ULTRAFILTRATION OF MODEL «OIL-IN-WATER» EMULSIONS WITH POLYSULFONAMIDE

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ABSTRACT
In this paper, studies have been carried out to determine the parameters of ultrafiltration separation of water-oil emulsions formed as a result of the activity of petrochemical, oil-producing and machine-building industries using polysulfonamide membranes of PES brand with a mass of cut off particles from 30 to 300 kDa. The surface of the membranes is hydrophilic, the contact angle of the surface wetting with distilled water was 76.1°. The thickness of the membrane PES with a mass of cut off particles of 300 kDa was 40 nm. The pore size varies from the membrane thickness, at the base is 0.4 µm, at a depth of 30 nm is 0.1 µm and decreases to 0.01 µm. The degree of separation of a 1% water-oil emulsion with particle sizes of 64-592 nm with a PES-300 membrane was more than 95% at a specific productivity of 528 dm³/m²·h, with membranes PES-100, 50, 30 was more than 99%, with specific Performance: 66, 14, 6 dm³/m²·hour, respectively. The dependence of the particle size and the absolute value of the z potential of the dispersed phase on the pore size of the PES membranes is established.

Keywords: emulsion, oil products, ultrafiltration, polysulfonamide, particle size.

INTRODUCTION
Thousands of enterprises in various industries annually consume millions of tons of oil-in-water emulsions, which are a source of oily waste water. During the operation, emulsions are contaminated with various impurities, are biologically damaged and, in the end, lose their technological potential. This circumstance leads to the need for frequent replacement of contaminated emulsions with freshly prepared ones, and waste products are merged into a neutralization system or directly into environmental objects.

Due to the complexity of the multicomponent composition, the resistance to the action of microorganisms, as well as the need to destroy the stable structure of the emulsion, the traditional methods of sedimentation, filtration and biological purification are not effective enough, which leads to their entry into natural aquatic ecosystems.

The use of membrane technologies allows solving simultaneously a number of problems: obtaining clean water, suitable for reuse for technical purposes or diversion into natural water bodies; reducing the costs of placing harmful waste production and creating a low-waste production process.

From the literature sources it is known about the successful use of membrane methods for the separation of water-oil emulsions [1-7]. The particle size of the dispersed phase of oil-in-water emulsions is from 50 to 10000 nm [8-10], on the basis of which, the most optimal is the use of ultrafiltration membranes with a pore size of 100 nm. During the purification of emulsions, membranes made mainly of hydrophilic materials, in particular from polysulfone, cellulose acetate, nylon, polytetrafluoroethylene and polyamide are used [2, 3, 11, 12]. The constructions of membrane modules of roll, hollow fiber and plane-parallel type are used [5, 12, 13].

In the process of ultrafiltration of the emulsion, water, salts and part of the surfactant pass through the membrane, while larger particles and oil droplets are retained, so-called concentrate containing oil in an amount of up to 25-50 % is formed. And a filtrate consisting of an aqueous phase is obtained. At an oil content of up to 70 %, the latter is mixed with fuel oil and burned in boiler units or subjected to further processing to obtain secondary products. A filtrate containing less than 20 mg/dm³ of dissolved petroleum...
products is used to wash products after treatment or is discharged into the sewage system after additional purification by reverse osmosis or activated carbon.

The efficiency of ultrafiltration separation of emulsions is influenced by a number of factors, such as: membrane permeability and the flow velocity of the separated mixture above the surface of the latter, operating pressure and temperature, as well as concentration, composition and pH of the medium to be separated.

As the permeability of the membrane increases, the productivity of the process increases, but the selectivity decreases. At a low operating pressure, the most significant hydraulic resistance of the membrane filter element and the productivity increase linearly with increasing operating pressure. At higher pressures, the performance does not depend on the named parameter. With increasing temperature, just as in the case of the previous factor, an increase in productivity is observed. An increase in temperature from 16 to 50 °C causes an increase in the parameter under consideration approximately by a factor of two [14], depending on the type of membranes. With increasing concentration of the mixture to be separated, productivity decreases logarithmically, but this factor has no effect on selectivity, since the solubility of oils in the aqueous phase of two-phase systems does not depend on the relative volumes of the two phases. The change in the pH of the emulsion, based on oils, has a significant effect on the stability of the system to be separated, its viscosity, the formation of precipitation, the release of free oil, the physico-chemical transformations of constituent emulsions, which in turn affects the performance characteristics. The optimal ranges for ultrafiltration separation of petroleum products and non-ionic surfactants from emulsion for membranes from polysulfonamide correspond to pH values from 2.1 to 2.9 [15, 16].

