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SEMI-PERMEABLE MEMBRANES FOR ULTRA-, MICROFILTRATION AND REVERSE OSMOSIS

Abstract. The results of theoretical and experimental studies in the field of synthesis and application of semipermeable synthetic membranes as the main component of modern non-waste environmentally friendly technologies are summarized. The methods for their preparation for baromembrane processes − reverse osmosis, ultra- and microfiltration, are considered. The features of the kinetics and formation mechanism of semipermeable polymer membranes of various types synthesized by polymerization or polycondensation of various monomers and chemical modification of the finished membranes are discussed. The results of studies to increase their selective permeability, physico-mechanical and electrochemical properties are presented.

The promising areas of their practical application for solving urgent problems of water treatment, industrial effluent treatment with the extraction of valuable components, separation of gas and liquid mixtures at high pressures and intensive mass transfer modes are identified.

Keywords: Membrane, filtration, baromembrane process, reverse osmosis, pores.

Currently, there are various methods of water purification using classical technologies based on the use of pressure, precipitation, sorption, ion exchange, and other filters. More and more attention is being paid to the search for promising new methods of water purification, more compact, cheap, easy to use compared to traditional ones. These include water purification methods using ultrafiltration and reverse osmosis membrane technologies. The widespread introduction of such processes into practice was made possible thanks to the development of polymer science and the use of synthetic high molecular weight film materials with active groups.

Membranes, like other filtering sorbents, can be considered as semi-permeable media: they pass water, but do not pass impurities. However, if conventional filtering is used to remove relatively large formations of dispersed and large colloidal impurities from water, then membrane technology is used to remove small colloidal particles, as well as dissolved compounds. To do this, they must have very small pores.

The driving force causing the liquid to penetrate the obstacle in the form of a thin partition may be: a) the applied pressure; b) the difference in the concentration of dissolved substances; c) temperature difference on both sides of the partition; d) electromotive force.

The main difference between membranes and conventional filter media is that they are thin, and the removed impurities are not retained in volume, but only on their surface. To do this, the so-called "tangential" scheme of water movement in the apparatus is used, in which water is collected from both sides of the membrane: one part of the flow passes through it and forms a filtrate, that is, purified water, and the other is directed along the membrane surface to wash off impurities and remove them from the filter zone. This part of the stream is called a concentrate or retentate, and is usually dumped into the drain. Thus, the membrane filtration unit has one inlet and two outlets, and part of the water is constantly spent on cleaning the film.

From the point of view of technological capabilities, membranes for ultrafiltration, nanofiltration and reverse osmosis are distinguished. In this series, the pore size decreases, and the working pressure increases.

Ultrafiltration membranes have the largest pores with a diameter of 1 to 0.05 microns ($1\mu m = 10^{-6}$ m) and usually work at pressures of 2-5 bar. They are used, for example, for the purification of drinking tap water from colloidal and high molecular weight contaminants, if the adjustment of its salt composition is not required.

Nanofiltration elements (pores of 5-50 nm, or 0.05-0.005 μm) are used to soften water with increased hardness, to remove heavy metal ions and organochlorine. Monovalent ions, such as Na, K, Cl, NO_3, are poorly retained − on average, no more than 10-30%. The nanofiltration working pressure usually does not exceed 5-7 bar.

Reverse osmosis membranes have pores with a diameter of less than 10 nanometers (less than 0.01 μm), operate at pressures up to 100 bar and allow deep desalination, or demineralization. Reverse osmosis is used to produce ultrapure water for industrial needs, as well as for desalination of sea and brackish groundwater, and the degree of desalination (selectivity) is usually not less than 92-97%.

Membranes can have various geometric shapes: tubular, hollow fiber and flat. Tubular are tubes with a diameter of several millimeters to 1-2 cm, made of a porous material, such as ceramic. Films in the form of hollow fibers also have a tubular shape, but their diameter is usually from 0.1 to 0.5 mm. Due to such a small size, a huge amount of fibers can be placed in a unit volume of the filter apparatus, and their total working surface will be tens of times higher than that of large diameter tubular membranes. Flat ones are produced in the form of films, as a rule, thin-film composite, that is, multilayer, and each layer is made of different chemical compounds [1].

Baromembrane processes are classified both by the size of the separated particles (molecules, ions) of the dissolved substance, and by the structure of the semipermeable membranes used.

These processes include the following membrane technologies: reverse osmosis, microfiltration, ultrafiltration and nanofiltration (nanometer – 1^{-9} m, or 0.001 microns: 1 nm = 10 angstroms = 0.001 microns).

Reverse osmosis (hyperfiltration) is the separation of aqueous solutions of low molecular weight compounds and salts due to the different mobility of the components in the pores of semipermeable membranes. The essence of reverse osmosis lies in the fact that when an external pressure is applied to an aqueous solution that exceeds the osmotic pressure, water molecules are transferred in the opposite direction – from the region of a weakly concentrated solution to a highly concentrated one. The mechanism of transfer of water molecules through a semipermeable membrane is activated diffusion – a process in which water and the substances dissolved in it are separated at the molecular level; on one side of the film, a flow of demineralized water (permeate) emerges, and pollution (concentrate) remains on the other side and merges into the drainage.

