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Research on structural and process properties of polysulfone membranes modified by CuO

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ABSTRACT

One of the problems associated with conducting a membrane filtration process is the accumulation of undesirable material on the surface of membranes. The deposited layer can significantly increase the resistance of the membrane, which leads to a reduction of the process efficacy. In many cases, the service life of the membranes is also reduced. One type of contamination that can accumulate on the surface of membranes are biological species (i.e., microorganisms). The process is called biofouling and can lead to a biofilm formation, which constitutes an integral layer resistant or completely invulnerable to many commonly used cleaning techniques. Various microorganisms, including bacteria, fungi and algae, proliferate and colonize the available surface of the membranes. Adhesion to the surface is enabled by secreted components known as extracellular polymeric substances, thanks to which a biofilm is formed on the surface. In order to reduce the intensity of biofouling, the membranes are subjected to various modification techniques. One of the modification techniques is the addition of particles with antimicrobial and anti-biofouling properties to the polymer at the stage of membrane production. In this study, copper oxide (CuO) was used as an antimicrobial material, which was added, as a nanopowder, to a polysulfone solution. From the prepared membrane-forming solution, flat ultrafiltration membranes were produced using the wet phase inversion method. The secondary solvent was the ultrapure water. The aim of the conducted research was to produce membranes with anti-biofouling properties and to characterize them in terms of structural and process characteristics. Anti-biofouling properties were determined using microbiological techniques based on standard test methods, appropriately adapted to obtain a representative result for typical realistic working conditions of separation material. Typical Gram-positive and Gram-negative bacteria found in the aquatic environment were selected for the study. Scanning electron microscopy, porosimetry and contact angle analysis were used to determine the structural properties. While characterizing the process properties, the filtration coefficient and the permeate flux change during the filtration process on an aqueous solution of bovine serum albumin were determined. Ultrafiltration membranes with pores 0.05–0.07 μm and permeability of 170 $dm^3/m^2/h \cdot bar$ have been obtained. Membranes have antibacterial properties against *Escherichia coli* and *Staphylococcus aureus*.

Keywords: Membrane filtration; Membrane modification; Anti-biofouling properties; Copper oxide

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1. Introduction

One of the problems associated with conducting membrane filtration processes is the phenomenon of biofouling. Biofouling is defined as the accumulation of biological materials on the surface of the membrane. The biofilm may include bacteria, fungi, algae, small animals and products produced by them [1]. The presence of biofouling has an adverse effect both on the material from which the membrane is made, as well as on the efficiency of the process itself. Organisms accumulating on the surface of the membrane accelerate the aging process of the membrane and deteriorate its mechanical properties. Moreover, the formed biofilm constitutes a new layer increasing the resistance of the membrane, as a result of which the permeate flux decreases. In addition, the resulting layer of organic material facilitates the retention of salt ions, which leads to concentration polarization. The phenomenon of concentration polarization reduces both the efficiency of the process and the purity of the product obtained. The formed biofilm also increases the energy consumption needed to increase the feed pressure in order to maintain the required permeate flux, and the energy demand to carry out more frequent cleaning of the system [2,3].

Several strategies are used to reduce fouling. One of the basic strategies is the selection of appropriate hydrodynamic conditions, in particular the velocity and the turbulence of the feed flow, ensuring a sufficiently high shear rate of the emerging biofilm. The hydrodynamic conditions of the flow depend on the volumetric flow and feed pressure as well as the design of the membrane module. Another way to reduce biofouling is the selection of appropriate conditions in which the process takes place and the physicochemical properties of the feed stream. The most important parameters affecting the intensity of biofilm formation are temperature, pH, salt concentration, turbidity, viscosity of the purified liquid and the content of ingredients that accelerate the growth of microorganisms. In turn, the basic strategy for the periodic removal of accumulated biofilm is washing the membranes with baths containing appropriate washing agents such as hypochlorite, detergents or enzymes [4–7]. Despite the proven effectiveness of these strategies, they do not provide a complete solution to the problem of biofouling, especially with regard to the growth of bacteria on the membrane surface. The intensity of the accumulation and development of microorganisms can be reduced by modifying the material from which the membrane is made. The purpose of such modification is to reduce the adhesion of biological material to the membrane surface and to limit the proliferation of microorganisms on its surface. The first effect can be achieved by changing the wettability, roughness and surface charge of the membrane [8]. In turn, limiting the development of microorganisms can be achieved by improving the bacteriostatic properties of the material from which the membrane is made. The compounds with antibacterial properties used to modify membranes are metals (Ag, Cu), metal oxides (AgO, CuO, ZnO, TiO_2), hydroxides ($Cu(OH)_2$, $Ca(OH)_2$, $Mg(OH)_2$, ZnOH), and various forms of carbon (carbon nanotubes, oxidized form of graphene) [9–11].

