAN-PGMG membranes in distilled water for 1h. Then we check the concentration of PGMG-chloride in permeate during the filtration of water through the modified membrane (Tab.3).

Studying the leaching of PGMG-chloride from the formed membrane, it can be concluded that with the increase of the concentration of PGMG-chloride in the casting solution to 3.0%, the amount of PGMG-chloride in the precipitation bath increases till 0.5% of the total amount of PGMG introduced into the membrane. PGMG-chloride was not detected in permeate after filtration throw washed modified PAN-PGMG membranes.

Table 3. *Leaching of PGMG-chloride in the process of membrane formation*

C_{PGMG} in casting solution, %	C_{PGMG} in precipitation bath, mg/l	C_{PGMG} in permeate after washing, mg/l
0	0	0
0,1	0	0
0,5	10,1	0
1,0	20,8	0
1,5	34,9	0
2,0	39,4	0
2,5	40,8	0
3,0	41,8	0

3.5. Preparation of PAN Membranes Filled with a Charged Cationic Oligourethane Compound

The molecule of the charged cationic oligourethane compound (COC) is characterized by the presence of a hydrophilic oligooxypropylene component of a three-ray branched structure, at the ends of which contains three pyridinium chloride groups – $N^+C_5H_5Cl^-$ [13], quaternary nitrogen which can contribute to the emergence of antibacterial properties of the membrane (Fig. 5).

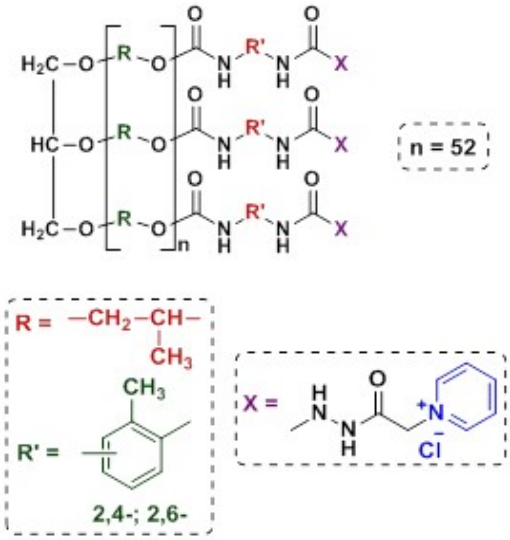


Fig. 5. *Scheme of the structure of oligourethane compound COC.*

3.6. Effect of COC adding on the characteristics of modified PAN membrane

Experimentally, the composition of the solution for the formation of PAN membranes from a mixture of PAN: (DMFA-X): X, where X is the concentration of the COC in the range from 0.1 to 3.0 % (wt.). The addition of macromolecular components to the casting solution change the working properties of PAN-COC membranes. The results of studies of the dependence of the concentration of COC in the casting solution on properties of PAN membrane are given in the Table. 4.

Table 4. *Dependence of concentration of COC on properties of PAN membranes.*

Membrane	Sample #	C $_{COC}$,%	J_v, l/(m^2×h)	R, %	ξ, mW*	Wetting angle, °
PAN	1	0	177	11,0	-11,2	86
PAN-COC	2	0,1	182	4,5	-11,0	68
	3	0,5	176	10,3	-10,0	59
	4	1,0	164	23,8	-9,2	58
	5	1,5	140	33,5	-8,0	52
	6	2,0	110	39,7	-5,2	48
	7	2,5	90	43,2	-1,0	45
	8	3,0	81	46,0	3,0	31

* Note: The ξ potential measured for the KCl solution of concentration $1 \cdot 10^{-3}$ M

The results of the study indicate that the water flux through modified PAN-COC membranes decreases twice with the increasing concentration of the introduced COC (Tab. 4), and retention of PEG 35 000 increases from 11 to 43%. Therefore, the presence of cationic COC in the casting solution leads to the formation of membranes

with a more fine porous structure. According to the results of the performed studies, leaching of the COC from the membrane surface in aqueous solutions does not occur.