The driving force of reverse osmosis (as well as ultra-, micro- and nanofiltration is the difference between the applied hydrostatic pressure and the osmotic pressure of the solution:

$$\Delta p = p - (p_1 - p_2) = p - \Delta p,$$

where p is the pressure above the initial solution, Pa; p_1 and p_2 are the osmotic pressures [Pa], respectively, of the initial aqueous solution at the surface of the membrane and permeate. The difference between reverse osmosis and microfiltration and ultrafiltration is determined by the pore size of the films used: reverse osmosis uses denser membranes with a minimum pore size, which have a large hydrodynamic resistance.

Microfiltration (MF) – a baromembrane process that occupies an intermediate position between ultrafiltration and filtration, is carried out under a pressure of 0.01-0.1 MPa and differs from other baromembrane processes carried out without phase transformations, the possibility of the formation of a solid phase on the membrane surface (salt precipitation). The pore sizes of microfiltration (MF) films are in the range from 10 to 0.05 μm, as a result of which the process is used to separate emulsions and suspensions of colloidal microparticles of water, defined as turbidity [2].

Ultrafiltration according to the technological scheme of the process occupies an intermediate position between microfiltration and reverse osmosis. The ultrafiltration method is based on the use of ultrafiltration (UV) membranes, the pore size of which is from 0.1 to 0.02 microns.

Nanofiltration (NF) occupies an intermediate position between reverse osmosis and ultrafiltration and is based on the method of its passage under pressure of about 6-8 MPa through selective nanofiltration (NF) membranes. Their main material is polysulfoamide, fluoroplast, cellulose acetate and other materials. The pore size, which varies from 0.001 to 0.01 μm, is selected in such a way that monovalent ions can pass through them, and divalent and larger ions and molecules are retained by the NF membrane.

Modern nanofiltration apparatuses are an alternative to ion-exchange water softeners. They are quite complex systems, the main functional elements of which are a selective NF membrane, a casing, and a pump supplying water to the filter casing for nanofiltration of water [3].

Filtration apparatuses working on the principle of baromembrane processes (reverse osmosis, micro-, ultra-, nanofiltration) are considered [4]; they are becoming increasingly used in industrial use and for domestic purposes. Their main feature is the presence of a semipermeable membrane based on ceramics, polymers, or nanocarbon materials with selective permeability to certain components of the mixture to be separated (charged metal cations, organic molecules, bacteria, viruses).

Osmosis phenomena play a very important role in the life of animals and especially plant organisms. Cell membranes are membranes that are easily permeable to water, but almost impermeable to substances dissolved in cell sap. Penetrating into cells, water creates quite a lot of pressure in them, which slightly stretches the cell membranes and maintains them in tension. That is why such soft organs of a plant as grassy stems, leaves, flower petals have a certain elasticity. If you cut a plant, then due to the evaporation of water through the cell wall, the volume of cell juice decreases, the cell wall falls off, becomes flabby - the plant withers. But once the plant has begun to fade, put in water, as osmosis begins, the cell membranes again strain and the plant takes its former form. Osmosis is one of the reasons that cause water to rise along the stem of a plant, cell growth, and many other phenomena.

Consider the principle of action of direct and reverse osmosis on graphic examples. Let chamber “A” contain an aqueous solution of inorganic salts, and chamber “B” contain pure water. Both chambers are separated by a semipermeable membrane capable of transmitting only water molecules. The initial state of the system in which the direct osmotic process is realized is shown in figure 1.

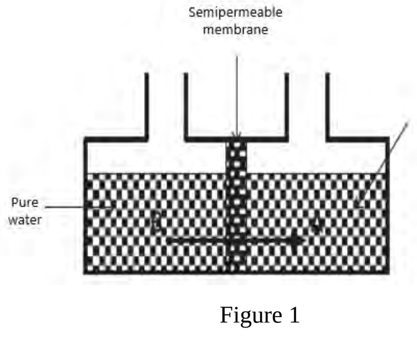

Figure 1

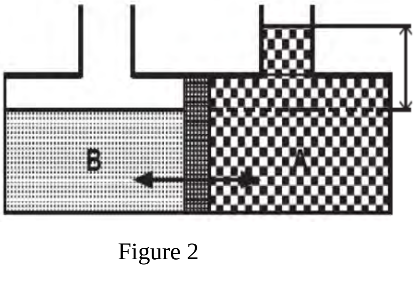

Figure 2

Due to the difference in pressure (concentration) of water molecules in different chambers (higher pressure in chamber “B”), water molecules pass through a semipermeable membrane into a volume with a lower concentration, i.e. into the camera "A". The volume of the solution is constantly increasing, the solution itself is diluted. The pressure difference of the water molecules will gradually decrease, inhibiting the further transfer of water molecules.

In other words, the water level in chamber A rises until the pressure created by the liquid column balances the flow of pure water. In this case, osmotic equilibrium is achieved. The magnitude of the generated hydraulic pressure is called the osmotic pressure of the solution in chamber "A" (figure 2).

If hydrostatic pressure exceeding the osmotic pressure is applied to the salt solution in this system, we find that pure water flows in the opposite direction to that described above, and that the salts are retained by the membrane. This phenomenon became known as reverse osmosis [5].

