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Spectroscopic study of MA-41P and MK-40 membranes in electromembrane purification of process solutions containing cobalt, copper, and cadmium ions

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Abstract: Infrared (IR) spectra were obtained for the surface layer of heterogeneous membranes — cation-exchange MK-40 and anion-exchange MA-41P — widely used in electromembrane processes. Spectra were recorded for air-dry, statically water-saturated, and operational (dynamically water-saturated) membrane samples. Dynamic water saturation was achieved during the electrodeionization purification of a solution containing cobalt, copper, and cadmium ions. Water saturation was found to increase the intensity and bandwidth of the absorption band at $\nu = 3000 \div 3700$ cm^{-1}, corresponding to the OH stretching vibration region. The appearance of an additional peak at $\nu \approx 3287$ cm^{-1} was attributed to the formation of stronger hydrogen bonds in the membrane pore space. The absence of shifts in the absorption bands corresponding to the membrane matrix components under air-dry, statically, and dynamically saturated conditions indicates their chemical stability. In the MA-41P membrane, after use in electrodeionization, changes were observed in both the intensity and position of absorption peaks in the $\nu \approx 1220 \div 1000$ cm^{-1} region, associated with the functional groups of the anion exchanger. The observed spectral changes were evaluated by calculating the normalized peak intensities of the absorption bands. It was shown that in the dynamically water-saturated state, both MK-40 and MA-41P membranes exhibit a reduction in the amount of weakly bound ("free") water and the formation of stronger hydrogen bonds. The results of optical density calculations for characteristic polyethylene absorption bands — the main component of the membrane matrix — are presented. Changes in optical density upon water saturation indicate conformational rearrangements of polyethylene macromolecules. The amounts of chemically unbound solute components retained within the membrane volume were quantified; these species do not affect the membranes' chemical stabiliy or operational performance.

Keywords: MK-40 membrane, MA-41P membrane, IR spectrum, water saturation, metal ions.

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Спектроскопические исследования мембран МА-41П и МК-40 в процессе электромембранной очистки технологических растворов от ионов кобальта, меди и кадмия

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Аннотация: Получены ИК-спектры поверхностного слоя гетерогенных мембран: катионообменной МК-40 и анионообменной МА-41П, широко применяемых в электромембранных процессах. Спектры представлены для воздушно-сухого, статиче-

ски и динамически водонасыщенного образцов мембран. Динамическое водонасыщение проводилось в процессе электродионизационной очистки раствора, содержащего ионы кобальта, меди и кадмия. Выявлено, что изменения в спектрах мембран, происходящие в результате водонасыщения, приводят к увеличению интенсивности и ширины полосы поглощения ν = 3000÷÷3700 см$^{-1}$ в диапазоне валентных колебаний OH^--групп. Появление дополнительного максимума при ν ~ 3287 см$^{-1}$ обусловлено образованием более прочных водородных связей в поровом пространстве мембран. Отсутствие смещения полос поглощения, определяющих соединения, составляющие матрицу мембран в воздушно-сухом, статически и динамически водонасыщенных состояниях, указывает на их химическую стабильность. Установлены изменения интенсивности и частоты поглощения пиков в диапазоне ν ~1220÷1000 см$^{-1}$, отвечающем за идентификацию функциональной группы анионита, для образца МА-41П после его использования в процессе электромембранной очистки. Наблюдаемые изменения в ИК-спектрах мембран оценивались на основании расчета приведенных пиковых интенсивностей полос поглощения. Установлено, что в мембранах МК-40 и МА-41П в динамически водонасыщенном состоянии уменьшается количество слабосвязанной «жидкой воды» и образуются более прочные водородные связи. Представлены результаты расчета оптической плотности характеристических полос поглощения полиэтилена, входящего в состав матрицы мембран. Показано изменение оптической плотности при водонасыщении, указывающее на конформационную перестройку в волокнах полиэтилена. Установлено количество химически не связанных компонентов разделяемого раствора, задерживающихся в объеме мембран и не оказывающих влияние на их эксплуатационные характеристики.

Ключевые слова: мембрана МК-40, МА-41П, ИК-спектр, водонасыщение, ионы металлов.

