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Separation of Water/Organic Mixtures Using Micro- and Nanostructured Membranes of Special Type of Wettability

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***Abstract*—**Both hydrophilic-oleophobic and hydrophobic-oleophilic membranes were obtained by coating of the substrate of membranes, presented by stainless steel meshes with various dimensions of their openings, with a composition that forms the special type of their surface wettability via spray-coating method. The surface morphology of resulting membranes was studied using SEM, the type of their wettability was identified by measuring the contact angle between the surface of membrane and a drop of studied liquid (water or organic liquid) and efficiency of continuous separation of water and organic liquid was studied on self-assembled setup.

***Keywords*—**Membrane, stainless steel mesh, oleophobicity, hydrophobicity, separation, water, organic liquids**.**

I. Introduction

SEPARATION of water and organic liquids is an important area not only in scientific view, but also in economic, social and environmental views [1], [2]. It is known that wastewater contaminated with organic pollutants, formed as a result of large-scale production of steels, aluminum, food, textiles, and petrochemicals is the largest pollutant to date [3]. At the same time, the notorious oil spills on the surface of water carry both a huge environmental threat and a large loss of energy [4].

In recent years, the phenomenon of wettability of the surface in the separation of water and organic liquids started to play an important role. Wettability is an inherent property of a solid surface, which determines the phenomenon of wetting the surface upon contact with the liquid. In the synthesis process it is possible to obtain materials with a specific type of wettability (superhydrophobic, superhydrophilic, superoleophobic, superolephilic) by varying the structure and composition. In this case, surfaces for special purpose can be obtained by usual combination of these properties. Summarizing the literature data, materials for controlled separation of water and organic liquids depending on the type of their wettability can be divided into two broad groups: materials that remove organic liquids from a mixture of “organic liquid - water” (hydrophobic) and materials that remove water from a mixture of “water - organic liquid”.

Typically, mesh structures (metal or polymeric) are used as the basis for creation of micro-porous filters. Superhydrophobic and superolephilic membranes were obtained in [5], [6] by etching a metallic mesh in acids (monoalkylsulfonic) at which nano-flakes of lamellar crystals were formed as a result of self-assembly of alkylphosphonates. These membranes have shown high efficiency in the separation of water and organic liquids.

Polyurethane and melamine surfaces can be used as polymer networks, which are coated with a certain composition that forms the type of its wettability. In [7], the authors coated polyurethane membrane with polystyrene microspheres, which increased its degree of hydrophobicity and oleophilicity, thus making it possible to use it in the separation of water and organic liquids.

Metal meshes, such as stainless steel and copper meshes formed by metal fibers, can be used as semipermeable barriers with a porous structure. Due to their strong mechanical properties, their simplicity of production, excellent performance and adjustable pore size, metal mesh membranes have always been of great scientific interest. To achieve the desired separation efficiency of a mixture of oil and water, the metal mesh must have selective permeability to water or oil due to increased wettability. As a rule, membranes of a metal mesh with special wettability are obtained by forming a micro-nanostructure and modifying the surface of a metal mesh substrate, which can enhance the surface roughness and enhance its wetting [8].

Materials that remove organic liquids from the "water-organic liquid" mixture can be obtained by two methods: chemical modification of porous surface by substances with a specific wettability and creation of a porous structure of a material with a specific wettability. The aim of this research is focused on obtaining membranes of special type of their wettability by spray-coating the substrate of membrane with compositions, which form their type of wettability and study their water-organic liquid separation efficiencies. For creation of hydrophilic-oleophobic membranes the composition based on poly(diallyldimethylammonium) chloride (PDDA) with additions of nanostructured particles of SiO_2 was used and for hydrophobic-oleophilic membranes the composition based on polytetrafluoroethylene (PTFE) was used [9], [10].

