1. Introduction

The synthesis of stable concentrated aqueous dispersions with desired physicochemical properties on the basis of silver nanoparticles is a necessary step during the further creation of nanostructured materials. The latter are currently used in microelectronics, electrochemistry, synthesis of optoelectronic sensors, pigments, decontamination materials, etc. [1]. In addition, a wide range of antimicrobial action of silver nanoparticles allows creating various drugs and biomedical materials with prolonged antimicrobial action [2]. The constraint to the wide involvement of water dispersions of silver nanoparticles in various industries is the lack of a universal synthesis method. This method should allow synthesizing storage-stable silver dispersions with a controlled particle size using minimum reagents and technological operations.

At present, there is a significant number of methods for the synthesis of silver nanodispersions, providing nanoparticles of different composition, morphology [3]. However, the variety of technological methods of synthesizing colloidal nanodispersions causes differences in properties. Moreover, with all the benefits, most of the existing methods require the use of reducing reagents, temperature regime maintenance, several technological stages, etc. These parameters narrow down further practical application and increase the cost of silver nanodispersions. In recent years, the use of plasma discharge for the synthesis of silver nanodispersions has become widespread. The processes based on plasma technologies using different plasma discharge generation units are considered promising and competitive. Most of them have not gone beyond laboratory studies, are multi-stage and power-intensive. Given this, the development of innovative high-performance plasma-chemical methods aimed at synthesizing nanosized silver particles and concentrated water dispersions on a basis is relevant.
solutions, electrolytes, technical and tap water) allow the generation of nonequilibrium plasma with a high concentration of reactive radicals at different pressures.

In turn, flows of energy and reactive particles of the discharge can affect the state of the liquid electrode, causing various physicochemical processes in it.

A number of papers have reported the possibility of synthesizing metal nanoparticles and oxides directly by means of plasma discharge generated between the electrodes immersed in a liquid [6, 7], at the gas-liquid interface at reduced pressure [8], the atmospheric pressure plasma in the interaction with the liquid [9], etc.

The papers [6, 7] report the possibility of plasma discharge generation between the electrodes immersed in a liquid. Thus, nanoparticles of noble metals (Au, Ag) and metal alloy (NiXFeX) were synthesized. The authors of [8–9] use plasma at the interface at atmospheric pressure to obtain colloidal aurum solutions. Platinum nanoparticles were synthesized by reduction of water-dissolved H2PtCl6 using plasma over water solution [9], Fe–NCs, Ni–NPs. NiXFeX nanoparticles were synthesized by plasma discharge generated between hollow metal pipes in the presence of acetylene C2H2 and hydrogen H2 [10–11]. Silver and platinum nanoparticles were synthesized by microwave induced plasma in a liquid without the addition of chemical reagents [12].

Among plasma-chemical discharges, the contact nonequilibrium low-temperature plasma (CNP) is promising in terms of practical application. Plasma discharge is generated between the electrode in the gas phase and the surface of the liquid with another electrode. Thus, chemical transformations at the interface are due to:

- the complex effect of electrophysical oxidation-reduction;
- photolysis reactions, initiated by UV irradiation;
- a stream of charged particles from the gas phase to the surface of the liquid medium [13].

The research has shown that by varying the composition of liquid phases, it is possible to control chemical transformations and obtain different inorganic synthesis products [13].

The paper [14] demonstrates the efficiency of CNP discharge for synthesizing nanosized ferrites MnFe2O4. However, in this case, the authors used only concentrated initial solutions in the alkaline medium. The resulting product was in powder form. The authors of [15] show the efficiency of plasma only for synthesizing gold nanoparticles from water solutions of tetrachloroaurate. The paper [16] investigated the effect of plasma-chemical treatment of water solutions of argon on the formation of silver particles. However, plasma-chemical treatment was carried out at low pressure. The final product was a gray residue that contained silver oxide through air drying. In addition, the work presents no analysis methods characteristic of nanosized materials research.

