# Preparation methods of bactericidal microfiltration membranes modified with compounds of silver, copper, and iodine

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## Abstract

**Aim and Scope:** Membrane technologies have become widespread in all fields of science and technology: Chemistry, petrochemistry, medicine, biology, pharmaceutics, electronic, and food industries. One of the directions of membrane use is sterilization, an antibacterial treatment of drinking water, chemical, biological, and medical solutions. **Materials and Methods:** The method of obtaining bactericidal membranes is an alternative method of struggle with bacterial contamination. The antibacterial microfiltration membranes were prepared in the work by treating an original membrane of nylon with silver, copper, and iodine compounds. **Result and Discussion:** The size of the silver particles deposited on the membrane surface was 102–617 nm, the size of copper particles made 249–415 nm, and the size of iodine particles made 206–359 nm. The elemental composition and the surface distribution of silver, copper, and iodine were determined by X-ray fluorescence analysis using a scanning electron microscope on the surface of modified membranes. The silver content on the surface of the modified membrane was 9.06%, the content of copper after the treatment with copper sulfate solution was 3.8%, and iodine content made 4.4%. **Conclusion:** There is a slight decrease in the specific productivity of membranes after the treatment with reagents. 100% bactericidal activity of membranes treated with silver nitrate solution was revealed. The membranes treated with the solutions of CuSO4 and J2 have a bacteriostatic property, and their antimicrobial activity manifests itself in the inhibition of microorganism growth.

**Key words:** Bacteria, copper, iodine, membranes, microfiltration, silver, total microbial number

## INTRODUCTION

The problem with the use of antibacterial membranes is the development of a biological film on a membrane surface at which the multiplication of microorganisms retained by the membrane occurs. Filtrate infestation is possible with the subsequent filtration. To prevent the destruction of the filtrate by microorganisms that occupy the surface of the membrane, there is a need for frequent replacement or the use of disposable membrane elements. Moreover, the use of disinfectants can lead to the destruction of the polymer membrane structure.

An alternative way to combat bacterial contamination can be the use of antibacterial membranes, but such membranes are absent in batch production, so the development of bactericidal membrane obtaining method is an urgent task. Bactericidal membranes should have a number of properties: High selectivity, bactericidal activity, and high specific productivity. The simplest and inexpensive way of obtaining bactericidal membranes is the chemical modification of serially produced membranes.

To obtain a bactericidal surface, the membranes are treated with the compounds of silver, copper, zinc, iodine solutions, chitosan, 1-bromododecane, graphene, and benzyl chloride.[1-8]

Among the metals, silver has the strongest bactericidal action. In this case, the interaction of not only the metal itself but also

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its ions with the cells of microorganisms causes their death. Silver shows a high bactericidal activity both in relation to aerobic and anaerobic microorganisms and to some viruses and fungi.

The studies have shown that the sensitivity of different pathogenic and non-pathogenic organisms to silver is not the same one. Pathogenic microflora is much more sensitive to silver ions than non-pathogenic one. Therefore, silver acts selectively, mostly destroying harmful microorganisms.[9]

The mechanism of silver action on the microbial cell is that the silver ions are absorbed by a microbe cell membrane, and thus, its cell remains viable, but some of its functions are violated, for example, the division (bacteriostatic effect). At that, the spectrum of antimicrobial action of silver is much broader than many antibiotics and sulfonamides. Silver has a more potent bactericidal effect than penicillin, biomycin, and other antibiotics and makes a disastrous effect on bacterial strains resistant to antibiotics.[10-12] Thus, it was proved that silver ions have a different antimicrobial effect, from bactericidal to bacteriostatic one (the ability to inhibit the growth of microbes).

The aim of this work was to investigate the method of bactericidal membrane obtaining from nylon modified with silver, copper, and iodine compounds, as well as to study their transport and bactericidal characteristics.

## MATERIALS AND METHODS

A microfiltration hydrophilic polymeric membrane made of nylon (manufacturer - "Phenex Filter Membranes," the pore size makes 0.45 μm) was used as the initial matrix for the preparation of bactericidal membranes. To obtain bactericidal properties, the membranes were treated with the following solutions: 1 molar solution of silver nitrate, 0.5 molar solution of copper sulfate, and 0.5% solution of iodine. The processing of the initial membrane was carried out under dynamic conditions using a laboratory membrane plant[13,14] by dead-end filtration of these solutions through a membrane. The membranes were washed with distilled water after drying.