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Introduction

Electromembrane systems are used for the desalination of solutions and for the removal of electrically conductive contaminants from wastewater. Cation- and anion-exchange membranes act as selective barriers that allow the passage of cations and anions, respectively. Based on microstructural differences, ion-exchange membranes are classified into two types: heterogeneous and homogeneous [1]. Heterogeneous membranes are produced by combining ion-exchange and polymer resin powders (mainly inert polymers), followed by hot pressing to form a film [2; 3]. Compared to homogeneous membranes, they exhibit superior mechanical strength, chemical stability, and lower production cost [4], although homogeneous membranes provide better electrochemical performance [5].

Studying the structure and properties of membranes is essential for determining the optimal operating conditions of electrodialysis units, improving membrane permeability, and enhancing ion selectivity. Research into membrane performance, including that of the domestically manufactured MK-40 and MA-41P grades — especially relevant following the cessation of foreign supplies and the absence of viable alternatives — is aimed at optimizing the technological parameters of electromembrane systems.

In [6], the authors presented the chronopotentiogram and *X*-ray diffraction pattern of the MA-41P membrane, both unused and after operation. These techniques were employed to investigate scale formation on the membrane surface. In [7], the surface of the MA-41P membrane was modified using polyelectrolytes, and the samples were analyzed before and after modification using scanning electron microscopy and *X*-ray fluorescence spectroscopy. Current-voltage characteristics of the membranes were also obtained. It was shown that chemical surface modification led to an increase in the concentration of quaternary ammonium groups and a decrease in secondary and tertiary amine groups in the conductive surface layer, thereby enhancing electroconvection and significantly increasing the transport rate of salt counter-ions across the membrane.

The study in [8] examined the effect of ammonium nitrate solutions on the structural and kinetic parameters of MK-40 and MA-41 membranes. Membrane resistance was measured using a contact potential difference method. In [9], during the separation of phenylalanine and sodium chloride using MK-40, MA-40, and MA-41 membranes, it was shown that simultaneous use of strongly acidic and strongly basic membranes was more effective for demineralization compared to membranes with moderate basicity. Separation efficiency was assessed via spectrophotometric methods.

The study of membranes using infrared (IR) spectroscopy provides detailed information on the structure and properties of their surface layers, as well as on

conformational rearrangements of the bonds within the polymer chains that make up the membrane. This method is widely used to identify organic contaminants on membrane surfaces after electrodeionization [10; 11], as well as to evaluate the effectiveness of membrane cleaning procedures [12; 13]. In the development of new cation- and anion-exchange membranes, IR spectroscopy is applied to confirm cross-linking reactions between reagents [14—16] or to assess surface modifications of widely used commercial membranes [17; 18]. This method is also used to determine the structure and surface properties of membrane surface layers [19; 20].

The aim of the present study was to investigate the structure of heterogeneous MK-40 and MA-41P membranes using IR spectroscopy and to determine the amount of not chemically bound metal ions in the cation-exchange membrane and sulfate ions in the anion-exchange membrane. The samples examined included air-dry, water-saturated, and operational (dynamically saturated during electrodeionization-based purification of aqueous copper, cobalt, and cadmium sulfate solutions) membranes.

Experimental procedure

The materials studied were industrially manufactured heterogeneous ion-exchange membranes produced in Russia by Shchekinoazot JSC, according to Technical Specifications TU 2255-001-95746392-2012: the strongly acidic cation-exchange membrane MK-40 and the strongly basic anion-exchange membrane MA-41P. Their properties are summarized in Table 1. These monopolar, weakly cross-linked heterogeneous membranes are intended for water treatment applications. The composite membrane layers are composed of polyethylene and nylon. The ion-exchange component of MK-40 is the strongly acidic cation-exchange resin KU-2, synthesized by sulfonation of a styrene copolymer containing 8 % divinylbenzene. In the MA-41P membrane, the ion-exchange component is the strongly basic anion-exchange resin AV-17-2, obtained via chloromethylation of a styrene copolymer with 2 % divinylbenzene, followed by amination with trimethylamine. The two membranes are similar in composition and structure, differing only in the type of functional group and, consequently, in their counter-ions.