The use of membrane technologies in the purification process of VMEs is based on the following advantages: reduction of the amount of chemical reagents required for purification; a smaller area of the service area; reduction of labor costs; Simplicity of automation on cost of system can compete with the traditional equipment.

The disadvantage of the method is contamination of the membrane due to the accumulation of components in the feed stream on the surface of the membrane - the phenomenon of concentration polarization, as well as clogging of pores due to adsorption phenomena [17].

There are three main mechanisms that lead to membrane contamination: narrowing of pores, blockage of pores, formation of sediment. The latter occurs when most of the particles in the flow are larger in size than the pore size of the membrane. Some degree of concentration polarization will always accompany the operation of the membrane system. However, the accumulation of a layer of gel or sediment is an extreme case in which a large amount of substance actually accumulates on the surface of the membrane. This process and the restriction of pores will occur only in those cases when the particles in the feed stream are smaller in size than the pore size of the membrane. Occlusion occurs when particles having dimensions similar to pore sizes get stuck in them. The effect of narrowing the pores is that the particles are adsorbed on the inner surface of the pores of the membrane. It is believed that a decrease in pore sizes leads to a further increase in concentration polarization and, consequently, an increase in the degree of contamination of the membrane [18].

As a result of the phenomena described above, the performance decreases until the process is completely stopped. In this connection, the issues of the optimal choice of effective methods for the preliminary purification of VMEs and membrane regeneration become topical [19].

METHODS
In this work, studies have been carried out to determine the parameters of ultrafiltration separation of water-oil emulsions formed as a result of the activity of petrochemical, oil-producing and machine-
building industries, using polysulfonamide membranes with a mass of cut off particles from 30 to 300 kDa.

Studies of the ultrafiltration separation of water-oil emulsions were carried out with flat membrane elements made of polyethersulfone (PES). PES is an amorphous polymer with high impact strength, tensile strength, resistance to ultraviolet radiation, water and aggressive chemical media. Preserves strength and rigidity at extremely low and high temperatures, as well as during sharp temperature changes. Has a high mechanical strength, is resistant to the action of disinfectants.

The particle size of the dispersed phase of oil-in-water emulsions was determined by the method of dynamic light scattering (DLS), and the ζ potential by the light scattering method with phase analysis (PALS) using the NanoBrook Omni analyzer.

The wettability of the test membrane samples was measured using a Kruss DSA 20E apparatus, which makes it possible to determine the contact angle of a drop of distilled water on the membrane surface.

Studies to determine the topography of the surface and the pore sizes of the membranes used were carried out on a scanning probe microscope of the brand "MultiMode V" from VEECO (USA).

As the main indicators of membrane separation of the emulsion, the specific productivity and the degree of separation of the water-oil emulsion were considered, which was calculated as the ratio of the content of petroleum products in the emulsion before and after separation, determined with the KH-3 concentrateometer.

For membrane separation, a 1% freshly prepared oil-in-water emulsion was used as the model emulsion. During the separation of distilled water and emulsions, the working pressure was 0.1 MPa, the temperature of the liquid was 25 °C.

**RESULTS AND DISCUSSION**

Figure 1 shows the distribution of the particle size of the dispersed phase of the water-oil emulsion in terms of intensity, and in Figure 2, the number of particles in the dispersed phase.

![Graph of the particle size distribution](image-url)

**Figure 1.** Graph of the particle size distribution (in terms of intensity) of the dispersed phase of the model 1% water-oil emulsion.
Figure 2. Graph of particle size distribution (by quantity) of the dispersed phase of a model 1% oil-water emulsion.

Table 1. Average values of the particle size and the z potential of the dispersed phase of the model 1% water-oil emulsion.