One of the compounds with high potential for modifying membranes in order to give them antibacterial properties is nano-sized copper oxide (CuO-NPs). The bacteriostatic mechanism of this compound is based on the penetration of nanoparticles through the bacterial cell membrane and the deactivation of enzymes. The advantages of copper oxide include effectiveness against Gram-positive and Gram-negative bacteria, high stability, antifungal activity, low cost of production and the ability to give the produced particles various sizes and shapes [12–16].

However, the modification of materials with metal oxide nanoparticles can affect a number of structural properties of membranes and related process properties. According to the literature data, the presence of nanoparticles can change the wettability and roughness of the membrane surface, porosity, pore size or membrane thickness. These parameters can significantly affect the permeability and selectivity of the membrane as well as its mechanical strength [17–20]. The influence of nanoparticles on the properties of membranes is particularly visible when the membranes are produced by the wet phase inversion method, which was used in the presented work. This effect results from the fact that the presence of metal oxide nanoparticles directly affects the rate of transport of solvent to the nonsolvent. This rate, in turn, has a significant impact on the pore diameter and porosity of the material [21,22]. For this reason, the aim of the presented work was to produce membranes with different concentrations of CuO-NPs by wet phase inversion and to determine the effect of CuO-NPs on the structural, process and antibacterial properties of the membranes.

2. Experimental set-up

2.1. Materials

Polysulfone (PS) polymer (Sigma-Aldrich, Finland Oy) was used to produce the membranes. N-methyl pyrrolidone (NMP) (Sigma-Aldrich, Poznan, Poland) (ACS reagent, ≥99.0%) was used as the solvent. The copper oxide (CuO-NPs) used to modify the manufactured membranes was developed and supplied by Bar Ilan University [23].

To determine the selective properties of the produced membranes, a 0.5 g/dm^3 aqueous solution of bovine serum albumin (BSA) was used (Sigma-Aldrich, Poznan, Poland). Water produced by the reverse osmosis process (RO water) with pH = 6.5, conductivity 35 μS/cm and surface tension 72 mN/m was used in the research.

2.2. Membrane preparation

The tested membranes were produced by the wet phase inversion method. A commercially available casting knife was used to obtain a film of the appropriate thickness. The temperature of the membrane-forming solution and non-solvent was 25°C.

The membrane-forming solution was prepared by dissolving polysulfone in NMP. The polymer concentration was 11% (w/w). This concentration was determined on the basis of our own research, the most important conclusions of which are presented in the further part of the work concerning the description of the obtained results. In turn, for the preparation of CuO-NPs-modified membranes, 0.5%, 1%, 2% or 5% by weight of CuO-NPs was added to the

solution relative to the weight of the polymer. CuO-NPs was added to the solution in the form of a suspension. Before forming the membrane-forming layer, the solution was intensively stirred and placed in an ultrasonic bath.

2.3. Testing of structure properties

To study the influence of CuO-NPs particles on the structural properties of the produced membranes, microscopic and porosimetric analysis was carried out and the static contact angle of the membrane surface was determined.

Scanning electron microscopy (SEM) was used for microscopic analysis. The SEM analysis was used to take photos of the surface and cross-section of the membranes. In addition, a visual topographical analysis of the membrane surface was carried out on the basis of photos of the membrane surfaces. SEM analyses were performed using the Phenom Pro apparatus (PhenomWorld, Eindhoven, the Netherlands). A special holder for non-conductive samples was used, which allows the observation of polymeric samples without prior sputtering.

