Currently, colloidal silver particles are used in the creation of electronic, optical, and sensor devices of a new generation. Silver-containing biocomposites (BNCs) were synthesized by immobilization of colloidal montmorillonite particles containing colloidal silver in a composition of sodium alginate and sodium salt of carboxymethylcellulose. Silver-containing montmorillonite particles Ag-Mt were obtained by replacing Na⁺ ions in layered silicate galleries with Ag⁺ ions, followed by the transformation of silver ions into silver particles. The introduction of Ag⁺ ions into the montmorillonite structure is justified by infrared spectroscopy. When studying the strength of biocomposites films, it was found that with an increase in the content of Ag-Mt particles in their composition, the strength increases and the deformation decreases.

It is found that the equilibrium values of the swelling constant are set in ~30 minutes. At the same time, with an increase in the Ag-Mt content in the biocomposite from 3 % to 10 %, the value of the equilibrium swelling coefficient (Ksw) decreases by 2.8 times. The replacement of Na⁺ ions with Ag⁺ ions in the montmorillonite structure is accompanied by a decrease in the swelling of biocomposites, which is explained by the lower hydration of Ag⁺ ions compared to Na⁺ ions. As another reason for the decrease in the swelling of bionanocomposites with an increase in the proportion of Ag-Mt in their composition, enhancing their ability to structure formation in the presence of a clay mineral is indicated.

The kinetics of the release of Ag⁺ ions from bionanocomposites into saline has been studied. It is shown that the release of Ag⁺ ions increases with increasing pH of the medium.

**Keywords:** colloidal silver, biocomposites, montmorillonite interlayer space, alginate, carboxymethylcellulose, tensile strength

1. Introduction

Recently, metal nanoparticles have been widely used in biotechnology, pharmacy, powder metallurgy and other innovative technologies. Colloidal silver particles possess valuable properties — unique optical properties due to surface plasma resonance, a highly specific surface area, catalytic activity, high-capacitance electric double layer, etc. [1]. Due to these properties, they are used to create new generation electronic, optical, and sensor devices.

The antiseptic properties of colloidal silver are of particular interest. The bactericidal properties of metal silver are well studied. The biological activity is shown not by molecules, but by silver ions, which attack various protein objects in the cell and affect intracellular processes. This valuable property of Ag⁺ ions allows them to fight against pathogenic bacteria that are highly resistant to narrow-acting antibiotics [2]. Silver ions Ag⁺ arise during the slow oxidation of metallic silver. An increase in the specific surface area of metallic silver leads to an increase in the concentration of Ag⁺ ions released from it. Therefore, Ag⁺ nanoparticles have the highest antibacterial activity. However, for the gradual release into the environment, silver ions must be immobilized on carriers. Therefore, obtaining composites of silver ions with various mineral and organic carriers is an urgent problem of modern bionanotechnology.

2. Literature review and problem statement

The search for effective antiseptics based on silver led to the establishment of a synergistic antibacterial action of a mixture of nanosilver and antibiotics in the fight against bacteria St. aureus and E. coli [3]. The high anticoagulant and bactericidal activity of the biocompatible polyelectrolyte layer of the lami-
nated polyethylene terephthalate film containing silver clusters was established. Such films can be used to modify the surface of various medical devices, in particular, cardiovascular implants.

A promising line of research is also the production of antibacterial textiles by impregnating them with solutions of silver nanoparticles. A simple and efficient industrial process is developed for impregnating woven and nonwoven fibers with 2 \(10^{-3}\) % solution of silver nanoparticles (3.2 nm), providing full bacteriostatic activity against Gram-positi
tive (St. aureus) and Gram-negative (E. Coli) microorganisms during ten wet treatments using detergents [4]. Animal testing has shown its complete safety for the skin.

This line of research has been developing successfully in recent years. To create bactericidal forms of silver compounds, bionanocomposites based on natural polymers – chitosan, Na-alginlate, pectins, cellulose derivatives, as well as various inorganic compounds are most often used [5, 6]. Antimicrobial efficacy of silver nanoparticles immobilized in Na-alginlate, polyvinylpyrrolidone, cellulose, hydroxypropyl cellulose against food microorganisms was shown [5]. Chitosan is used to immobilize silver compounds in gels [6, 7] and films [8]. In these works, the main attention is paid to elucidating the relationship between the structural features of nanocomposites and the antimicrobial activity of colloidal silver particles immobilized in them.