Samples were prepared in three states: air-dry, statically water-saturated, and operational (i.e., dynamically saturated during electrodeionization). The MK-40 and MA-41P membranes in the operational state were used as part of an electrodeionization module in a laboratory setup designed for the separation of a multicomponent solution containing copper sulfate (15 mg/dm^3), cobalt sulfate (20 mg/dm^3), and cadmium sulfate (20 mg/dm^3). These concentrations simulate industrial electroplating wastewater. The solution had a pH of 3.2.

Membrane samples were cut from regions with the most uniform thickness. Water-saturated samples were equilibrated in deionized water for 2 h, followed by gentle blotting of surface moisture with filter paper. Operational membrane samples were rinsed with deionized water and blotted dry in the same manner. All samples were stored in a desiccator at 20 °C. Infrared (IR) spectra were collected using a Jasco FT/IR 6700 Fourier-transform infrared spectrometer (JASCO International Co., Ltd., Japan) over the range of $\nu = 500 \div 4000$ cm^{-1}, with a resolution of 4 cm^{-1} and 32 scans.

Ion desorption from the membranes was carried out as follows. Operational membrane samples without any visible damage, stains, or deposits were used in the experiment. For the desorption procedure, operational ion-exchange membrane samples with the most uniform thickness were selected. Each used membrane sample, previously employed in electrodeionization-based separation of copper, cobalt, and cadmium sulfate solutions, was placed in a 500 cm^3 vessel filled with distilled wa-

Table. 1. **Properties of the studied membranes**

Таблица 1. Характеристики исследуемых мембран

Parameter	MK-40	MA-41P
Ion-exchange group	$-SO_3H$ (sulfo group)	$-N+(CH_3)_3$ (quaternary ammonium base)
Counter-ion	Na^+	Cl^-
Moisture content, max, %	40 ± 5	31.2 ± 1
Ion-exchange capacity, mmol/cm^3	1.58 ± 0.06	0.92 ± 0.02
Thickness, μm	535 ± 10	535 ± 10

ter. Every 24 h, the sample was transferred to a fresh vessel with distilled water. Desorption was conducted over a period of four days, which was sufficient for the complete release of retained substances from the membranes. The concentration of substances transferred into the distilled water was determined daily in the used solution by photometric methods (for metal cations) and titrimetric analysis (for sulfates). Based on the obtained data, the concentrations of substances distributed within the membrane volume were calculated.

Results and discussion

The results obtained, presented in Figs. 1 and 2, provide information on the functional groups present in the studied membranes and their structural features, which is essential for understanding the processes involved in electromembrane treatment of solutions containing non-ferrous metal ions.

Fig. 1 shows the infrared (IR) spectra of MA-41P anion-exchange membrane samples in three states: air-dry, statically water-saturated, and operational (dynamically water-saturated). All spectra contain distinct characteristic absorption bands corresponding to functional groups of the membrane components, including C—H, O—H, aromatic (C_6H_6), and N—C groups [21—23].

Polyethylene, a component of the membrane matrix, is identified by asymmetric ($\nu \sim 2914$ cm^{-1}) and symmetric ($\nu \sim 2846$ cm^{-1}) C—H stretching vibrations. The doublet at $\nu \approx 1472$ and 1470 cm^{-1} corresponds to asymmetric and symmetric C—H scissoring vibrations. Asymmetric and symmetric rocking vibrations of crystalline polyethylene are observed at $\nu \approx 717$ and 714 cm^{-1}.

Minor stretching vibrations in the range of $\nu = 3900 \div 3600$ cm^{-1} observed in all spectra are attributed to trace amounts of water. A broad absorption band at $\nu = 3600 \div 3100$ cm^{-1} corresponds to water associates exhibiting various hydrogen bond energies. The minimum at $\nu \approx 1646$ cm^{-1} is associated with the bending vibrations of —OH groups in hydration water.

The absorption band at $\nu \approx 1541$ cm^{-1} corresponds to stretching vibrations of conjugated C=C bonds in the benzene ring. In-plane deformation vibrations of C—H and C—C groups of a disubstituted benzene ring are observed at $\nu \approx 900$, 830, and 770 cm^{-1}. The increased intensity of these bands in the water-saturated sample is explained by the higher water content.

