Modification of polymeric membranes with unipolar corona discharge to intensify the separation of oil-in-water emulsions

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Abstract. The data on the unipolar corona treatment of polymer membranes made of polyethersulfone and polyacrylonitrile and their use for the separation of a 20% model oil-in-water emulsion based on an “I-20A” industrial oil stabilized by a “Kosintol-242” surfactant are given. It is shown that corona treatment of polymer membranes contributes to an increase in membrane productivity and the efficiency of separation of water-oil emulsion. It has been determined that corona discharge treatment leads to a decrease in the degree of crystallinity of the membranes, roughness due to oxidation of the surface with ozone produced during corona processing and the edge wetting angle, which indicates an increase in hydrophilic characteristics.

1. Introduction

In connection with the intensive development of industrial production, it is formed a greater amount of wastewater (WW), which containing various impurities in its composition. A special place in the problem under consideration is occupied by WWs containing petroleum and petroleum products. Crude oil, as well as its numerous refined products, flow in large quantities into storm sewage, industrial wastewater. At the same time, they can partially or completely dissolve in water, form emulsions or form a slick on the water surface.

Various methods are used for cleaning WW containing water-insoluble petroleum products in the form of corresponding emulsions – flotation [1-3], coagulation [4, 5], adsorption [6-8], etc. In recent years worldwide for purifying WW including those containing petroleum products, membrane methods are being intensively developed. As a rule, ultrafiltration processes using polymer membranes are used to remove petroleum products.

In order to improve the efficiency and selectivity of the release of pollutants from aqueous environments, the membranes are subjected to modification, which is carried out by treatment: using chemical reagents [9-11], flame, plasma, corona discharge, laser radiation and high-energy radiation.

Recently, the industrial scale widely used processing of polymeric materials using corona discharge, mainly to change their adhesive characteristics. It is also shown that the corona discharge may be used for processing polymer membranes, however, it is indicated that corona discharge
treatment leads to hydrophilization of the surface and an increase in the rate of emulsion separation through the membrane. At the same time, it should be noted that a variable corona discharge is mainly used abroad. In contrast, a constant (unipolar) corona discharge can not only modify the surface of dielectric materials, but also give them electret properties, i.e. the ability for a long time to maintain a polarized state after the removal of external influences. This circumstance leads to the polarization of this dielectric, which then creates a quasi-permanent electric field in the surrounding space [9]. This circumstance helps to increase the performance of polymer membranes when cleaning emulsions of the type “oil in water”.

2. Methods
In light of the above, we carried out experiments on the separation of 20% water-oil emulsion (WOE) using polyethersulfone (PES) and polyacrylonitrile (PAN) membranes with a mass of cut-off particles 10, 30, 50 and 10, 25, 60 kDa, respectively. The emulsion was prepared by mixing 200 cm$^3$ of industrial oil of the “I-20A” brand from 20 cm$^3$ of surfactant of the “Kosintol-242” brand and 780 cm$^3$ of distilled water until an aggregate-stable disperse system was formed. The chemical oxygen consumption (COC) of the resulting emulsion was 1,66550 mg O / dm$^3$. Using the “Malvern ZetasizerNano ZS” brand nanoparticle analyzer, the particle size of the dispersed phase of the emulsion, 179 nm, was determined using the dynamic light scattering method, which corresponds to the pore size range of selected ultrafiltration PES and PAN membranes. The separation process was carried out in a membrane module with a “cross-flow”, a filtration area of 47 cm$^2$ at a temperature of 20-25 °C and a pressure of 2 bar. Corona processing of the membranes was carried out at a voltage of $U = 5$, 10 or 15 kV of negative polarity and exposure time $\tau = 0.5$, 1.0 or 1.5 minutes.

3. The results
Analysis of the performance of the initial and modified PES membranes showed an increase in the flow of WOE with an increase in the mass of cut-off membrane particles, which is quite natural. At the same time, the largest increase in the indicator under consideration from 10 to 20 dm$^3$/(m$^2$∙h) for modified filter elements compared to the initial ones is observed for membranes with a mass of 50 kDa cut-off particles. For membranes with a mass of cut-off particles of 10 and 30 kDa, the increase in productivity of separation of WOE after corona processing occurs from 2 to 4 dm$^3$/(m$^2$∙h) and from 12 to 15 dm$^3$/(m$^2$∙h). COC values are presented in table 1.

| Table 1. Values of COC WOE before and after separation of the original and corona-treated PES membranes with a mass of cut-off particles of 10, 30 and 50 kDa. |
|---|---|---|---|
| Mass of cut-off particles of PES membrane, kDa | Corona discharge voltage $U_a$, kV | COC values, mgO / dm$^3$ | Corona time $\tau$, min |
| | | 0.5 | 1.0 | 1.5 |
| 10 | 5 | 13202 | 11316 | 12731 |
| | 10 | 10373 | 8487 | 11316 |
| | 15 | 28290 | 18860 | 11788 |
| The filtrate after separation of the emulsion by the original membrane | 9902 |
| 30 | 5 | 3920 | 784 | 3920 |
| | 10 | 2352 | 1960 | 3136 |
| | 15 | 2352 | 784 | 1568 |
| The filtrate after separation of the emulsion by the original membrane | 7056 |
| 50 | 5 | 34215 | 6077 | 13554 |
| | 10 | 23520 | 9985 | 14525 |
The filtrate after separation of the emulsion by the original membrane

