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Polysulfonamide electret membranes for hydrocarbon emulsion separation

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Abstract. Wastewater containing emulsified petroleum products poses a serious threat to the environment. Hydrocarbons change the physicochemical properties of the environment, poison the body of living organisms, and envelop their bodies, leading to the suppression of biocenosis and degradation of ecosystems. In this regard, polysulfonamide membranes for water purification from emulsified oil have been studied. To increase resistance to oiling and improve performance, the filters were treated with corona discharge at a voltage of U = 5–35 kV for 1–5 minutes. As a result of corona treatment, the efficiency increased from 74.9 to 84.5%, while productivity increased by up to 11 times. This circumstance is explained by a change in the contact properties of the surface of the modified membranes, as shown by the results of this study.

Keywords: wastewater, petroleum products, polysulfonamide membranes, industrial oil, corona treatment, emulsion

Oil and petroleum products are fundamental components of the economic security of any state. At the same time, excessive intake of hydrocarbons into the environment leads to a decrease in the stability of ecosystems and pollution of the biosphere, as a result of which living organisms die, soil fertility decreases, water becomes unsuitable for drinking and fish farming, and air contributes to environmental diseases of the cardiovascular and respiratory systems. In the end, the person himself is exposed to the negative effects of adverse environmental factors, as a result of which the quality of life and work capacity decrease. The solution to this issue is the use of energy- and resource-saving technologies (Altapova et al. 2017; Dryakhlov et al. 2015; Fedotova et al. 2016; Zainullin, Abzalova 2019; Zainullin, Shaigallyamova 2019; Zainullin et al. 2005).

In this context, the use of membrane technologies for water purification from hydrocarbons is relevant. The advantages of polymer membranes include high efficiency, a wide range of sizes for cleaning contaminants (from ions to suspended solids), and a relatively small area occupied by equipment, which is important in industrial settings. The disadvantage is the concentration polarization of hydrocarbons on the filter surface during separation, which leads to oiling of the membrane and a decrease in the performance of emulsion cleaning. To address this issue, the treatment of membranes with corona discharge is proposed.

In recent decades, the corona discharge has attracted increasing attention in both scientific and practical circles due to its unique properties and potential applications. A corona discharge is an electric discharge that occurs in a gas when the voltage exceeds a certain threshold, but does not reach the level necessary to create a full arc discharge. This phenomenon is widely studied in the context of electrophysics, materials science, and energy technologies.

Processing of polymer materials using corona discharge is a promising method that allows modifying their surfaces to improve adhesion, hydrophilicity, and other performance characteristics. Modern technologies require highly efficient approaches to polymer processing due to the growing needs of materials science and engineering. Corona discharge, as a physical process, ensures the creation of active centers on the surface of polymers, which opens up new possibilities for their functionalization.

When exposed to corona discharge, charged particles are formed, initiating a physical and chemical modification on the surface of the treated material to impart the necessary characteristics, as in the case of membranes, to increase wettability. The AC corona is characterized by the groups O–, HOO–, H_2O_2, and O_3. At higher humidity levels, the concentration of OH groups increases, while O– and O_3 – concentrations decrease. CO_3 ions are also formed during negative corona discharge.

Modification of polymer membranes by corona discharge is an effective method of modifying and improving their surface properties, which significantly improves their functionality and applicability in various industries.

The key advantages of this method include:

1. Increased adhesion. Corona discharge increases the wettability of the membrane surface, which contributes to the repulsion of the hydrocarbon phase and increases selectivity to water.

2. Improved separation efficiency. Corona discharge can increase the permeability of membranes to gases and liquids, which is particularly beneficial in wastewater treatment.

3. Antibacterial properties. Corona discharge facilitates the formation of functional groups with antimicrobial activity, which can enhance operational characteristics of the membrane.

Experimental studies (Shaikhiev et al. 2015; 2016a; 2016b; 2020a; 2020b; 2021) show that processing parameters such as discharge power, exposure time, and distance to the surface significantly affect the final properties of membranes. Properly optimizing these parameters is crucial to achieving the desired balance between improving the properties and maintaining the initial characteristics of polymers.

