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X-RAY STRUCTURAL STUDY OF MEMBRANES BASED ON Na-CMC AND CS-CI FOR WATER PURIFICATION

The level of environmental pollution is increasing year by year. Solving this problem requires the development and application of new effective technologies and materials for wastewater treatment and processing of accumulated waste. One of the alternative directions is membrane technologies, in particular, the development of biodegradable nanocomposite membranes.

Anionic polyelectrolyte – Na-carboxymethyl cellulose with molecular weight $M_w \sim 90000$ and cationic polyelectrolyte – low molecular weight chitosan were used to create these membranes. Polymeric membranes were formed by mixing aqueous solutions of chitosan hydrochloride and Na-carboxymethylcellulose in different ratios.

Analysis of X-ray diffractograms of polyelectrolyte complexes showed that with a gradual increase in the content of cationic polyelectrolyte from 5 % to 17 %, the structure of polyelectrolyte complexes changes dramatically. Whereas, the diffractograms of polyelectrolyte complexes with chitosan content from 29 % to 84 % are similar.

The effectiveness of the obtained membranes was tested on a barometric device at different pressures. It was established that membranes based on polyelectrolyte complexes with a stoichiometric ratio of anionic and cationic polyelectrolytes turned out to be the most productive.

The degree of water purification was checked by indicators of color selectivity. The obtained results allow us to conclude that with an increase in the duration of purification, the selectivity increases

Key words: *biodegradable nanocomposite membranes, water purification, polysaccharide, polyelectrolyte complex, polymer membrane, structure*

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Introduction. Growing amounts of environmental pollution require the development of new effective technologies and materials for wastewater treatment and processing of accumulated waste. One of such promising directions is membrane technology, which allows to solve a significant number of environmental problems today. Especially these concerns to the development of biodegradable nanocomposite membranes that can be used in a wide variety of fields, including pharmaceuticals, the food industry, and medicine [1–13]. The main components of such membranes are polymers of natural origin, which are characterized by high biological activity and, at the same time, are non-toxic, biocompatible and biodegradable materials. This ensures both environmental friendliness and high efficiency at the same time.

Experimental part. For creating of polymer membranes based on polyelectrolyte complexes, an anionic polyelectrolyte – Na-carboxymethyl cellulose (Na-CMC) with a molecular weight of $M_w \sim 90,000$, (a product of Merck company); cationic polyelectrolyte – chitosan of low molecular weight, degree of deacetylation $\sim 85\%$, $M_w \sim 50,000$ – $190,000$, a product of the Aldrich company was used.

Protonation of amino groups of chitosan was performed by adding HCl to its 5% aqueous solution until complete dissolution (pH = 6,8).

Polymer membranes were formed by mixing aqueous solutions of chitosan hydrochloride (CS-CI) and Na-CMC in different ratios.

Features of the amorphous and amorphous-crystalline structure of polymer membranes were studied by the method of wide-angle X-ray diffraction on a DRON-4-07 diffractometer, the X-ray optical scheme is made "for the passage" of the primary beam of radiation through studied sample.

The heterogeneous structure (at the nanoscale level) of the obtained samples was studied by the method of small-angle scattering of X-rays using a KRM-1 camera equipped with a slit collimator of the primary radiation beam, made according to the Kratky method. The geometric parameters of the camera satisfy the condition of infinite height of the

primary beam. The profiles of the intensity were normalized by the size of the scattering volume of X-rays and the attenuation factor of the primary beam by studied sample.

All X-ray structural studies were carried out in Cu K_{α} radiation, monochromatized by a Ni filter, at $T = 20 \pm 2$ °C.

For checking of the effectiveness of the obtained membranes, they were tested in a barometric installation at different pressures (3, 4 and 5 atm). Color indicators were determined using a photoelectric concentration CFC colorimeter – 2MP.

Results and their discussion. Analysis of wide-angle X-ray diffractograms of anionic and cationic polyelectrolytes, on the basis of which polymer membranes were formed, showed, that Na-CMC has an amorphous structure. On the diffractogram of this polyelectrolyte there are two asymmetric diffraction maxima with a significant angular half-width. The angular position of these maxima are 8.5 ° and 20.0 ° (Fig. 1, curve 1).