Porosimetric analysis was used to determine the pore diameter distribution of the produced membranes. For this purpose, the flow method was used. Porosimetric analysis was performed using the Capillary Flow Porometer iPore −1200 A device (PMI, Ithaca, NY, USA).

The static contact angle was used to determine the surface wettability of the manufactured membranes. In the tests, the sessile drop method was used. A 0.5 μm droplet of RO water was deposited on the membrane. The OCA 25 device was used (DataPhysics Instruments, Filderstadt, Germany).

2.4. Testing of process properties

For tests in the flow system, flat membranes with dimensions of 0.125 m × 0.135 m (0.0169 m^2) were produced. The membranes were placed in a self-produced, reusable module. The construction of the module ensures that the filtration process is carried out in a cross-flow system. A laboratory filtration installation was used to carry out the tests in the flow system. Its structure, apart from the membrane module, includes a circulation pump, feed tank, control valves and pressure gauges. The filtration process was carried out in a closed system with continuous permeate recirculation. The tests were carried out at a pressure of 1 bar and a retentate flow of 36 dm^3/h.

On the basis of the tests carried out in the flow system, permeability for RO water, permeate volumetric flow and BSA retention were determined. In order to determine changes in the volume flow during the process, the time of collecting a sample of 15 mL was measured. The collected samples were also used to determine the concentration of BSA in the permeate. Samples were collected after 1, 15, 30 and 60 min from the start of the process. The retention of BSA was determined based on Eq. (1):

$$R_{\mathrm{BSA}} = \frac{c_N - c_P}{c_N} \times 100\% \tag{1}$$

where c_N is the BSA concentration in feed (g/dm^3), c_P is the BSA concentration in permeate (g/dm^3).

To determine the concentration of BSA, UV-Vis spectroscopy was used, performed with a Genesys 10S UV-Vis apparatus (Thermo Fisher Scientific, Waltham, MA, USA).

2.5. Testing of antibacterial properties

The assessment of antibacterial properties was carried out using ASTM E2149-13a "Standard Test Method for Determining the Antimicrobial Agents Under Dynamic Contact Conditions".

The tests were carried out for two strains of bacteria commonly found in the aquatic environment: *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive). Each test was repeated three times, and the results were averaged.

The percentage reduction in the number of bacteria was determined based on Eq. (2):

$$R = \frac{B - A}{B} \times 100\% \tag{2}$$

where A – cells concentration after 1 h of contact with the sample (CFU/mL), B – cells concentration after 1 h in the control sample (CFU/mL).

3. Results and discussion

In the first part of the research, on the basis of the tests carried out, it was determined that the concentration of the membrane-forming solution of 11% ensures the production of membranes with reproducible properties. A lower polymer concentration reduces the viscosity of the solution, which makes it difficult to form a uniform membrane-forming layer. As a consequence, this leads to the formation of membranes with a non-homogeneous structure. In addition, the membranes have pores with a significantly larger diameter than ultrafiltration or microfiltration membranes. On the other hand, with the increase of the polymer concentration, the viscosity of the membrane-forming solution increases significantly, as a result of which the transport of the solvent in the extraction process is hindered. The slower transport of the solvent leads to the formation of membranes with higher stiffness and the formation of cracks on the membrane surface. The resulting cracks reduce the strength of the membrane and reduce its selectivity.

3.1. Microscopy analysis

In the next part of the research, the influence of the presence of CuO-NPs on the structural properties of the manufactured membranes was determined. For this purpose, 0.5%, 1%, 2% or 5% CuO-NPs by weight to the weight of PS polymer was added to the polymer solution. Then the SEM analyses of the prepared membranes surface were performed. The obtained photos of the surface of the unmodified membrane and the membrane containing 0.5%, 1% and 2% CuO-NPs are shown in Fig. 1 (magnification 500x) and Fig. 2 (magnification 2,000x). Pictures of the membrane surface with a CuO-NPs concentration of 5% are shown in Fig. 3.