A probabilistic method was developed [6] for assessing the porosity of nanofiltration and reverse osmosis membranes with a rigid structure. The size distribution of transport pores based on porous glass is experimentally obtained. The proposed theoretical functions describe the obtained experimental data with good accuracy.

The development of such methods is one of the progressive directions of science and technology. The electrochemical activity (change in the ion transport numbers in the pores) of the membranes is highly dependent on the pore size. For coarsely dispersed systems (electrokinetic radius $\chi R \geq 20$, where χ is the Debye parameter, R is the pore radius), an increase in ion transport numbers (in comparison with a free solution) is weakly expressed due to the small contribution of DEL to the properties of the liquid in the pores. The technological requirements for membranes (chemical resistance to active media, mechanical strength, relative cheapness, etc.) in most cases do not allow optimally combining high charge and large pore sizes in industrial membranes [7].

One of the unique methods for producing new reverse osmosis membranes is the radiation grafting of active monomers (as well as polyelectrolytes) to mechanically strong substrates, which makes it possible to obtain materials with high electrochemical activity. However, these methods are laborious and unsafe. A promising direction in membrane technology is the use of polyelectrolyte complexes based on both weak and strong polyelectrolytes (PE) [8]. Films based on polyelectrolyte complexes can be obtained with the required permeability and selectivity. A known method of adsorption modification by multiple sequential deposition of layers up to 10-12 of oppositely charged PE [9]. By adjusting the number of PE layers, membranes with desired properties (controlled charge density, permeability, and selectivity) are obtained.

A macroporous nylon film was modified [7] with polyelectrolyte associates based on oppositely charged synthetic polyelectrolytes and surfactants. The modifying effect of polycomplexes of surfactants is evaluated by the value of ion transport numbers. To increase the strength of fixing the polycomplex on the surface of the macroporous nylon membrane, a benzene solution with different polystyrene contents is added. The optimal amount of polystyrene (30% wt.) Was determined. The modified membrane increases the transport number of the ion having a charge sign opposite to the charge of the polyelectrolyte macromolecules.

Membrane methods are a modern tool for implementing a number of priority areas for the development of science, technology and technology, their practical significance is associated primarily with the solution of global problems facing humanity in the 21st century: the creation of high technologies, ensuring safe living, the production of environmentally friendly food , high-quality drinking water, as well as the formation of the proper balance between solving socio-economic problems and preserving the environment [10].

Among such methods, baromembrane processes, in which the transfer of matter through the film under the influence of a pressure difference, are most demanded. First of all, they include microfiltration and ultrafiltration (I. Behhold, 1907) and reverse osmosis (I. Manegold, 1929). The classification of baromembrane separation methods and their position with respect to conventional filtration are shown in figure 3.

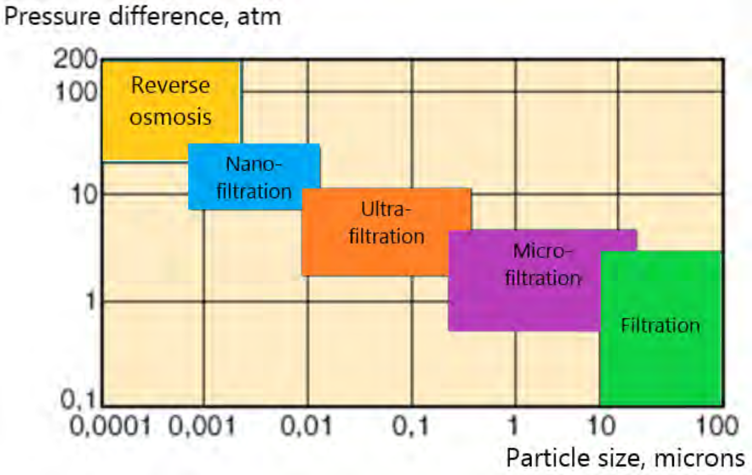

Figure 3 – Classification of baromembrane methods

The authors of [11] discuss the practical significance of baromembrane processes for various areas of the sphere of human activity. The methods of forming semipermeable films and evaluating their characteristics are considered. The advantages of the electrochemical method for the synthesis of polymer membranes (electropolymerization) are shown. A comparison is made of the methods for studying their supramolecular structure (phase composition, pore size, total porosity, asymmetric structure). The advantages of video microscopy for their study in a swollen state are shown. The prospects of baromembrane technologies are determined.

Membrane methods for the separation, purification and concentration of organic and mineral substances are widely used to create economical and low-energy and reagent-free technologies. The leading place in this area belongs to baromembrane filtration, electrodialysis, and a new direction in the development of membrane processes – pervaporation.

Pervaporation is a new direction in the development of membrane processes used for dehydration of organic solvents, in which the phase transition from liquid in the feed phase to vapor in permeate is carried out. In recent years, this promising method has attracted great attention of researchers. A wide range of practical use of the method requires expanding the assortment of membranes. To this end, tests were carried out of electro-synthesized polymethylolacrylamide films as pervaporation films for ethanol dehydration.

The possibility of using electro-synthesized ultrafiltration membranes for the concentration and purification of phenolic impurities of aqueous extracts of arabinogalactanis also shown. The possibility of using polymethylolacrylamide materials for pervaporation separation of water-ethanol mixtures was revealed. It has been established that surface modification of ion-exchange membranes by ionogenic surfactants of various nature makes it possible to increase the separation of mono- and divalent ions by a factor of 2-3 compared with industrial ones.