Scientists are interested in establishing the relationship between the antibacterial activity of colloidal silver and the rate of release of silver ions from it [9]. It is noted that the rate of release of silver ions into solution from the chitosan–Ag-polyvinylpyrrolidone (PV P) nanocomposite is determined by the rate of dissolution of the oxide layer from the surface of nanoparticles and the rate of oxidation of metallic silver. In bionanocomposites containing colloidal particles of montmorillonite and silver, the rate of release of Ag\(^+\) ions is determined by the rate of diffusion of Ag atoms and the rate of their oxidation [10]. The paper [11] presents the results of research of the antibacterial activity of films of Ca-alginlate containing colloidal particles of silver [11]. It is shown that silver ions immobilized in polymer matrices exhibit high antimicrobial activity. However, the combination of polymer and mineral components in the composition of carriers could extend the life of such antimicrobial composites due to the different mechanism of binding of silver ions to carriers. The reason for this may be including silver ions in the structure of the mineral. An attempt to obtain such composites was undertaken in [5, 6]. It is shown that composites of silver ions with clays can be obtained both by introducing Ag\(^+\) ions into the interlayer space of clays and by their adsorption on the surface of clay particles, however, the use of polymers requires the selection of their concentration and ratio. All this suggests that for the purposeful regulation of the properties of composites of silver ions with polymers and clays, it is necessary to study in detail the mechanism of interaction of all components of these systems, the swelling of composites and the kinetics of release of Ag\(^+\) ions from them.

The aim and objectives of the study

The aim of this work is to optimize the conditions for immobilization of colloidal silver in nanocomposites of montmorillonite, natural polymers and the release of Ag\(^+\) ions from them.

To achieve this goal, the following objectives are set:

- to obtain composites of colloidal silver with montmorillonite, Na-alginlate and Na-carboxymethylcellulose in the form of films;
- to determine the influence of the concentration of “silver montmorillonite” on the degree of film swelling in water;
- to study the kinetics of the release of Ag\(^+\) ions from composites.

4. Materials and method

4. 1. Object of research

In this work, silver nitrate AgNO\(_3\) of the “pure for analysis” brand produced by “Reachim” (Russia) was used.

The following biopolymers were also used:
- sodium salt of alginic acid–Na-alginlate (NaALG) with a number average molecular weight (\(M_n\)) of 1.08*10\(^3\) (Sigma, USA);
- sodium salt of carboxymethylcellulose (NaCMC) with medium viscosity (Sigma, USA).

The source of montmorillonite (Mt) was pink bentonite clay from the Tagan deposit in the East Kazakhstan region.

4. 2. Research methods

4. 2. 1. Preparation of clay

To isolate the enriched montmorillonite, natural clay was ground in an impact mill at a grinding unit rotation speed of 22,000 rpm for 3 hours. Then 50 g of dispersed clay was suspended in distilled water (5.0 L), intensively mixed for 10 minutes and left to sediment microheterogeneous particles of non-clay materials – sand, other components – for 20 hours. Then the upper layer of the suspension was separated by decantation, the colloidal dispersed fraction of montmorillonite was precipitated from it by centrifugation; it is activated by the method [5]. Next, the thermally activated clay was treated with a 10 % aqueous solution of sulfuric acid at the temperature of a boiling water bath for 2 hours with periodic stirring. The suspension is neutralized with ammonia solution and washed with sodium chloride solution, dried at 80 °C in a drying oven.