The presentation of photos, in various magnifications, of the membranes surface facilitates the observation of two

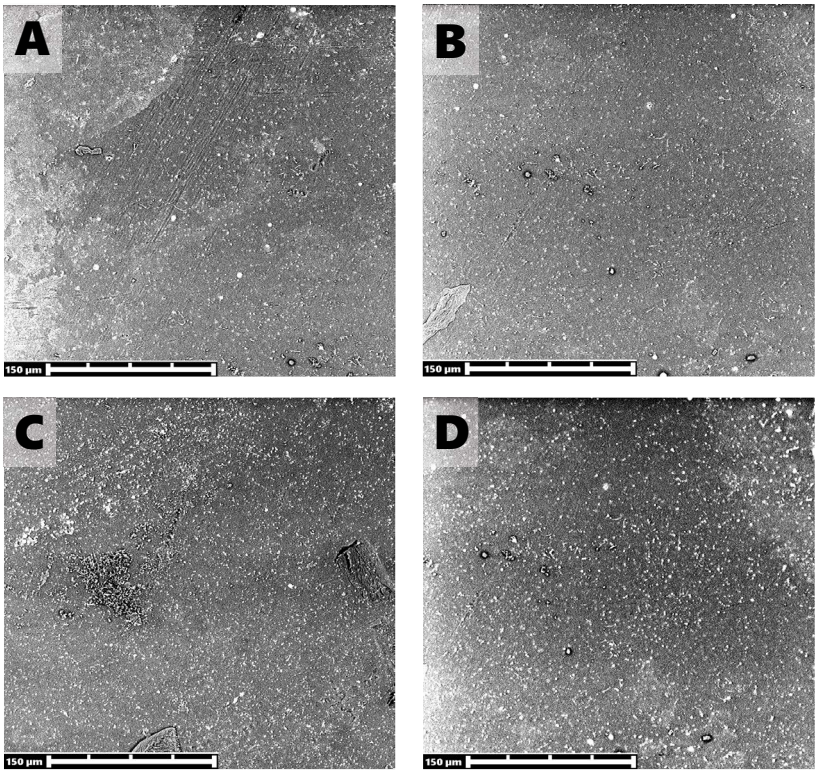

Fig. 1. Scanning electron microscopy image of the surface of the unmodified membrane (A) and membranes with CuO-NPs concentrations of 0.5% (B), 1% (C), and 2% (D) – magnification 500x.

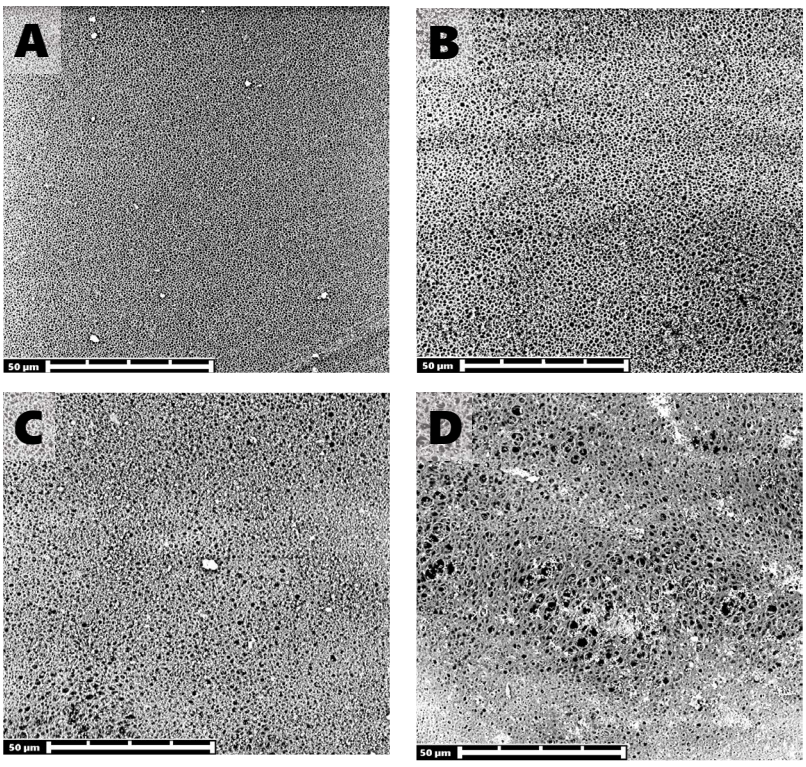

Fig. 2. Scanning electron microscopy image of the surface of the unmodified membrane (A) and membranes with CuO-NPs concentrations of 0.5% (B), 1% (C), and 2% (D) – magnification 2000x.

