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Preparation of Silvered Colloidal Compositions for Nanocosmetic Drugs

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Abstract

The article presents the results of obtaining nanosilver aqueous suspensions by electrolysis method with variations in the quality and composition of water, the type, and quantity of modifying additives, as well as the creation of colloidal compositions consisting of silicon dioxide and nanosilver emulsion as a result of mechanochemical treatment of the system. As a modifier of silver nanoparticles, citric acid, glycerin, and ether-cellulose were used, which can form the thinnest layers on the surface of the metal particle, preventing particles from sticking together and precipitating them. It is shown that the use of modifiers in the preparation of a colloidal solution with silver particles and ultrasonic treatment of the system provide an increase and stabilization of the activated state of colloidal systems with silver nanoparticles and silicon dioxide. Obtained under the influence of ultrasonic treatment homogeneous and resistant to delamination soft gel systems containing silver and having antimicrobial activity are promising for the manufacture of drugs for cosmetic purposes.

1. Introduction

A distinctive feature of nanocosmetic is that such drugs contain active nanoparticles, which due to their size can penetrate into the deep layers of skin: the epidermis and dermis. As a result, the deep layers of the skin receive nutrients and active components that do not lose their useful properties and help to eliminate the existing focal points of infection or aging [1]. Active substances in the form of various microelements and vitamins make up whole nanocomplexes, and with their participation, the protective properties of the skin increase, which makes it more effective to fight against the harmful effects of the environment, as well as the destructive action of free radicals [2, 3]. As biologically active substances, alcohols, acids, various organic compounds of synthetic and natural origin, having a certain functional purpose, are used [4].

Also, dozens of microelements are needed to preserve the beauty and elasticity of the skin. One of the main directions of rapidly developing nanotechnology is the use of inorganic nanoparticles, in particular, those obtained based on silicon oxide [5, 6], as well as in combination with various metals: gold, silver, platinum. The use of metals allows creating of carriers possessing a number of unique properties. Metal nanoparticles can effectively penetrate deep into the epidermis. Special attention is paid to the use of silver nanoparticles in the composition of cosmetic preparations, the presence of which has an anti-inflammatory and tonic effect, stimulates reparative and metabolic processes in the skin, promotes rapid healing of microtrauma, abrasions, and other skin lesions [7, 8]. In this direction, intensive work is carried out in many cosmetic companies around the world [9–11]. The presence of silver in creams and ointments eliminates acne and removes any inflammatory processes of the skin, stimulates the protective forces of the skin and regulates the sebaceous glands. In modern cosmetology used colloidal, that is, “dissolved” in water silver, is used.

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Both physical and chemical methods are used to produce silver nanoparticles. One of the simplest and most effective methods of saturation of aqueous solutions with silver is the method of electrolysis (ionization) of silver. At the concentration of silver in water 0.1–0.2 mg/l the process of suppression and disinfection of dangerous microorganisms begins. Therefore, silver water is used to solve many problems in the medical and cosmetic fields. It is found that at a concentration of silver ions in water of 50–100 μg/l growth and reproduction of bacteria is restrained and at a concentration of 150–200 μg/l bacteria die [12]. To stabilize the aqueous solution of silver nanoparticles, various substances are introduced into it, which provide surface modification of silver nanoparticles in the solution. Chemical modification of the surface of nanoparticles is carried out to change the existing properties and impart them new ones, as well as to prevent coagulation of particles. Depending on the goals, a modifier of the corresponding nature is chosen. The modification process is associated with the electrostatic interaction of organic molecules with the surface of silver particles resulting in the change of their physical and chemical characteristics [13].

This paper presents the results on the synthesis of nanosilver depending on the quality of the input medium and modifying additives, as well as the creation of colloidal compositions consisting of silicon dioxide and nanosilver emulsion as a result of mechanochemical treatment of the system. To ensure the stability of the state and high activity with respect to physical and chemical characteristics, the obtained colloidal compositions were subjected to ultrasonic treatment. The synthesized colloidal systems are designed as a carrier of various active additives of synthetic and natural origin and are introduced into the gel base to obtain cosmetic products for various functional purposes.

