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Distillation of Petroleum Products from Water by Hydrophobic Membranes

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ABSTRACT

Distillation of petroleum products by means of microfiltration hydrophobic membranes with a pore of 0.47 microns size on running installation with selection of a filtrate for the quantitative chemical analysis was studied. Hydrophobic membrane made of polytetrafluoroethylene (PTFE) and hydrophilic nylon membrane was used to separate of petroleum products. Nylon membrane was kept in toluene to give hydrophobic properties before distillation. 1:1 mixture of tetrachloromethane and water and 1:1 mixture of hexane and water have been separated. Membrane distillation experiments were conducted at working pressure 0.1 MPa and temperature was 25° C. Tetrachloromethane flow speed through the PTFE membrane was 14.4 cm3/cm2min, through the nylon membrane was 13.8 cm3/cm2min. Hexane is lighter than water, as is known, and between membranes and hexane is layer of water. To bring the hexane to the membrane surface through the layer of water, mixture mixed at a speed of 1000 rpm during the filtration. Filtration speed during passing hexane through PTFE membrane was 9.6cm3/cm2min, for nylon membrane filtration speed was 3.1 cm3/cm2min. Optimal parameters of membrane separation processes were chosen. Oil products content in water after filtration were was studied. The initial concentration of oil products was 500 g/dm3.Residual content of oil products during filtration of hexane-water mix through PTFE membrane is 1140 mg/dm3, and for nylon membrane is 1230 mg/dm3. Residual content of hydrocarbons in water is associated with dissolution of hexane and formation of an emulsion hexane in water as a result of mixing during filtration.

Keywords: Membranes, polytetrafluoroethylene, nylon membrane, Emulsions

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Introduction

Petroleum products are the most common pollutants of sewage - group of hydrocarbons of petroleum, fuel oil, kerosene, oils and their impurity. According to UNESCO, there are among the most dangerous environmental pollutant because of their high degree of toxicity. Petroleum products can be emulsifying, dissolved in solution and to form a floating layer on water surface.

The main sources of petrol and oil products pollution are extractive enterprises, transfer and transportation systems, oil terminals and oil base, storages of oil products, railway transport, river and sea oil tankers, petrol complexes and stations. Also oil products enter on surface water from activity of petrochemical enterprises and from using lubricating and cooling fluid in metalworking. The volume of waste from oil products and oil pollution that has accumulated on individual objects stand at ten and hundred thousands of cubic meters.

Traditional methods of sewage purification, that contains oil products, such as flotation, water precipitation, coagulation and filtration don't meet the increased requirements for degree of sewage purity. That is the reason that oil products transferring into surface water and, as a consequence, substantial pollution of environment objects [1].

Purification of oil-containing sewage must fulfill the following requirements: extraction of valuable impurities for use for the intended purpose, use of the purified sewage in technological processes, a minimum release of wastewater into water reservoir. Membrane methods of cleaning of oily water have such properties among existing methods [1-7]. Membrane technology is one of the most perspective branch of chemical technologies to solve a number of important practical tasks. Membrane methods are based on division of the homogeneous or heterogeneous mixes consisting of two or more components by means of membranes, under the influence of the driving force applied to system. Membrane division is carried out without phase transformations, and energy is spent, generally for creation of pressure of initial solution, his movement in the device and breakdown through a membrane [8].

For improvement of selective properties and productivity of membranes carry out chemical, physical and physical and chemical modification of the last. For improvement of water repellency and hydrophily treat one of types of chemical modification of membranes: processing of membranes various reagents, for example, solutions of acids, alkalis, amines, and also solutions of chemically active polymers. Water repellency the membrane is given processing of the last, in particular, benzene, toluene, nitrobenzene that are used when cleaning water environments of oil and oils. Hydrophily of membranes, and with it water penetration are raising after processing of membranes substances with a low superficial tension, such as surfactants solutions, acetone, alcohols, air, polyethyleneglycol, and others.

The hydrophilic type of membranes has the high superficial potential caused by violation of power balance of intermolecular forces in a polymeric matrix of a membrane with formation of limit of the section of phases at her contact with water and education on a surface of a membrane of a layer of the connected water which physical and chemical properties strongly differ from water in a free state. At hydrophobic membranes superficial potential or very low, or opposite polarization. Their surface isn't moistened with water – on the contrary molecules of water gather in discrete balls which easily roll down from a membrane surface. Than less superficial tension of liquid and the more superficial tension of material of a membrane the is thicker and stabler the connected layer on her surface. The superficial tension of multicomponent solutions isn't additive and can cause a stir from a superficial tension of free liquids considerably. Microparticles are potential pollutants of membranes, in the water environment usually gidrofobna, for example: hydroxides of iron and aluminum; compounds of silicon, humic and fulvic acids; colloidal polysaccharides; molecular units with a diameter of 10^{-7}-10^{-9} m in the form of emulsions or suspensions, oils, paraffin, surfactant, greasings [9].