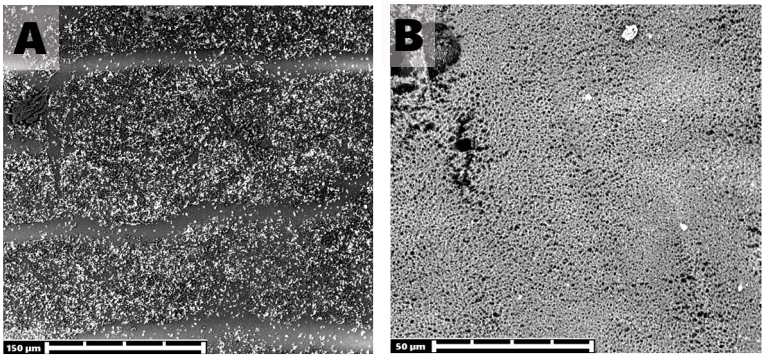

Fig. 3. Scanning electron microscopy image of the surface of the membranes with 5% CuO-NPs concentrations; A – magnification 500x, B – magnification 2,000x.

effects related to the presence of CuO particles. The images with a magnification 500x can confirm the presence of CuO-NPs on the surface of the modified membranes. In addition, with the increase of CuO-NPs concentration, nanoparticles amount on the membrane surface increases. However, for membranes with a CuO-NPs content of 1% and 2%, a large amount of agglomerates of filler particles are found. A large number of agglomerates and their distribution on the membrane surface prove that the concentrations of CuO-NPs used are relatively too high for this compound. On the other hand, observing the images taken with a magnification 2,000x, it can be stated that the presence of CuO-NPs also affects the porosity of the membrane at its surface. With increasing concentration, an increase in pore diameter can be seen. In addition, for membranes containing 1% and 2% of fillers, pores with a clearly larger diameter appear, and the homogeneity of the surface and the regularity of pore distribution on the membrane surface decrease. The increase in membrane porosity and pore diameter is related to the hydrophilic nature of CuO-NPs particles. The presence of hydrophilic particles facilitates the penetration of non-solvent (water) into the formed membrane-forming film. In addition, the presence of hydrophilic particles reduces the affinity of the solvent (NMP) to the polymer chains. Both the facilitated penetration of water and faster diffusion of NMP into the non-solvent volume accelerates the extraction process, resulting in increased porosity and pore diameter [18–22,24,25]. In addition, interactions may occur between the CuO-NPs and the polymer chains, causing interfacial stresses. The shrinking volume of the polymer phase facilitates the formation of pores [17,19].

As the concentration of CuO-NPs increases, the effects described above are more intense. Particularly intense agglomeration of particles occurs; it can be observed on the basis of a photo of the membrane surface with a CuO-NPs content of 5% (Fig. 3a). In addition, the viscosity of the membrane-forming solution increases with the increase in the fillers concentration. The increase in the viscosity of the membrane-forming solution hinders the diffusion of NMP into the water. Slowing down the solvent transport slows down the extraction process, which in turn results in a reduction in porosity and pore diameter (Fig. 3b). However, a large number of agglomerates causes the formation of free spaces on the surface and inside the membrane, the size of such spaces is significantly larger than the diameter of the pores. As a result, the produced membranes with a CuO-NPs concentration of 5% were characterized by low selectivity and their mechanical strength was reduced. For this reason, membranes containing 5% CuO-NPs will not be further analyzed.

In addition, on the basis of SEM photos with magnification 2,000x, surface topographies of the manufactured membranes were made (Fig. 4) using internal application of microscope. On the basis of the obtained images of membrane surface topography, it can be concluded that the surface roughness increases with the increase in CuO-NPs concentration. The roughnes of unmodified membrane was R_a = 414 nm and R_z = 2.3 μm, while for membrane containing 2% of CuO-NPs the roughness was R_a = 720 nm and R_z = 3.7 μm. The increase in roughness results from the presence of agglomerates of CuO-NPs on the surface of the membrane and the inhomogeneous distribution of nanoparticles.