Protonated chitosan (CS-Cl), in turn, has a well-defined amorphous-crystalline structure. Protonation of chitosan by HCl leads to a significant changing in its structure. This can be seen from the fact that the angular position of the diffraction maxima changes, and their shape becomes more symmetrical (Fig. 2, curves 1, 2). These changes are a consequence of the existence of intense Coulomb interactions involving ionogenic groups.

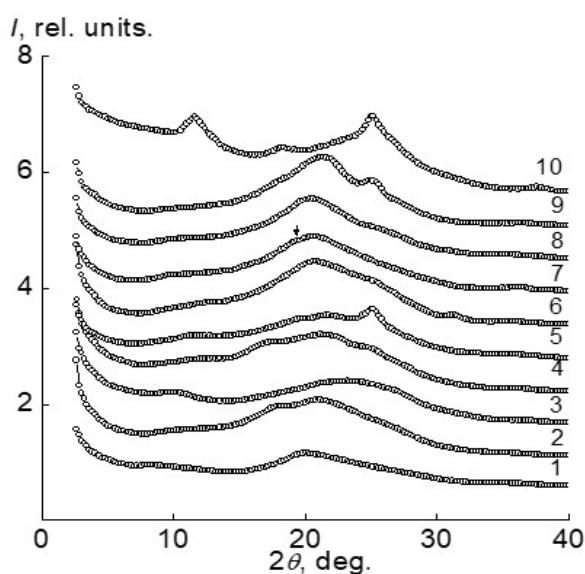


Fig. 1 – Wide-angle X-ray diffractograms of original polyelectrolytes Na-CMC (1) and CS-Cl (10) and PEK with different content of cationic polyelectrolyte: 5 % (2), 6 % (3), 9 % (4), 17 % (5), 29 % (6), 50 % (7), 71 % (8) and 84 % by weight (9)

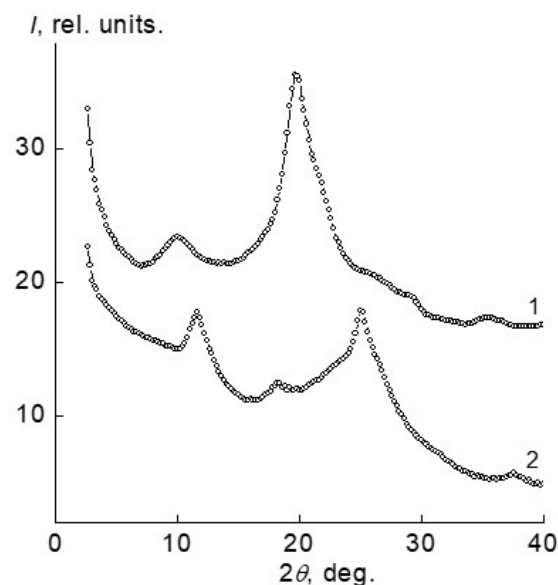


Fig. 2 – X-ray diffractograms of chitosan and chitosan hydrochloride

The analysis of X-ray diffractograms of PEK showed that the structure of PEK changes dramatically with a gradual increasing of the mole fraction of cationic PE from 0.05 to 0.17 in the composition of these polymer systems (Fig. 1, curves 2–5). Meanwhile, the diffractograms of PEK with the mole fraction of CS-Cl, which varies from 0.29 to 0.84 (Fig. 1, curves 6–9) are similar.

It is noteworthy that on the diffractograms of PEK with the molar fraction of CS-Cl, which varies from 0.09 to 0.84, a diffraction maximum is observed. The angular position of maximum coincides with the position of the main diffraction maximum on the diffractogram of the original cationic polyelectrolyte (at $2\theta_{\max} = 25,0$ °) (Fig. 1).

Evaluation of the effective size of the crystallites of the studied samples, was carried out according to the Scherrer method [1]:

$$L = K \lambda (\beta \cos \theta_m)^{-1},$$

where K is a constant related to the shape of the crystallites (at their shape is unknown, $K = 0.9$), and β is the angular half-width (width at half the height) of the singlet diffraction maximum of a discrete type. It showed that the average value of $L \approx 4.5$ nm (the most clear diffraction maxima were used for calculations at $2\theta_{\max} = 25,0$ ° on curves 5, 9).