In work [10] division of emulsions oil in water with use of two membranes with different water repellency is investigated. The variation of water repellency of membranes is carried out at their chemical modification that allows to optimize process of division owing to specific interaction between a membrane and components of emulsions. Modification of chemical structure of methylcellulose membranes 1,2 epoxybihexyl is analysed by methods X-ray electronic and IK-spectroscopy with Fourier transformation.

It is known what hydrophobic microfiltration membranes can be used for an oil emulsion deemulsation in water owing to a koalestsention of droplets of oil in a membrane time. On result of researches conclusions are drawn that hydrophilic polymeric membranes can be used for a deemulsation of the surfactant-stabilized oil emulsions in water. It is defined that the deemulsation depends on type of an emulsion and a membrane [11].

In work experiments on membrane division of the regenerated oils with a pressure in the pressure head channel of 0.1-0.5 MPa, temperature of 40-140 °C and the speed of 1-3 m/s were made. Optimum parameters of process of membrane division are picked up. The clarified engine oil on polymeric, ceramic-metal and carbon membranes is received. It is shown that degree selectivity on monoethanol amine and asphaltic compounds of engine oil depends on material of a membrane and the sizes of the applied membranes [12, 13].

RESULTS AND DISCUSSION

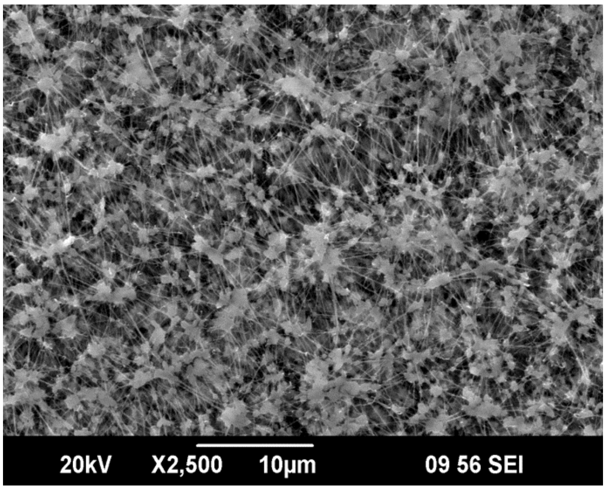
In the present scientific work researches of process of division of the following water-oil product mixes are conducted: water-tetrachlormethane, water-hexane in the ratio 1:1 by means of polymeric microfiltration membranes.

For membrane division of mixes water-oil product used microfiltration membranes from a politetraftoretilen (PTFE) and nylon of Phenex Filter Membranes firm. Characteristics and properties of membranes are presented in table 1. Membranes differ only in water repellency and hydrophily in relation to water.

Table 1: Characteristics and properties of the studied membranes

Membrane	Relative to the water	Water absorbtion, g/g	Average size of pore, mcm	Working pressure, MPa	Diameter of a membrane, mm
Phenex (PTFE)	Hydrophobic	0.55	0.45	0.05-0.1 MPa	47
Phenex (nylon)	Hydrophilic	<0.001	0.45	0.05-0.1 MPa	47

Research of a surface of membranes was fixed by means of the scanning electronic microscope of the Jeol JSM-6390 LA brand. The image of a surface of PTFE and nylon membranes in increase in 2500 times is presented to fig. 1.



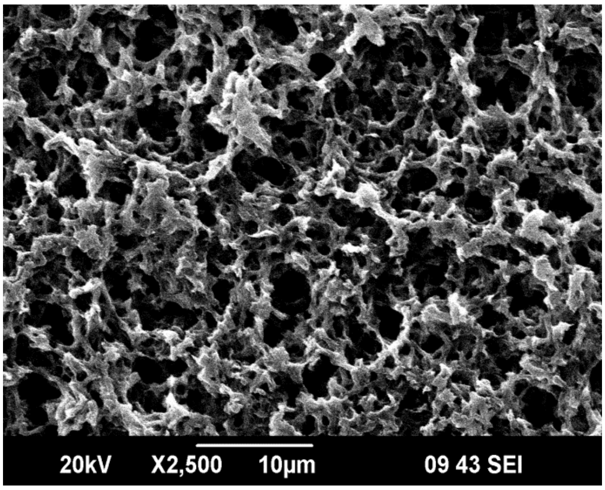


Figure 1: Morphology of a surface of membranes in increase in 2500 times: at the left there is PTFE, on the right nylon.