On the basis of cross-sectional SEM photos of the membranes produced (Fig. 5), it can be concluded that these membranes have a characteristic, classic amorphous structure with finger-like pores linked by sponge walls. On the basis of these images, the presence of CuO-NPs agglomerates on the surface of the pores of the modified membranes should also be confirmed. This is especially visible for membranes with CuO-NPs content of 1% and 2%. However, based on the analysis of the photos, it can be concluded that the presence of CuO-NPs does not significantly affect the structure of the inner pores.

3.2. Contact angle measurement

Based on the results of the static contact angle (Fig. 6) for the unmodified membrane surface, it can be concluded that such a membrane has a slightly hydrophilic character, which is consistent with the literature data [17,26,27]. In addition, based on the results of the contact angle, it can be concluded that the presence of CuO-NPs did not significantly affects the wettability of the membrane surface. Only for the membrane containing 2% CuO-NPs, a slightly greater change in the contact angle can be observed. The slight influence of CuO-NPs on the surface wettability of the modified membranes may be related to the small amount of CuO-NPs on the membrane surface. However, an increase

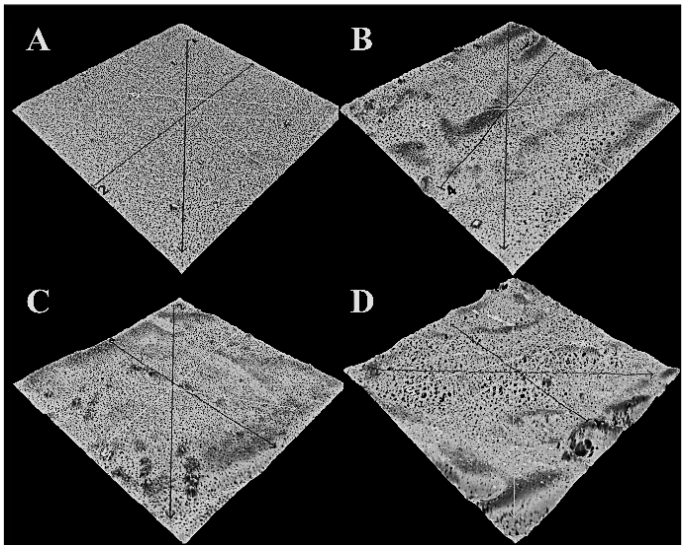

Fig. 4. Topographic analysis of the surface of the unmodified membrane (A) and membranes with CuO-NPs concentrations of 0.5% (B), 1% (C), and 2% (D).

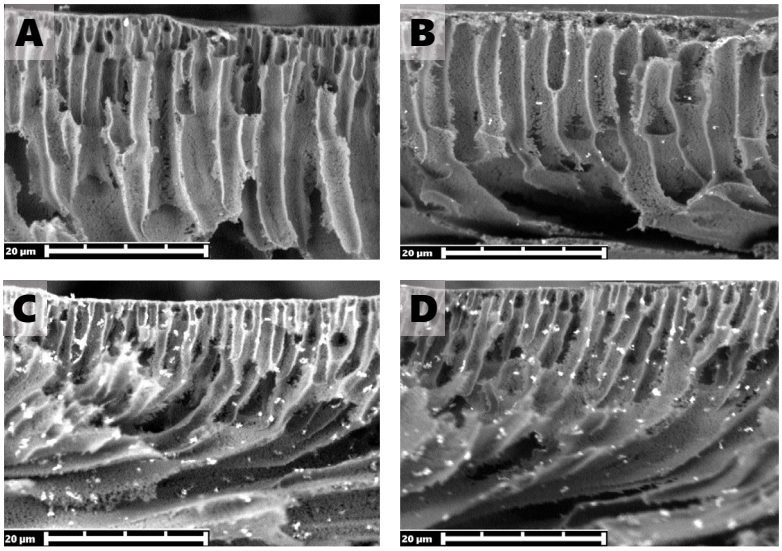

Fig. 5. Scanning electron microscopy image of the surface of the unmodified membrane (A) and membranes with CuO-NPs concentrations of 0.5% (B), 1% (C), and 2% (D) – magnification 5,000x.

in surface roughness and porosity may also be responsible for the increase in surface wettability of the modified membranes. The increase in both roughness [28,29] and porosity [30,31] of hydrophilic materials causes a decrease in the value of the contact angle of its surface.