<table>
<thead>
<tr>
<th>Emulsion</th>
<th>Particle size, nm</th>
<th>ζ-potential, mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% oil-water emulsion</td>
<td>64 – 592</td>
<td>-75.2±7.5</td>
</tr>
</tbody>
</table>

The particle size of the dispersed phase of the water-oil emulsion, according to Fig. 1 and tab. 1 is from 64 to 592 nm. According to Fig. 2, in the emulsion the particles of the dispersed phase with sizes from 64 to 126 nm are greatest, and the number of particles with sizes from 126 to 592 nm is not more than 10%. Therefore, to separate this emulsion, the average pore size of the membranes should not be more than 0.1 µm, and for the complete removal of oil particles, the pore size should be 0.05 µm. The value of the ζ potential by the disperse phase of the emulsion has a negative sign and is equal to -75.2 mV.

The results of measuring the wettability of PES membranes are shown in Figure 3.
According to Fig. 3, with distilled water, the surface of the PES membrane acquires a semicircular shape, the contact angle of the distilled water is 76.1°. Such a surface is hydrophilic.

With the help of probe microscopy, histograms of the pore size of the investigated PES membrane with a mass of cut off particles of 300 kDa, shown in Fig. 4, were obtained.

According to Fig. 4, the thickness of the PES membrane with a mass of cut off particles of 300 kDa is 40 nm. The membrane pore size varies from the membrane thickness, at the base is 0.4 μm, at a depth of 30 nm is 0.1 μm and decreases to 0.01 μm.

Specific productivity of PES membranes based on distilled water and 1% water-oil emulsion was determined (Table 2).

**Table 2. Specific productivity of membranes**
Membrane | Specific capacity of membranes, dm³/m²·hour |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>for distilled water</td>
</tr>
<tr>
<td>PES-300 (300 kDa)</td>
<td>5915</td>
</tr>
<tr>
<td>PES-100 (100 kDa)</td>
<td>951</td>
</tr>
<tr>
<td>PES-50 (50 kDa)</td>
<td>131</td>
</tr>
<tr>
<td>PES-30 (30 kDa)</td>
<td>28</td>
</tr>
</tbody>
</table>

According to the table, high specific productivity is observed in the 300 kDa membrane, with a decrease in the pore size of membranes, productivity is reduced.

Specific productivity is reduced by a factor of 10 when the 1% water-oil emulsion is separated from the filtration of distilled water.

To restore the initial productivity of the membranes after filtering the emulsion with a volume of 500 cm³, the membranes were washed backwashing with a 5% solution of sodium dodecyl sulfate and then rinsed with distilled water.

PES membranes in specific capacity for the separation of water-oil emulsion are inferior to membranes with a pore size of 0.2 µm "nylon-PANI" (1260 m³/m²·h) [2] and PTFE-PANI (420 m³/m²·h) [3], also used to separate similar oil-water emulsions under the conditions given above. The performance is not inferior to polysulfonamide membranes of the brand "UPM-100" (the mass of the cut off particles is 100 kDa) (12-42 m³/m²·h) [20], cellulose acetate membranes of the brand "UAM-150" (mass of cut off particles 150 kDa) (54 m³/m²·h) [21] upon separation of the emulsion.

The results of the oil-water emulsion separation using PES membranes are shown in Table 3. The degree of separation was determined from the residual concentration of petroleum products in the filtrate.

**Table 3.** Degree of separation of petroleum products from 1% water-oil emulsion

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Mass of cut off particles, kDa</th>
<th>Concentration of oil products, mg/dm³</th>
<th>Degree of separation,%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>before cleaning</td>
<td>after cleaning</td>
<td></td>
</tr>
<tr>
<td>PES-300</td>
<td>300</td>
<td>462±46,2</td>
<td>95,4</td>
</tr>
<tr>
<td>PES-100</td>
<td>100</td>
<td>32,7±7,8</td>
<td>99,7</td>
</tr>
<tr>
<td>PES-50</td>
<td>50</td>
<td>18,7±4,5</td>
<td>99,8</td>
</tr>
<tr>
<td>PES-30</td>
<td>30</td>
<td>12,5±3,0</td>
<td>99,9</td>
</tr>
</tbody>
</table>

According to Table 3, it is obvious that the degree of removal of petroleum products from the emulsion with decreasing mass of the cut off particles increases. When the emulsion is separated from the membranes by a mass of cut off particles of 100 kDa or less, the degree of removal of petroleum products is more than 99%.
Figure 5. The graph of the particle size distribution (by quantity) of the dispersed phase of the initial 1% oil-water emulsion and PES membrane filtrates.