2. Experimental

To obtain a nanosilver emulsion, a saturation of water with silver was carried out by the electrolysis method using the ionizer "NEVOTON IP-112". The silver content in the system was determined by the AA-6200 atomic adsorption spectrophotometer. The data were processed was carried out using the software in the MS-Windows system.

To obtain a system consisting of silicon dioxide saturated with silver, synthetic amorphous silicon dioxide of 99.9% purity was used. Silicon dioxide powders were subjected to mechanochemical treatment (MCT) in a ball laboratory mill ML-1R. Grinding was first carried out in an alcohol-water solution, and then a colloidal silver solution stabilized with various organic compounds was introduced. The prepared compositions were processed in ultrasonic multifunctional apparatus "Malysh" (Model UZTA-0.05/27-O) with the frequency of exciting oscillations 27 kHz and power of 100 W. Electron-microscopic and energy-dispersive elemental analyses of the powder were carried out on a scanning electron microscope Quanta 3D 200i Dual system, FEI.

The quality of the resulting compositions was evaluated by pH, conductivity, and viscosity. Determination of pH was carried out by the pH-meter "pH-150MI", which is designed to measure the activity of hydrogen ions (pH), redox potentials (Eh) and the temperature of aqueous solutions. Measurement pH is carried out in a digital form using a measuring transducer and a set of electrodes and meets the requirements of group 3 (Interstate Standard 22261-94. Means for measuring electrical and magnetic quantities. General specifications. #6, October 21, 1994). Conductimetric analysis on the TDS/EC meter HM COM-80 was used to determine the conductivity. This instrument is a meter of electrical conductivity (EC Range), total dissolved salt (TDS Range) and temperature of liquids. The viscosity of colloidal systems was determined on a rotary viscometer EAC-2M, designed for operational control over rheological parameters of various substances.

3. Results and discussion

To obtain a nanosilver emulsion by the electrolysis method, boiled, filtrated tap water and water from in mineral spring of "Koktem" health resort in Almaty with a high concentration of silicon oxide was used. The silicon component in mineral water exerts an anti-toxic, anti-inflammatory and analgesic action providing an effective treatment of a whole number of diseases including skin and traumatic injuries. Table 1 presents the physico-chemical characteristics of tap boiled, filtrated and mineral water in the initial state and after ultrasonic treatment (UST).

The largest number of elements dissolved in water is present in mineral water, the smallest–in filtered water, which is reflected accordingly on the conductivity values. UST of water helps to increase the ppm values (the number of elements dissolved

Table 1
Physical and chemical characteristics of water: hydrogen index (pH), the amount of elements dissolved in water (ppm) and electrical conductivity (µs)

Water	UST time, min	Property indicators		
		pH	ppm	Electroconductivity, µs
Boiled	0	7.47	212	437
	2	7.32	232	467
Filtrated	0	7.53	97	202
	2	6.15	145	301
Mineral	0	7.83	842	1680
	2	7.53	974	1834

in water) and electrical conductivity, which may be due to the decomposition of particles of various suspensions and their transfer to the solution under the influence of the cavitation effect. Preparation of nanosilver by electrolysis method was carried out with a variation of ionization-time (from 20 to 60 min). The amount of silver in the aqueous solutions obtained varies from 0.1 to 30 mg/l.

As stabilizers of silver nanoparticles, citric acid, glycerin, and ether-cellulose were used, capable of forming the thinnest layers on the surface of a metal particle, preventing particles from sticking together and precipitating them. To ensure the modification of silver nanoparticles by organic molecules, aqueous silver solutions with additives of organic stabilizers were subjected to mechanochemical treatment in the mode of ultrasonic action [14, 15]. A mechanical shock impact when cavitation effects [16] the passage of ultrasonic waves in an aqueous medium lead to the destruction of aggregates. In addition, as a result of mechanochemical treatment of an aqueous solution in the ultrasonic mode and modification of the surface of particles, there also takes place an additional chemical reduction of silver from complex formations present in the aqueous solution of silver. As a result, the percentage of metal silver nanoparticles in the solution increases (Table 2).