| Mass of cut-off particles of PAN membrane, kDa | Corona discharge voltage $U_a$, kV | COC values, mgO / dm$^3$ | Corona time $\tau$, min |
|----------------------------------------------|-----------------------------------|--------------------------|-------------------------|
|                                              | 0,5                               | 1,0                      | 1,5                     |
| 10                                           | 5                                 | 1850                     | 4040                    | 1400                    |
|                                              | 10                                | 1190                     | 3830                    | 2720                    |
|                                              | 15                                | 1280                     | 1620                    | 1430                    |
|                                              | The filtrate after separation of the emulsion by the original membrane | 1900                     |                         |                         |
| 25                                           | 5                                 | 10002                    | 7803                    | 7639                    |
|                                              | 10                                | 6578                     | 5642                    | 6810                    |
|                                              | 15                                | 6812                     | 6339                    | 7462                    |
|                                              | The filtrate after separation of the emulsion by the original membrane | 8520                     |                         |                         |
| 60                                           | 5                                 | 31591                    | 19126                   | 34023                   |
|                                              | 10                                | 20112                    | 24783                   | 44326                   |
|                                              | 15                                | 43989                    | 44045                   | 45760                   |
|                                              | The filtrate after separation of the emulsion by the original membrane | 61046                    |                         |                         |
|                                              | The original emulsion              | 166550                   |                         |                         |

According to the results of table 1, it is obvious that the best effect of corona processing was noted, as in the case with the performance parameter for membranes with a larger mass of cut-off particles — 30 and 50 kDa. At the same time, the efficiency for the indicated membranes as a result of corona processing increased from 95.8 to 99.5% ($\tau = 1$ min and $U_a = 5$ and 15 kV) and from 88.6 % (initial PES membrane 30 kDa) up to 96.3% ($U_a = 10$ kV and $\tau = 0.5$ min), respectively.

Unlike PES membranes for PAN membranes with the smallest pore size (10 kDa), the increase in productivity as a result of corona processing was not revealed and is $\approx 15$ dm$^3$/(m$^2$·h), at the same time for membranes with a mass of cut-off particles 25 and 60 kDa marked increase in the parameter under consideration after exposure to corona discharge with 10 to 20 dm$^3$/(m$^2$·h) and from 20 to 35 dm$^3$/(m$^2$·h), respectively. Values of COC of the filtrates are given in table 2.

**Table 2.** The values of COC WOE before and after separation of the original and corona-treated PAN membranes with a mass of cut-off particles 10, 25 and 60 kDa.

Analysis of the data in table 2 shows that the greatest effect of the corona discharge in terms of COC, namely more than 3 times the decrease in the values of the indicator is observed for membranes with a mass of 60 kDa cut-off particles, in which case the lowest corona rending effect on performance is noted.

The surface and structural characteristics of the original and most effective coronaned membranes were determined by IR spectroscopy of internal reflection, sessile drop, atomic force microscopy, and diffractometry. It should be noted that in the infrared spectra of corona-treated membranes in most cases there is a decrease in the intensity of the absorption bands compared to those of the original sample, which is a consequence of the partial destruction of the polymer material of the membrane.

The above is confirmed by a decrease in the degree of crystallinity of the polymer membrane matrix of a corona-treated membrane compared to the initial one with $Y = 0.14$ to $Y = 0.12$ (from 14 to 12%), as determined by X-ray analysis using a “RigakuUltima IV” diffractometer. Using the device
“Krus DSA 20E” revealed that as a result of exposure to a unipolar corona discharge is increased wettability as evidenced by a decrease in contact angle of a corona-treated membrane compared to the original $\alpha = 59^\circ$ to $48^\circ$ for PAN membranes, in particular.

Using a probe microscope “MultiMode V”, images and histograms of the surface topography of the original (untreated) and corona-discharged PAN membranes are presented, shown in figure 1. Hereinafter, the surface height at a given point relative to the base plane is taken into account as the main topographic parameter, which in this case represents the plane in contact with the lowest point of the surface under consideration.

![Surface images with corresponding histograms of PAN membranes](image)

**Figure 1.** Surface images with corresponding histograms of PAN membranes:a) source membrane;b) 10 kDa, $U_s = 10$ kV, $\tau = 0.5$ min

On the basis of the presented images of the surfaces of the original and corona-treated PAN membranes, a reduction in roughness was revealed. This circumstance can be explained from the following positions. It is known that under the action of a corona discharge, ozone is formed [12], which contributes to the oxidation of protruding parts of the membrane surface. Its action is based on the destruction of the crystallites of the polymer, while the reaction products are mainly dicarboxylic acids.

Thus, it has been shown that the use of a corona discharge, in order to intensify the separation of WOEs, is advisable not only for PAN and PES membranes, but also suggests the possibility of such a modification for other polymeric materials.

On the basis of a comparative analysis of the results of our own research [13–17] and foreign authors [18–20], it was found that as a result of the effect of a corona discharge on the surface of polymer membranes, their performance characteristics change - performance and efficiency. The latter depend on changes in the surface properties of the membranes, the most significant of which are their thickness, roughness, hydrophilicity, porosity and pore size and the presence of charge, which, in turn, depend on the corona discharge parameters — the exposure time and power (voltage) of the corona. In this regard, the main task of research on the modification of polymer membranes by corona discharge
is to identify the dependencies of membrane properties on corona parameters, followed by the
determination of targeted membrane treatment modes, which increase their performance in a specific
field of science and technology.

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