The possibility of using electrodialysisis determined by the selectivity of ion transfer through membranes, which depends on their composition and structure, electrodialysis conditions: electrolyte composition, hydrodynamic conditions near the membranes, and current density. In order to create selectively permeable ion-exchange membranes, most studies are aimed at modifying their surface. The most widespread is their chemical conversion with polyethyleneimine, which leads to a noticeable decrease in the transfer of divalent ions as compared with monovalent ions both through cationite and anionite membranes [12, 13].

In terms of natural water consumption and wastewater discharge, dyeing and finishing shops occupy one of the leading places in textile enterprises. The specific consumption of natural water and, accordingly, the wastewater in them is from about 70-400 m^3 per ton of product. It has been established that more than 50 types of organic and mineral compounds are present in the wastewater of the dyeing and finishing shops [14]. Depending on the size of the particles contained in the water, pollution is divided into three types (table).

Depending on the class of the dye, the type of material to be painted, and other parameters 5-50% of the initial amount of the dye passes into the wastewater. Maximum allowable concentrations in water are relatively low and range from 0.1-0.0025 mg/l [15].

Classification of textile industry wastewater pollution

Particle size	Pollution form	Pollution Composition	Environmental Impact
Less than 10^{-8} m	True solutions	Cu^{2+}, Al^{3+}, Fe^{3+}, Cr^{3+}, Zn^{2+}, Pb^{2+}, Be^{2+}, CrO_4^{2-}, ClO^-, NO_3^- and etc.	excess MPC and as a result - high toxicity
10^{-8}-10^{-5} m	Colloidal solutions	dyes, syntheticsurfactants, detergents	change in organoleptic properties of water, toxicity
More than 10^{-5} m	Coar seimpurities	fibrous waste, kaolin, pectin breakdown products, mineral oils	change in the organoleptic properties of water

For the first time [16], the membrane elements of the world's leading manufacturers were experimentally determined using reverse osmosis technology to purify cyanide-containing recycled water from hydrometallurgical production. The Amur Hydrometallurgical Plant is the only enterprise operating in Russia in 2015 that uses autoclave technology for the processing of refractory gold-bearing sulfide ores. The company uses its own reverse osmosis water purification system for repeated reuse in production, to implement the concept of “near-zero liquid runoff”, NZLD. A feature of this hydrometallurgical production is its sensitivity to chloride and cyanide ions in recycled water, which reduce the extraction of precious metals. In a specially set series of experiments, cyanide ion selectivity in-dices were obtained at high permeate selection coefficients. It was found that all the studied membrane elements show low selectivity of nothigher than 65 and 61% for cyanide ion with permeate selection coefficients of 0.6 and 0.7, respectively.

The problem of wastewater treatment of various industries from difficultly oxidized organic compounds is very relevant. Traditional cleaning methods are not always effective, which adversely affects the environmental friendliness of projects. One of the promising methods of wastewater treatment from organic pollution is ozonation. The results of a study of the influence of nature, the concentration of coagulants, flocculants and ozonation on the degree of wastewater treatment at the Ufa Plywood-Tile Plant are presented [17]. $Al_2(SO_4)_3$ and $FeCl_3$ were used as coagulants, and the most accessible natural active silicic acid (ACC) and synthetic organic polyacrylamide were used as flocculants. Quantitative chemical analysis of the investigated wastewater showed that it is advisable to carry out ozonation using the coagulant $Al_2(SO_4)_3$ and the flocculant ACC. At the same time, the degree of purification from phenol reaches 0.05 g/dm^3, and COD decreases by 1.8 times.

Real wastewater from chemical and machine-building enterprises contains both organic and inorganic compounds in their component composition, which must be extracted from wastewater due to their value, toxicity and the possibility of secondary use. Metal-containing wastewater contains mainly inorganic salts, and the effluents of chemical plants contain both organic and inorganic components. For example, aniline contained in the effluents of chemical plants along with other compounds is used in the manufacture of dyes and rubbers.

There is a need for research and application of the reverse osmosis separation method for effluents of engineering and chemical enterprises [18].

The widespread use of the reverse osmosis separation process is constrained by the poorly studied mass transfer kinetics and the lack of hardware and technology design for its implementation. An experimental reverse osmosis unit with a single-module roll apparatus and a method for studying specific productivity and retention coefficient through an MGA-95 membrane during the separation of inorganic salt solutions were developed [19]. Experimental studies of specific productivity and retention coefficient through the MGA-95 membrane for aqueous solutions of zinc, iron, and tin sulfate were carried out. The effect of dissolved inorganic substances on the specific productivity and the retention coefficient through the membranes of OPM-K and MGA-100 in the separation of aqueous aniline-containing solutions was studied.