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II. Experimental

A. Synthesis of Hydrophilic-Oleophobic Membranes Based on PDDA with Addition of Nanostructured Particles of SiO_2

To obtain a hydrophilic-oleophobic compound, silica particles (0.1 g) were dispersed in an aqueous PDDA solution (35 ml, 1 mg/ml) by ultrasonic treatment for 30 minutes. After creating a homogeneous dispersion of silicon dioxide particles in the PDDA solution, 8 ml of a 0.1 M solution of the ammonium salt of pentadecafluorooctanoic acid was added dropwise with constant stirring. When a certain concentration of the ammonium salt of pentadecafluorooctanoic acid in the mixture was reached, a pulp precipitate was formed due to the coordination of the anions of the ammonium salt of pentadecafluorooctanoic acid with the quaternary amine groups of PDDA. The resulting precipitate was repeatedly washed with distilled water and dried at room temperature.

A certain amount of a dried compound based on PDDA, pentadecafluorooctanoic acid with the addition of particles of silicon dioxide was dissolved in ethanol (95%), after which the resulting mixture was applied to a substrate - a pre-cleaned metal mesh with specific openings sizes by spray-coating methods. The mesh coated with the compound was dried at room temperature for 2 hours until ethanol was completely evaporated, after which it was exposed to microwave air plasma (50 W) for one minute with the formation of polar hydrophilic groups on the membrane surface to enhance the hydrophilic-oleophobic effect.

B. Synthesis of Hydrophobic-Oleophilic Membranes Based on PTFE

Teflon was selected to create a hydrophobic compound that is applied to the substrate of the membrane. A homogeneous emulsion containing Teflon - PFTE 30 wt. %, adhesive - PVA, 10 wt. %, dispersant - polyvinyl acetate, 8 wt. %, surfactant - sodium dodecylbenzenesulfonate, 2 wt. % and diluent - distilled water, 50 wt. % was prepared. The starting reagents were mixed in a proportional amount by stirring until the mixture was completely homogenized.

When applying a hydrophobic-oleophilic compound to a metal mesh by spraying, a spray gun was used. A mixture under pressure of 0.2 MPa sprayed with a thin film to the surface of the metal mesh. Then, the samples were heated at 350 °C in an electric furnace for 30 minutes for thermal decomposition of the adhesive and dispersion agent, after which a thin film of a hydrophobic-oleophilic reaction component remained on the surface.

C. Study of the Efficiency of Separation of Water/Organic Liquids by Obtained Membranes

The efficiency of separation of water and organic liquids by the obtained hydrophilic-oleophobic membranes was studied on an assembled setup, which consisted of two fittings screwed into each other and glass tubes attached to them. The membrane with the size less than the internal diameter of the fittings was placed in the internal cavity of fitting, where it was tightly sealed. The fittings were tightened, thereby ensuring the tightness of the entire system to eliminate the slightest smudges (Fig. 1).

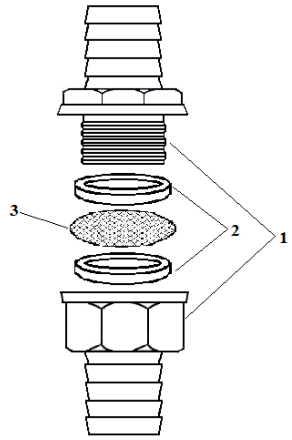

Fig. 1 Installation for determining the efficiency of separation of water and organic liquids obtained hydrophilic-oleophobic membranes where 1 is fittings, 2 is rubber seals, 3 is obtained membrane

III. Results and Discussion

Fig. 2, which shows the surface morphology of the membrane based on a stainless steel mesh 200 coated with the PDDA/SiO_2 compound, shows that in this case the coating is uniform along all the wires that make up the grid framework. With an increase, it is seen that the PDDA/SiO_2 compound forms a large number of globules and protrusions, which can favorably affect the membrane oleophobicity.

Fig. 3 presents SEM images of the surface of a membrane based on a stainless steel mesh 200 coated with a hydrophobic-oleophilic compound based on PFTE by spray-coating method. Figure shows that the hydrophobic-oleophilic compound is evenly distributed along the entire surface of the membrane substrate; some protrusions that reduce the actual size of the holes of the membrane base are seen. The coating has globular formations, tightly adjacent to the surface of the wires of the membrane base.

To determine the quality of the coating of the substrate with the developed compounds, the wetting angle of the surface of the obtained membrane with a drop of the studied liquid (water or organic liquid) was measured. For this, a drop of liquid was applied to the surface of the membrane, after which the contact angle between the drop and the surface of the membrane was measured (Fig. 4).