The results of the measurement of the ξ-potential of the surface of the PAN-COC membranes. Adding of cationic COC causes recharging of the surface, i.e. the membrane acquires a positive charge.

The introduction of COC into the structure of the obtained PAN membranes also contributes to a significant hydrophilization of their surface compared to the unmodified membrane, as evidenced by a substantial decrease in the value of the water wetting angle of the surface of the modified membranes. Therefore, COC is altering the surface properties of membranes, in particular, the surface charge and its hydrophilicity, due to the fixation in the structure of the membrane of cationic ionic groups.

3.7. Generalization of properties of modified PAN membranes obtained by phase inversion method

The phase inversion method is an easy technique to get membranes of any structure, changing only the parameters of the process of polymer transition from the liquid phase to solid. We developed the methods of introducing into the PAN casting solution of functional antibacterial substances (PVP-I_3 complex, PGMG, COC), which provide the surfaces of membrane hydrophilicity, charge, bactericidal properties and other functional properties.

Thus, with an increase in the concentration of antibacterial additives (COC and PGMG) in the casting solution to 3% wt. the water flux of the modified membranes decreases (Fig. 6) and the PEG 35 000 retention rate increases (Fig. 7). And concerning the membranes formed with the addition of the PVP-I_3 complex, an inverse dependence is observed, which gives grounds to claim its influence as a pore-forming agent.

The results of the hydrophilicity study of the modified membranes confirmed that after the introduction of antibacterial components into the volume of PAN membranes, a significant hydrophilization of their surface was observed (Fig. 8). And changing the values of the ξ-potential of the membrane surface (Fig. 9) means that the PAN membrane changes the initial value of the surface charge from –11.2 mV to +9.0 mV (PAN-PGMG membranes) and +3.1 mV (membranes) PAN-COC). Such results indicate the presence of a large number of amino groups on the membrane surface. The surface charge of the PAN surface of the membrane modified

PVP-I_3 remained virtually unchanged.

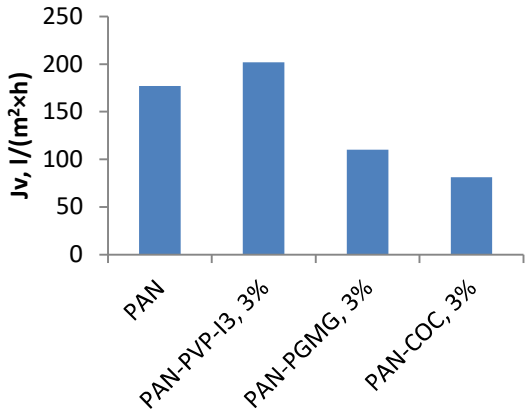


Fig. 6. *Dependence of water flux vs. different type modifiers (3% wt.).*

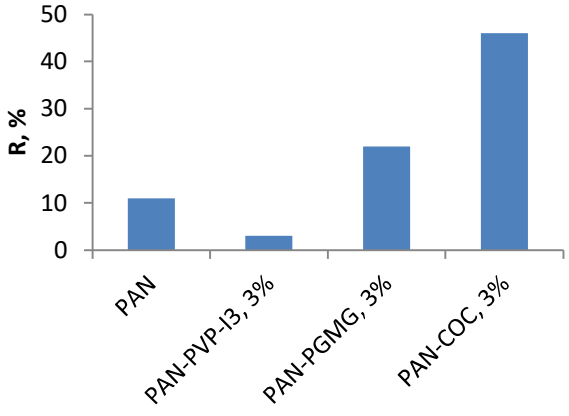


Fig. 7. *Dependence of the retention factor PEG 35 000 vs. different type modifiers (3% wt.).*