Membrane barometric separation processes include microfiltration, ultrafiltration, nanofiltration and reverse osmosis [3, 20-24], which differ in the size of the recovered particles. Microfiltration retains particles larger than 0.1-1 microns (large colloids, suspensions, bacteria). Working pressure, as a rule, up to 2-3 atm. Ultrafiltration retains particles an order of magnitude smaller − 0.01-0.1 microns, these include colloids, proteins; microbiological pollution of water is reduced by 4-6 orders of magnitude, large organic molecules (with a molecular weight of over 1000 Da) are retained. Nanofiltration effectively retains components of substances with a size of 0.001-0.01 microns, organics with a molecular weight of more than 500 Da. Chroma, organic matter, pesticides, microbiological contaminants, hardness salts, multiply charged ions are removed. Working pressure − from 3 to 20 atm. Reverse osmosis removes all dissolved salts (filter rating 0.0001-0.001 microns), organic matter (with a molecular weight of less than 500 Da). Working pressure is up to 100 atm.

For the purification of solutions from ionic impurities, reverse osmosis and nanofiltration methods are used [25]. Separation by reverse osmosis removes all cations and anions from the water with a close degree of extraction − 98-99%. An effective separation of one and two charge ions does not occur. During nanofiltration, single and doubly charged ions are extracted with significantly different coefficients. For Na^+, the selectivity of the membranes is 40-60%, and for Ca^{+2}, Mg^{+2}– 95-99%, which basically makes it possible to separate them. Previously, the study of such processes was carried out mainly in the field of concentrations close to drinking water. In the promising area of high concentrations of research, very little. Preliminary experimental results show that with an increase in concentration to tens of g/l, a significant change in the selectivity of the membrane for single and doubly charged ions occurs. For some membranes, Na^+ selectivity can tend to 0 with Ca^{+2}, Mg^{+2} selectivity reaching 50-80% and even higher for multivalent heavy metal ions. In practice, this makes it possible to isolate valuable components from saline solutions or organize the reverse use of regeneration solutions of ion-exchange filters.

It is well known that one of the decisive factors in the habitability of the ships of the Navy, which directly determines the success of the tasks of the training and combat activities of naval specialists, is water supply. Providing the crew of ships with high-quality fresh drinking water has always been a difficult multi-stage hygiene and technical task.

Desalination of sea water, as the first stage of this task, has long been achieved in the Navy by using mainly desalination plants of the evaporative type. However, this method, despite its effectiveness, has a number of disadvantages. So, when receiving the distillate, a large amount of energy is consumed, for its further mineralization the operator’s manual labor is used, storage of sets of salts and chemicals for the subsequent disinfection of water requires the allocation of additional ship areas. In addition, the production of certain types of these desalination plants has been discontinued, as well as the production of salt kits for the mineralization of distillate. Given the above, the relevance of the search for new ways to solve the problem of supplying ships with quality fresh water has increased.

To improve the water treatment process, a method of desalination of sea water using reverse osmosis plants, which has recently been used on some ships of the civilian fleet, has been proposed. Installations of this type have such advantages as lower energy consumption, full automation of the process, small overall dimensions, the possibility of application in the coastal zone, balanced physico-chemical composition of the desalinated water obtained, its bacteriological safety. However, despite the already begun use of reverse osmosis plants, comprehensive studies of the effect of the consumption of desalinated water with their help on the body were not carried out, which makes it impossible to use them on the ships of the Navy. The preliminary studies [26] allow us to consider the use of reverse osmosis units as a promising area for optimizing the water supply system of the ships of the Navy.

On seagoing vessels, bottled water isused to provide seafarers with high-quality drinking water, but its characteristics deteriorate during long-term storage. In addition, this method is expensive. Recently, the consumption of high-quality water obtained in desalination plants of the membrane type with the “reverse osmosis” effect has increased. This process takes place at the molecular level and relates to nanotechnology. Cleaning is carried out in filters using a thin film membrane. All kinds of impurities are removed from the water, including the main one – sodium chloride salts. Molecules of water and oxygen can freely pass through the pores of the membrane with a size of 0.0001 microns, and the remaining elements of the periodic table - only in a limited amount. So, from sea water with a total salinity of 35 g/l of salts, water with a total salinity of about 0.25 g/l is obtained, which meets the WHO water requirement. Consider [27] the production of environmentally friendly and high-quality drinking water on marine vessels using nanotechnology. A description of the relevant desalination plant is provided.

A number of regions of our country have large reserves of groundwater with a total salinity of 1 to 35 g/l, not used for water supply due to the high content of salts dissolved in water. These waters can become sources of water supply only if they are further desalinated.

When water is desalinated by the reverse osmosis method, sea water is passed through semipermeable membranes under the influence of pressure significantly exceeding the difference between the osmotic pressures of fresh and sea water (for sea water 25-50 atm) [28]. Such membranes are made by the domestic industry from polyamide or cellulose acetate and are available in the form of hollow fibers or rolls. Small water molecules can freely penetrate through the micropores of these membranes, while larger salt ions and other impurities are retained by the membrane.

Reverse osmosis has been used in our country since the beginning of the 1970s in various technologies for purifying water from impurities, including for desalination of water [17]. Modern industrial reverse osmosis plants include a fine water filter, a reagent preparation system, a high pressure pump, a filter module unit, and a chemical washing unit.