Table I presents data on the wetting angles of the synthesized membranes. The table shows that membranes based on stainless steel meshes coated with PDDA/SiO_2 exhibit hydrophilic-oleophobic properties. The membrane based on the mesh 400, which has smaller dimensions of its openings than mesh 200, exhibits the greatest oleophobicity, the contact angle between its surface and a drop of organic liquid is 116 °, while water passes through it easily. On the other hand membranes coated with PTFE are hydrophobic, the wetting angles of their surfaces is up to 145°. At the same time, the synthesized membranes exhibit high oleophilicity, a drop of organic liquid does not stay on the membrane surface, passing through it.

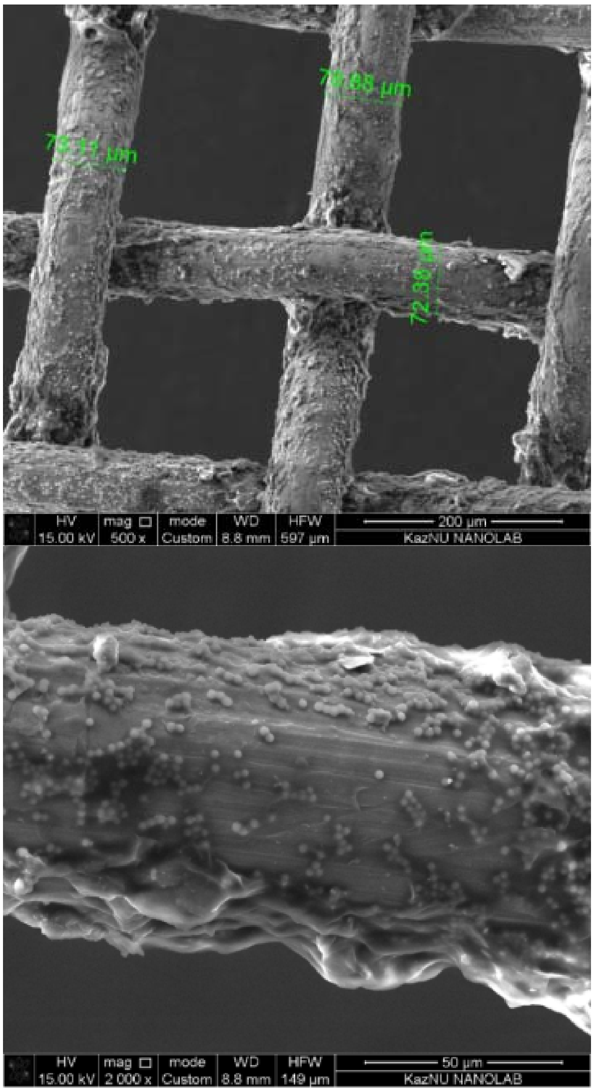

Fig. 2 SEM images of the surface of membranes based on a stainless steel mesh 200 coated with PDDA/SiO_2

TABLE I
VALUES OF WETTING ANGLES OF THE SYNTHESIZED MEMBRANES

Type of mesh	Membrane wetting angle depending on the coating composition, organic liquid / water, °	
	PDDA/SiO_2	PTFE
Stainless steel mesh 200	103/-	-/131
Stainless steel mesh 400	116/-	-/145

To study the process of separation of water and organic liquids using the obtained membranes, the setup was assembled. The setup consists of two metal fittings into which glass tubes are tightly inserted (for visualization of the process of separation of water and organic liquids) with a diameter of 10 mm A membrane with a diameter of 10 mm is inserted into the cavity between the two fittings, where it is tightly fixed with rubber seals. As a result, a cavity with a diameter of 6-7 mm is formed, on the surface of which there is a contact of water and organic liquid with the membrane.