Thus, at present, there are no data concerning the plasma-chemical synthesis of stable water dispersions of silver nanoparticles. Therefore, it is of scientific and practical interest to investigate the possibility of applying the contact nonequilibrium plasma discharge for the formation of silver nanodispersions.

3. The aim and objectives of the study

The research was aimed at synthesizing stable water nanodispersions of silver using contact nonequilibrium low-temperature plasma. To achieve this aim, the following objectives were accomplished:

- to synthesize silver nanodispersions from a water solution of silver nitrate under plasma discharge without the introduction of additional reagents and in the presence of sodium alginate;
- to synthesize silver nanodispersions by conventional methods of chemical reduction in solutions and photochemical deposition and compare with plasma-chemically synthesized dispersion systems;
- to investigate the dimensional characteristics of silver particles and the aggregate stability of plasma-chemically synthesized dispersions.

4. Materials and methods of synthesis of silver nanodispersions and characterization

Plasma-chemical synthesis of silver nanodispersions was carried out in a 100 ml batch gas-liquid reactor. The discharge was generated between the water cathode (with the immersed metal electrode) and the metal (steel) interdigitated anode (Fig. 1).

![Fig. 1. Photo of plasma discharge in a batch plasma-chemical gas-liquid reactor](image)

The electrodes made of H18N10T stainless steel were used. The cathode (d=4 mm) was located in the liquid part, and the anode (d=2.4 mm) – at a distance of 10 mm from the solution surface. The solution volume in the reactor was 70 ml. Cooling of the reaction mixture was provided by a continuous circulation of cold water. The reactor pressure was 80±4 kPa. For the plasma discharge generation, a voltage of 500–1,000 V was applied to the electrodes. The current strength was maintained at 120–6 mA.

Plasma-chemical synthesis of silver nanodispersions was carried out by treatment of 0.5 g/l silver nitrate solution (in the first case) and the mixture of 0.5 g/l silver nitrate and 3.0 g/l sodium alginate (in the second case) for 5 min.

Chemical synthesis of silver nanodispersions was carried out by the reduction of 0.5 g/l silver nitrate by ascorbic acid (1.0 g/l) in the ratio of 1:2, respectively, without the presence of sodium alginate stabilizer while stirring for 15 min.

Photochemical synthesis of silver nanodispersions was carried out by treatment of 0.5 g/l silver nitrate solution on the UV installation, the irradiation range 250–400 nm, DKB-7 lamp (7 W) for 15 min.

To characterize the silver nanoparticles formed, the reaction mixture was analyzed using spectrophotometry. The spectra of colloidal solutions were obtained on the UV-5800PC
spectrophotometer using quartz cuvettes in the wavelength range of 300–700 nm.

Microphotographs of the nanoparticles were obtained on JEOL JSM-6510LV (France) and REM-106I (Ukraine) scanning microscopes. The disperse phase of the solution, obtained by plasma-chemical treatment, dried in the air at 25 °C was investigated using the Ultima IV Rigaku X-ray diffractometer (Japan).

The yield of silver nanoparticles was estimated by the difference between the silver ions in the initial solution and after plasma discharge treatment. For measurements, the “ELIS-131Ag” silver-selective electrode was used.

Infrared spectroscopy was performed on the (NICO-LET3700) spectrometer (USA) to form a KBr tablet, in the frequency range of 400–4,000 cm⁻¹.

5. Results of the research on the efficiency of plasma-chemical synthesis of silver nanoparticles in comparison with conventional methods

The efficiency of the plasma-chemical method of synthesizing silver nanoparticles in comparison with the conventional method of chemical reduction in solutions and photochemical deposition is investigated.

According to the Mie-Drude theory, optical properties of colloidal solutions of metal nanoparticles are characterized by the presence of a pronounced resonance absorption band of surface plasmon resonance (SPR) in the visible spectrum. The positions of SPR peaks serve as the characteristics of both the form of existence of colloidal silver in the aqueous medium, and the size [17, 18]. It is now well established that the maximum absorption of 10–80 nm silver nanoparticles is characterized by the maximum absorption in the range of 395–465 nm [19].