X-ray diffractograms of the studied membranes based on polyelectrolyte complexes show that they have an amorphous-crystalline structure. This structure differs from the amorphous-crystalline structure of the cationic polyelectrolyte, but has some of its features. For example, a diffraction maximum of varying intensity and clarity is observed on all PEK diffractograms, the angular position of which $2\theta_{\max}=25,0^\circ$ is similar to the angular position of the most intense diffraction maximum on the diffractogram of chitosan hydrochloride (Fig. 1).

Relative level of crystallinity (X_{cr}) of the cationic polyelectrolyte was evaluated according to the Mathews method [3]:

$$X_{cr} = Q_{cr} (Q_{cr} + Q_{am})^{-1} \cdot 100,$$

where Q_{cr} is the area of diffraction maxima that characterize the crystalline structure of the polymer; $Q_{cr} + Q_{am}$ is the area of the entire diffractogram in the range of scattering angles ($2\theta_1 \div 2\theta_2$) in which the amorphous-crystalline structure of the polymer is manifested. It showed that it is about 55 %, and PEK with different molar ratios of Na - CMTS and CS-Cl have $X_{cr} \approx 20-30\%$.

The analysis of the profiles of the intensity of small-angle X-ray scattering showed that there is no heterogeneous structure in the volume of the anionic polyelectrolyte – Na-CMC.

This means that in this case the electron density contrast $\Delta\rho \approx 0$. At the same time, a heterogeneous structure is present ($\Delta\rho \neq 0$) in the volume of the cationic polyelectrolyte XT3-Cl and PEK. That is, there are two types of regions of heterogeneity: crystallites and amorphous regions.

The absence of an interference maximum on the intensity profiles indicates the stochastic nature of the distribution of the heterogeneity areas in the volume of HTZ-Cl and PEK based on them (Fig. 3).

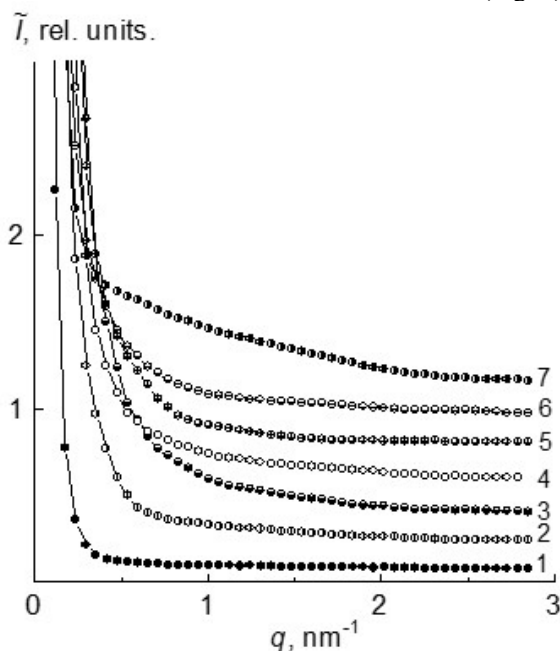


Fig. 3 – Profiles of small-angle scattering of X-rays (slit collimation) for Na-CMC, CS-Cl and PEK obtained on their basis with different content of cationic polymer: 6 % (2), 17 % (3), 50 % (4), 71 % (5) and 84 % (6)

For comparison, let's look at graphs of the dependence of $s^3 \tilde{I}(s)$ on s^3 for the initial anionic (Na-CMC) and cationic (CS-Cl) polyelectrolytes (Fig. 4). These graphs show that in the absence of charge imbalance ($\Delta\rho \approx 0$) the Ruland graph has the form of a straight line that passes through the origin. This means that in this case the structure of the polymer is homogeneous. In the presence of a charge imbalance ($\Delta\rho \neq 0$), the linear approximation of the rectilinear part of the Ruland graph (at $s \rightarrow \infty$) passes through the point x_0 on the ordinate axis. This means that the structure of the polymer is heterogeneous.

In order to estimate the effective size of the regions of heterogeneity of CS-Cl and PEK, the range of heterogeneity l_p was determined.