4. 2. 2. Preparation of silver montmorillonite Ag-Mt

The silver form of Mt (Ag-Mt) was obtained by replacing Na\(^+\) ions in Mt with Ag\(^+\) ions according to [12]. For this, 5 g Mt was dispersed in 100 ml 0.2 mol/L NaCl solution by mixing for 4 hours at room temperature. Then the Na-Mt particles were separated by centrifugation at a speed of 10,000 min\(^{-1}\) for 15 minutes, washed 3 times with bidistilled water. Next, Na-Mt was treated in turn with AgNO\(_3\) solutions with a concentration of 5.0*10\(^{-2}\)%, 1.0*10\(^{-1}\)% and 5.0*10\(^{-1}\)% in a vessel protected from ultraviolet radiation. After treatment with Na-Mt with a solution of AgNO\(_3\) with the lowest concentration 5.0*10\(^{-2}\)% at a temperature of 70 °C for 3 hours under stirring conditions, the Ag-Mt particles were separated by centrifugation at a speed of 10,000 min\(^{-1}\) for 15 minutes and treated with AgNO\(_3\) solutions with a concentration of 1.0*10\(^{-1}\)% and 5.0*10\(^{-1}\)% under the above conditions. Then, the Ag-Mt particles isolated after the third treatment were washed 3 times with bidistilled water to remove the AgNO\(_3\) residues, and dried in a vacuum at a temperature of 80 °C for 8 hours.

4. 2. 3. Preparation of films

NaALG film was obtained by drying to a constant weight at room temperature (20 °C) 10 ml of its 2 % aqueous

3.7. A. 1.08. 10^3 (Sigma, USA);
solution introduced into a polystyrene Petri dish with a diameter of 85 mm.

NaCMC film was also obtained by drying at a temperature (20 °C) to a constant weight of 10 ml of its 3 % aqueous solution introduced into a polystyrene cup with a diameter of 85 mm.

Films of bionanocomposites (BNC) based on NaCMC, Ag-Mt, and NaALG were obtained by the method [12]. For this, aqueous solutions of NaCMC (3 %) and NaALG (2 %) were prepared separately. Then they were mixed at a ratio of 1:2. Suspensions of Ag-Mt were also prepared in a 50 % aqueous solution of ethanol with concentrations of 3 %, 6 %, 8 % and 10 % (based on the composition of BNC) with stirring at high speed in a magnetic stirrer for 20 minutes. Next, the water-ethanol suspension of Ag-Mt was introduced into a mixed solution of NaCMC and NaALG with stirring at high speed for 20 minutes. 10 ml of the resulting suspension was introduced into a polystyrene Petri dish with a diameter of 85 mm and dried to constant weight at 20 °C. The thickness of the films measured using the MT-531 thickness gauge was ~30 mkm.

NaCMC/NaALG/Ag-Mt film containing 3 % Ag-Mt is designated BNC–3, 6 % Ag-Mt is BNC–6, 8 % Ag-Mt is BNC–8, and the film with 10 % Ag-Mt is BNC–10.

4. 2. 4. Film thickness measuring

The MT-531 thickness gauge (Russia) is designed for measuring the thickness of sheet materials in laboratory rooms at a temperature of 20±15 °C and a relative humidity of 65±15 %. Limits of permissible measurement error are ±0.02 mm. The material to be measured is inserted between the tip and the base. In the free position, the measuring surfaces are closed.

4. 2. 5. Determination of the tensile strength of films

To determine the tensile strength and elongation of the films, the film break mass was found on the MT-160 device (Russia). The principle of operation of the device is based on the change in the tension force in the measuring resistor sensor. Tensile strength and elongation at break were calculated using the formulas given in the work [13].

4. 2. 6. Study of film swelling and kinetics

The kinetics of swelling of the films was determined from the rate of increase in their weight over time (W). For this, 0.2 g (W0) of an air-dry sample of films was poured into 30 ml of bidistilled water with pH values. The solution of HCl with concentration 1 mol/L was used for changing the pH values. After a certain time (t) at 20 °C its weight was determined (Wt) on the Kern analytical balance (KERN &Sohn GmbH, Germany) with an accuracy of 0.0001 g.

\[ K_{swell} = \frac{(W_t - W_0)}{W_0} \]

Each Kswell value is the average of its three values.

4. 2. 7. Study of the kinetics of the release of silver ions

The kinetics of the release of silver ions was determined from the rate of change in its concentration in the solution (F=Ct/C∞, where Ct is the concentration of Ag⁺ ions released at time t; C∞ is the maximum possible concentration of Ag⁺ ions provided that all ions are released). To do this, 0.1 g of air-dry sample was filled with 30 ml of the saline solution was mixed using a magnetic stirrer at 20 °C. The concentration of Ag⁺ ions was determined using an Agilent 8453E UV spectrophotometer (Agilent Technologies Deutschland GmbH, Germany) at a wavelength of 302 nm using a previously constructed calibration curve. The experiment was repeated three times.