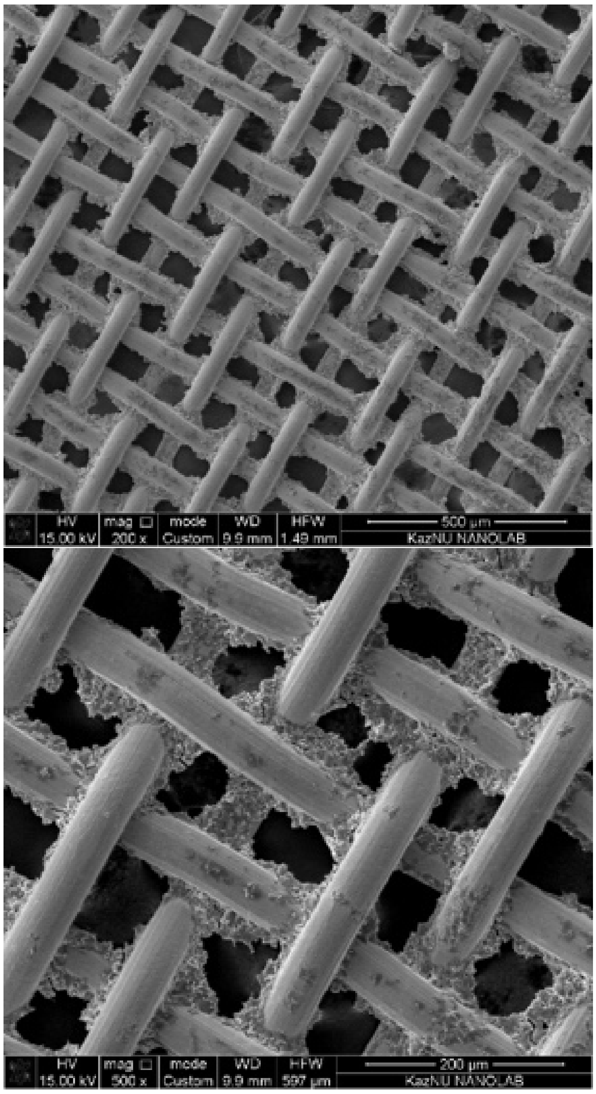

Fig. 3 SEM images of surface morphology of membranes based on stainless steel mesh 200 coated with PTFE

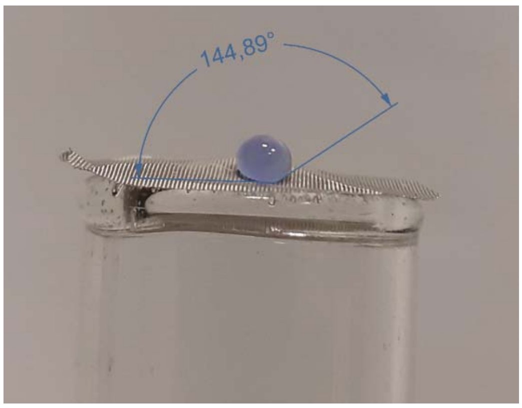

Fig. 4 The wetting angle of the membrane based on a stainless steel mesh 200 coated with PTFE

Fig. 5 shows the process of separation of water and kerosene, dyed with a special dye for organic liquids "Sudan", by a hydrophilic-oleophobic membrane based on a mesh 400 coated with PDDA/SiO_2 compound. It can be seen from the figure that this membrane effectively transmits water (20 ml of water in 4-5 seconds); however, after complete passage of water, this membrane does not pass kerosene through its structure.

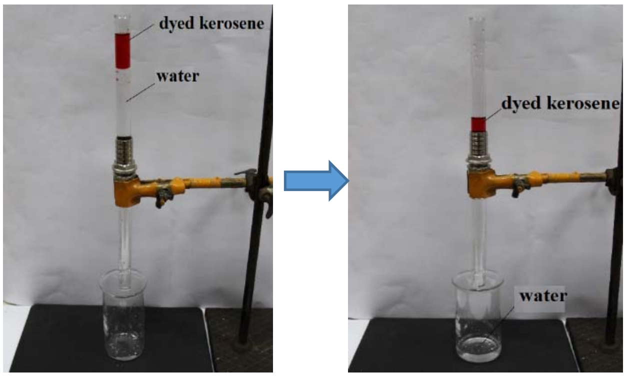

Fig. 5 The process of gravitational separation of water and organic liquid using hydrophilic oleophobic membranes