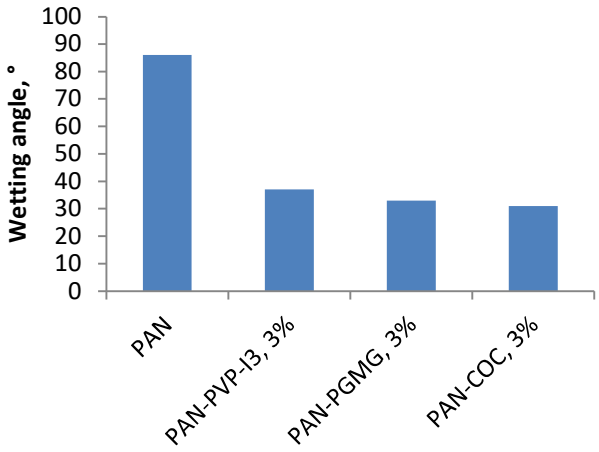


Fig. 8. *Dependence of the wetting angle of the membrane with water (θ, °) vs. different type modifiers (3% wt.).*

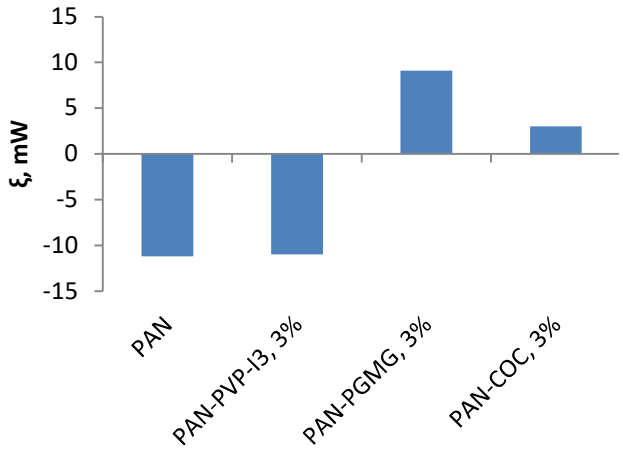


Fig. 9. *Dependence of surface charge (ξ, mW) vs. different type modifiers (3% wt.).*

3.8. The effect of positively charged PGMG-chloride on the selectivity of modified membranes to low molecular weight electrolytes

The presence in the structure of polyhexamethyleneguanidine quaternary ammonium ionic groups for PAN-PGMG membranes with a positive charge creates the prerequisites for a significant change in the characteristics of the modified PAN membranes concerning low molecular weight electrolytes. In support of this assumption, the process of selective detention of Ca^{2+} ions by PAN-PGMG, depending on the concentration of PGMG-chloride in it (Fig. 10).