4. 2. 8. FTIR spectroscopy

Infrared spectra (FTIR) of Na-Mt, Ag-Mt, and BNC samples were recorded using a Cary 660 FTIR spectrophotometer (Agilent Technologies, USA) in the wavelength range of 4,000–450 cm⁻¹ and intensities up to 61 %. The samples were pressed on a Crush IR press (Pike Technologies, USA).

5. Results

5. 1. Synthesis and properties of composites of colloidal silver with montmorillonite, Na-alginate and Na-carboxymethylcellulose

5. 1. 1. IR spectroscopy of bionanocomposites polymer-Ag-Mt

For information on the mechanism of interaction of the Ag⁺ ions with montmorillonite, IR spectra of Na-Mt and Ag-Mt are withdrawn (Fig. 1). For the synthesis of the Ag-Mt composite, natural bentonite was converted to sodium form by treating its suspensions with a sodium chloride solution.

![Fig. 1. IR spectra of montmorillonite composites with metal ions: a - sodium (Na-Mt); b - silver (Ag-Mt)](image-url)
The interpretation of the IR spectra of Na-Mt and Ag-Mt systems according to [14] indicates the presence of silicon and hydrogen bonds with oxygen in these samples (Fig. 1). The pronounced broad band at 1036.32 cm\(^{-1}\) corresponds to stretching vibrations of Si–O–Si bonds of the tetrahedra of the silicon-oxygen framework, and the bands at 470.82 and 527.03 cm\(^{-1}\) correspond to deformation vibrations of Me-O bonds. The 913.62 cm\(^{-1}\) band is related to the vibrations of Si–O–Si rings of SiO\(_4\) tetrahedra. The intense bands at 1634.05, 3436.51 and the band at 3626.88 cm\(^{-1}\) are related to stretching and bending vibrations of O–H bonds of free and bound water [14].

The appearance in the spectrum of Ag-Mt of a band at 1401.17 cm\(^{-1}\), related to the Ag–O bonds, indicates the presence of Ag\(^{+}\) ions in the object under study. This band shifts to higher frequencies with an increase in the Ag\(^{+}\) ions content in Ag-Mt particles. The presence of Ag\(^{+}\) in the Ag-Mt structure is evidenced by double peaks at ~2,400 cm\(^{-1}\) [15]. In Fig. 1, these peaks are not of high intensity, but are found between peaks of 3436.68 cm\(^{-1}\) and 1638.54 cm\(^{-1}\).

To study the dependence of the structure of bionanocomposite films on the Ag-Mt concentration, the IR spectra of NaCMC/NaALG/Ag-Mt with the same composition and different Ag-Mt contents: 3 %, 6 %, 8 %, and 10 % were obtained (Fig. 2). This is evidenced by similar IR spectra, differing in the intensity of absorption in the infrared region.

| Bonds   | Peaks nature of Mt, cm\(^{-1}\) | Peaks of Ag-Mt, cm\(^{-1}\) |
|---------|---------------------------------|-----------------------------|
| -OH     | 1634.15                         | 1638.34                     |
|         | 3436.51                         | 3436.68                     |
|         | 3626.88                         | 3629.72                     |
| Si-O-Si | 913.62                          | 913.62                      |
|         | 1036.32                         | 1039.97                     |
| Me-O    | 470.82                          | 470.78                      |
|         | 527.03                          | 527.43                      |
| Ag-O    | –                               | 1401.17                     |
| Ag\(^{+}\)| –                              | 2400.00                     |

The IR spectra of bionanocomposites (Fig. 2) have peaks indicating the presence of carbonyl groups (absorption maximum at 1,600–2,800 cm\(^{-1}\)) and hydroxyl groups (absorption maximum at 1,400–1,600 cm\(^{-1}\)) in the films [15].

The peaks at 600–1,000 cm\(^{-1}\) refer to metal and silicon oxides [15].