The analysis of the data obtained (Fig. 2, curve 2) shows that treatment of the silver nitrate solution by low-temperature plasma discharge on the spectrum results in the SPR absorption peak (λ_{max}) at 420 nm (D=0.83), characterizing the formation of silver nanoparticles. Application of plasma discharge in the presence of sodium alginate stabilizer (Fig. 2, curve 1) contributes to a sharp increase in the SPR peak intensity to D=2.7. A slight shift to the short-wave region to 414 nm, corresponding to the nanoparticles is observed. Such data can be explained by the formation of a larger amount of silver nanoparticles and/or size reduction.

The possible reason is that an increase in the number of carboxyl and hydroxyl groups of sodium alginate facilitates the complex formation between Ag⁺ and the polymer molecular matrix. Moreover, a greater number of hydroxyl groups, as is known [20], contributes to Ag⁺ reduction.

Chemical synthesis of silver nanodispersions was carried out by the reduction of 0.5 g/l silver nitrate by ascorbic acid (1.0 g/l) in the ratio of 1:2, respectively, without/in the presence of sodium alginate stabilizer while stirring for 15 min.

Photochemical synthesis of silver nanodispersions was carried out by treatment of 0.5 g/l silver nitrate solution on the UV installation, the irradiation range 230–400 nm, DKB-7 lamp (7 W) for 15 min.

Application of conventional methods, as expected, also allows synthesizing silver nanoparticles with a characteristic absorption peak (λ_{max}) at 414–430 nm, but lower absorption intensity (D=0.35–0.43), compared to the plasma-chemical method. This is known to indicate a lower concentration of the formed silver nanoparticles [16–18].

![Fig. 2. Dependence of the absorption intensity (D) on the wavelength (λ) of solutions of silver nanodispersions synthesized by different methods: 1, 2 – plasma-chemical synthesis without (AgNO₃=0.5 g/l, τ=5 min, I=120 mA, P=0.8 MPa) and in the presence of AlgNa (AgNO₃=0.5 g/l, AlgNa=5.0 g/l, τ=5 min, I=120 mA, P=0.8 MPa); 3, 4 – chemical deposition without and in the presence of AlgNa (AgNO₃=0.5 g/l, ascorbic acid 1.0 g/l, AlgNa=5.0 g/l, τ=15 min); 5 – photochemical deposition of AgNO₃=0.5 g/l, τ=15 min)](image)

To confirm the preliminary data and efficiency of the investigated methods for synthesizing silver nanoparticles, the quantitative yield of silver nanoparticles in dispersions was estimated. Table 1 shows the yield of silver nanoparticles depending on the synthesis method.

### Table 1

<table>
<thead>
<tr>
<th>Synthesis method</th>
<th>Yield of nanoparticles, %</th>
</tr>
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<tbody>
<tr>
<td>Contact nonequilibrium low-temperature plasma</td>
<td>95.10</td>
</tr>
<tr>
<td>without the stabilizer in the presence of AlgNa</td>
<td>97.17</td>
</tr>
<tr>
<td>Chemical deposition</td>
<td>93.9</td>
</tr>
<tr>
<td>without the stabilizer in the presence of AlgNa</td>
<td>93.9</td>
</tr>
<tr>
<td>Photochemical deposition</td>
<td>20.0</td>
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</tbody>
</table>

The data obtained agree with the previous results. CNP discharge gives a highly effective yield of silver nanoparticles and provides the yield of Ag⁺ silver particles of 95.1 % without the stabilizer and 97.17 % under plasma discharge in the presence of sodium alginate stabilizer.