The content of silver in the solution after ultrasonic treatment increases most significantly when glycerin or ether-cellulose is used as a modifier-stabilizer when natural mineral water is used for silvering. Thus, when obtaining a silver solution by the electrolysis method, the determining factors are the choice of modifier, the use of mineralized water and the ultrasonic treatment of the system.

Measurements of the physicochemical characteristics of the obtained silver aqueous solutions based on mineral water have shown that the choice of modifier and its optimal amount determine the effectiveness of the subsequent use of the solutions (Table 3).

Table 2
Changes in the content of silver content in the aqueous solution from the time of ionization, under the influence of ultrasonic action and the type of modifying additives

Water	Ionization time, min	UST time, min	Silver content, mg/l			
			Modifier, 1%			
			No modifiers	Citric acid	Glycerin	Ether-cellulose
Boiled	20	0	0.0307	0.091	0.0821	0.112
	60	0	0.0507	0.109	0.092	0.112
	60	2	0.1086	0.920	0.312	0.822
Filtrated	20	0	3.6711	2.431	9.420	16.340
	60	0	11.4584	7.120	22.312	28.521
	60	2	1.9810	10.930	27.666	32.232
Mineral	20	0	4.9890	3.550	12.987	17.321
	60	0	11.6938	9.713	26.215	30.147
	60	2	17.432	11.650	31.410	36.216

Table 3
Results of measuring the properties of silver solutions obtained by electrolysis method on mineral water depending on the type of modifying additives and UST

Modifier	UST time, min	Property Indicators		
		pH	ppm	Elecroconductivity, µs
Without modifier	0	8.34	805	1619
Glycerin 0.5%	2	8.30	881	1750
Glycerin 1%	2	8.13	816	1603
Glycerin 2%	2	7.15	788	1565
Citric acid 0.01%	2	4.24	902	1798
Citric acid 0.05%	2	3.15	1025	2036
Citric acid 0.5%	2	1.72	1764	3449
Citric acid 1%	2	1.40	2485	4937
Citric acid 2%	2	1.40	2658	5282
Ether-cellulose 0.05%	2	5.43	868	1780
Ether-cellulose 0.1%	2	5.16	837	1691
Ether-cellulose 0.2%	2	3.68	786	1688

It follows from the presented results, that when glycerin is used as a stabilizer, its amount should not exceed 0.5%. In this case, the content of silver in solution increases and so does its electrical conductivity. The limiting amount of the introduced ether-cellulose, providing an increase in the characteristics of the solution, is 0.05%. Moreover, the use of ether-cellulose provides optimal indicators for hydrogen potential, i.e. a neutral medium is formed over pH. The use of citric acid as a stabilizer leads to a sharp increase in the acidity of an aqueous solution. This ensures stabilization of the ionized state of silver, i.e. its highly active state, which is reflected in the high electrical conductivity of the solution. However, this level of acidity of solution (pH less than 2), is unfavorable for its use in cosmetic preparations and the choice of the amount of the introduced modifier should be determined in total with the other introduced ingredients [17]. To assess the biological antimicrobial activity of the obtained silvered aqueous solutions (i.e. salts saturated with silver ions and nanoparticles), a known method for changing the acidity of milk was used (State standard #3624-92. Milk and dairy products. Titrimetric methods for the determination of acidity, Moscow, 2002).