The particle size of silver, copper, and iodine compounds in membrane processing solutions was determined by the method of dynamic light scattering, and the ζ potential was determined by the light scattering method with phase analysis using the NanoBrook Omni analyzer.

The presence of silver on the surface of the modified membranes was identified by X-ray fluorescence analysis using Jeol JSM-6390 LA scanning electron microscope with EX-230**BU energy-dispersive system.

Specific productivity and bactericidal activity were considered as the main characteristics of modified membranes. Tap water was used, aged for 2 days at the temperature of 25°C ± 1°C in the studies of modified membrane bactericidal action. The number of microorganisms in water before and after filtration with membranes was evaluated by the measurement of total microbial number, the bacteria content in 1 ml of the water under study made CFU/ml.

The specific productivity of the initial and treated membranes was determined by filtration through 500 $cm^3$ membrane of distilled water in terms of 1 min and on area of 1 $cm^2$. During the filtration of the water under study, the working pressure of 0.1 MPa was applied, the water temperature was 21°C, the type of filtration was dead-end, and the conversion was 100%.

## RESULTS AND DISCUSSION

According to Figure 1 and Table 1, the particle size of silver in $AgNO_3$ solution makes 102–617 nm. The size of copper particles is in the range from 249 to 415 nm and iodine - from 206 to 359 nm. The smaller the particle size of the antibacterial modifier, the more effective the destruction of microorganisms. The effect is achieved due to a large specific surface area, which increases the area of silver contact with bacteria or viruses, significantly improving its bactericidal action. To determine the compounds of silver, copper, and iodine on the surface of modified membranes, the membranes were examined by X-ray fluorescence analysis using a scanning electron microscope.

Table 2 presents the results of an elemental composition study concerning the surface of initial and modified membranes.

According to Table 2, the elemental composition has changed after the treatment of the original membrane. The silver content in the modified membrane was 9.06%, the copper content after treatment with copper sulfate solution was 3.8%, and the iodine content was 4.4%.

After the processing of the membrane with $AgNO_3$ solution, silver is uniformly distributed over the entire surface in the form of particles from 0.1 to 1.5 μm, but there are separate

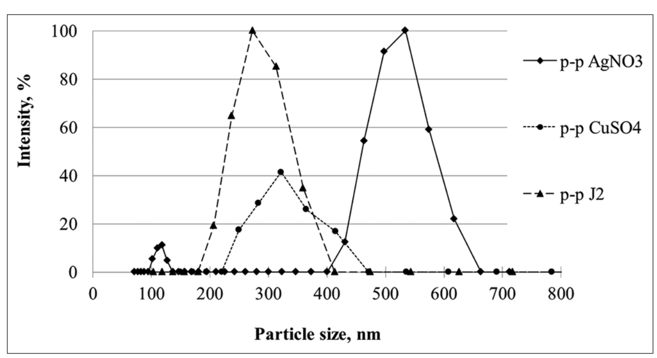


**Figure 1:** The graph of silver, copper, and iodine particles distribution in solutions for membrane treatment

areas of silver compound accumulation the size of which makes 10–50 μm [Figure 2]. When the membrane is treated with $CuSO_4$ solution, a non-uniform distribution of copper with particle sizes from 0.2 to 0.5 μm is observed on the surface of a membrane. When a membrane is treated with an iodine solution, a uniform distribution is observed throughout a membrane surface.

The results of specific membrane productivity after the modification with silver compounds are presented in Table 3.

After the treatment of membrane with the solutions of $AgNO_3$, $CuSO_4$, and $J_2$, the specific productivity of membranes is insignificantly reduced. The maximum productivity is observed when the membrane is treated with the solution of $J_2$, and minimal productivity is observed when the membrane is treated with the solution of CuSO4.

The results obtained after the incubation of the filtrates were interpreted as follows: If the increase of total microbial number (TMN) on the filtrate of the test membrane after incubation at 37°C for 5 days was completely absent, then this filter was considered as bactericidal one. The membranes were considered to be bacteriostatic, on the filtrate of which the number of colonies of the test culture did not exceed 10 units 5 days after the incubation in Petri dishes with meat-pentagon agar at 37°C.[15]

It can be seen from Table 4 that, after the filtering of water through the nylon membrane, TMN decreases. The membranes treated with the solution of silver nitrate are characterized by 100% bactericidal activity, the TMN in the membrane filtrate is zero. This can be explained by the fact that the silver particles which are present on the surface and in the pores of the membrane provide a high surface concentration of silver ions, which determines the increased chemical activity of silver particles against microorganisms contained in water. The membranes treated with the solutions of $CuSO_4$ and $J_2$ have a bacteriostatic property, and their antimicrobial activity is manifested in the inhibition of microorganism growth.