Based on the above, further research was conducted on the separation of water-oil emulsions (WOE) using industrial oil grade 'I20-A' (3%) and the surfactant 'Kositol 242' (0.2%) with polysulfonamide (PSA) membranes with a pore size of 0.1 μm. To intensify the process and increase resistance to fouling, the polymer filters were subjected to corona discharge plasma for 1–5 minutes at voltages ranging from 5 to 35 kV. As shown by the data in the table, the modification resulted in an increase in the separation efficiency to approximately 90%, with productivity increasing by up to 10 times. The results suggest that the tested ultrafiltration membranes can be effectively used for the purification of wastewater containing emulsified oils, such as those found in spent lubricating and cooling fluids or cleaning solutions.

Atomic force microscopy (AFM) using a MultiMode V probe microscope was used to obtain images of the surface of both the original (untreated) and modified PSA membranes.

Infrared (IR) spectra of the examined membrane samples were obtained using an IR Fourier spectrometer (Infralum FT-08) over the frequency range of 600–4000 cm^{-1}.

The initial stage of the research involved studying the separation of WOE using PSA membranes with a pore size of 0.01 μm pre-treated treated with corona discharge. The corresponding productivity graphs over the duration of the process are presented in Figure 1, and the COD values of the permeates are provided in Table 1.

Based on the data in Figure 1, an increase in the performance of the modified membranes up to 11 times is observed, with the highest values of productivity occurring at the maximum exposure time to corona discharge. At the same time, Table 1 indicates that the lowest COD value, corresponding to the highest efficiency of 84.5%, was achieved at τ = 5 min and U = 25 kV. This was accompanied by the lowest productivity, likely due to partial pore blockage. The efficiency of the initial membrane was 74.9%.

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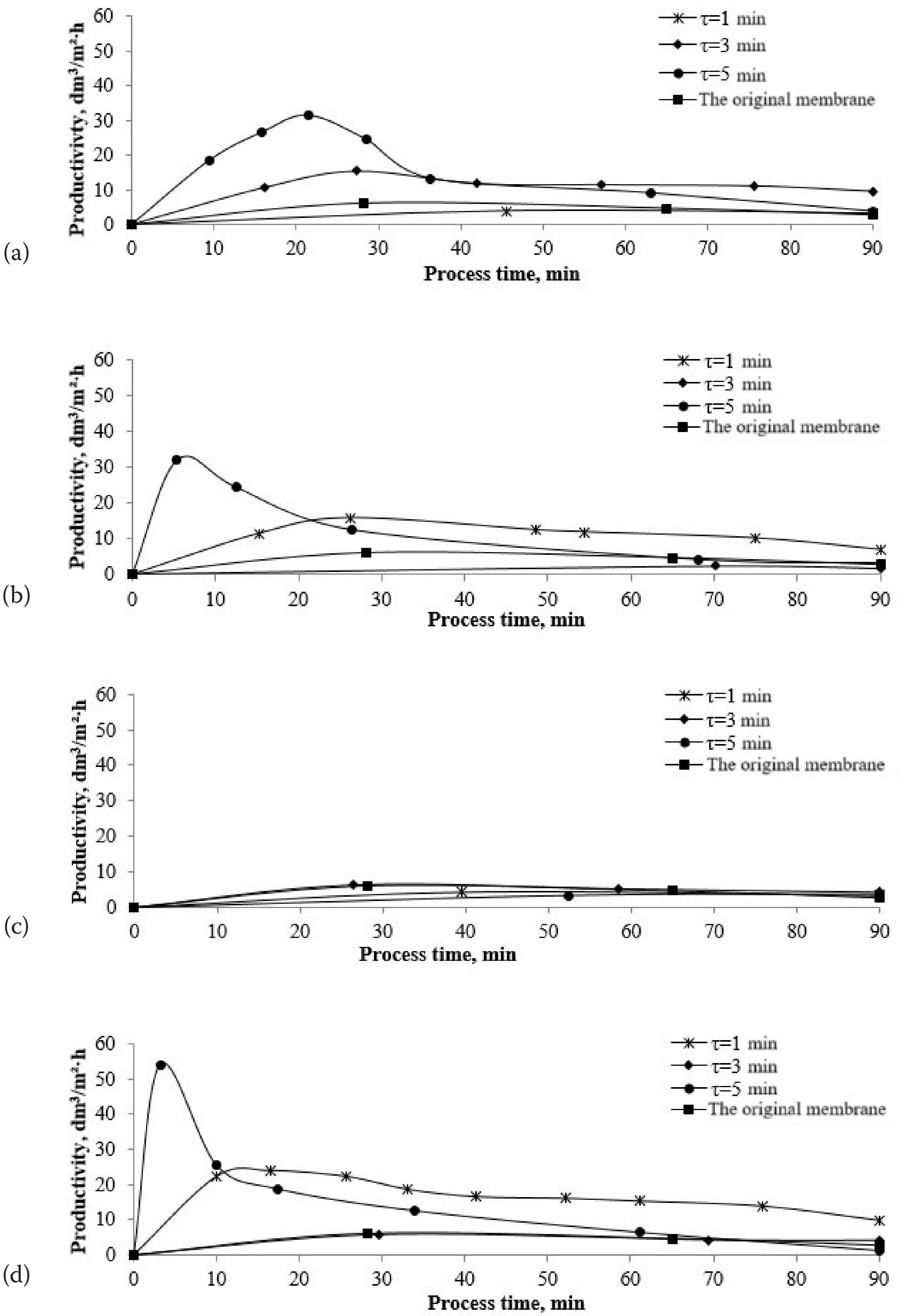

