



*V.I. Vernadskii Institute
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MEMBRANE AND SORPTION MATERIALS AND TECHNOLOGIES: PRESENT AND FUTURE



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CHAPTER 4**POLYMER MEMBRANES WITH ENHANCED
STABILITY TO BIOFOULING**P.V. Vakuliuk¹, I.M. Furtat¹, O.O. Yatsenko¹¹National University of Kyiv-Mohyla Academy,

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Abstract. *The major problem in membrane separations is biofouling as it leads to more frequent chemical cleaning, higher operating pressures, shortened membrane life, and compromised product water quality. Methods of creation of new polymer composite membranes with increased resistance to biofouling by bulk and surface modification of membranes have been developed, separation and functional properties of the received membranes have been investigated. The performed researches allowed to create a number of new functionalized membranes with a wide range of properties and to improve the technological processes of obtaining hydrophilic, charged and bactericidal polymer membranes to increase their usage for water treatment, concentration and separation of substances of different nature.*

Keywords: *polymer membranes, biofouling, bulk and surface modification.*

Introduction. The relevant issue is creation of new polymer composite membranes and improvement of modification method of commercial polymer membranes with the use of new types of bactericidal modifying agents. The modifying agents of bactericidal action must meet the requirements of high bactericidal stability and, at the same time, the ability to both effective surface and volume modification of membranes. Ultimately, it will create new types of competitive membranes with the necessary transport characteristics and long-term resistance to biofouling.

Our attention is focused on the involvement of polymer ultra- and microfiltration membranes in the process of modification, especially with ion-containing oligomers of various chemical nature and molecular architecture, as well as ion-containing polymers and their complexes. The study of the influence of chemical nature of modifying agents, as well as modification methods of surface and structure chemical nature of the resulting composite membranes, their functional properties, in particular the resistance to biofouling, has practical value in the fundamental plans and in the aspects of applied application.

Numerous studies in the field of membrane technology show that the creation of new membranes is economically unprofitable; therefore, modification is the main method of solving this problem. The attachment of bacterial cells to the membrane surface is the first step in the formation of biofilm. There are many factors that affect the ability of cells to attach. Conditionally, they can be

divided into bacterial characteristics, membrane characteristics and technological parameters. In our work, attention at membrane charge and the hydrophobicity of its surface was focused.

The aim of the work is to extend the life of the membranes due to the creation of increased resistance to biofouling by modifying the surface with substances that either prevent unwanted interactions (adhesion) between the pollutants and the membrane, or destroy the microorganisms that settle on the surface of the membrane. Conditionally these strategies can be divided into strategies of “defending” and “attacking”. The strategy of “defending” provides surface characteristics that would not allow the bacteria to join the surface of the membrane, for example, hydrophilicity. The strategy of “attacking” involves the functionalization of bactericidal agents, which, in the case of cell contact, lead to their death.

The methods of bulk and surface modification for different types of polymer membranes, characterization of the influence of modification methods and the nature of modifying agents on the selective surface layer characteristics and the structure of composite membranes, selectivity, as well as creation of composite polymeric membranes with increased resistance to biofouling was also aimed.

Experimental. In this study two polymers – polyacrylonitrile (PAN) and polyethylene terephthalate (PETF) were selected for creating of the membranes. Membranes from PAN polyacrylonitrile were made by phase inversion. PETF is industrial membrane, which is a model object for study. The difference between the membranes consists in structure points: PAN - asymmetric with a selective layer, PETF membranes have cross-cut straight pores.

In our work, modifying agents are selected according to the “defending” and “attacking” strategies. N-vinyl-2-pyrrolidone and methacrylic acid have been selected to create “defending” effect. The difference between these modifiers is that methacrylic acid provides carboxyl groups of the membrane surface, and N-vinyl-2-pyrrolidone provides amide-carbonyl $-N-C=O$ groups. In order to implement the “attacking” strategy, GO (guanidine-containing oligomer) and PVP-I₃ were selected.

Bactericidal agents are selected depending on the mechanism of action against bacterial cells. Guanidin-containing oligomers, penetrating through the cell wall, are embedded in the phospholipid layer of the immiscible metamorphic membrane, resulting in its defragmentation. There is a loss of vitality of the cell. The main effect of *Povidone-iodine* is the oxidation of amino acids of bacterial cell proteins by the release of iodine complex, inhibition of the synthesis of toxins (alpha-hemolysin, phospholipase C and lipase), and inhibition of the activity of enzymes (elastase, beta-glucoronidase). For example, representatives of *Pseudomonas* produce elastase, which is a factor in pathogenicity. Iodine suppresses the activity of this enzyme.

Results and discussion. Surface modification of the membranes by methacrylic acid leads to contact angle decreasing of the PAN and PETF membranes from 40° to 20°, respectively, and by vinyl pyrrolidone - from 30 ° to 15 °. Surface recharging as a result of the modification of polyacrylonitrile and polyethylene terephthalate membranes with methacrylic acid gives the surface a negative charge that repels bacterial cells, which is associated with repulsion of charges of the same name.

Modification with polyvinylpyrrolidone does not create the phenomenon of recharging the surface. Modification with guanidinium oligomer leads to a positive charge on the surface, which promotes the contact of negatively charged bacteria (Table 4.1). While membranes with immobilized polyvinylpyrrolidone iodine complex, membrane charge does not change.

Table 4.1. Adhesion of bacteria on membrane surface,%

Membrane	<i>P. fluorescens</i> 8573	<i>S. aureus</i> ATCC25923	<i>E. coli</i> ATCC 25922	<i>C. stationis</i> Ukm Ac 719
PAN	98	71	84	81
PETF	90	67	79	77
“Protection” strategy				
PAN-PMAA	38	17	25	20
PAN-PVP	41	19	20	24
PETF-PMAA	43	23	32	30
PETF-PVP	48	26	37	32
“Attack” strategy				
PAN-PMAA-GO	41	19	20	24
PAN-PVP-I ₃	34	16	23	21
PETF-PMAA-GO	48	26	37	32
PETF-PVP-I ₃	39	19	26	18

Conclusions. Modification of membranes with methacrylic acid and polyvinylpyrrolidone results in surface and prevents the adhesion of hydrophobic test cultures, implementing the strategy of “defending”. The most effective “protective” agent is methacrylic acid.

Modifying membrane surface with more hydrophobic polymer based on polyacrylonitrile reduces the adhesion of test cultures to the surface by 50-60%, and for polyethylene terephthalate membranes with less hydrophobic properties by 40-45%.

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ПОЛІМЕРНІ МЕМБРАНИ З ПІДВИЩЕНОЮ СТІЙКІСТЮ ДО БІОЗАБРУДНЕННЯ

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Резюме. Основною проблемою в процесах мембранного розділення є біозабруднення мембран, адже це призводить до підвищення робочих тисків, скороченого терміну експлуатації мембран, необхідності очищення мембран тощо. Розроблені методики створення нових полімерних композитних мембран з підвищеною стійкістю до біозабруднення за допомогою об'ємного та поверхневого модифікування мембран та досліджені розділові та функціональні властивості одержаних мембран. Виконані дослідження дозволили створити низку нових функціалізованих мембран з широким діапазоном властивостей і удосконалити технологічні процеси одержання гідрофільних, заряджених та бактерицидних полімерних мембран для підвищення ефективності їх використання в галузях водопідготовки, концентрування та розділення речовин різної природи.

Ключові слова: полімерні мембрани, біозабруднення, об'ємне і поверхневе модифікування.