Weak absorption bands in the range of $\nu = 1250 \div 950$ cm^{-1} (at approximately 1218, 1114, 1040, and 975 cm^{-1}) correspond to quaternary trimethylammonium groups, which are the principal functional groups of the anion-exchange resins used in the membrane. Additional weak peaks at $\nu \approx 890$ and 825 cm^{-1} are associated with C—N vibrations adjacent to the benzene ring.

The weak vibrations detected in the $\nu \approx 2350 \div 2255$ cm^{-1} range for all membrane samples are due to the absorption of atmospheric CO during sample preparation.

The IR spectrum of the cation-exchange membrane (Fig. 2) shows substantial overlap with that of the MA-41P anion-exchange membrane over a broad spectral range. Differences are observed in the regions of $\nu \approx 1300 \div 800$ cm^{-1} and $700 \div 600$ cm^{-1}, where the peaks correspond to vibrations associated with the presence of sulfonic acid groups in the membrane structure.

The bands at $\nu \approx 1171$, 1122, 1036, and 1006 cm^{-1}

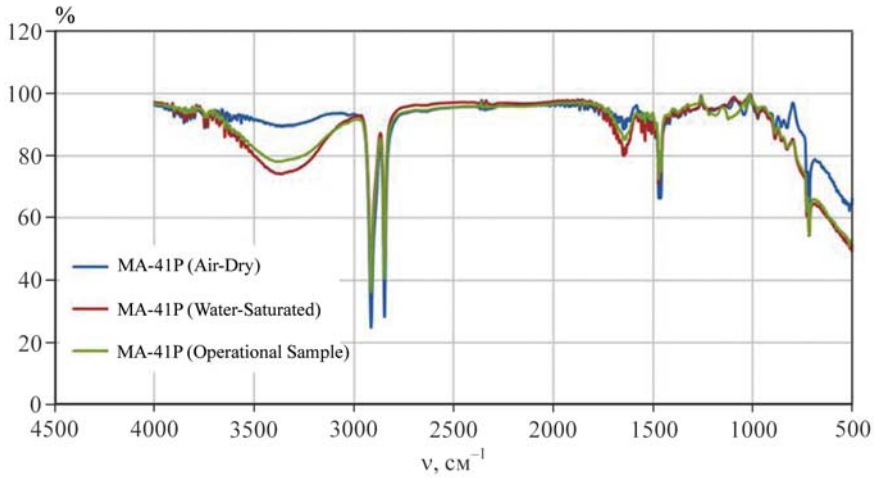

Fig. 1. IR spectra of MA-41P membrane samples

Рис. 1. ИК-спектрограмма образцов мембран МА-41П

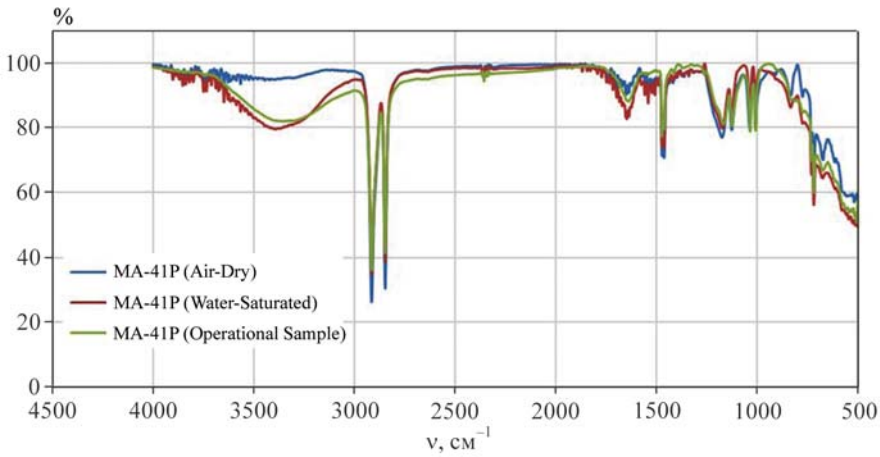

Fig. 2. IR spectra of MK-40 membrane samples

Рис. 2. ИК-спектрограмма образцов мембран МК-40

correspond to the asymmetric and symmetric stretching vibrations of sulfonic acid group atoms. The bands at $\nu \approx 671$ and 618 cm^{-1} are attributed to bending vibrations of C—S bonds attached to benzene rings.

