

SUMMARY
of the PhD thesis on the specialty 6D060600 – Chemistry
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“Hydrophobization of track-etched membranes based on poly(ethylene terephthalate) for water treatment by membrane distillation”

General characteristics of the dissertation research

This work is devoted to the study of modification methods of track-etched membranes (TeMs) based on polyethylene terephthalate (PET) in order to obtain hydrophobic membranes and control the colloid-chemical properties of the surface, the study of their physicochemical properties and testing in the processes of membrane distillation for the purification of natural and waste water from salts, pesticides and low-level liquid radioactive waste.

The dissertation work is presented in the form of a series of articles published by a doctoral student in accordance with the requirements of paragraph 5-1 of the Rules for awarding degrees, approved by order of the Minister of Education and Science of the Republic of Kazakhstan dated March 31, 2011 No. 127 (registered in the Register of State Registration of Normative Legal Acts under No. 6951) with the change, introduced by the order of the Minister of Education and Science of the Republic of Kazakhstan dated April 30, 2020 No. 170 and in accordance with the order of the Minister of Education and Science of the Republic of Kazakhstan dated March 09, 2021 No. 98.

Topicality of the research

In connection with the growing problem of shortage of drinking water in the world, including in Kazakhstan, research on methods for obtaining and purifying water is becoming extremely relevant.

The main water pollutants are oil and oil products, surfactants, pesticides, phenols, heavy metals, dioxins, etc. In addition, there is the problem of purification and concentration of radionuclides in liquids of both natural and anthropogenic nature (nuclear reactors, Semipalatinsk nuclear test site). Among the methods of water purification, a special place is occupied by membrane processes, characterized by low energy consumption, high selectivity and efficiency.

Membrane distillation (MD) is a process for purifying and/or concentrating liquid media based on vapor permeability and liquid impermeability of a membrane.

There are various types of membranes used for cleaning purposes: isotropic, anisotropic, composite; flat, tubular, fiber; braided, sintered or molded. Most of the works are devoted to the study of fibrous membranes in MD processes. However, track-etched membranes (TeMs) based on polyethylene terephthalate (PET) produced in Nur-Sultan also have a high potential for use in MD, since TM are characterized by a regular pore geometry with the ability to control their number per unit area and a record narrow distribution of pores over sizes. All this ensures high membrane selectivity.

The main characteristics of PET are high strength and optical characteristics, low swelling and shrinkage, and thermal stability. However, these parameters are

not universal advantages for all applications. The effective use of PET TeMs in MD requires a significant expansion of the range of their characteristics (pore structure, hydrophobicity/hydrophilicity, creation of special chemical groups on the surface). Thus, the development of methods for the directed modification of PET TeMs with the preservation of the pore structure in order to obtain membranes with desired physicochemical properties and performance characteristics is an important scientific and technical task.

The degree of development of the problem. For the first time, the term "membrane distillation" appeared in the patent of B. Bodell and in the work of M. Findley in 1967, various materials (aluminum foil, cellulose paper, glass) were investigated and requirements were established for them for the direct contact membrane distillation process [1,2].

Alhudhiri's paper considers the types of membrane distillation configurations and membrane characteristics. The review showed the need to collect data from large-scale studies, develop membranes with high hydrophobic properties and further study the influence of operating parameters [3].

Hydrophobicity is a basic membrane property that plays an important role in the membrane distillation process. Mainly membranes with large contact angle (over 90°) and LEP over 2.5 bar are used.

The authors of [4] studied the possibilities of using nanofiber membranes obtained by electrospinning. Low selectivity, the thickness of the membrane used adversely affects the thermal conductivity.

The use of microporous hydrophobic nanofiber PVDF membranes was studied by Simone [5]. Among the disadvantages, it is worth noting the low selectivity of membranes and productivity, as well as the gradual contamination of the membrane surface.

The authors studied the modification of polyethersulfone (PES) membranes by the sol-gel method [6]. The low performance of the membranes is explained by the uneven hydrophobic coating

A number of authors proposed the modification of PES membranes made of polyacrylonitrile (PAN) by plasma treatment in an atmosphere of carbon tetrafluoride [7,8]. The main disadvantage is the high toxicity and corrosiveness of fluorine ions.

The modification of PES and PVC membranes by radiation graft polymerization was studied in the works of Tooma and Liu [9,10]. The need for membrane distillation using vacuum is a major disadvantage.

To date, there are no works devoted to the use of track-etched membranes in membrane distillation. A characteristic feature and advantage of track-etched membranes is the regular geometry of pores with the ability to control their number per unit area and a narrow pore size distribution, small thickness, which will solve the problems of selectivity and productivity.