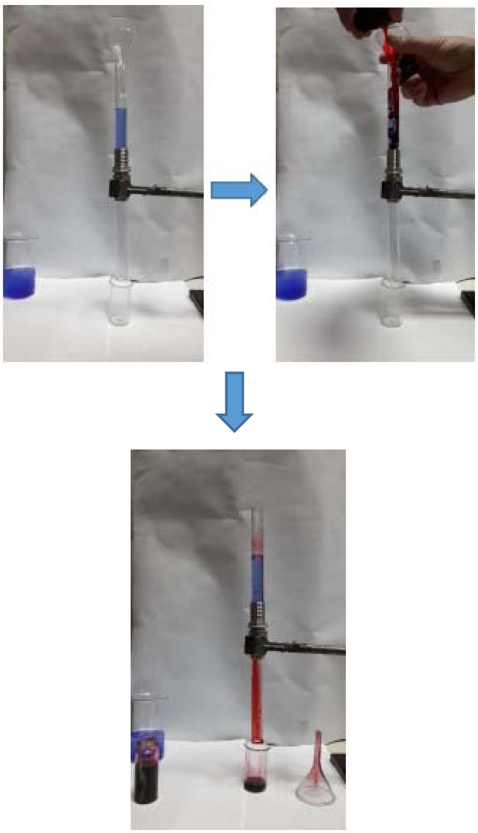

Fig. 6 Study of the efficiency of separation of chloroform and water by a hydrophobic oleophilic membrane based on a stainless steel mesh of grade 400, coated with PTFE

In the case of chloroform, whose density is higher than water, it is clearly seen that it displaces water and sinks to the bottom of the system. Wetting the membrane chloroform passes through it at high speed due to its oleophilicity. After complete passage of chloroform through the membrane, it is clear that water repelled by its surface due to the formed hydrophobicity, not passing through the membrane (Fig. 6).

A mixture of water and organic liquid was fed from above through a glass tube into the assembled setup, after which the liquids decomposed in densities, i.e. water, having a higher density than that of an organic liquid, fell down, contacting and wetting the membrane. The efficiency of separation of water and organic liquids by membranes was determined by the rate of separation of measured volumes of liquids and the presence of organic liquid in the receiving tank after complete separation.

Investigation of efficiency of gravitational separation of water and organic liquids showed that a membrane based on stainless steel mesh 400 coated with PDDA/SiO_2 exhibits excellent hydrophilic and oleophobic properties. The flow rate of 20 ml of water is 4-5 seconds (as with a mesh-based membrane 200); however, this membrane does not pass through its structure kerosene. The passage of 10 ml of kerosene through the membrane was not observed within 40 minutes of pressure of a liquid column on its surface. At the same time, the passage rate of 10 ml of oil decreased to 20-21 minutes. A membrane based on stainless steel mesh 400 coated with PFTE exhibits a high degree of hydrophobicity. It was experimentally confirmed that it practically does not pass water; the waiting time was 2 hours, while the presence of water in the receiving tank was not visually observed. Moreover, this membrane exhibits oleophilicity - the passage rates of 10 ml of chloroform and kerosene were 90 and 50 seconds, respectively.

IV. Conclusion

The membranes of special type of wettability based on stainless steel meshes spray-coated with developed compositions were obtained. The surface morphology of membranes is presented by rough structure, with formed protrusions and pores influencing on their wetting properties. The efficiency of separation of organic liquids from mixture of water and organic liquids of hydrophilic and oleophobic membrane coated with PDDA/SiO_2 is following: the flow rate of 20 ml of water through the membrane is 4-5 seconds, while the passage of 10 ml of kerosene through the membrane was not observed within 40 minutes of pressure of a liquid column on its surface, the passage rate of 10 ml of oil decreased to 20-21 minutes. In case of hydrophobic and oleophilic membrane coated with PTFE the results of study of their oil/water separation efficiencies are following: it practically does not pass water, the waiting time was 2 hours, while the passage rates of 10 ml of chloroform and kerosene through it were 90 and 50 seconds, respectively. We believe that these materials are perspective candidates for complex and continuous separation of water and organic liquids.

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