A comparison of the IR spectra in the $\nu = 1500 \div 600$ cm^{-1} region of the studied samples provides insight into the chemical stability of the macromolecular structure in the active layer of the membranes. For MK-40, the spectra show complete agreement in the frequencies of the absorption bands corresponding to the structural elements of the functional groups, without any detectable shifts. In contrast, for MA-41P, a shift in peaks is observed in the range of $\nu \approx 1220 \div 1000$ cm^{-1} in the operational membrane compared to the air-dry and statically water-saturated samples. Both the intensity and frequency of the absorption bands are altered. This spectral region is characteristic of the quaternary ammonium groups that serve as the membrane's ion-exchange sites.

Changes in the spectrum are characterized by a shift in peaks, but they do not disappear completely. It is known [23] that trimethylamine forms water complexes with a symmetric top configuration, where the water molecule is able to rotate freely about the symmetry axis defined by the trimethylamine moiety. The observed shifts and changes in band intensity in this range are likely related to displacement of the trimethylamine symmetry axis caused by bond rearrangements under dynamic exposure.

A comparison of the IR spectra (Figs. 1 and 2) in the OH stretching vibration region ($\nu \approx 3000 \div 3700$ cm^{-1}) for water-saturated and air-dry membranes indicates a substantial increase in the full width at half maximum (FWHM) of the absorption band at $\nu \approx 3392$ cm^{-1} (see Table 2), along with asymmetry in the band shape and the clear appearance of an additional peak at $\nu \approx 3287$ cm^{-1} in the water-saturated membranes. Additionally, the intensity and FWHM of the absorption band at $\nu \approx 1646$ cm^{-1}, corresponding to H—O—H bending vibrations of water molecules, increase as well. A comparative analysis of OH vibration frequencies and calculated hydrogen bond energies for MK-40 and MA-41P membranes is provided in Table 2.

The hydrogen bond energy was calculated using the equation [24]

$$E_{OH} = \frac{1}{K} \frac{\nu_0 - \nu}{\nu_0},$$

where $\nu_0 = 3650$ cm^{-1} is the absorption frequency of a free hydroxyl group, ν is the observed absorption frequency of the hydrogen-bonded OH group, and $1/K = 2.625 \cdot 10^2$ kJ/mol is the equilibrium constant.

The maximum absorption band for both membranes is observed at $\nu = 3392$ cm^{-1}, with a full width at half maximum (FWHM) of 403 for MK-40 and 424 for MA-41P. This frequency is significantly lower than that of a free OH group ($\nu_0 = 3650$ cm^{-1}), indicating hydrogen bonding. The similar peak intensities across all membrane types reflect the stability of the membrane matrix under both static and dynamic water saturation. The appearance of an additional low-frequency peak in the water-saturated membranes suggests the formation of stronger hydrogen bonds

Undoubtedly, these spectral features indicate that pore-confined water OH groups interact with all components of the membranes' polymer system, forming energetically diverse hydrogen bonds.

To assess the observed changes in the IR spectra, normalized peak intensities at $\nu = 1646$, 2846, and 3550 cm^{-1} were monitored relative to the C—H bending

Table. 2. **Observed frequencies of OH stretching vibrations in MK-40 and MA-41P membranes at 20 °C**

Таблица 2. Наблюдаемые частоты валентных колебаний ОН-групп мембран МК-40 и МА-41П при температуре 20 °С

Parameter	MK-40			MA-41P		
	Air-dry	Water-saturated	Operational	Air-dry	Water-saturated	Operational
ν_1, cm^{-1} (FWHM)	3392 (160)	3392 (403)	3392 (356)	3392 (170)	3392 (424)	3392 (360)
E_{OH}, kJ/mol	19.97	19.97	19.97	19.97	19.97	19.97
$\nu_д$, cm^{-1}	–	3285	3289	–	3288	3284
E_{OH}, kJ/mol	–	29.41	28.81	–	28.9	29.26
ν_2, cm^{-1} (FWHM)	1646 (48)	1646 (64)	1635 (58)	1646 (56)	1646 (73)	1646 (71)

