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Absorption of Ag^+ Ions on Polymer Membranes Based on Chitosan and Na-Carboxymethylcellulose

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Abstract. In this study, composite film membranes of different ratios based on local chitosan and Na-carboxymethylcellulose (KMS) were obtained and their silver ion absorption was studied and analyzed using modern physicochemical methods. The obtained polymer membrane is suitable for use in industry for the absorption of various metal ions due to its good sorption properties.
Keywords. Carboxymethylcellulose, polymer membrane, sorption properties, chitosan.

INTRODUCTION

One of the main ways to expand the field of application of polymers in modern chemistry, to create the desired properties in them is to modify these polymers.

An important method in the modification of polymers is the production of polymer complexes. It has been found that components with different properties in polymer complexes can exhibit new, original, special properties in the case of mutual existence, or that the properties of individual components can be directed to a specific purpose. For example, polymer-based complexes have been used successfully in the formation of various fibers, in the formation of layers for microcapsules, as a drug carrier in medicine, as well as in the absorption of metal ions [1].

Polysaccharides impregnated with silver ions have been found to have high antibacterial properties, can effectively treat skin infections and fungal diseases by 99.9%, and improve ion circulation and metabolism. Similarly, silver ions are firmly fixed in the chitosan-Na-KMS polycomplex and exhibit the above properties.

Research in the field of polymers, especially polysaccharides, shows that biopolymer-based films, including chitosan and cellulose derivatives, have very important and improved adsorption properties [2].

It is known that the resulting polymer complexes and the resulting properties of the films based on them depend on the molecular factor of the polymer components and the environment in which they are obtained. Molecular factors are determined by: molecular mass, chain charge density, macromolecular conformation, and chemical nature of functional groups.

In our studies [3] the formation of an interpolymer complex based on chitosan and Na-carboxymethylcellulose (Na-KMS) by the method of "artificial layering" in analytical ultracentrifugation was successfully carried out. In this study, the optimal conditions for the formation of the polymer complex of the two components were determined depending on the above factors. However, this method determines the reaction kinetics of the formation of the polymer complex, the thickness, symmetry and transparency of the resulting film.

The fact that chitosan and polyanionic Na-KMS form a cross-interpolymer complex and exhibit excellent properties has been studied by many practitioners and scientists. Chitosan-based films, especially modified compositions with silver ions, are widely used in medical practice as an antibacterial coating on wounds. This

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feature of chitosan products will inevitably develop in Uzbekistan in the future, and this research is part of the work in this direction. Another important aspect of these biopolymers is that they are of local importance and are isolated from the natural resources of Uzbekistan [4].

In addition to polymer compounds, various porous adsorbents, various adsorbates on clay minerals on the thermodynamics of sorption Rakhmatkarieva G.U. and others conducted research. This research work serves to enrich the knowledge on adsorption and absorption [5-17]. Based on these data, polymer membranes also help to study the laws of sorption.

MATERIALS AND METHODS

Chitosan used for films based on chitosan and Na-KMS was provided by the Institute of Polymer Chemistry and Physics of the Academy of Sciences of the Republic of Uzbekistan [18] and isolated from silkworm moth (Bombyx Mori) by the method described in the study. Samples of Na-KMS were obtained from OOO "Karbonam" and prepared in accordance with the specifications [19.

Data on the samples used to obtain the interpolymer film in the Chitosan-Na-KMS pair are given in Table 1.

TABLE 1. Molecular mass, moisture, exchange rate, acetylation levels of Chitosan and Na-KMS samples used for film production.

Sample	Humidity (%)	Exchange rate, %	Acetylation rate, %	Molecular mass, g / mol
Chitosan	8.20		95	100000
Na-KMS	7,20	0,81		120000

Three proportions of components were obtained to obtain an interpolymer composite film based on chitosan-Na-KMS. These ratios and the pH of the interaction are given in Table 2. 4.5 value of pH medium $0{,}4MCH_3COOH / 0{,}4MCH_3COONa / 0{,}2MNaCl$ stabilized using an acetate buffer. The films interacted by gently transferring the Na-KMS solution to the surface of the chitosan solution as a layer so that the solvents evaporated at room temperature for 24 h.

TABLE 2. Chitosan - Quantitative ratios of Na-KMS used for interaction and pH of the reaction medium.