The yield of silver particles, when synthesized by the conventional chemical method, is 93.9 %. by the photochemical – 20 %. Thus, application of CNP for synthesizing silver nanoparticles, both using the AlgNa stabilizer and without it is an effective way compared to the known conventional methods. In addition, it should be noted that the duration of plasma discharge treatment for the formation of silver nanodispersions is 3–5 min, compared with the duration of synthesis by conventional methods (15 min).

In addition to the yield efficiency of the particles, description of the properties of the synthesized dispersions is
necessary in the study of new synthesis methods. One of the main parameters that characterize silver dispersions and determines the further practical application is aggregate stability. The level of aggregation of metal nanoparticles can be effectively estimated by changing the absorption characteristics: the shift of the SPR peak in the spectrum and its intensity. Fig. 3 shows the spectra of silver nanodispersions synthesized by different methods when stored for 4 days. The analysis of the data obtained shows a high aggregate stability of plasma-chemically synthesized nanodispersions compared to the methods of chemical reduction in solutions and photochemical deposition. In the plasma-chemical synthesis, in the spectra of silver dispersions (Fig. 3, a, b), there are no significant changes in the SPR band intensity and structure in 4 days after the synthesis. These results indicate the absence of rapid aggregation processes in silver dispersions. In the spectra corresponding to the chemical and photochemical synthesis methods, a significant decrease in the absorption intensity, indicating the coagulation of nanoparticles and possible recrystallization, is observed in 4 days due to the SPR peak shift.

To further evaluate changes in the properties and stability of silver dispersions synthesized by different methods, changes in the acidity of freshly synthesized silver solutions during storage were investigated as a pointer to dimensional changes (Fig. 4). Unlike other methods, the plasma-chemical synthesis of silver nanodispersions is characterized by the absence of a clear change in pH during storage.

Characteristics of dimensional and morphological parameters of silver nanodispersions synthesized by chemical and photochemical methods are sufficiently investigated today and some are given in [20, 21]. It was of scientific interest to determine the dimensional characteristics of plasma-chemically synthesized silver nanoparticles. According to the electron microscopy data, a dispersed phase of particles up to 100 nm is formed under plasma discharge without and in the presence of AlgNa (Fig. 5). The solid phase of both samples of plasma-chemically synthesized silver nanodispersions was investigated by the X-ray diffraction analysis.

In both cases, the data obtained (Fig. 5) indicate the presence of reflexes from the crystallographic planes 111, 200, 220, 311, and 222. The characteristic peaks are at angles of 38.1°, 44.3°, 64.4°, 77.4°, and 81.6°, respectively, corresponding to silver metal particles in accordance with [22].

As shown by the data on the quantitative yield of nanoparticles during the plasma-chemical synthesis, sodium alginate, probably, acts as both the stabilizer of the formed nanoparticles, and additional reducer. The interaction of AgNPS with sodium alginate is confirmed by the analysis of IR spectroscopy (Fig. 7). In the AlgNa alginate spectra, the peak within 3,200–3,600 cm⁻¹ corresponds to deformation oscillations of the hydroxyl group bond. Peaks at 1,412 cm⁻¹ and 1,591 cm⁻¹ characterize the COO⁻, symmetric and asymmetric deformation oscillations, respectively. The small and expanded peak within 1,327–1,370 cm⁻¹ can be explained by the C–O bond. Two peaks at wavelengths of 1016.5 cm⁻¹ and 1078 cm⁻¹ are characterized by deformation oscillations of C=O and C–O–C. Absorption peaks within 1,030–1,200 cm⁻¹ are characteristic of natural polysaccharide.

When comparing the alginate spectrum with AgNPS/Alg, one can observe a significant shift of the wave position from 1591 cm⁻¹ for alginate to 1,640 cm⁻¹ for AgNPS, with a decrease in intensity. This shift confirms the interaction of oxygen carboxyl groups in the alginate structure with AgNPS. The peak shift within 3,200–3,500 cm⁻¹, 1,084 cm⁻¹ can be attributed to the chemical transformation during the reduction of Ag⁺ to Ag⁰ [23].