As can be seen from Fig. 2, with an increase in the Ag-Mt content in the bionanocomposite, i.e. with a change in the ratio of the polymer matrix to Ag-Mt, the intensity of absorption of infrared radiation increases, since the IR transparency of the modified bentonites decreases. Accordingly, the height of the peaks also increases: for spectrum a – the maximum height is in the range of 50–60 % of the transmittance, for b – 60–70 %, for c – above 70 %.

![Fig. 2. IR spectra of bionanocomposite NaCMC/NaALG/Ag-Mt films with different content Ag-Mt: a – BNC–3; b – BNC–6; c – BNC–10](image-url)
5.1.2. Mechanical properties of bionanocomposite films

The effect of colloidal particles of montmorillonite containing silver nanoparticles ("silver montmorillonite", Ag-Mt) on the properties of bionanocomposites has been studied. For this purpose, Ag-Mt was first synthesized according to the method [12]. It was found that with an increase in the concentration of the AgNO₃ solution, from which Ag⁺ ions are adsorbed on the colloidal particles of Mt, which are then transformed into colloidal particles of silver.

With this method of obtaining Ag-Mt, the maximum content of colloidal silver is 0.037 g/g [16]. The presence of characteristic bands at 290 nm, 350 nm, and 450 nm in the UV spectrum of surface plasmolysis indicates the presence of residual amounts of Ag⁺ ions and silver nanoparticles with an average size of 2 nm, 10 nm, and 40 nm in Ag-Mt [12].

Ag⁺ ions are incorporated into the Mt matrix as a result of their exchange with Na⁺ ions located in the inter-package space, in the so-called galleries of Mt. Analysis of the spectra of wide-angle X-ray scattering and X-ray photoelectron spectroscopy of Na-Mt and Ag-Mt particles obtained in the presence of chitosan (Cs) made it possible to confirm the presence of the latter nanoparticles of metallic silver (Ag) and AgO/Ag₂O in the clay galleries [12].

A sample of "silver clay" containing 0.037 g/g of colloidal silver particles was used when BNCs films were obtained from the suspension. It was found that with an increase in the Ag-Mt concentration in the biocomposite from 3 % to 10 %, the film changes color from light brown to dark brown (Fig. 3).

Similar results were obtained in the study of films of bionanocomposites of chitosan with Ag-Mt [6]. The introduction of colloidal particles of Mt into the structure of bionanocomposites of methylcellulose and Na-alginate, as is known, improves their mechanical properties [14]. In this regard, this work also studied the effect of the concentration of Ag-Mt in the composition of bionanocomposites on their strength and elongation at break (Table 2).

The initial film obtained from 2 biopolymers – NaALG and NaCMC – has a low strength, the value of the tensile strength is 10.95 MPa. In the presence of 3 % Ag-Mt particles, the film strength increases to 12.70 MPa, an increase in the Ag-Mt concentration to 10 % increases the film strength to 35.20 MPa. However, an increase in the content of silver ions in bionanocomposites leads to a decrease in elongation at break.

5.2. Influence of the "silver montmorillonite" concentration on the film swelling

The interaction of bionanocomposites with water is one of the most important properties that determine the areas of practical use of these materials. Fig. 4 shows the kinetics of swelling of bionanocomposites in water. It may be noted that the subject bionanocomposites quickly swell – the equilibrium values of them to swell are set for ~30 minutes. Furthermore, with increasing content of Ag-Mt in bionanocomposite the swelling ability is reduced: with increasing content of Ag-Mt from 3 % (BNC–3) to 10 % (BNC–10), the value of the equilibrium ratio of swelling ($K_{swell}$) is reduced to 2.8 times.

### Table 2

| No. | Film samples | Tensile strength, MPa | Elongation at break, % |
|-----|--------------|-----------------------|------------------------|
| 1   | NaALG–NaCMC  | 10.95                 | 2.25                   |
| 2   | BNC–3        | 12.70                 | 1.75                   |
| 3   | BNC–10       | 35.20                 | 1.45                   |

Fig. 3. Image of bionanocomposite films: 1 – BNC–3; 2 – BNC–10

Fig. 4. Kinetics of swelling of the BNC films with varying content of Ag-Mt: a – the first 30 minutes, b – over 24 hours
From a colloidal-chemical point of view, bionanocomposites are a type of filled polymer materials consisting of a continuous dispersion medium of a polymer and a dispersed phase – colloidal filler particles – in this case, Ag-Mt particles. Rheological, as well as mechanical, properties of such systems are determined by the coagulation structure formation of filler particles with each other through the adsorbed polymer layer. This process is accompanied by the strengthening of the adsorption layer of the polymer as a result of the interaction of the segments of macromolecules with the surface of the filler particles, which has excess Gibbs free energy.