The increase in acidity is related to with the cleavage of lactose, the accumulation of lactic and other organic acids and is expressed in Turner degrees (0T), i.e., the number of ml of 0.1 n sodium hydroxide solution (NaOH) necessary to neutralize the acids contained in 100 ml of milk. Stale milk has acidity in degrees Turner 23 and more. Plastic bags were impregnated with water silver sols obtained by stabilizing them with additives of glycerin, citric acid and ether-cellulose, i.e. with pH of 3 or more, dried and filled with fresh milk. After aging in a package at a temperature of 4–5 °C, the acidity of milk was determined. For the experiment, silver gel obtained on mineral water was used. Glycerin and ether-cellulose were used, as the most effective modifiers for stabilization of a silver solution. In containers treated with silver sols, the acidity of the milk increased more slowly

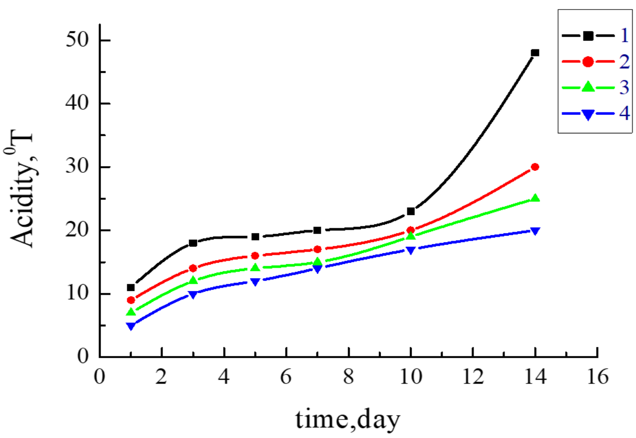

Fig. 1. Change of acidity of milk according to Turner depending on time in an ordinary package (1) and in a package treated with silver sol obtained by the electrolysis method and subjected to UST with 0.5% glycerin (2), 0.05% citric acid (3) and 0.05% ether-cellulose (4).