Table. 3. **Relative absorption band intensities of MK-40 and MA-41P membranes at 20 °C**

Таблица 3. Относительная интенсивность полос поглощения мембран МК-40 и МА-41П при температуре 20 °С

Parameter	MK-40			MA-41P		
	Air-dry	Water-saturated	Operational	Air-dry	Water-saturated	Operational
$I(1646)/I(1472)$	0.33	0.67	0.44	0.32	0.77	0.42
$I(2846)/I(1472)$	2.53	2.57	2.26	2.48	2.6	2.6
$I(3550)/I(1472)$	0.07	0.45	0.23	0.03	0.59	0.42

vibration at ν = 1472 cm^{-1} (expressed as $I(X)/I(1472)$). The frequency at 3550 cm^{-1} corresponds to weakly bound or "free" water [25]. The results are presented in Table 3. These data show that the relative intensity of all analyzed absorption bands increases in statically water-saturated membranes compared to air-dry samples, while in dynamically saturated membranes it decreases relative to the statically saturated ones. Based on these results, it can be concluded that in the pore space of the active layer, static water saturation leads to an increased amount of weakly bound (liquid-like) water, whereas in dynamically saturated membranes, this fraction decreases and is replaced by more strongly bound water. This indicates minor structural changes within the membrane matrix.

Polyethylene serves as the base material of the MK-40 and MA-41P membrane matrices. Upon water saturation, conformational changes occur in its macromolecular structure, as indicated by variations in the optical density of characteristic absorption bands. The bands at 1472 cm^{-1} (CH_2 scissoring vibrations) and 717 cm^{-1} (CH_2 rocking vibrations) are considered characteristic for polyethylene [26].

Optical density was calculated using the formula:

$$D = \lg (I_0 / I),$$

where I_0 and I are the intensities of the incident and transmitted radiation, respectively, determined using the baseline method. Table 4 presents the calculated values for these characteristic bands.

Upon water saturation, the optical density of the membranes decreased and remained unchanged under dynamic conditions. These results indicate conformational rearrangements of polyethylene macromolecules due to water uptake, caused by the redistribution of bonds involving CH_2 groups within the polymer structure in the presence of adsorbed water. The similar optical density values observed for water-saturated and operational samples suggest that conformational changes in the polyethylene macromolecules result primarily from water saturation and are not caused by the potential difference applied across the membrane.

The electrodeionization process is accompanied by the sorption of solutes from the solution onto the membrane surfaces [27; 28]. The obtained results show that fouling of the membranes by extractable

Table. 4. **Optical density variation in MK-40 and MA-41P membranes at 20 °C**

Таблица 4. Изменение оптической плотности мембран МК-40 и МА-41П при температуре 20 °С

Показатель	MK-40			MA-41P		
	Air-dry	Water-saturated	Operational	Air-dry	Water-saturated	Operational
ν_1, cm^{-1}	1472	1472	1471	1472	1472	1472
D	0.12	0.11	0.1	0.13	0.09	0.09
ν_2, cm^{-1}	717	717	717	717	717	717
D	0.091	0.087	0.077	0.11	0.08	0.08

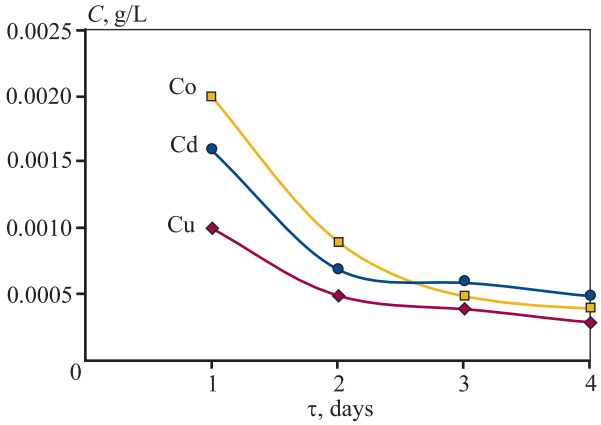

Fig. 3. Desorption of metal ions from the MK-40 cation-exchange membrane into distilled water at 20 °C

