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Separation of oil water emulsions using microfiltration membranes with a surface layer of polyaniline.

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ABSTRACT

Water-oil emulsions containing mostly oil and surfactants formed by the use of cutting fluids (coolant) in the metal, as well as oil production plants. Membrane techniques are often used to clean the oil water emulsions. But high concentrations of oil result in reduction of membrane performance. For membranes with high performance and the degree of purification is carried out modification of the membrane. In this paper we prepared composite membranes with the modified polyaniline surface layer on a substrate of nylon, cellulose acetate and PTFE. The results of the study of membranes by IK-spectroscopy of the molecular structure of polyaniline and some materials on its basis. Determined moisture content, specific productivity and the degree of purification of oil water emulsions of oil products for the original and modified membranes. An analysis of the infrared absorption spectra of the original and the modified membranes showed the presence of polyaniline matrix in the modified membranes. After modifying polyaniline an increase in the degree of purification of oil water emulsions of oil. The specific membrane performance after modification significantly reduced. The most optimal for specific performance (14.2 cm^3 / cm^2 · min) and purity (96.5%) of petroleum products is a membrane modified polyaniline membrane of cellulose acetate grade AC-PANI.

Keywords: membrane, polyaniline, nylon, polytetrafluoroethylene, cellulose acetate, IK-spectroscopy, oil-water emulsion, oil.

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INTRODUCTION

Wastewater containing emulsified oil and petroleum products produced in almost all engineering companies as a result of the use of cutting fluids, as well as oil companies, large tank farms, river and sea ports, gas transmission companies.

Emulsions are characterized by a high kinetic and thermodynamic stability, their purification by traditional methods such as flotation, sedimentation, coagulation, is inefficient and in some cases impossible.

Membrane technology is one of the most promising branches of chemical technology, allows you to split water-oil emulsion. Membrane separation methods based on homogeneous or heterogeneous mixtures of two or more components using a membrane under the influence of forces applied to the driving system [1].

In recent widespread method finds oil water emulsions membrane separation using polymeric membranes [2-5]. Application of the last has a number of advantages, such as small equipment area, lack of reagents, high selectivity for the shared components, the possibility of return of the filtrate for reuse, etc. However, during the separation of emulsions with the oil water oil high specific capacity decrease occurs membranes associated with the occurrence of concentration polarization and membrane formation on the surface of the gel layer [6, 7]. Improving the efficiency and productivity of the membrane separation oil water emulsions is now urgent.

To improve the selective properties and performance of membranes for chemical, physical and physical-chemical modification of the latter [8, 9]. The advantage of chemical modification is the lack of complex technological systems, high efficiency, and a disadvantage is the use of aggressive chemicals as modifying agents.

Currently attention as a modifying reagent, including polymeric membranes attracted polyaniline (PANI) [10]. The polymer chain conductive PANI consists of regularly alternating benzene rings and nitrogen-containing groups. This circuit structure provides polyconjugation (regular alternation of single and double bonds). Centers oxidation of PANI are nitrogen atoms, not involved in the chemical valence bonds a pair of electrons. In the oxidation, i.e. withdrawal of one of the electrons, the positive charge [11] appears in the polymeric chain.

According to the literature it is known that the polymerization of aniline products are protonated oligoaniline containing quinone diimine and fenoldiaminnye fragments [12, 13].

According to infra red spectroscopic analysis of chemical structure made of composite systems based on nylon or PTFE and electrically conductive polymer - PANI.

METHODS

In this paper obtained ion-exchange membrane, a working layer which is PANI.

As template for the polymerization of aniline was used brand polytetrafluoroethylene (PTFE) membrane Phenex AF0-0514, brand nylon Phenex AF0-0504 a 0.45 micron membrane and cellulose acetate (CA) brand MFA-MA9 with 0.2 micron. The synthesis of membranes with surface distribution of PANI polymerization of aniline was performed directly in the matrix membranes. The membrane was preincubated for 2 h in a solution of 1 mol of aniline hydrochloride. The membrane was placed in a 1 mol solution of ammonium persulfate. The polymerization was carried out for 10 minutes at a temperature of 25 °C. After the reaction, the membrane was washed with distilled water [14-18].