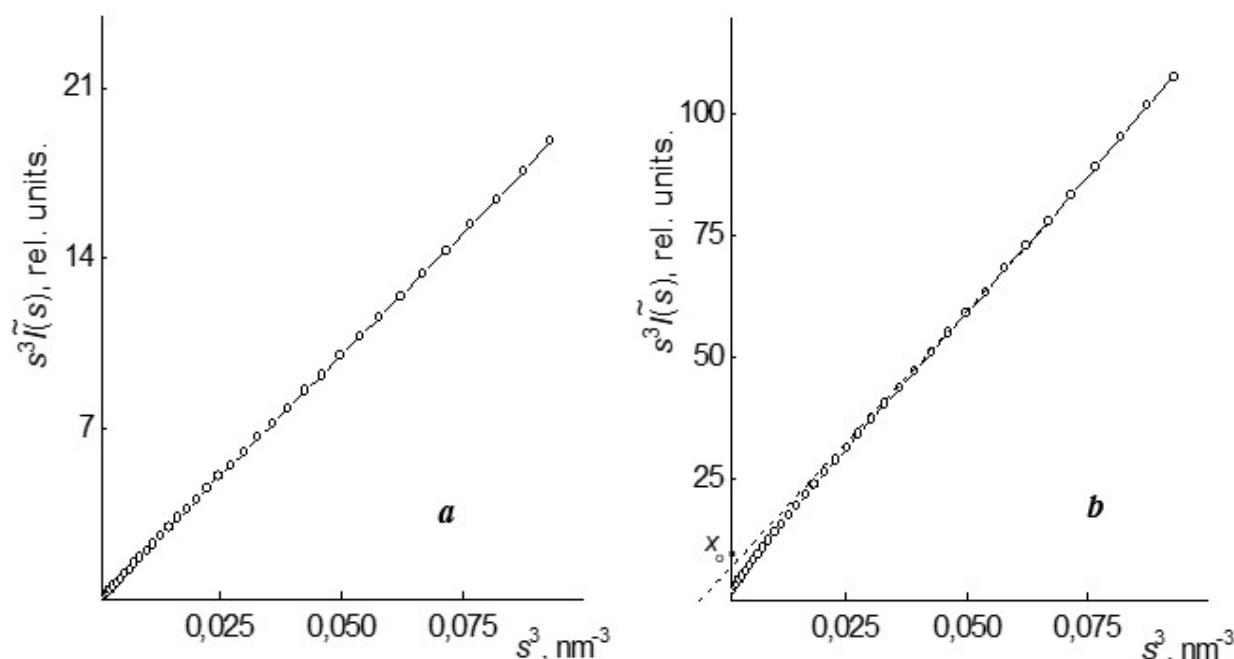


Fig. 4 – Profiles of the intensity of small-angle scattering of X-rays (slit collimation) of Na-CMC (a) and CS-Cl (b). The graphs are built according to the function $s^3 \tilde{I}(s)$ from s^3

From table 1 we can see that the values of l_p change extremely as the content of cationic polyelectrolyte in the volume of polyelectrolyte complexes increases gradually.

Table 1 – Structural parameters of PEK based on Na-CMC and CS-Cl

Mole fraction of PE in PEK		l_p , nm	Q' , in one unit
Na-CMC	CS-Cl		
1	0	0	5.5
0.94	0.06	9.8	7.0
0.83	0.17	12.8	8.3
0.50	0.50	15.0	8.4
0.29	0.71	33.1	7.0
0.16	0.84	10.0	7.6
0	1	7.6	10.8

At the same time, the largest value of the effective size of the regions of heterogeneity is observed for the PEK sample in which the most stoichiometric composition is realized. That is, when the mole fraction of cationic PE – CS-Cl in the composition of these polymer systems is 0.71.

One of the important structural characteristics of polymer systems with a pseudo-two-phase morphology is the level of heterogeneity of their structure. For a semi-quantitative assessment of this level, the calculation of the Porod invariant Q' was carried out. The values of Q' (Table 1) show that it has an extreme concentration dependence, reaching a maximum at an equimolar ratio of anionic and cationic polyelectrolytes in PEK.

To check the effectiveness of the obtained membranes, they were tested on a barometric device at different pressures. Membranes based on polyelectrolyte complexes with a stoichiometric ratio of anionic and cationic polyelectrolytes proved to be the most productive. The degree of water purification was checked by indicators of color and color selectivity (Fig. 5).