In plants for desalination of salt water by the reverse osmosis method, pipes are made of a porous material lined on the inside with a cellulose acetate film that acts as a semipermeable membrane. The desalination plant consists of many similar pipes laid parallel to each other, through which high-pressure pump (50-100 bar or 5-10 MH/m^2) is continuously pumped with sea water, and two flows are discharged − desalted (permeate) and water with concentrated salts (concentrate), which merges into stock. The flow of fresh water through the membrane is proportional to the applied external pressure. The maximum pressure is determined by the inherent characteristics of the reverse osmosis membrane. If the pressure is too high, the membrane may burst, become clogged with impurities present in the water, or allow too many dissolved salts to pass through. If the pressure is too low, the process slows down.

Reverse osmosis has significant advantages compared to other methods of desalination: energy costs are relatively small, installations are structurally simple and compact, their work can be easily automated. The reverse osmosis system is controlled in semi-automatic and automatic modes. Precipitation inhibitors are used to reduce the formation of unwanted salt deposits in pipe cavities. To remove salt deposits from the surface of the membranes, a chemical washing system is used; to control the quality of water purification and pH values, flow measuring salinity and pH meters are used. Permeate and concentrate consumption is controlled by flow meters [28, 29].

The 21st century will be characterized by a further exacerbation of the shortage of fresh water on a global scale. It is noted that two-thirds of drinking water is consumed for agricultural activities (for example, for irrigation and cultivation of crops). The problem of desalination of sea and ocean water is also compounded by the fact that the planet’s population is growing rapidly (more than 80 million people a year) and by 2025 at least 2 billion people on the planet will systematically experience an acute shortage of fresh water [30]. Of the 30% of fresh water, approximately 70% are frozen in snow, glaciers and permafrost, most of the remaining reserves are in aquifers, from where we pump it out much faster than nature can make up for losses.

A modern technology called reverse osmosis involves passing water through a salt retaining membrane. Although this method requires less energy than distillation, it is still quite expensive and energy-intensive: the manufacture and operation of membranes is associated with high energy and economic costs (desalination of 1 cubic meter of sea water requires at least 400 kW of electricity and pressure up to 6, 5 MPa – 65 atm). It should not be forgotten that with any type of desalination, a concentrated salt solution will inevitably form, which can be dangerous for the environment and even for the natural reserves of fresh water. It is difficult to get rid of the saline solution, as the salinity of sea or ocean water rises: after cleaning with reverse osmosis, concentrated solutions will be returned back to the sea or ocean, further deepening the desalination methods. Currently, at least $6 \cdot 10^{10}$ liters of fresh water are produced daily by about 15 thousand desalination plants around the world [30, 31].

Reverse osmosis as a method of water treatment is used, as a rule, in continuous processes. Desalinated water enters the tank made of a corrosion-resistant material (polyethylene, polypropylene, stainless steel). Desalinated water is supplied from the reservoir to the consumer using a pump made of stainless steel (in some cases, after a reverse osmosis installation, a mixed-action filter is installed on the line). Particular advantages of reverse osmosis are its high environmental safety. Neither acid nor alkali are used here, which drastically reduces the load on wastewater and improves production safety. Examples of the practical application of the method: Drinking water obtained from sea and brackish water – Cooling water – Air purifiers – Feed water for boilers – Humidifiers – Sterilizers [32].

Membrane separation on reverse osmosis or nanofiltration membranes is widely used in everyday life and technology. However, the theory of such a separation is still much unclear and systematic theoretical and experimental studies are required. The diffusion of alkali metal and ammonium chlorides through an OPMN – KMZ composite nanofiltration membrane depending on the electrolyte concentration on both sides of the membrane was studied [33]. A model is proposed for calculating the diffusion coefficients, taking into account the change in the electrolyte concentration in the selective pores of the film. The diffusion coefficients are calculated in the framework of the proposed model and using the Fick equation. The influence of the orientation of the membrane with respect to the diffusion flux on the diffusion coefficients of salts is analyzed.

The solution to the problem of environmental pollution by heavy metal compounds is possible on the basis of a radical change in existing approaches to wastewater treatment systems, as well as in the creation of local block-modular systems based on the latest achievements of science and technology in this field. Improving the water supply and sanitation systems of galvanic production is associated with an increase in the effluent treatment efficiency while ensuring the flexibility and reliability of such systems that exclude environmental pollution.

In the process of plating, the bulk of the water falls on washing operations (about 95-98%). It is advisable to return the water from the washing baths after cleaning to the process. The difficulty here lies in the fact that traditional methods of treating such waters require either the use of reagents or the use of sophisticated expensive equipment, for example, ion-exchange or adsorption units and are associated with high energy costs [34]. The disadvantage of reagent methods is the irretrievable loss of valuable components with precipitation. In addition, precipitation is usually carried out by lime, which is why purified water contains a large amount of calcium salts, which makes it difficult to use it in the circulating water supply [35].

Unlike traditional methods, membrane methods look more advantageous and have a number of advantages: compact equipment, simplicity of devices and the ability to increase capacities due to the modular design of the equipment, fairly low energy consumption, full automation of processing and water quality control. However, it should be noted that reverse osmosis membranes require preliminary treatment of water, which consists in the removal of suspended particles, dissolved iron and neutralization of oxidizing agents. The disadvantages include relatively low productivity, increased pressure in the system, which necessitates special equipment seals and the phenomenon of concentration polarization, which leads to a decrease in productivity, degree of separation, and membrane life [34, 35]. The creation of closed water circulation in galvanic production is the most appropriate solution. In this case, as a result of purification of polluted waters, concentrated liquid wastes are formed that are suitable for the further extraction of valuable components. There are several options for organizing drainless galvanic production. Some of them suggest the presence of several non-flowing trap baths, in which the loss of water from evaporation is replenished in the last bath part along the movement. Other methods are based on the use of combined wetting of parts over a working bath, followed by immersion in a trap. Known methods of using water-air and air blowing parts above a plating bath, as a result of which it is possible to reduce the flow rate of wash water several times [36]. Analysis of the state of wastewater treatment in galvanic plants allows us to conclude that the creation of a closed cycle for water and recoverable components is possible using the reverse osmosis method.