The object of the research. The objects of study are track-etched membranes based on polyethylene terephthalate (PET TeMs), chemical reactions on the membrane surface: polycondensation of silanes (dichlorodimethylsilane and perfluorododecyltrichlorosilane), UV-graft polymerization reactions of

triethoxyvinylsilane, styrene, immobilization of hydrophobic nanoparticles based on silicon oxide on the membrane surface, physicochemical properties of modified track-etched membranes.

The aim of the research. The aim of this work is to develop methods for directed surface modification of TeMs to control their chemical and hydrophobic properties and to study them in membrane distillation processes for the purification of model solutions and wastewater.

The objectives of the dissertation research. In the course of the dissertation work, the following tasks were set and solved:

- general patterns of increasing the hydrophobicity of track-etched membranes based on polyethylene terephthalate

- study of the patterns of changes in the physicochemical properties of track-etched membranes based on polyethylene terephthalate (wetting contact angle (CA), liquid entry pressure (LEP), the degree of grafting) on the conditions of the polycondensation reaction of silanes (dichlorodimethylsilane and perfluorododecyltrichlorosilane) on the membrane surface

- patterns of changes in the physicochemical properties of track-etched membranes based on polyethylene terephthalate on the conditions of the UV-photoinitiated grafting polymerization of styrene and triethoxyvinylsilane on the membrane surface

- patterns of changes in the physicochemical properties of track-etched membranes based on polyethylene terephthalate with a simultaneous change in the chemical composition of the surface and the roughness of the membranes by immobilizing hydrophobic nanoparticles based on silicon oxide on the membrane surface

- identification and determination of the structure of compounds modified on the surface of membranes, determination of the contact angle (CA), liquid entry pressure (LEP), degree of grafting using a complex of instrumental physicochemical methods of analysis: ultraviolet (UV) spectroscopy, infrared (FTIR) spectroscopy, XPS, energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM)

- study of modified membranes in the purification of water from salts, pesticides and liquid radioactive waste by the MD method in the direct contact mode.

The scientific novelty. The scientific novelty of the dissertation research is as follows:

- for the first time, in order to increase hydrophobicity, the reaction of polycondensation of silanes (dichlorodimethylsilane and perfluorododecyltrichlorosilane) on the surface of track-etched membranes was studied. The main factors influencing the degree of grafting, the change in pore diameters, CA and LEP, the mechanism of the polycondensation reaction have been established;

- for the first time, in order to increase hydrophobicity, UV-photoinitiated graft polymerization of triethoxyvinylsilane, styrene, on the surface of track-etched membranes based on polyethylene terephthalate was studied. The main factors influencing the degree of grafting, the change in pore diameters, CA and LEP, the

mechanism of the polymerization reaction on the membrane surface have been established;

- for the first time to increase the hydrophobicity of the membrane, the method of coating its surface with silicon nanoparticles with vinyl groups was applied. The thermal initiator fixed on the membrane surface made it possible to attach silicon nanoparticles to the membrane surface by forming covalent bonds.

- for the first time, modified track-etched membranes based on polyethylene terephthalate were used in membrane distillation processes for water purification from NaCl, pesticides and radionuclides.

Statements for the defense:

- polycondensation of silanes (perfluorododecyltrichlorosilane and dichlorodimethylsilane) on the surface of track-etched membranes based on polyethylene terephthalate under reaction conditions of a 20 mM solution of perfluorododecyltrichlorosilane in 2-propanol, reaction time - 24 h provides a high degree of membrane hydrophobization, while the value of the contact angle (CA) is $109 \pm 5^\circ$, liquid entry pressure (LEP) - 3.4 bar, pore diameter up to 210 nm;

- the optimal parameters for the reaction of UV-photoinitiated graft polymerization of triethoxyvinylsilane (TEVS) are: 20% solution of TEVS in dichloroethane with the addition of N-vinylimidazole in an amount of 3.3%, reaction time - 1 hour, distance to the UV source - 10 cm. In this case, an increase in the liquid entry pressure - LEP > 4.3 bar with pore diameters of 200 nm, the contact angle reaches values up to $105 \pm 5^\circ$, which is slightly less than for silanes ($109 \pm 5^\circ$);

- the optimal parameters for carrying out the styrene polymerization reaction are: styrene concentration - 40%, reaction time - 1 hour, distance to the UV source - 7 cm. The CA was 99° , with a pore diameter of ~ 210 nm, the LEP value was 3.4 bar;

- simultaneous change in the chemical composition of the surface and the roughness of the membranes by immobilizing hydrophobic nanoparticles based on silicon oxide on the membrane surface provides the highest degree of hydrophobization with an increase in the CA up to 125° with a pore diameter of 315 nm, the LEP value was 3.5 bar;

- the use of obtained PET TeMs with a regular pore geometry with the ability to control their number per unit area and a record narrow distribution of pores by size, as well as with sufficiently high values for LEP and CA (LEP > 2.5 bar, CA > 90°) provides high selectivity of membranes in the processes of water purification from salts, pesticides and radionuclides by the MD method.