Filled polymers are characterized by an extreme dependence of their mechanical properties on the filler content in them. This is due to a change in the proportion of adsorption layers of macromolecules oriented on the surface of filler particles with increasing filler concentration [15]. The minimum filler concentration at which a spatial coagulation structure appears in the filled polymer decreases with an increase in the degree of dispersion of the filler.

5.3. Kinetics of Ag$^+$ ions release from bionanocomposites

As noted above, the kinetics of the release of silver ions from its colloidal silver particles immobilized in bionanocomposites is mainly determined by the water absorption of these particles. In this regard, in this work, it was studied the release of Ag$^+$ ions from bionanocomposites. As can be seen in Fig. 5–7, the release of Ag$^+$ ions is not instantaneous, but a kinetic process – within 15 days at pH=1.2, only 1.2 to 4.5 % of immobilized Ag$^+$ ions are released, depending on the Ag-Mt content of the BNCs. For fifteen days, this process is not over yet. With an increase in the pH of the medium, the release of Ag$^+$ ions is accelerated (Fig. 6, 7).

Fig. 5. Kinetics of Ag$^+$ ions release from bionanocomposites NaALG/NaCMC/Ag-Mt, containing 3 %, 6 %, 8 % and 10 % Ag-Mt, into saline solution at pH 1.2 and $T=20^\circ C$: a – first 120 minutes; b – during 15 days

Fig. 6. Kinetics of Ag$^+$ ions release from NaALG/NaCMC/Ag-Mt bionanocomposites, containing 3 %, 6 %, 8 % and 10 % Ag-Mt, into saline solution at pH 5.0 and $T=20^\circ C$: a – first 120 minutes; b – during 15 days
Comparing these data with the kinetics of swelling of the considered BNCs in water (Fig. 4), it can be noted that the better the BNCs swells in water, the faster the Ag\(^{+}\) ions are released from it, as found in [17].

6. Discussion of experimental results

6.1. Incorporation of Ag\(^{+}\) ions into the structure of montmorillonite and bionanocomposites

To justify the occurrence of Ag\(^{+}\) ions in the structure of montmorillonite, it is necessary to compare the IR spectra of the sodium and silver forms of montmorillonite (Fig. 1). Both spectra are very similar to each other, but after processing with Ag\(^{+}\) ions, noticeable peaks appear on the IR spectrum of clay at a frequency of 1,401 cm\(^{-1}\) and 2,400 cm\(^{-1}\), which can be attributed to Ag–O bond vibrations. This is evidence of the entry of Ag\(^{+}\) ions into the structure of montmorillonite as a result of exchange with Na\(^{+}\) ions in the interlayer space of clay. The bands at 470.82 cm\(^{-1}\) and 527.03 cm\(^{-1}\) are caused by deformation vibrations of the Me–O bonds, where Me are other metals that are part of the clay (K, Ca, Mg, Fe). Other peaks characteristic of Si–O–Si and O–H bonds of silicate ions and bound water remain unchanged.

In the IR spectra of bionanocomposites, the peaks at 1,401 cm\(^{-1}\) and 2,400 cm\(^{-1}\) indicating the presence of Ag\(^{+}\) ions in the montmorillonite structure are shifted to 1,415–1,417 cm\(^{-1}\) and 2,147–2,192 cm\(^{-1}\), respectively. In addition, they have peaks corresponding to carbonyl (1,600–2,800 cm\(^{-1}\)) and hydroxyl groups (1,400–1,600 cm\(^{-1}\)) [4]. As the Ag-Mt concentration increases, the intensity of these peaks decreases, which indicates the formation of a composite that includes biopolymers – alginate and carboxymethylcellulose, as well as montmorillonite with Ag\(^{+}\) ions.