Table 4. Average values of the particle size and the z potential of the dispersed phase of the initial 1% oil-water emulsion and PES membrane filtrates

<table>
<thead>
<tr>
<th>Emulsion</th>
<th>Particle size, nm</th>
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<td>1% oil-water emulsion</td>
<td>64 – 592</td>
<td>10066</td>
<td>-75,2±7,5</td>
</tr>
<tr>
<td>the membrane filtrate of PES-300</td>
<td>100 – 139</td>
<td>462</td>
<td>-63,0±6,3</td>
</tr>
<tr>
<td>the membrane filtrate of PES-100</td>
<td>95 – 124</td>
<td>32,7</td>
<td>-41,6±4,2</td>
</tr>
<tr>
<td>the membrane filtrate of PES-30</td>
<td>36 – 80</td>
<td>12,5</td>
<td>-28,4±2,8</td>
</tr>
</tbody>
</table>

According to Fig. 5 and Table 4, after separation of the emulsion with the PES-300 membrane, particles with a particle size larger than 139 nm are completely cut off, when the particle with a size of more than 124 nm is separated from the PES-100 membrane and when the membrane with PES-30 is separated, particles larger than 80 nm. The absolute value of the z-potential of the emulsion decreases after separation of the PES by the membranes, and the smaller the pore size of the membranes, the less the ζ-potential of the emulsion filtrate and the residual content of oil products in the filtrate.

CONCLUSIONS

The particle size of the dispersed phase of the water-oil emulsion is from 64 to 592 nm. In the emulsion the particles of the dispersed phase with sizes from 64 to 126 nm are greatest, and the number of particles with sizes from 126 to 592 nm is not more than 10%, for the complete removal of oil particles, the membrane pore size should be 0.05 μm.
The contact angle of the surface of the membrane PES of the membrane with distilled water was 76.1°. Such a surface is hydrophilic.

The thickness of the PES membrane with a mass of cut off particles of 300 kDa leaves 40 nm. The membrane pore size varies from the membrane thickness, at the base is 0.4 µm, at a depth of 30 nm is 0.1 µm and decreases to 0.01 µm.

Specific productivity for distilled water at the membrane of PES-300 is 5915 m³/m²·h, with a decrease in the pore size of the membranes, the productivity is reduced for the membrane PES-30 (the mass of the cut off particles is 30 kDa) is 28 dm³/m²·hour. The specific productivity is reduced to 15 times when the 1% water-oil emulsion is separated from the filtration of distilled water.

The degree of separation of a 1% water-oil emulsion for a PES-300 membrane is 95%, and for membranes with a mass of cut off particles of less than 100 kDa, the degree of separation is more than 99%. After separation of the emulsion with PES membranes, the particle size of the dispersed phase of the filtrate decreases. A decrease in the absolute value of the ζ potential of the emulsion is also observed, and the smaller the pore size of the membranes, the less is the ζ potential of the emulsion filtrate.

SUMMARY

In this work, studies have been carried out to determine the parameters of ultrafiltration separation of water-oil emulsions formed as a result of the activity of petrochemical, oil-producing and machine-building industries, using polysulfonamide membranes with a mass of cut off particles from 30 to 300 kDa. The degree of separation of a 1% water-oil emulsion with particle sizes of 64-592 nm with a PES-300 membrane was more than 95% at a specific productivity of 528 m³/m²·h, with membranes PES-100, 50, 30 was more than 99%, with specific Performance: 66, 14, 6 m³/m²·h, respectively. The dependence of the particle size and the absolute value of the z potential of the dispersed phase on the pore size of the PES membranes is established.

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REFERENCES