**Fig. 3.** Dependence of the absorption intensity (D) on the wavelength (λ) of silver nanodispersions synthesized by different methods during storage: a, b — plasma-chemical synthesis without (AgNO₃ 0.5 g/L, τ=5 min, I=120 mA, P=0.8 MPa) and in the presence of AlgNa (AgNO₃ 0.5 g/L, AlgNa 5.0 g/L, τ=5 min, I=120 mA, P=0.8 MPa); c — chemical deposition without and in the presence of AlgNa (AgNO₃ 0.5 g/L, ascorbic acid 1.0 g/L, AlgNa 5.0 g/L, τ=15 min); d — photochemical deposition of AgNO₃ 0.5 g/L, τ=15 min)
Fig. 4. Dependence of the acidity of solutions with different plasma discharge treatment times on storage time: 1, 2 — plasma-chemical synthesis without (AgNO₃ = 0.5 g/l, ṭ = 5 min, I = 120 mA, P = 0.8 MPa) and in the presence of AlgNa (AgNO₃ = 0.5 g/l, AlgNa = 5.0 g/l, ṭ = 5 min, I = 120 mA, P = 0.8 MPa); 3, 4 — chemical deposition without and in the presence of AlgNa (AgNO₃ = 0.5 g/l, ascorbic acid 1.0 g/l, AlgNa = 5.0 g/l, ṭ = 15 min); 5 — photochemical deposition of AgNO₃ = 0.5 g/l, ṭ = 15 min.

Fig. 5. SEM images of plasma-chemically synthesized silver dispersions: a — without AlgNa; b — with AlgNa.

Fig. 6. X-ray photograph of plasma-chemically synthesized silver dispersions: a — without AlgNa; b — with AlgNa.

Fig. 7. IR spectroscopy of the samples: 1 — sodium alginate; 2 — plasma-chemically synthesized silver nanoparticles with sodium alginate.

6. Discussion of the results of the research on plasma-chemical synthesis of silver nanodispersions

In [13], it was reliably determined that in the treatment of water solutions with contact nonequilibrium low-temperature plasma, a large number of reactive particles are generated in the treated medium. These are free and solvated electrons, protons, radicals, charged and excited atoms and molecules (2). The interaction proceeds in nonequilibrium conditions due to the nonequilibrium of plasma discharge and irreversibility of interaction of radical particles in gas and liquid phases,

\[ n \cdot H_2O \rightarrow e^-_n, H^+ \rightarrow OH^-, H, H_2O^+, H_2O. \]  

(2)

As is known, the solvated electron \( e^-_n \) and \( H^+ \) are strong oxidizers: \( E(\cdot H_2Oe^-) = -2.87 \text{ V} \), \( E(\cdot H^+/H^+) = -2.3 \text{ V} \). The latter easily reduce metal ions to the zerovalent state (1). Neutral Ag atoms react with excess \( Ag^+ \) ions to form \( Ag_2 \) (3). Thus, the aggregation process does not stop and leads to the formation of silver nanoparticles (6).

\[ AgNO_3 \rightarrow Ag + NO_3^- \]  

(3)

\[ Ag + e^-_n \rightarrow Ag^0 \]  

(4)

\[ Ag^0 + Ag \rightarrow Ag_2 \]  

(5)

\[ Ag^+ + Ag^0 \rightarrow Ag_2^+ \]  

(6)

To prevent the aggregation of silver dispersions and increase the yield efficiency of particles during the synthesis, stabilizing/reducing reagents are used. The analysis of foreign scientific papers indicates the effectiveness of using sodium alginate for the synthesis of stable silver nanoparticles and materials that are characterized by antibacterial properties. In addition, the advantage of sodium alginate is its environmental friendliness and compatibility for pharmaceutical, biomedical and other applications. Given the above-mentioned properties of sodium alginate, the plasma-chemical synthesis of colloidal solutions of silver nanoparticles in the presence of sodium alginate as a stabilizing/reducing reagent was investigated. Based on the experimental data obtained, the following mechanism of AgNP₃ synthesis in the
sodium alginate solution during irradiation by the CNP discharge was proposed (Fig. 8).