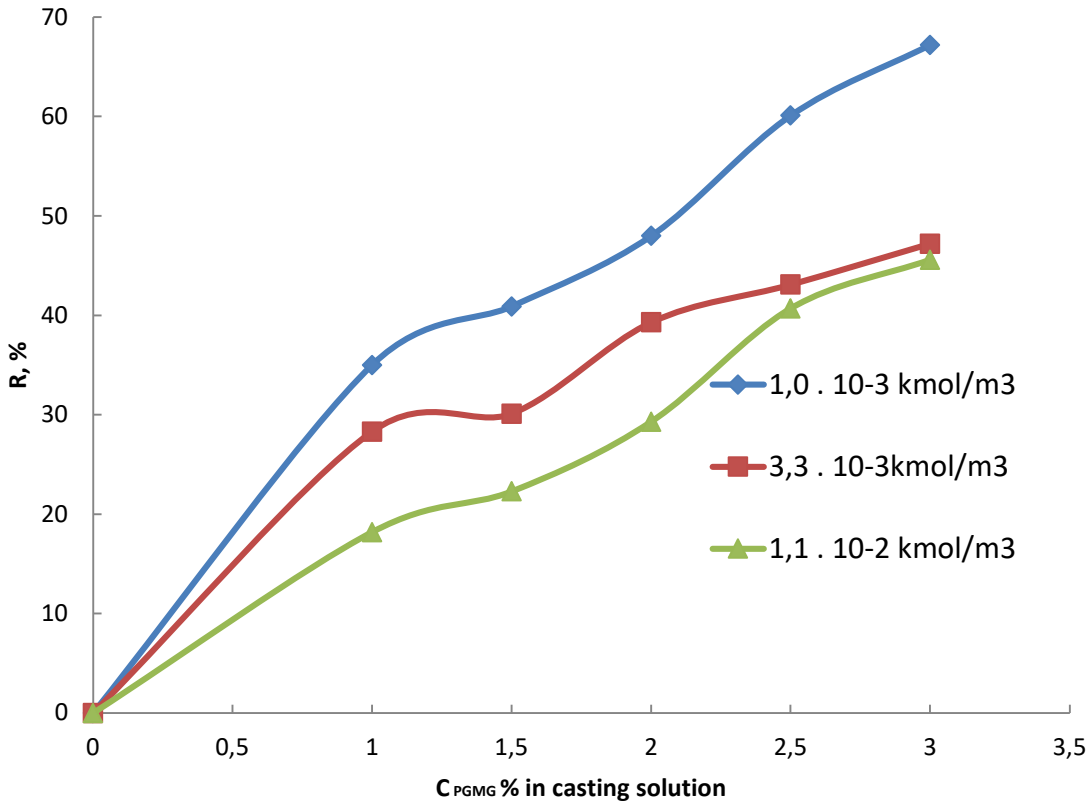


Fig. 10. Retention coefficient of Ca^{2+} by PAN-PGMG membranes vs. C $_{PGMG}$ % in the casting solution.

Analysis of the results showed that the selectivity of PAN-PGMG modified membranes is higher than that of native PAN membranes. Since the retention of Ca^{2+} ions on charged membranes occurs by an electrochemical mechanism, there is slight retention of Ca^{2+} ions on membranes without PGMG. The higher the value of the positive charge of the membrane, the higher the retention coefficient of Ca^{2+} ions.

3.9. Antibacterial properties of PAN membranes

We compared the antibacterial properties of modified PAN and native PAN membranes against gram-positive (*S. aureus* CCM 209) and gram-negative (*E. coli* HB 101) cultures.

We show (Table 5) that for the concentration of the introduced antimicrobial compounds 2% wt. and more membrane has antibacterial properties.

Table 5. *The dependence of the bactericidal properties of the membranes on the concentration of the modifier of different types*

C, % wt.	The bactericidal nature of the membranes, %					
	Escherichia coli HB 101			*Staphylococcus aureus* CCM 209		
	PAN-PVP-I_3	PAN-COC	PAN-PGMG	PAN-PVP-I_3	PAN-COC	PAN-PGMG
0	++++	+++++	+++++	+++++	+++++	++++

1,0	+	+	++	++	+	+
1,5	+	-	+	+	-	+
2,0	-	-	+	+	-	+
2,5	-	-	-	-	-	-
3,0	-	-	-	-	-	-

Note: "–" signifies that the growth of microorganisms is absent; "+" stands for single colonies, and "++++" denotes a confluent growth. The parent unmodified PAN membrane did not exhibit antibacterial properties; that is, confluent growth of the test culture was observed.

The concentration in the casting mixture of bactericides <2% wt. causes unstable bactericidal properties of the membrane as their content decreases over time due to leaching from the surface and pores of the membrane.

We show the effect of the duration of leaching of antibacterial additives on the bactericidal properties of the membranes in Tab. 6.

Table 6. *Dependence of bactericidal activity of PAN membranes on the duration of their keeping in water*

Antibacterial additives	Bacterial growth *Escherichia coli* HB 101/ *Staphylococcus aureus* CCM 209						
	Duration of leaching, days						
	0	10	20	30	40	50	60
PAN	++++	++++	++++	++++	++++	++++	++++
PAN-PVP-I_3	-/-	-/-	+/+	++/++	++/++	++/++	+++/+++
PAN-COC	-/-	+/+	+/+	+/++	+/++	+/++	+++/+++
PAN-PGMG	+/+	+/+	+/+	+/+	+/+	+/+	++/++

Note: "–" signifies that the growth of microorganisms is absent; "+" stands for single colonies, and "++++" denotes a confluent growth. The parent unmodified PAN membrane did not exhibit antibacterial properties; that is, confluent growth of the test culture was observed.