To prove the modification polyaniline membranes, the infra red spectra of the initial PTFE membranes were measured, nylon, atsatatatsellyulozy and modified membranes and nylon-PANI, PTFE-PANI, AC-PANI. Since, when compared with the spectrum of the spectrum substance whose presence is supposed to find a spectrum of a mixture of all of the absorption band of the reference material. If the spectrum of the test sample contains all of the absorption band of the reference material, it can be assumed that the substance actually contained in the sample. The study of the infra red spectra of the samples PTFE membranes and nylon was performed on FT infra red spectrometer “Bruker Vector 22”. Samples of the membranes of cellulose acetate was investigated by FT- infra red spectrometer brand “InfraLUM FT-08”.

To investigate wetness membrane samples with a diameter of 45 mm and 22 were wetted with distilled water and the moisture content was determined using a moisture analyzer “A & D MX-50”.

The specific productivity was determined by passage through the membrane a certain volume of distilled water, and water-oil emulsion (VME) per minute, based on the area of 1 cm^3.

To study the degree of purification of the modified membrane "nylon-PANI", passed through a membrane containing petroleum VME 1100 mg / dm^3. The emulsion was passed under a pressure of 0.01-0.03 MPa. The concentration of oil in the emulsion was determined by infra red spectrometry analyzer mark "KN-3".

The degree of purification of oil membrane was calculated by the formula:

$$\phi = (Cf - Cp) / Cf, \qquad (1)$$

where Cf - initial concentration of oil in the emulsion and the concentration;
Cp - oil in the filtrate [7, 18].

RESULTS AND DISCUSSION

Figure 1 shows the absorption infra red spectra of PTFE membrane samples before and after modification PANI.

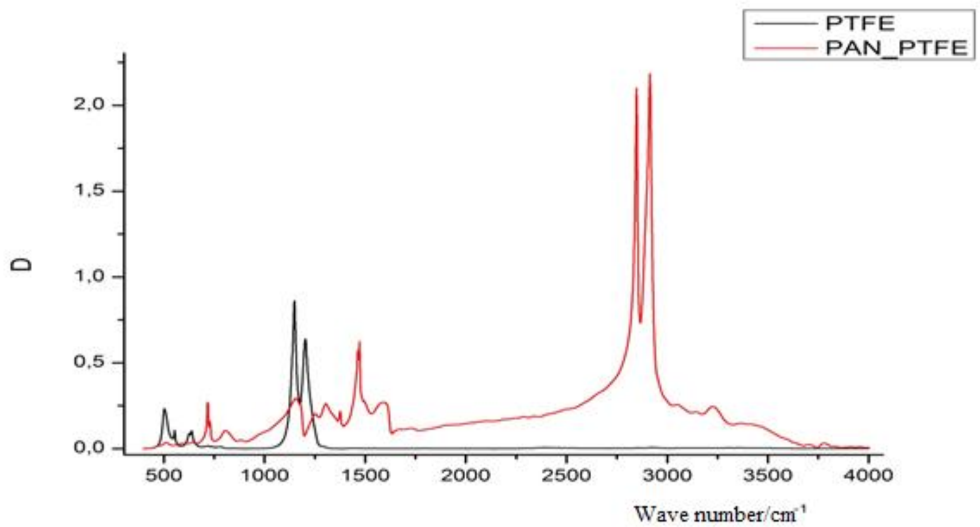

Figure 1. PTFE absorption infra red spectra: the bottom - PTFE high - PTFE-PANI system

A comparison of the infra red spectra of PTFE and PTFE-PANI found a number of differences. They consist in the appearance of the spectra of PTFE PANI additional bands with frequencies of 720, 790, 1313, 1490, 2823, 2900 cm^{-1} and change the shape and the intensity ratio of the majority of the bands (Figure 3). One reason for the observed changes in the spectrum appearance can be in the field of new bands associated with the emergence of new groups. Since the absorption bands at 720, 790 and 1154 cm^{-1} correspond to the deformation and-of-plane vibrations of CF_2 groups at 1233 cm^{-1} - vibration ν (SS), which manifests itself in the form of a bend, the band at 1313 cm^{-1} can be attributed to the stretching and symmetrical deformation CN vibrations of aromatic amines, and at 1490 cm^{-1} correspond to a planar stretching vibrations of C = C and C-quinonediimine C PANI fenildiaminnyh fragments [17].