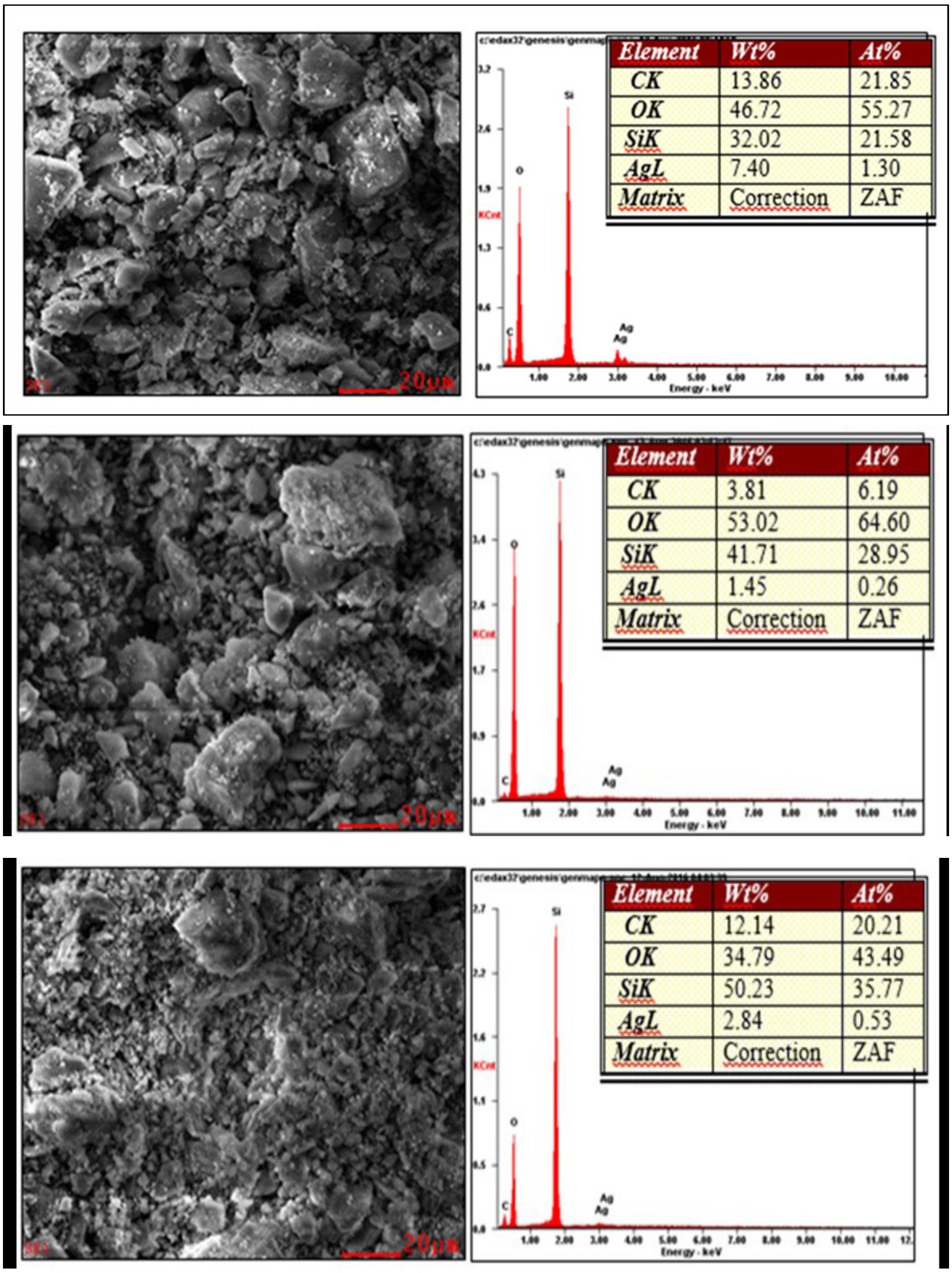

Fig. 2. SEM images (a, c, e) and spectral analysis (b, d, f) of silicon dioxide powder after HCT in a ball mill for 6 h with colloidal solution of nanosilver stabilized with citric acid (a, b), glycerin (c, d) and ether-cellulose (e, f).

than for the reference sample in the untreated package (Fig. 1). The greatest effect of antimicrobial activity was found for silvered aqueous solutions stabilized by ether-cellulose additives, i.e. with the highest silver content, both in the form of nanoparticles and in the ionized state.

Thus, the results of the studies showed the effectiveness of the use of natural mineral water to produce silver sols by electrochemical method, as well as mechanochemical treatment under the conditions of ultrasonic action to modify silver particles and stabilize the colloidal solution of nanosilver.

Then, the preparation of ultrafine silvered silicon dioxide, which is intended as a filler for cosmetic and pharmaceutical preparations on a gel basis was considered. Powders of amorphous silicon dioxide were crushed in a ball mill in an alcohol-water solution to a dispersion of 1–20 mm. Then, the crushed silicon dioxide was mixed with nanosilver ash (50/50) and re-subjected to mechanochemical treatment (MCT) in the mill for 2 to 6 h. With the increase in MCT time, dispersion of the system increases, and the surface of silicon dioxide particles is saturated with silver.

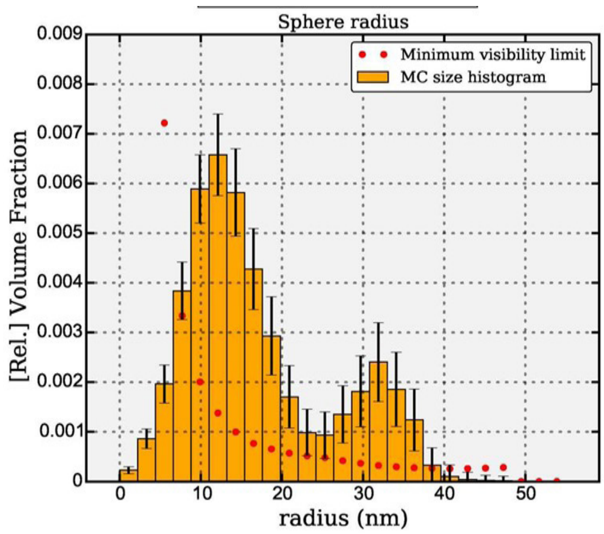

Fig. 3. Distribution of nanosized particles of silicon dioxide treated in a colloidal silver solution by the method of small-angel X-ray scattering.