Therefore, the introduction into the polymer solution of the complex PVP-I_3 in the amount of 3 wt.%. improves antibacterial properties against gram-positive and gram-negative bacteria. However, the antibacterial properties of the PAN-PVP-I_3 membranes are only stable for 7 days, since complex PVP-I_3 slowly leaching and removed from the structure of the membrane. The introduction into the casting solution of oligomeric compounds containing quaternary ammonium groups or guanidine groups COC and PGMG in the amount of 3 wt.%, promotes bacteriostatic properties for PAN-COC membranes, which persist for 40 days. The most effective and long-lasting bactericidal action up to 50 days is characteristic of membranes containing 3 % wt PGMG.

4. Conclusions

We show the method of preparing the PAN membranes by the phase inversion with

the introduction into the casting solution the modifiers PVP-I_3, PGMG and COC. The regularities of the formation of new polymer membranes with the introduction of antibacterial substances into the casting solutions of polyacrylonitrile polymers have been established, and the practical ability to regulate the working and antibacterial properties of the obtained membranes by introducing appropriate components into the casting solution is shown. Dependences of change of hydrophilicity, ξ-potential and bactericidal properties of the formed membranes on the type and amount of ionic substances and polymers introduced into the polymeric structure have been established. The wetting angle of the membrane with water is 37°, 33°, 31° for PAN-PVP-I_3, PAN-PGMG, PAN-COC membranes respectively. The surface charge of different type modifiers is

+3 mW for PAN-COC, +9 mW for PAN-PGMG.

The application of PGMG, COC in the formation of membranes made it possible to obtain ultrafiltration membranes with charged (both positive and negative) and hydrophilized surface, which provided an increase of retention of PEG 35 000 and Ca^{2+} ions; as well as increasing the lifetime of membranes by reducing their contamination with substances of various origin, including biocolloid in separation processes. Water flux through modified PAN membranes is 201, 110,

81 l/(m^2×h) and retention factor PEG 35 000 is 3, 22, 46% for PAN-PVP-I_3, PAN-PGMG, PAN-COC membranes respectively. Prepared charged membranes with a hydrophilic surface promote bacteriostatic properties against the gram-negative bacterium *Escherichia coli* HB 101 and gram-positive *Staphylococcus aureus* CCM 209. The most long-lasting bactericidal action up to 50 days is characteristic of membranes containing 3 % wt PGMG.

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СТВОРЕННЯ ТА ДОСЛІДЖЕННЯ ПОЛІАКРИЛОНІТРИЛОВИХ МЕМБРАН З АНТИБАКТЕРІАЛЬНИМИ ВЛАСТИВОСТЯМИ

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Основною проблемою розділення, фракціонування та очищення води є розробка методів модифікування промислових ПАН мембран для запобігання біологічному забрудненню, включаючи утворення біоплівки на поверхні мембрани, та продовження їх використання. Ми описуємо спосіб утворення поліакрилонітрильних мембран з антибактеріальними властивостями шляхом додавання в поливальний розчин антибактеріальних полімерних сполук: полігексаметиленгуанідину хлориду, олігоуретансемикарбазиду з кінцевими катіонними піридиній хлоридними групами та комплексу полівінілпіролідон-йоду. Ми досліджували вплив додавання антибактеріальних сполук до формувального розчину на фізико-хімічні, транспортні та антибактеріальні властивості отриманих мембран. Показано, що збільшення концентрації бактерицидних добавок у формувальному розчині до 3% (мас.) приводить до зміни досліджуваних фізико-хімічних та транспортних характеристик мембрани, а саме об'ємного потоку води та коефіцієнту затримання поліетиленгліколю та низькомолекулярного електроліту типу 2-1 ($CaCl_2$). Ми виявили, що мембрани, сформовані з поливального розчину з 3% (мас.) антимікробних речовин, характеризуються високою антибактеріальною активністю до 50 днів.

Ключові слова: *поліакрилонітрильні мембрани, антибактеріальні властивості, антибактеріальні сполуки.*