Experience	Chitosan		Na-KMS		
	Sample, molecular mass	Concentration (%)	Sample, molecular mass	Concentration (%)	pH
A	Ch-1, M=100000	10	CMC, M=120000	90	4,5
Б	Ch-1, M=100000	90	CMC, M=120000	10	4,5
C	Ch-1, M=100000	70	CMC, M=120000	30	4,5

Experiments on the absorption of silver ions of chitosan-Na-KMS-based interpolymer composite film were carried out at the Center for High Technologies in Tashkent under the German ZEISS EVO electron scanner, energy solution, which allows qualitative and quantitative analysis of elements. The samples were tested at 20 kV.

Adsorption properties of samples with different quantitative ratios of Na-KMS and chitosan solutions were studied. The average thickness of the film obtained from 10% of chitosan in solution, 90% by mass fraction of Na-KMS was 0.065mm, the average thickness of the film in the ratio of 30-70% was 0.060mm, and the average thickness of the film in the ratio of 90-10% was 0.068mm. It can be observed that the thickness of the film is almost close to each other in 3 ratios obtained for the experiment. This means that Na-KMS and chitosan interacted in all of the ratios obtained and the film-forming property was preserved. However, microscopic analysis showed that the ratio of 10-90% of the system of Chitosan and Na-KMS is flat and homogeneous compared to other samples.

To determine the silver ion absorption properties of the films, all film samples were immersed in 10%, 20%, 40% solutions of $AgNO_3$ and stored for 2,6,12 and 24 hours. As a result, 36 samples with different salt concentrations, time durations, and component ratios in the film were compared for comparison. Samples in ratios of

30–70% and 10–90%, stored for 24 h at all concentrations of the $AgNO_3$ solution, swelled to a high degree in solution, reaching a partial melting point and becoming gel-like. This situation is explained by the fact that it is formed at the expense of water-soluble Na-KMS. The film with a ratio of 90-10% of components retains the appearance of a mechanically stable film at all times and under conditions of concentration. Based on the above, qualitative and quantitative analyzes of the absorption of silver ions in films were carried out in samples with a concentration of $AgNO_3$ solution of 20.40% in the absorbed samples for 6 hours.

Qualitative and quantitative measurements of the sorption properties of the samples relative to the silver ion were combined with elemental microanalysis, energy-enhanced digital scanning complex electron microscope ZEISS eVO (Germany). Qualitative and quantitative elemental microanalysis. The samples were examined under an accelerating pressure of 20 kV.