When using a colloidal nanosilver solution obtained in the presence of various stabilizers that exclude agglomeration of the particles and their precipitation, simultaneously with the grinding of amorphous silicon dioxide particles, their saturation with silver is clearly registered, the amount of which depends on the conditions for preparation of the silver solution. According to the results of the experiment, the most amount of silver is fixed in the powder of silicon dioxide treated with a silver solution stabilized with citric acid, and the least amount is observed when the solution is stabilized with glycerin (Fig. 2).

Intermediate values for the saturation of silicon dioxide with silver were found when stabilizing solutions cellulose with ether-cellulose. The study on the distribution of nanoscale particles of silicon dioxide treated in a colloidal solution of silver by small-angle X-ray scattering on the Hecus S3-MICRO diffractometer (Cu-radiation with W-filter) showed that after 6 h of MCT, the bulk of silicon dioxide particles in the colloidal system made up 10–15 nm (Fig. 3).

As a coordinate of scattering, the value of the scattering vector length $q = 4\pi\sin\Theta/\lambda$ was used, where 2Θ is a scattering angle, λ is the length of the used radiation (λ = 1.54A, 2Θ = 0.008÷8°). Scattering intensity was registered in the range of q from 0.006 to 0.6 $Å^{-1}$. Dispersity of the colloidal system silicon dioxide +aqueous solution of silver increases with the introduction of modifying additives (in the amount of 1–2%) and treatment with ultrasound and makes up not more than 5–10 nm.

The structural changes affect the indices of the obtained composition properties. The results of measuring the properties of colloidal systems of silicon dioxide with silvered water obtained by the electrolysis method are presented in Table 4.

The system viscosity significantly decreases (by one order, in some cases-by two orders) due to introduction of a modifying additive and action of UST, the system consistency becomes more

Table 4
The change in the indices of the properties of colloidal systems silicon dioxide + silvered water (50/50) depending on the quality of water, type of modifying additives and ultrasonic action

Water	Modifier, 1%	UST time, min	Indices of properties			
			pH	pm	Viscosity, (Pa*S)	Electro-conductivity, (μs)
Boiled	Without modifier	0	6.30	91	17.200	190
	Citric acid	2	3.84	1124	0.36	2623
	Glycerin	2	6.17	103	1.800	413
	Ether-cellulose	2	6.0	125	1.707	570
Filtered	Without modifier	0	5.9	69	11.4	62
	Citric acid	2	3.2	1089	0.32	2567
	Glycerol	2	5.79	81	2.080	268
	Ether-cellulose	2	5.4	109	0.354	340
Mineral	Without modifier	0	6.5	107	37.0	205
	Citric acid	2	3.52	1239	0.33	2464
	Glycerol	2	5.4	153	0.95	440
	Ether-cellulose	2	5.0	178	0.58	650

homogeneous and stable to separation, this being promising for the preparation of soft gel systems of a cosmetic purpose. Also, the electroconductivity of a colloidal system considerably increases. This effect is most important when using mineral water for silvering and citric acid and ether-cellulose as modifying additives. The presence of citric acid in the system provides an acid medium resulting in a considerable increase in the amount of dissolved elements and electroconductivity of the colloidal system silicon dioxide + silver sol.

When considering colloidal systems with a filler from powder nanodisperse silicon dioxide the particles of which are saturated with silver ions during MCT in a mill, we can make a conclusion about the possibility of assessing the biochemical activity of the system by measuring its electroconductivity. This conclusion is vividly confirmed by the results on the assessment of the microbiological activity of the colloidal system containing silver particles by the disco-diffusion method [18, 19].