For the formation of AgNP$_S$, the standard mechanism involves two stages, namely, formation and polymerization of atoms. In the first stage, a part of metal ions in the solution is reduced by available reduction groups. The atoms formed in this way act as nucleation centers and catalyze the reduction of residual metal ions in the solution. Compared with other water-soluble polymers, alginate is an anionic polymer with high charge density. Negatively charged alginate facilitates the attraction of positively charged silver ions to polymer chains, which are then reduced by means of existing groups. Preformed silver atoms adsorb Ag$^+$ on the surface through dimerization or association with excess ions due to the binding energy between metal atoms. Surface ions are decreased again, then the atoms merge, leading to the formation of metal clusters. Thus, the aggregation process does not stop and leads to the formation of larger particles.

The process is stabilized in the presence of sodium alginate, preventing further coalescence. Probably, the metal clusters will be fixed through strong bonds between the AgNP$_S$ surface and the “O” atom of the (COO$^-$ and OH) functional group of sodium alginate [23]. So, the negative surface charge of alginate carboxyl groups stabilizes silver nanoparticles against aggregation due to electrostatic and steric effects.

Thus, the complex effect of active compounds of plasma discharge provides an almost complete reduction of silver ions in the solution to metallic silver. In this case, the simultaneous presence of the sodium alginate stabilizing reagent in the solution prevents aggregation of the formed particles. As a result, it is possible to synthesize silver dispersions with a particle size up to 100 nm. The synthesized dispersions are environmentally friendly and storage stable. This will allow expanding the areas of their application and increasing the antimicrobial functionality of materials on their basis, as well as producing materials on their basis with multifunctional properties and increasing the competitive capacity of known materials.

The research was conducted using a wide range of analysis methods. The possibility and efficiency of plasma discharge application for the controlled formation of silver nanoparticles are also confirmed by quantitative particle yields. The dimensional and morphological characteristics are given.

For a more detailed description of the plasma-chemically synthesized silver nanoparticles, determination of the size distribution and characterization of antimicrobial properties of dispersions were expedient.

Optimizing factors of plasma-chemical effects on water solutions are discharge current strength, reactor pressure, plasma effect duration, solution concentration, temperature and acidity. Further research may be aimed at determining the influence of these factors on the formation of silver nanodispersions. The study of the effect of the specified parameters on antimicrobial properties of the synthesized silver dispersions can also be a probable development. The main difficulty of further research is the transition from the discrete-type laboratory reactor to the flow industrial one.

7. Conclusions

1. The possibility of applying the discharge of contact nonequilibrium low-temperature plasma for synthesizing silver nanodispersions from water AgNO$_3$ solutions is established. The efficiency of plasma-chemical synthesis without the use of additional reducing reagents and in the presence of sodium alginate stabilizing reagent is shown. The process is more efficient in the presence of the stabilizer.

2. It is found that the yield of silver nanoparticles in the plasma-chemical synthesis is higher by 1.5–2% and 75–78%, in comparison with the conventional method of chemical reduction in solutions and photochemical precipitation, respectively. At the same time, the duration of the synthesis process is reduced almost 3 times. It is found that the introduction of sodium alginate stabilizer contributes to the increase of the yield of silver nanoparticles and allows synthesizing stable colloidal silver solutions.

3. The formation of silver nanodispersions under plasma discharge is characterized by the presence of the peak $\lambda_{max}=400–420$ nm. The formation of silver nanoparticles was confirmed by the X-ray diffraction analysis. Microscopic examination (SEM) indicates that the size of the formed silver particles is up to 100 nm. The scheme of synthesizing silver nanoparticles in the sodium alginate solution under plasma discharge is proposed.

References