Fig. 1. Graphs showing the change in productivity of WOE separation using PSA membranes with a pore size of 0.01 μm, treated with corona discharge at a) U = 5 kV; b) U = 15 kV; c) U = 25 kV; d) U = 35 kV as a function of process time

Table 1. COD values of the permeates obtained from the separation of WOE using corona-treated PSA membranes with a pore size of 0.01 μm

Corona treatment time, τ, min	COD values, mg O/dm³			
	Corona treatment voltage, U, kV			
	5	15	25	35
1	6480	7020	5040	7020
3	6660	6480	7020	6840
5	5760	6660	**4860**	7200
Permeate after emulsion separation with the original membrane	**7880**			
Original/Initial emulsion	**31360**			

Subsequently, the effect of different types of plasma on the surface structure and internal structure of PSA membranes was evaluated using instrumental methods. In particular, Figure 2 shows images of the membrane surfaces after exposure to glow and corona discharge plasma.

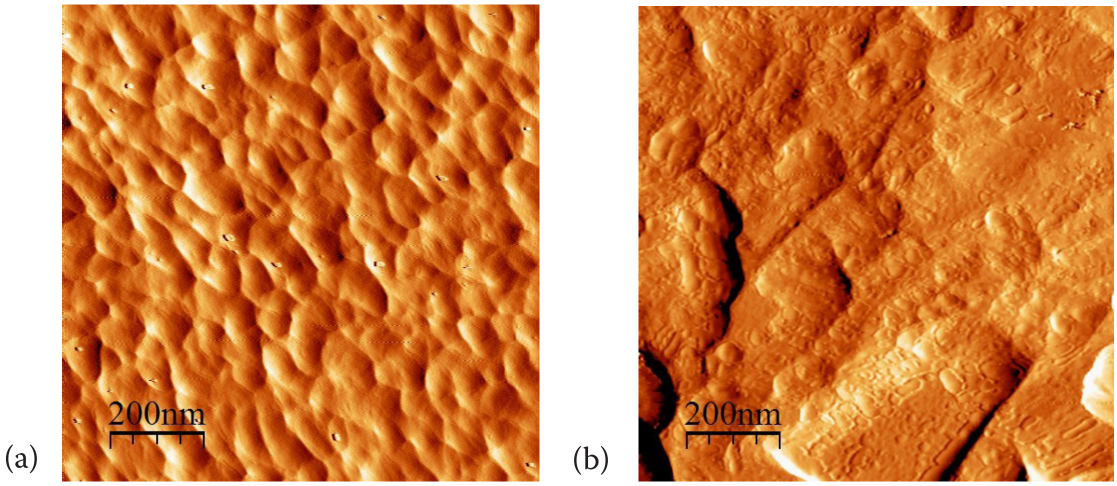

Fig. 2. Images of the surface of the PSA membrane: a) original; b) plasma-treated in corona discharge

Based on AFM analysis (Fig. 2), surface deformations were observed on the modified membrane, resulting in an increase in roughness. The height of the protrusions increased from 100 nm to 750 nm.