In an agarized medium with bacteria, a hole was cut out into which solution of the preparation understudy was pleased. The preparation diffuses along the layer of agar and if it possesses an anti-microbial activity, it leads to the appearance around the hole of the so-called lysis (death) zone of cells or a zone of inhibition of cell growth seen visually. The preparation activity can be judged by the size of such a zone [20, 21]. A bacterial culture *Bacillus mycoides* was taken as a strain. It was introduced into a solid nutrient medium and placed in a Petri dish. In the central part of the object, a hole of a definite size was cut out which was filled

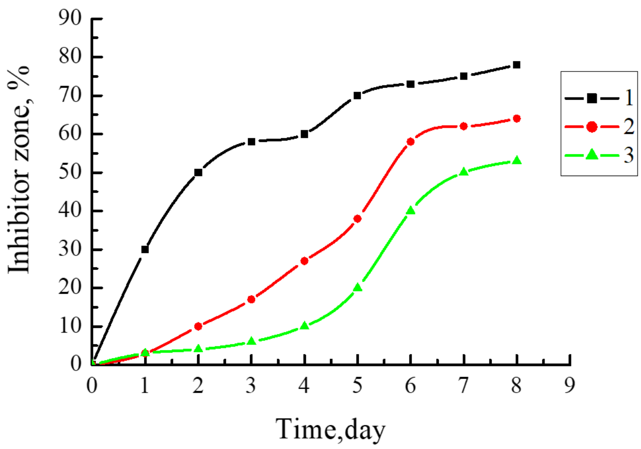

Fig. 4. Change in the size of the inhibitor zone depending on the contact time of agar sample infected with a bacterial strain with a colloidal solution of silicon dioxide with silver obtained with different stabilizers: citric acid (1); glycerin (2); ether-cellulose (3).

up with silicon dioxide gel containing an aqueous solution of silver obtained using different modifiers for stabilization of silver ions and particles according to Table 4. In 24 h, we registered the presence and sizes of the zone of bacteria inhibition due to diffusion of the substance from the composition of the silvered sample being tested. The preparation activity was evaluated in relative units of the infected zone sizes decrease depending on the time of contact with the sample of colloidal system of silicon dioxide with an aqueous solution of silver (Fig. 4). The size of the inhibition zone depending on the time of contact with the preparation containing silver increases. It is clearly visible that the preparation activity depends on the conditions for preparing an aqueous solution of silver, i.e. by chemical reduction or electrolysis method, as well as on the type of the modifier used.

The greater the electroconductivity value of the system under study the higher are kinetics and efficiency of action of containing silver colloidal systems based on silicon dioxide. Consequently, in this case, the destructive bacteria action of silver is likely to be related to the accumulation of the charge on the cell surface, i.e. suppression of growth and destruction of bacteria proceeds by the electrochemical mechanism. Thus, measurement of the system electroconductivity can serve as an express method to evaluate the activity of the being developed preparation based on silvered silicon dioxide gel.

So, the results of the carried-out investigations have shown that the use of modifiers for obtaining a colloidal solution with silver particles and ultrasonic treatment of the system provide the increase and stabilization of the activated state of colloidal systems with nanoparticles of silver and silicon dioxide. And the activated state of the material can be evaluated by the results on the measurement of its electroconductivity.

4. Conclusions

Thus, the carried-out investigations resulted in obtaining aqueous suspensions of silver by the electrolysis method varying the quality and composition of water, type and amount of modifying additives. The use of natural water of the of mineral spring of the health resort "Koktem" in Almaty (Kazakhstan) was shown to be effective for obtaining silver sols by the electrochemical method also, MCT under the conditions of ultrasonic action proved to be effective for modification of silver particles and stabilization of a colloidal solution of nanosilver.

Composition colloidal systems based on silicon dioxide and silver solutions with different modifiers were obtained by grinding in the mill in the course of MCT. It is stated that the use of polymer forming additives of the type ether-cellulose as modifiers the system was the most effective for structural changes of silicon dioxide. Ultrasonic treatment of the composition contributes to the homogeneity of the composition and stabilization of the structure of silicon dioxide particles as well as to the increase in the content of silver and electroconductivity and, consequently, to the activated state of the colloidal compositions under study. It is shown that under the action of UST, there form homogeneous and stable to splitting soft gel systems which are promising for cosmetic gels.

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