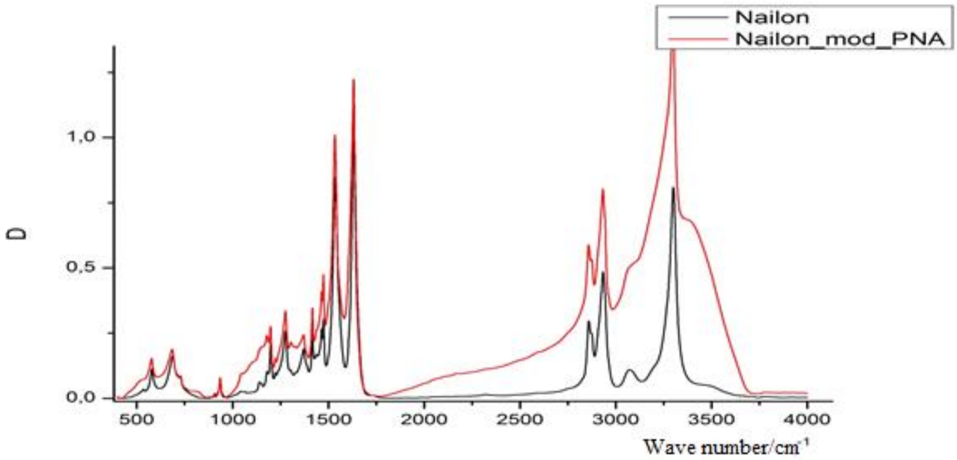

Figure 2. Nylon absorption infra red spectra: the bottom - nylon, upper - a system of nylon-PANI

Investigation of the obtained membranes, represented in Figure 2 by FT infra red spectroscopy showed that the spectrum of the composite absorption bands at 1260 cm^{-1}, characteristic of the radical cation, and in the fields 1581-1600 cm^{-1} and 1494-1500 cm^{-1}; corresponding quinone diimine and fenildiaminnym fragments [17].

Nylon modification leads to a polyaniline in infra red spectra of samples of well-resolved absorption bands characteristic for polyaniline (1589, 1506, 1313, 1164 and 833 cm^{-1}) as well as for nylon (1635, 1539 cm^{-1}). Thus, the comparison of the infra red spectra of the membranes with the infra red spectrum of the starting nylon reveals their qualitative agreement. In both spectra contain strong absorption bands in the regions 1580-1590 cm^{-1} and 1490-1510 cm^{-1}, corresponding to a planar stretching vibrations of the C = C and C-quinone diimine C-fenildiaminnyh fragments PANI, from the ratio of intensities that can assess the degree of polymer oxidation. Intense bands at 1164 cm^{-1} and 1313 cm^{-1} can be attributed to the stretching and bending vibrations of symmetrical CN bonds in the aromatic amines. The absorption band at 833 cm-1 in the IR spectra corresponds to deformation vibrations of CH group in 1,4-substituted benzene ring[17].

The composite infrared spectrum shows a shift of the absorption bands 1584, 1496, 1295 cm^{-1} and 1141 cm^{-1}, characteristic of PANI, to longer wavelengths and bands 1643 cm^{-1} and 1544 cm^{-1}, characteristic of nylon - at shorter wavelengths. These spectral changes indicate the formation of hydrogen bonds between PANI and nylon. [17]

Figure 3 shows the Infra red absorption spectra of polyaniline initial and modified cellulose acetate membrane.