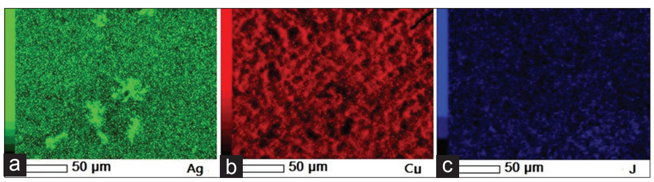


**Figure 2:** The distribution of antibacterial components on the membrane surface after treatment: (a) Ag, (b) Cu, and (c) J

**Table 1:** The size of the particles and ζ-potential of the dispersed phase

| Solution | Particle size, nm | ζ-potential, Mv |
|---|---|---|
| 1 mole of $AgNO_3$ solution | 102–127, 431–617 | −7.6±0.8 |
| 0.5 mole of $CuSO_4$ solution | 249–415 | −0.31±0.03 |
| 0.5% of iodine solution | 206–359 | −2.8±0.3 |

## CONCLUSIONS

According to the results of the study, the membranes modified with silver nitrate have a bactericidal action, which allows to perform the disinfection of water under dynamic conditions in a short time. The membranes treated with $CuSO_4$ and $J_2$ solutions exhibit bacteriostatic properties. Specific productivity of membranes after the treatment with $AgNO_3$, $CuSO_4$, and $J_2$ solutions decreases slightly from the initial indices. The silver content in the modified membrane was 9.06%, the copper content after the treatment with copper sulfate solution was 3.8%, and the iodine content was 4.4%. The particles of silver are distributed on the membrane surface in the form of particles from 0.1 to 5 μm. When a membrane is treated with $CuSO_4$ solution, a non-uniform distribution of copper with the particle of 0.2–0.5 μm is observed on a membrane surface. The compounds of iodine distributed over the entire surface of the membrane in the form of particles from 0.2 to 5 μ.

**Table 2:** Element composition of initial and modified membrane surface

| Element | Mass content, % | | | |
|---|---|---|---|---|
| | Nylon | Nylon ($AgNO_3$) | Nylon ($CuSO_4$) | Nylon (5% p−p J2) |
| Carbon (C) | 43.7 | 35.6 | 37.5 | 40.7 |
| Nitrogen (N) | 38.3 | 35.4 | 35.5 | 36.8 |
| Oxygen (O) | 18.0 | 19.9 | 21.9 | 18.1 |
| Silver (Ag) | - | 9.06 | - | - |
| Aluminum (Al) | - | 0.04 | - | - |
| Copper (Cu) | - | - | 3.8 | - |
| Sulfur (S) | - | - | 1.3 | - |
| Iodine (J) | - | - | - | 4.4 |
| Total | 100 | 100 | 100 | 100 |

**Table 3:** Specific productivity of the initial and treated membranes by distilled water

| Membrane name | Specific productivity of membranes in distilled water, $cm^3/cm^2$ min |
|---|---|
| Nylon | 9.3 |
| Nylon (1 molar solution of $AgNO_3$) | 9.0 |
| Nylon (0.5 molar solution of $CuSO_4$) | 8.8 |
| Nylon (5% of $J_2$) | 9.2 |

**Table 4:** Antibacterial properties of membranes treated with $AgNO_3$, $CuSO_4$, and $J_2$ solutions

| Water sample | Total microbial number (TMN) of CFU/ml | CFU/ml standard |
|---|---|---|
| Original water | 510 | No more than 50 (according to SanPiN 2.1.4.1074-01) |
| Nylon membrane filtrate | 16 | |
| Nylon membrane filtrate ($AgNO_3$) | - | |
| Nylon membrane filtrate ($CuSO_4$) | 6 | |
| Nylon membrane filtrate ($J_2$) | 4 | |

## SUMMARY

The result of the original microfiltration membrane modification from nylon with the compounds of silver, copper, and iodine solution is the demonstration of bactericidal and bacteriostatic activity by membranes with respect to microorganisms. The method of membrane processing is simple, and it does not require complicated equipment and energy costs, at which an effective antibacterial membrane is obtained.

## ACKNOWLEDGMENTS

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