Рис. 3. Десорбция металлов из катионообменной мембраны МК-40 в дистиллированную воду при температуре 20 °С

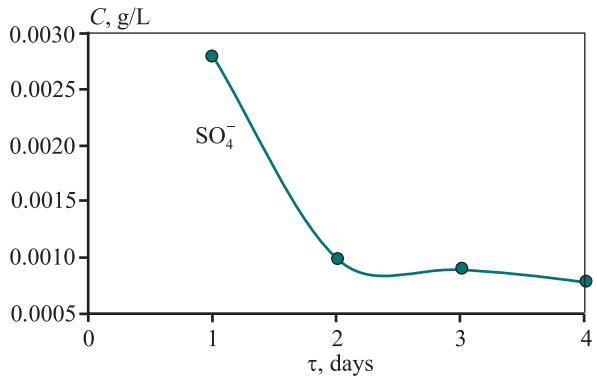

Fig. 4. Desorption of sulfate ions from the MA-41P anion-exchange membrane into distilled water at 20 °C

Рис. 4. Десорбция сульфат-ионов из анионообменной мембраны МА-41П в дистиллированную воду при температуре 20 °С

components does not affect their structure or chemical stability.

To assess desorption, the amounts of copper, cobalt, and cadmium ions, as well as sulfate ions, that were not chemically bound to the membrane components but were retained during electrodeionization and had no effect on the membranes' operational characteristics were determined (Figs. 3 and 4).

The desorption profiles of metal and sulfate ions from the MK-40 cation-exchange and MA-41P anion-exchange membranes consistently show a rapid release during the first 24 h, followed by a gradual decrease over the next three days. The difference in concentrations of desorbed Cu^{2+}, Cd^{2+}, and Co^{2+} is attributed to the selectivity of the KU-2 cation-exchange resin used in the MK-40 membrane. The amounts of unbound metals retained in MK-40 were 0.11 mg/g of copper, 0.17 mg/g of cadmium, and 0.19 mg/g of cobalt. The amount of sulfate retained in the MA-41P membrane was 0.26 mg/g of membrane mass.

Conclusion

1. Infrared spectral analysis demonstrated that the matrices of the MK-40 and MA-41P membranes retain their chemical stability after the electromembrane purification of process solutions from cobalt, copper, and cadmium ions, and do not undergo degradation under the influence of the applied potential difference or components of the treated solution.

2. The macromolecules in the active layer of the MK-40 membrane remain stable, whereas in the active layer of the MA-41P sample, dynamic water saturation leads to a rearrangement of bonds within the ion-exchange group (quaternary ammonium bases). These changes indicate that anion-exchange membranes should be replaced more frequently than cation-exchange membranes in order to maintain the performance characteristics of the electromembrane separation process for copper, cadmium, and cobalt solutions.

3. Static water saturation of the membranes results in an increased amount of weakly bound water in the pore space of the active layer, whereas dynamic saturation is characterized by a decrease in weakly bound water and the formation of stronger hydrogen bonds, indicating minor structural changes in the membrane matrices.

4. In the polyethylene that forms the basis of the MK-40 and MA-41P membrane matrices, water saturation causes a redistribution of bonds involving CH_2 functional groups and, accordingly, a conformational rearrangement of the macromolecules. The similar calculated optical density values for water-saturated and operational membrane samples suggest that this rearrangement is due to water saturation and is not related to the effect of the applied potential difference or the presence of metal sulfates from the treated solution.

5. The amount of chemically unbound metals sorbed within the volume of the MK-40 cation-exchange membrane was 0.11 mg/g for copper, 0.17 mg/g for cadmium, and 0.19 mg/g for cobalt. The amount of sulfate retained in the MA-41P membrane was 0.26 mg/g relative to the membrane's mass. Thus, the transfer of contaminant components from the treated solution into the volume of the membranes does not affect their chemical stability.

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