Figure 3. Infra red absorption spectra atsetatatsellyulozy: lower - atsetatatsellyulozy, upper - the system cellulose-PANI acetate (AC-PANI)

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Representative spectra are spectra for atsetatatsellyulozy 1740, 1430, 1370, 1318, 1230, 1160, 900 and 1050 cm^{-1}. After modification of the original atsetatatsellyulozy membrane in the infrared spectrum of the sample membrane AC-PANI has additional absorption bands characteristic of polyaniline: 1589, 1506 and 833 cm^{-1}. Also in the modified membrane of polyaniline in wave numbers of 2000 cm^{-1} is observed strong background absorption, which is characteristic of one form of polyaniline - emeraldina salt.

Thus, the infra red data show that ion-exchange membranes in modified polyaniline salt form produced in emeraldina containing phenylamino quinonediimine and fragments.

Table 1 – The physical properties of the membranes

Membrane	Pore Size, micron	Moisture capacity, %
Nylon-PANI	~ 0.20	59
AC-PANI	~ 0.20	52
PTFE-PANI	~ 0.25	3,6
The original Nylon membrane Phenex AF0-0504	0.45	55
The original cellulose acetate membrane-brand MFA-MA9	0.4	47
The original PTFE membrane Phenex AF0-0514	0.45	<0,1

Moisture-absorbing ability of the membranes are the most important characteristics of ion-exchange membranes that define the availability of ion-exchange groups and ion exchange rate of establishment of equilibrium. As a result of the modification nylon membrane moisture content increased by 4% cellulose acetate membrane increased by 5%, the PTFE membrane after the modification become hydrophilic. Increased moisture-absorbing ability of the membranes due to the presence of polyaniline in the membrane structure.

Table 2 – Specific performance membranes

Membrane	Time processing membrane ammonium persulfate, min	Specific performance membranes cm^3 / cm^2 • min	
		distilled water	for oil-water emulsion
The original PTFE membrane Phenex AF0-0514*	-	8.9	4.6
PTFE-PANI *	10	7.9	3.2
The original Nylon membrane Phenex AF0-0504	-	9.3	6.6
Nylon-PANI	10	8.7	5.2
The original cellulose acetate membrane-brand MFA-MA9	-	15.1	8.4
AS-PANI	10	14.2	7.3

* before filtration membrane wetting with acetone.

From the data shown in Table. 1, it follows that all the membranes after treatment aniline hydrochloride and ammonium persulfate, the specific productivity decreases. The high specific productivity observed in AC-PANI membranes, compared with the PTFE-PANI membrane and Nylon-PANI. Moreover, it is obvious that the said parameter depends on the composition of shared fluid. Maximum performance of the original and the modified membranes observed by passing distilled water, and the minimum - the separation of oil-water emulsion.

Results of the study treatment much oil in water emulsion of mineral oil are presented in Table 3.

Table 3 – The degree of purification of oil in water emulsion from oil-modified membranes

№ п/п	Membrane	The concentration of oil, mg / dm^3		The degree of purification, %
		The stock solution	After cleaning	
1	PTFE-PANI*	1100±110	60.4±12.1	94.5
2	PTFE*		142±28.4	87.1
3	Nylon-PANI		35.2±7.0	96.8
4	Nylon		107±21.3	90.3
5	AC-PANI		38.5±7.7	96.5
6	Cellulose acetate MFA MA-9		116±23.1	89.5

* before filtration membrane wetting with acetone.

The extent of the removal of oil from the oil-water emulsion of the model using the original and the modified membranes is high. Moreover, in the membrane of the modified ammonium persulfate, after an hour soaking in a solution of aniline hydrochloride, the degree of removal of oil increases. The highest degree of purification of oil-water emulsions of oil products is achieved with the membrane Nylon-PANI.

CONCLUSIONS

Analysis of the infra red absorption spectra of the original and the modified membranes showed the presence of polyaniline matrix in the modified membranes. After modification of polyaniline, an increase dehumidifying membrane capacity and the degree of purification of the water-oil emulsion of oil. The specific membrane performance after modification significantly reduced. The most optimal for specific performance (14.2 cm^3 / cm^2 • min) and purity (96.5%) of petroleum products is a membrane of modified cellulose acetate membrane polyaniline brand AC-PANI.

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