The widespread introduction of reverse osmosis is associated with objective difficulties, the main of which are: the creation of highly selective membranes resistant to aggressive fluids; the manufacture of compact reverse osmosis modules that would allow a small volume to concentrate a large area of the membranes; lack of comparative technical and economic tests of various reverse osmosis apparatus as applied to specific tasks of wastewater treatment; lack of recommendations on the optimal areas of application of reverse osmosis apparatus in technological processes of wastewater treatment [34-36]. The solution to these issues is based on comprehensive studies to determine the necessary parameters of the reverse osmotic separation.

The possibility of using the reverse osmosis process for the treatment of wash water containing heavy metal salts was considered [36]. The dependences of the influence of the working pressure on the solution on the separation selectivity are investigated. Based on the obtained dependences, a technology for cleaning the wash water of the galvanic section is proposed.

The most “significant” problem in the operation of reverse osmosis systems is the formation of various deposits on the membranes: primarily calcium carbonate, as well as calcium sulfate, iron hydroxide, colloidal and organic substances. The problem of operating reverse osmosis plants is solved with the simultaneous use of two types of reagents:

– by dosing inhibitors (antiscalants) into the source water. Their role is to slow down the rate of precipitation of carbonate and calcium sulfate;

– using regular chemical washes to dissolve and remove precipitates of calcium carbonate, iron hydroxide, colloidal and bacterial deposits.

Both industrial and laboratory experience has been accumulated in assessing the effectiveness of inhibitors. The properties of inhibitors – various substances capable of an inhibitory effect – were revealed, and the ways of their synthesis and production were outlined [37].

The first reverse osmosis plant in the energy sector of the Russian Federation for the preparation of additional boiler water was put into operation at the Zuevskaya experimental VTI CHPP exactly 20 years ago. The appearance in the energy sector of a new technology for desalination of water, which practically does not require the consumption of reagents and does not pollute the environment, eliminates phase transitions, is relatively simple to manufacture and operate, has caused general interest and hope for a radical improvement in the environmental performance of water treatment plants in power plants.

Twenty years ago, the traditional schemes of water treatment plants based on the use of parallel-flow ion-exchange filters and, sometimes, energy evaporators, were characterized by specific consumption of sulfuric acid in the range of 2.2-3.7 g-equiv/g-equivalent of sorbedcations, caustic soda in the range of 2.5-3.5 g-equiv/ g-equivalent of sorbed anions, sodium chloride in the range of 3.0-4.0 g-equivalent/g-equivalent of sorbedcations of hardness. Environmental and economic problems caused by large overruns of reagents for the regeneration of ion-exchange materials were aggravated by the huge production volumes of demineralized and softened water at domestic power plants. The total capacity of desalination water treatment plants for feeding power boilers was 50 thousand cubic meters per hour, and for feeding the heating system over 100 thousand cubic meters per hour. As a result of a combination of technical imperfection of the water treatment equipment used and the enormous volumes of water production, the total salt discharge from the water treatment plants of power plants amounted to 1.5-2.0 million tons per year [38].

A comparative characteristic of various water treatment methods is carried out [39]. High efficiency of membrane cleaning technologies is emphasized, especially in terms of reducing environmental pollution.

Of the methods of desalination of sea water, the most common are thermal and reverse osmosis methods. The operating experience of thermal desalination plants shows that a significant proportion of operating costs (~ 60%) is accounted for by the thermal component. This circumstance, together with the increase in fuel prices and a decrease in its resources, puts forward the tasks of using secondary energy resources (SER) for the thermal desalination (TD) of sea waters. In the energy sector, emissions of the combustion products of gas turbines, power boilers, and cooling systems of power equipment are of practical interest as SER. The low energy intensity characteristic of the reverse osmosis desalination (OD) method stimulates the development of energy-saving technologies based on a rational combination of OD and TD methods [40].

The technological aspects of combined desalination of sea water based on the methods of reverse osmosis and thermal distillation using SER were studied [40].

Currently, reverse osmosis occupies a leading place in desalting natural waters, it removes ion exchange, evaporation, electrodes, etc. This is due to a number of advantages: low energy consumption, minimal amount of reagents used, relatively low operating costs, and ease of maintenance. However, along with the advantages listed above, which are the basis of reverse osmosis, there are also significant disadvantages: a large number of concentrations are required that must be used, mandatory preliminary preparation of water is required for objective studies in order to fully determine weighty substances, which cannot exceed the cost of capital the cost of the symbol itself [41].