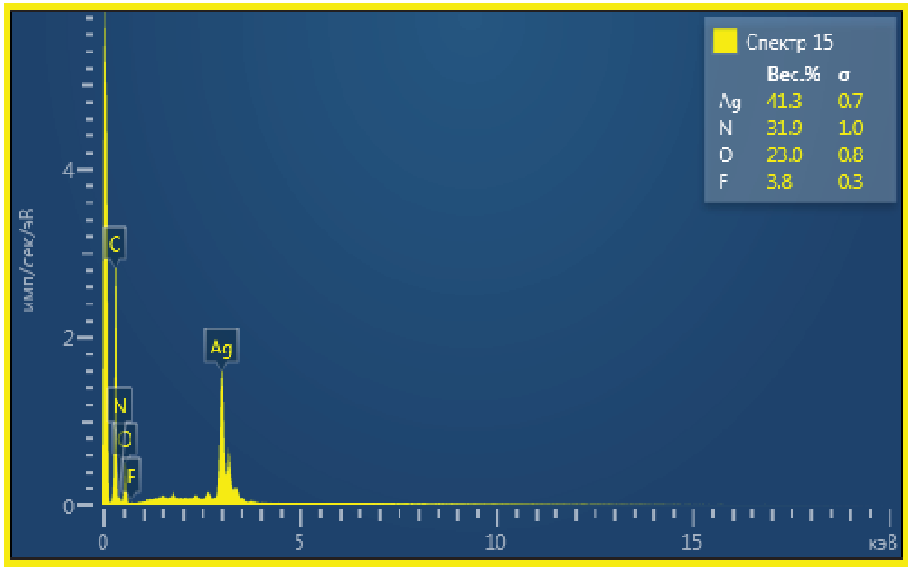


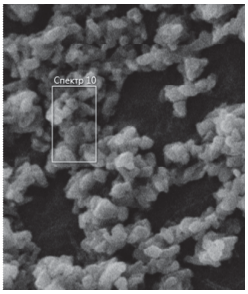
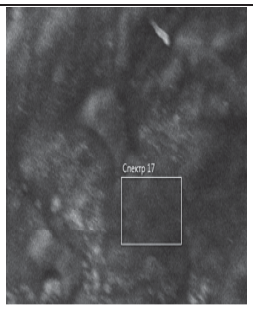
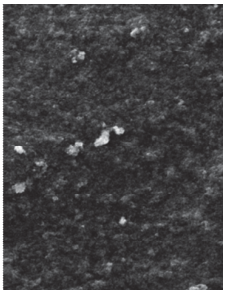
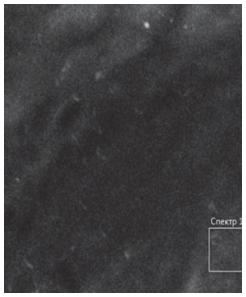
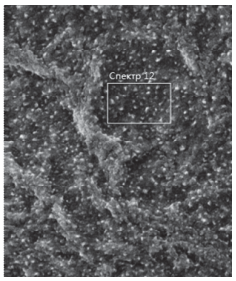
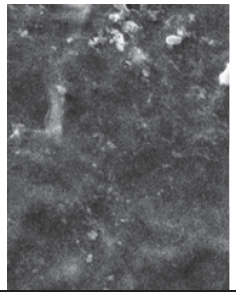
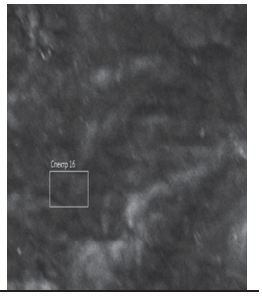
FIGURE 1. Chitosan: Microscopic rate of Na-KMS 10:90 film ratio.

Microscopic analysis and images show that certain amounts of silver ions are absorbed into the examined films, but their distribution across the film is statistical in nature. The amount of silver in the films was probe-examined under a microscope in a sample with sides of 2 cm and calculated as a percentage of the total mass of silver in the examined area. Figure 1 shows an example of a microscopic measurement diagram and shows how silver is absorbed into a film. Comparative analyzes on individual polymer components and films in the polymer complex are given in Table 3. The microscopic images that correspond to these results are shown in Table 4.

TABLE 3. Chitosan, Na-KMS and chitosan: Ag^+ absorption indicators of Na-KMS polycomplex films.

Sample	**Ch**	**Ch-KMS**	**Ch: Na-KMS 90:10**	**Ch : Na-KMS 10:90**
Solution concentration C_{Ag+}, mg / ml			quantities of Ag^+, %	
20	13,10	41.84	54.66	41.28
40	48.26	-	56.44	44.88

TABLE 4. Microscopic images of polymers of chytosan and Na-KMS and polycomplex films based on them.

Sample	Ch	Ch-KMS	Ch: Na-KMS 90:10	Ch : Na-KMS 10:90
C_{Ag+}, 20mg / ml				
C_{Ag+},40 mg / ml		-		

At the same time, we can see that the ratio of Chitosan-90 and Na-KMS-10 in both 20% and 40% absorbed Ag + mass up to 56%. The analysis of microscopic scanning images shows that the silver ion has a relatively high sorption volume in a sample of Chitosan: KMS complex in a ratio of 90:10, and the high sorption property in this sample is higher than in a ratio of 10:90 and an individual polymer. However, it can also be seen that Chitosan: KMS is homogeneous in the distribution of silver ions on the sample surface in a 90:10 ratio.

Chitosan complex with Na-KMS for the formation of metal complexes exhibited high absorption properties. In the sample of chitosan-90 and Na-KMS-10, the absorption property of Ag ion is relatively low. Thus, chitosan itself has a high sensitivity to metal ions. However, we can see that the sorption property of Chitosan is further stabilized with Na-KMS.

Silver nitrate solutions were prepared in water and experiments on sorption of silver ions were carried out to assess the sorption capacity of the obtained complex membranes of Chitosan and Na-KMS. To do this, sample mixtures were prepared with pre-determined concentrations of silver nitrate (20 and 40%). With complex membranes of chitosan and Na-KMS, silver nitrate was mixed in an AVU-3 apparatus for shaking in liquids with a frequency of at least 100 vibrations per minute for 24 hours at a certain interval in water. Upon completion of the experiments, the samples are analyzed to determine the amount of silver. The results obtained by this method also showed that silver absorbs up to 56%.

CONCLUSION

The polycomplex, consisting of chitosan and Na-KMS, is sensitive to the silver ion and absorbs it from the solution. It should also be noted that the quantitative value of such absorption is within the values specified in the literature. In the studied films, a sample of Chitosan: Na-KMS complex in a ratio of 90:10 showed the highest absorption property. Hence, the mutual complex of local raw materials Chitosan and Na-KMS can be used in the future in the separation of silver ions.

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