PTFE membrane represents set of the weaved threads of a fluoroplastic 0.5–5 microns of long and with polymer clots in points of connection of threads. The membrane surface nylon possesses high porosity and a roughness. The size of a time makes from 0.1 microns to 3 microns. Owing to rather high porosity the membrane nylon possesses high water-absorbing ability of 0.55 g/g. Therefore before process of a filtration the nylon membrane was kept in toluene, for giving of hydrophobic properties.

Experiments on division were made on laboratory membrane installation which scheme is submitted in figure 2. Initial mixes water-oil product moved on the membrane module (1) with the microfiltration membrane. Under the influence of the pressure generated by the compressor (5) and registered by the manometer (6) there was a division into water and oil products. The last gathered in reception capacity (4), water in process of division collected in the working camera of the membrane module (1).

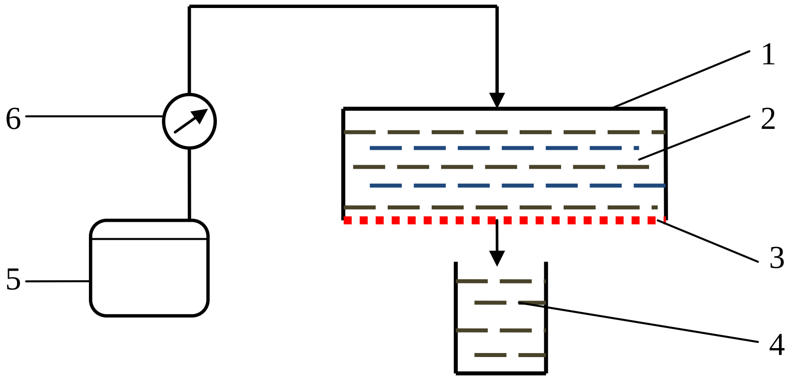


Figure 2: Scheme of laboratory installation of membrane division: 1 – the membrane module, 2 – mix water-oil product, 3 – a microfiltration hydrophobic membrane, 4 – the reception capacity of oil products, 5 – the compressor, 6 – the manometer.

Specific productivity of membranes was defined by a transmission by membranes of a certain volume of the distilled water, also mixes of tetrachlormethane and water in the ratio 1:1, hexane and water in the same ratio. For giving of hydrophily moistened with acetone PTFE membrane, the membrane nylon was moistened with toluene for water repellency giving. Membrane division of oil products it was carried out with a working pressure of 0.1 MPa, temperature of 25 °C and the volume of the divided environments has made 100 cm3. As it is known hexane is lighter than water, and between a membrane and hexane there is a sheet of water. For supply of hexane to a membrane surface through a sheet of water, mix during a filtration mixed with a speed of 1000 rpm. Results are presented in table 2.

Table 2: Specific productivity of membranes

Membrane	Specific productivity, $cm^3/cm^2 min$		
	on the distilled water	mix of tetrachloromethane -water	mix of hexane-water
Phenex (PTFE)	8.9*	14.4	9.6
Phenex (nylon)	9.3	13.8**	3.1**

* the membrane was moistened with acetone

** the membrane was moistened with toluene

High efficiency on division of oil products has PTFE membrane. And mix division tetrachlormethane-water has higher speed of a filtration than division of mix hexane-water. At a membrane nylon the mix division speed processed by toluene hexane-water is 3 times lower in comparison with PTFE membrane.

After filtration investigated the content of oil products in water. Initial concentration of oil products in mixes was 500 g/dm^3. During a microfiltration, working pressure has made 0.1 MPa, temperature and volume of the divided environments of 25 °C and 100 cm^3 respectively. Content of oil products after membrane division in water was determined by an IK-spectroscopy method. Results of measurements are presented in table 3.

Table 3: Extent of division of mix hexane-water

Membrane	Hexane concentration, g/dm^3		Extent of division, %
	Starting	After division	
Phenex (PTFE)	500	1.14	99.8
Phenex (nylon)		1.23	99.8

Residual content of oil products at a mix filtration hexane-water through PTFE membrane was 1.14 g/dm^3, and for nylon membrane was 1.23 g/dm^3. Residual content of hydrocarbons in water is connected by both hexane dissolution, and formation of an emulsion hexane in water as a result hashing during a filtration.

CONCLUSION

Mix of water-oil product was separated with microfiltration hydrophobic PTFE membranes and processed by toluene nylon membranes. PTFE membrane has the best specific productivity and extent of division of oil products. The membrane concedes nylon to PTFE a membrane the specific productivity and need of continuous wetting by toluene before division process, otherwise the membrane begins to absorb and pass water. The membrane of PTFE is recommended for division of liquid mixes water-oil product.

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