The technology [42] for deep desalination of water with reverse osmosis treatment at the second stage with a degree of conversion of up to 90% was considered. To determine the likelihood of salts precipitating on the membrane, it is proposed to use preliminary ion-exchange softening, the regeneration solution is ready for conversion into a reverse osmosis concentration, which contains sodium ions. All this together allows you to increase the amount of permeate and significantly reduce the amount of concentrated wastewater.

To obtain drinking water in the practice of water and wastewater treatment, coagulation with a low consumption of coagulant is traditionally used, followed by settling or filtering on pressureless filters. Chlorine-based oxidizing agents are traditionally used to disinfect water. But in the case of severe contamination with suspended particles, pesticides, viruses of high color and hardness, such treatment does not allow to obtain water corresponding to Sanitary regulations2.1.4.559-96. In the territory of the Russian Federation, two main classes of water have been identified, which cause difficulties in processing with the aim of obtaining drinking water. The first class includes water from surface sources contaminated with natural technogenic organic impurities. These impurities reduce the organoleptic characteristics of water. In the case of treatment of these waters with strong oxidizing agents (chlorine, ozone), the formation of secondary organic impurities is possible, the maximum permissible concentration of which is extremely low. In some cases, these impurities have carcinogenic properties. The second class of waters includes waters from artesian springs with high salinity. The high mineralization of these waters is caused by the presence of a large number of hardness ions and sulfates, the concentration of which is significantly higher than Sanitary regulations 2.1.4.559-96. Long-term use of such water leads to serious illness. The rapid growth in the importance of membrane technologies based on nanofiltration in the field of drinking water purification and related areas is due to the challenges facing humanity today on a global scale:

– providing the population with drinking water, the quality of which meets the requirements of Sanitary regulations 2.1.4.559-96;

– reduction of natural water consumption due to processing and reuse of generated liquid wastewater;

– minimization of both the volume of liquid effluents arising in the course of economic activity, and the amount of salts discharged into the environment [43].

Ion-exchange membrane materials have come a long way since its inception and the first applications in water treatment in the early 50s. Kazakhstani scientists have made and continue to make a significant contribution to this process [44, 45]. New technical capabilities that have appeared today allow you to penetrate deeper into the structure of ion-exchange materials, to better understand the relationship of the structure with various properties and to find effective ways to improve these materials. The use of hybrid technologies combining baro-, electromembrane, and other processes leads to highly efficient, environmentally friendly and economical productions, where it is possible to carry out closed cycles both in water and in dissolved substances. Today, without membranes, not only production associated with separation processes is unthinkable, but also alternative energy. As the director of Osmonics (USA) D. Paulson said: “The possibilities of using membranes are so great that they are only restrained by our imagination”.

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Резюме

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УЛЬТРА-, МИКРОФИЛЬТРАЦИЯҒА ЖӘНЕ КЕРІОСМОСҚА АРНАЛҒАН ЖАРТЫЛАЙ ӨТКІЗГІШ МЕМБРАНАЛАР

Қазіргі таңда қалдықсыз экологиялық таза технологиялардың басты құрамдас бөлігі ретінде саналатын жартылай өткізгіш синтетикалық мембраналарды синтездеу және қолдану саласындағы теориялық және эксперименттік зерттеулердің нәтижелері қорытыланды. Баромембранды процестер – кері осмос, ультра және микрофильтрация үшін оларды алу тәсілдері қарастырылды. Полимерлеу немесе әртүрлі мономерлерді поликонденсациялау және дайын мембраналардың химиялық модификациясы әдістерімен синтезделген жартылай өткізгіш полимерлі мембраналардың пайда болу механизмі мен кинетикасының ерекшеліктері талқыланды. Олардың селективті өткізгіштігін, физика-механикалық және электрохимиялық қасиеттерін арттыру бойынша зерттеу нәтижелері алынды.

Су дайындаудың өзекті проблемаларын шешу үшін оларды практикалық қолданудың перспективалы бағыттары анықталды, құнды компоненттерді ала отырып, өнеркәсіптік өндіріс ағындарын қайта өңдеу, жоғары қысым мен масса алмасу қарқынды режимдері кезінде газ және сұйық қоспаларды бөлу.

Түйін сөздер: мембрана, фильтрация, баромембраналы процесс, кері осмос, кеуек.

Резюме

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ПОЛУПРОНИЦАЕМЫЕ МЕМБРАНЫ ДЛЯ УЛЬТРА-, МИКРОФИЛЬТРАЦИИ И ОБРАТНОГО ОСМОСА

Обобщены результаты теоретических и экспериментальных исследований в области синтеза и применения полупроницаемых синтетических мембран, как главной составляющей современных безотходных экологически чистых технологий. Рассмотрены способы их получения для баромембранных процессов − обратный осмос, ультра- и микрофильтрации. Обсуждены особенности кинетики и механизма образования полупроницаемых полимерных мембран различных типов, синтезированных методами полимеризации или поликонденсации различных мономеров и химической модификацией готовых мембран. Представлены ре-зультаты исследований по повышению их селективной проницаемости, физико-механических и электрохимических свойств.

Определены перспективные направления их практического применения для решения актуальных проблем водоподготовки, переработки стоков промышленных производств с извлечением ценных компонентов, разделения газовых и жидких смесей при высоких давлениях и интенсивных режимах массопереноса.

Ключевые слова: мембрана, фильтрация, баромембранный процесс, обратный осмос, поры.