From Fig. 5 it can be seen that the selectivity increases at increasing of the duration of cleaning. It can be explained by the fact that at long-term cleaning, the pores of the membrane become clogged, and its permeability decreases, while the cleaning efficiency increases.

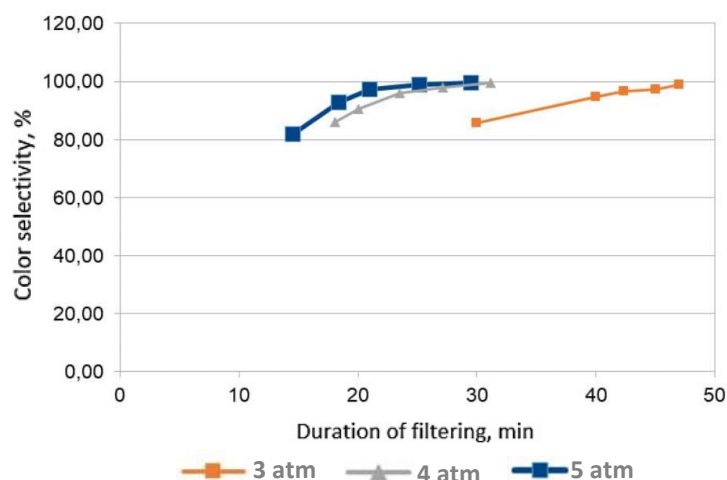


Fig. 5 – Color selectivity

Conclusions. Thus, as a result of the research, it was established that the structure of PEK is determined by the interaction between macromolecular chains of anionic and cationic polyelectrolytes. The most stable PECs are formed by the interaction of macromolecular chains that have similar sizes and shapes. The level of heterogeneity of the PEK structure depends on the ratio between anionic and cationic polyelectrolytes. It was established that polymer membranes are most productive with a stoichiometric combination of anionic and cationic polyelectrolytes.

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РЕНТГЕНОСТРУКТУРНЕ ДОСЛІДЖЕННЯ МЕМБРАН НА ОСНОВІ Na-КМЦ ТА ХТЗ-СІ ДЛЯ ОЧИЩЕННЯ ВОДИ

З року в рік рівень забруднення довкілля зростає. Вирішення цієї проблеми потребує розробки та застосування нових ефективних технологій та матеріалів для очищення стічних вод та переробки накопичених відходів. Одним з альтернативних напрямків є мембранні технології, зокрема, розроблення біорозкладаних нанокомпозитних мембран, які можуть бути використані в різноманітних сферах.

Для створення цих мембран використовували аніонний поліелектроліт – Na-карбоксиметилцелюлози з молекулярною масою M_w близько 90 000 та катіонний поліелектроліт – хітозан низької молекулярної маси. Протонування аміногруп хітозану виконували шляхом додавання хлористоводневої кислоти до його 5 %-го водного розчину до повного розчинення ($pH = 6,8$). Полімерні мембрани формували шляхом змішування водних розчинів гідрохлориду хітозану і Na-карбоксиметилцелюлози у різних співвідношеннях.

Аналіз рентгенівських дифрактограм поліелектролітних комплексів показав, що при поступовому зростанні вмісту катіонного поліелектроліту від 5 % до 17 % структура поліелектролітних комплексів різко змінюється. Тоді як, дифрактограми поліелектролітних комплексів із вмістом хітозану від 29 % до 84 % є подібними.

Перевірку ефективності отриманих мембран було проведено на барометричній установці при різних тисках. Встановлено, що найбільш продуктивними виявилися мембрани на основі поліелектролітних комплексів із стехіометричним співвідношенням аніонного та катіонного поліелектролітів.

Ступінь очищення води перевіряли за показниками селективності по кольоровості. Отримані результати дозволяють зробити висновок, що при збільшенні тривалості очищення селективність зростає. Це може пояснюватися тим, що при тривалому очищенні забиваються пори мембрани і її пропускна здатність падає, при цьому ефективність очищення зростає.

Ключові слова: біодеградабельні нанокомпозитні мембрани, очищення води, полісахарид, поліелектролітний комплекс, полімерна мембрана, структура

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