- results of the application of track-etched membranes hydrophobized with silanes, triethoxyvinylsilane, polystyrene, immobilization of silicon nanoparticles on the membrane surface for water purification from sodium chloride. A comparative analysis of the productivity and degree of water purification from salts showed that the membranes obtained by the immobilization of silicon nanoparticles have the highest productivity value ($15000 \text{ g/m}^2 \cdot \text{h}$) and the degree of purification ($\sim 93\%$) with a pore diameter of ~ 315 nm. With pore diameters of 200 and 250 nm, the productivity was 2200 and $6500 \text{ g/m}^2 \cdot \text{h}$, and the degree of purification was 99% and 98%, respectively;

- the results of the application of track-etched membranes modified with polystyrene for the treatment of low-level liquid radioactive waste of the second cooling circuit of the WWR-K research reactor (Institute of Nuclear Physics, Almaty). The decontamination factor for membranes with a pore diameter of 220 nm was >85 for ^{60}Co , >1727 for ^{137}Cs , and 5 for ^{241}Am . According to the degree of purification, the obtained membranes surpassed commercial nanofiber PTFE membranes by 4 times.

Practical significance of the research outcomes:

The established patterns of changes in the physicochemical properties of membranes depending on the conditions of chemical reactions of polycondensation, polymerization, and immobilization of hydrophobic silicon nanoparticles on the membrane surface expand and deepen the understanding of membrane modification and are a significant contribution to the theory and practice of directed surface modification of track membranes. Four modifications of track-etched membranes based on polyethylene terephthalate have been obtained. The resulting membranes were tested in the purification of aqueous media from salts, pesticides, low-level liquid radioactive waste by membrane distillation. Treatment of water from low-level liquid radioactive waste obtained from the second circuit of the WWR-K reactor at the Institute of Nuclear Physics (Almaty) with the help of MD will, in the long term, make it possible to overcome the problem of burying a large amount of low-background liquid radioactive waste from nuclear reactors and concentrate them by volume. The results of these studies are a significant contribution to solving the problem of lack of drinking water and environmental pollution.

Personal contribution of the PhD student consists in planning, direct execution of the experimental part of the work, processing and interpretation of the data obtained. The results of studying the surface of modified membranes by SEM and AFM methods were discussed jointly with employees of the technological laboratory of track membranes and the laboratory of solid state physics of the Astana branch of the Institute of Nuclear Physics of the Ministry of Energy of the Republic of Kazakhstan. The study by X-ray photoelectron spectroscopy was carried out at the Ural Center for Collective Use "Modern Nanotechnologies". The results obtained were discussed jointly with the supervisor and a foreign consultant.

Relationship of work with research programs. The work was carried out within the framework of the grant funding project AP05132110 "Obtaining track membranes with desired properties for membrane distillation and direct osmosis" (2018-2020).

Approbation of the thesis outcomes. The results of the dissertation research were presented at the international scientific conference "Global science and innovations IV", (Sofia, Bulgaria, 2018), at the XIV International scientific conference of students and young scientists "Science and education – 2019", (Nur-Sultan, Kazakhstan, 2019), at the III Forum of young scientists "Burabay Forum: international cooperation of Kazakhstan", (Nur-Sultan, Kazakhstan, 2019), at the 20th international conference "Radiation Effects in Insulators" (Nur-Sultan, Kazakhstan, 2019), at the I International School-Conference "Atom. Science.

Technologies” (Almaty, 2021), at the III International Scientific Forum “Nuclear Science and Technology” (Almaty, 2021).

Publications. The main results of the dissertation research were published in 14 printed works that fully correspond to the topic of the dissertation research, of which 5 articles (including 1 review article) in peer-reviewed scientific journals with a non-zero impact factor included in the Scopus and Web of Science databases (Polymers - (IF- 4.329, Q1), Separation and Purification Technology - (IF-5.774, Q1), Progress in Nuclear Energy (IF-1.508, Q2), Chemical Papers (IF-1.68, Q3), Membranes (IF-3.094, Q2):

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5. Korolkov I.V, Kuandykova A., **Yeszhanov A.B.**, Güven O., Gorin Y.G., Zdorovets M.V. Modification of PET Ion-Track Membranes by Silica Nanoparticles for Direct Contact Membrane Distillation of Salt Solutions // Membranes – 2020. – Vol.10(11):322. – P.1-15 **(IF-3.094, Q2)** <https://doi.org/10.3390/membranes10110322>

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