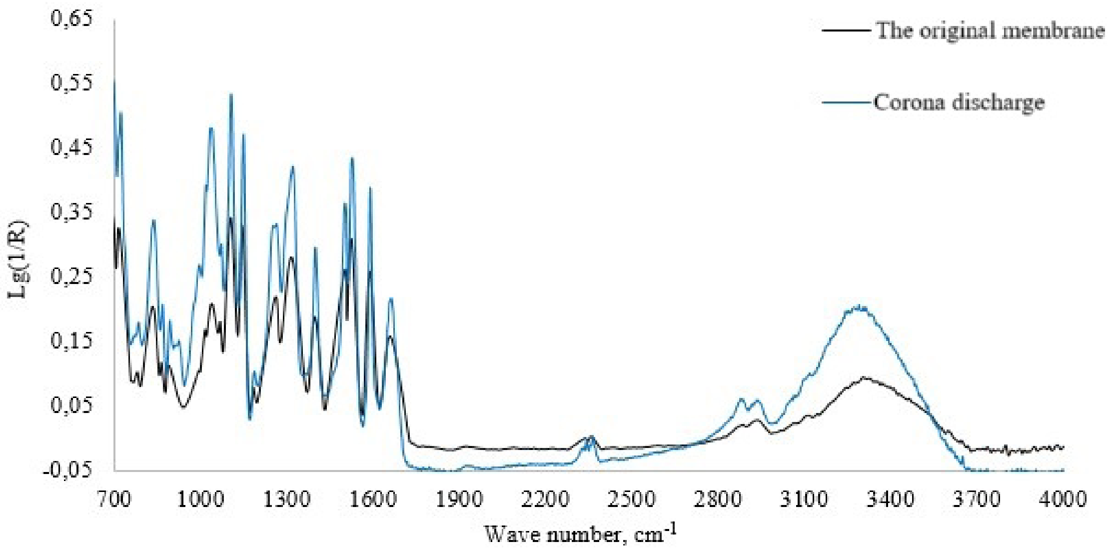

Fig. 3. IR spectra of PSA membranes before and after plasma treatment

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IR spectroscopy (Fig. 3) identified the following fragments of PSA: C–H, SO_2, C–S, C–O, N–H, C–C, and CH_2. Corona discharge treatment introduced oxygen-containing functional groups, which enhanced the hydrophilicity of the membrane surface, leading to improved operational characteristics.

Conclusions

The data obtained from this study indicate that corona discharge plasma treatment significantly improves the operational characteristics of polymer membranes, specifically in terms of productivity and efficiency in the separation of water-oil emulsions. These improvements are attributed to changes in both the topography and chemical structure of the membranes, as confirmed by AFM and IR spectroscopy, respectively.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

All the authors contributed to the discussion of the final work and participated in writing the article.

References

Altapova, R. F., Sanatullova, Z. T., Shaikhiev, I. G. (2017) Udalenie maslyanykh plenok s poverkhnosti vody valyanymi i vojlochnymi otkhodami proizvodstva (monooksid ugleroda), obrabotannymi kremnijorganicheskimi zhidkostyami [Removal of oil films from the water surface by felting and felt production waste (carbon monoxide) treated with organosilicon liquids]. *Vestnik Tekhnologicheskogo universiteta — Bulletin of the Technological University*, 20 (19), 111–116. (In Russian)

Dryakhlov, V. O., Shaikhiev, I. G., Abdullin, I. Sh. et al. (2015) Vliyanie parametrov plazmy ponizhennogo davleniya na effektivnost' membrannogo razdeleniya vodomaslyanykh emul'sij [Impact of low-pressure plasma parameters on membrane separation efficiency of oil-water emulsions]. *Voda: khimiya i ekologiya — Water: Chemistry and Ecology*, 2 (80), 25–30. (In Russian)

Fedotova, A. V., Shaikhiev, I. G., Dryakhlov, V. O. et al. (2016) Vliyanie plazmy nizkogo davleniya na strukturu polisul'fonamidnykh membran i ikh razdelitel'nye kharakteristiki otnositel'no vodoneftyanoj emul'sii [Influence of low-pressure plasma on the structure of polysulfonamide membranes and their separation characteristics relative to a water-oil emulsion]. *Vestnik Belgorodskogo gosudarstvennogo tekhnologicheskogo universiteta imeni V. G. Shuhova — Bulletin of Belgorod State Technological University named after V. G. Shukhov*, 5, 167–173. (In Russian)

Shaikhiev, I. G., Altapova, A. F., Sanatullova, Z. T. (2016a) Issledovanie vliyaniya parametrov plazmennoj obrabotki na effektivnost' udaleniya devonskogo masla s poverkhnosti vody valyal'nymi i vojlochnymi otkhodami proizvodstva (monooksid ugleroda) [Investigation of the effect of plasma treatment parameters on the efficiency of removal of devonian oil from the water surface by felting and felt production waste (carbon monoxide)]. *Vestnik Tekhnologicheskogo universiteta — Bulletin of the Technological University,* 19 (23), 161–166. (In Russian)