It is known that the introduction of colloidal clay particles into the structure of bionanocomposites of methylcellulose and Na-alginate can improve their mechanical properties [12]. In this regard, we also studied the effect of Ag-Mt concentration in bionanocomposites on their strength and elongation at break (Table 2). The results of the study show that the strength of films increases with increasing Ag-Mt concentration in bionanocomposites. However, the process of film hardening in the presence of Ag-Mt is accompanied by a certain increase in the brittleness of the samples — a decrease in elongation when they break. Probably, Ag-Mt particles introduced into the mixture of two biopolymers have a cross-linking effect on their macromolecules, reducing their flexibility. This leads to an increase in the strength and a decrease in the elasticity of the films.

6.2. Effect of Ag\(^{+}\) ions on the swelling of bionanocomposite films

To explain the phenomenon observed in Fig. 4, one can turn to modern representatives about the mechanism of hydration of ion-exchange resins, taking the considered bionanocomposites as such due to the presence of functional –COO\(^{-}\) groups in them, as in weakly acidic ion exchangers.

This process begins with the interaction of water molecules with a counterion, in this case, with Na\(^{+}\) ions in the Na-CMC film and with Ag\(^{+}\) ions — in a film of a bionanocomposite with Ag-Mt. The counterion, by attaching the first water molecule, is somewhat removed from the group (–COO\(^{-}\)) fixed on the polymer matrix. Subsequent hydration layers are formed both between the counterion and the fixed group and around them. With an increase in the radius of the counterion, its hydration weakens due to a decrease in the ion charge density. Thus, reducing the swelling of films at the transition from NaCMC to BNC–3 and BNC–10 can be explained by an increase of content of Ag\(^{+}\) ions, which are less hydrated than Na\(^{+}\) ions. On the other hand, it can be assumed that the colloidal particles of montmorillonite, structuring the bionanocomposite, also reduce its swelling capacity. Con-
sequently, the observed decrease in the swelling ability of bionanocomposites, containing colloidal particles of Ag-Mt, can be considered as the superposition of two of these effects.

Similar results were obtained in the work [17] when studying the kinetics of swelling of bionanocomposites of chitosan, Na-Mt and Ag-Mt and the kinetics of release of Ag⁺ ions from these bionanocomposites. In the study of water uptake of films of chitosan and its composition with Na-Mt and Ag-Mt, it is found that chitosan composite comprising 10% Na-Mt has the highest water absorption. The lowest water absorption is present in a film of pure chitosan, a composite film containing 10% Ag-Mt, and, in these indicators, has an intermediate position. The increase in water absorption of the chitosan film in the presence of Na-Mt is explained by the high affinity of layered aluminosilicate for water, and its decrease upon the introduction of Ag-Mt instead of Na-Mt is attributed, following [18], to the “hardness” of Mt particles and their interaction with chitosan macromolecules.

As mentioned above, bionanocomposite films are a type of filled polymers, where colloidal Ag-Mt particles play the role of filler. Therefore, the mechanical properties of such systems are determined by the structure formation of filler particles with each other through the adsorption layer of the polymer.

6.3. Kinetics of Ag⁺ ions release from bionanocomposites

Analysis of data on the kinetics of the release of Ag⁺ ions into saline solution (Fig. 5–7) shows that this is a rather long process. Moreover, the higher the pH of the medium, the greater the yield of silver ions in the medium. Another factor contributing to the release of Ag⁺ ions is their concentration.

Similar results were obtained in [12] in the study of water absorption by composites of chitosan and Ag-Mt, as well as the kinetics of the release of Ag⁺ ions from them. The higher the content of Ag-Mt in the composite, the faster the Ag⁺ ions are released. Note that in the cited work, the Ag⁺ ions diffuse in the positively charged matrix of the polymer (chitosan), when released from BNCs. In the BNCs based on CaALG and NaCMC, the Ag⁺ ions diffuse in a negatively charged polymer medium. In this case, the passage of an ion exchange process is not excluded. The release of Na⁺ ions from the BNC and Ag⁺ ions from Na-Mt is attributed, following [18], to the “hardness” of Mt particles and their interaction with chitosan macromolecules.