Shaikhiev, I. G., Dryakhlov, V. O., Fazullin, D. D. (2020a) Membrannaya ochistka vody, soderzhashchej otrabotannye smazochnye materialy [Membrane purification of water containing spent lubricants]. *Chernye metally — Ferrous metals*, 7, 46–50. (In Russian)

Shaikhiev, I. G., Dryakhlov, V. O., Galikhanov, M. F. et al. (2020b) Razdelenie maslyanoj emul'sii s ispol'zovaniem poliakrilonitril'nykh membran, modifitsirovannykh koronnym razryadom [Separation of oil emulsion using polyacrylonitrile membranes, modified by corona discharge]. *Neorganicheskie materialy: Prikladnye issledovaniya*, 11 (5), 1160–1164. (In Russian)

Shaikhiev, I. G., Sanatullova, Z. T., Farnosova, T. F. (2021) Per'ya indejki — perspektivnyj sorbtsionnyj material dlya udaleniya nefti i masel iz vodnykh sred [Turkey feathers are a promising sorption material for removing oil and oils from aqueous media]. In: *Innovatsionnye tekhnologii zashchity okruzhayushchej sredy v sovremennom mire. materialy Vserossijskoj nauchnoj konferentsii s mezhdunarodnym uchastiem molodykh uchenykh i spetsialistov [Innovative technologies for environmental protection in the modern world. materials of the All-Russian scientific conference with international participation of young scientists and specialists]*. Kazan: Kazan National Research Technological University Publ., pp. 519–524. (In Russian)

Shaikhiev, I. G., Safina, G. Sh., Alekseeva, M. Yu. et al. (2016b) Vliyanie parametrov odnopolyarnogo koronnogo razryada na selektivnost' i proizvoditel'nost' razdeleniya vodomaslyanoj emul'sii polisul'fonamidnoj membranoj [Influence of parameters of a unipolar corona discharge on the selectivity and productivity of separation of a water-oil emulsion by polysulfonamide membrane]. *Vestnik Tekhnologicheskogo universiteta — Bulletin of the Technological University*, 19 (5), 89–92. (In Russian)

Shaikhiev, I. G., Safina, G. Sh., Dryakhlov, V. O. et al. (2015) Intensifikatsiya razdeleniya vodoneftyanykh emul'sij polisul'fopamidnymi membranami, obrabatyvaemymi v oblasti odnopolyarnogo koronnogo razryada [Intensification of separation of water-oil emulsions by polysulfopamide membranes treated in the field of unipolar corona discharge]. *Vestnik Tekhnologicheskogo universiteta — Bulletin of the Technological University*, 18 (17), 217–220. (In Russian)

Zainullin, A. M., Abzalova, A. G. (2019) Kompleksnaya fiziko-khimicheskaya ochistka stochnykh vod proizvodstva TNRS [Complex physico-chemical wastewater treatment of TNRS production]. In: *Innovatsionnye podkhody k resheniyu sovremennykh problem ratsional'nogo ispol'zovaniya prirodnykh resursov i okhrany okruzhayushchej sredy. Sbornik dokladov Mezhdunarodnoj nauchno-tekhnicheskoj konferentsii [Innovative approaches to solving modern problems of rational use of natural resources and environmental protection. Collection of reports of the International Scientific and Technical Conference]*. Belgorod: BSTU Publ., pp. 188–191. (In Russian)

Zainullin, A. M., Shaigallyamova, L. S. (2019) Ochistka stochnykh vod proizvodstva nitrosoedinenij aromaticheskogo ryada [Wastewater treatment of the production of aromatic nitro compounds]. In: *Innovatsionnye podkhody k resheniyu sovremennykh problem ratsional'nogo ispol'zovaniya prirodnykh resursov i okhrany okruzhayushchej sredy. Sbornik dokladov Mezhdunarodnoj nauchno-tekhnicheskoj konferentsii [Innovative approaches to solving modern problems of rational use of natural resources and environmental protection. Collection of reports of the International Scientific and Technical Conference]*. Belgorod: BSTU Publ., pp. 192–195. (In Russian)

Zainullin, A. M., Shaikhiev, I. G., Friedland, S. V. (2005) Issledovanie kataliticheskoj ochistki stochnykh vod proizvodstva diazodinitrokhinona [Investigation of catalytic wastewater treatment of diazodinitroquinone production]. *Bezopasnost' zhiznedeyatel'nosti*, 7, 46–47. (In Russian)