Comparison of the results of the study of the release of Ag⁺ ions from bionanocomposites, conducted in [12], shows that this is a rather long process. Moreover, the higher the pH of the medium, the greater the yield of silver ions in the medium. Another factor contributing to the release of Ag⁺ ions is their concentration.

Similar results were obtained in [12] in the study of water absorption by composites of chitosan and Ag-Mt, as well as the kinetics of the release of Ag⁺ ions from them. The higher the content of Ag-Mt in the composite, the faster the Ag⁺ ions are released. Note that in the cited work, the Ag⁺ ions diffuse in the positively charged matrix of the polymer (chitosan), when released from BNCs. In the BNCs based on CaALG and NaCMC, the Ag⁺ ions diffuse in a negatively charged polymer medium. In this case, the passage of an ion exchange process is not excluded. The release of Na⁺ ions from the BNC and Ag⁺ ions from Na-Mt is attributed, following [18], to the “hardness” of Mt particles and their interaction with chitosan macromolecules.

As mentioned above, bionanocomposite films are a type of filled polymers, where colloidal Ag-Mt particles play the role of filler. Therefore, the mechanical properties of such systems are determined by the structure formation of filler particles with each other through the adsorption layer of the polymer.

Therefore, the kinetics of the release of Ag⁺ ions from the BNC studied in this work should differ from the analogous process established in BNCs based on chitosan [12].

Comparison of the results of the study of the release of Ag⁺ ions into saline solution (Fig. 5–7) shows that this is a rather long process. Moreover, the higher the pH of the medium, the greater the yield of silver ions in the medium. Another factor contributing to the release of Ag⁺ ions is their concentration.

Similar results were obtained in [12] in the study of water absorption by composites of chitosan and Ag-Mt, as well as the kinetics of the release of Ag⁺ ions from them. The higher the content of Ag-Mt in the composite, the faster the Ag⁺ ions are released. Note that in the cited work, the Ag⁺ ions diffuse in the positively charged matrix of the polymer (chitosan), when released from BNCs. In the BNCs based on CaALG and NaCMC, the Ag⁺ ions diffuse in a negatively charged polymer medium. In this case, the passage of an ion exchange process is not excluded. The release of Na⁺ ions from the BNC and Ag⁺ ions from Na-Mt is attributed, following [18], to the “hardness” of Mt particles and their interaction with chitosan macromolecules.

The main disadvantage of the study is the lack of testing bionanocomposites for bactericidal activity. This would make it possible to determine the minimum concentration of Ag⁺ ions necessary for the manifestation of bactericidal properties, since an excess of silver is also undesirable due to their possible toxic effect. In addition, research is needed to describe the storage conditions of films.

Research in this area can be developed using mathematical modeling methods and using modern research methods, such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM). However, this requires preliminary experiments to determine the variable parameters and the limits of their change. SEM and TEM studies also require information about the possible degree of dehydration of films, since it is difficult to obtain information about the morphology of their surface when the films are excessively dehydrated.

7. Conclusions

1. In order to expand the range of antimicrobial, biocidal preparations and products based on colloidal silver, colloidal silver particles were synthesized from Ag⁺ ions immobilized in the structure of layered silicate-montmorillonite. The structure of the synthesized composite was studied using IR spectroscopy. It is found that the introduction of Ag⁺ ions into the clay structure is accompanied by the appearance of new absorption bands in the IR spectrum at 1401 cm⁻¹ and 2400 cm⁻¹ due to fluctuations in Ag-O bonds.
2. Synthesized colloidal particles of silver-containing montmorillonite Ag-Mt are immobilized in the structure of films based on NaALG and NaCMC biopolymers. It was found that with an increase in the Ag-Mt content in bionanocomposites, the swelling of films decreases due to the replacement of more hydrated Na⁺ ions with less hydrated Ag⁺ ions and the strengthening of structure formation in the system under the influence of montmorillonite.

3. The kinetics of the release of Ag⁺ ions from synthesized bionanocomposites into saline solution at pH values of 1.2, 5.0, and 7.4 was studied. It is shown that the release of Ag⁺ ions increases with increasing Ag-Mt content in BNC and with an increasing pH of the medium.

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