3.3. Porosimetry analysis

Based on the results of the porosimetric analysis (Fig. 7), it can be concluded that with the increase in the CuO-NPs concentration, the pore diameter distribution flattens out and shifts towards larger diameters. The effect of CuO-NPs on porosity and pore diameter results from the effects described in the section on microscopic analysis. Thus, the obtained results of the porosimetric analysis confirm the conclusions formulated during the microscopic analysis.

3.4. Filtration tests

On the basis of the tests carried out in the flow system, the influence of the presence of CuO-NPs on the process properties of the produced membranes, that is, water permeability (Fig. 8), permeate volumetric flow (Fig. 9) and the BSA retention (Fig. 10), was determined.

Based on the obtained permeability value of the unmodified membrane, it can be concluded that the obtained value is within the range of literature values [17,30,31]. In turn, based on the obtained results (Fig. 8), it can be seen that

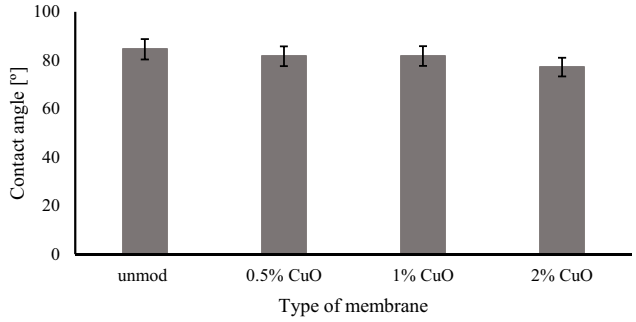

Fig. 6. Contact angle of membranes' surface.

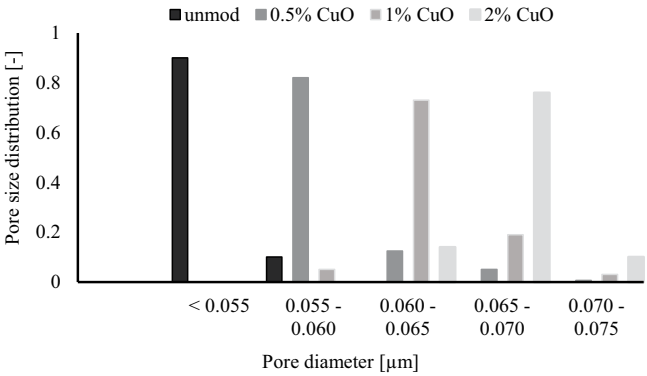

Fig. 7. Pore-size distribution.

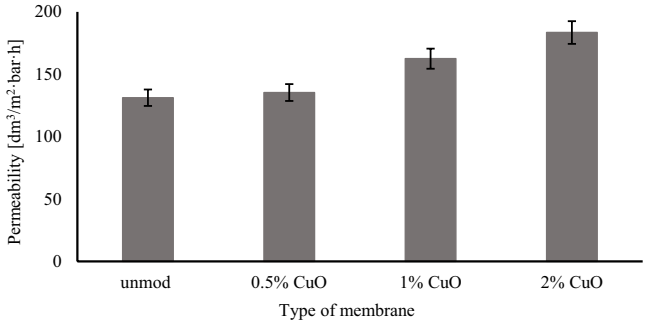

Fig. 8. Water permeability for different types of membranes.

the permeability of the produced membranes increases with the increase in CuO-NPs concentration. This is due to the increase in porosity and pore diameter of the membranes, which is confirmed by the results of microscopic and porosimetric analysis (Fig. 7).

The increase in the permeability of the produced membranes is also confirmed by the results of the permeate volumetric flow (Fig. 9). Based on the obtained results, it can be concluded that the permeate volumetric flow for BSA filtration increases with the increase in CuO-NPs concentration. However, a small change in the previously discussed contact angle and membrane roughness does not significantly affect the percentage decrease in the permeate flux during the process.

Based on the analysis of the BSA retention by the manufactured membranes (Fig. 10), it can be concluded that

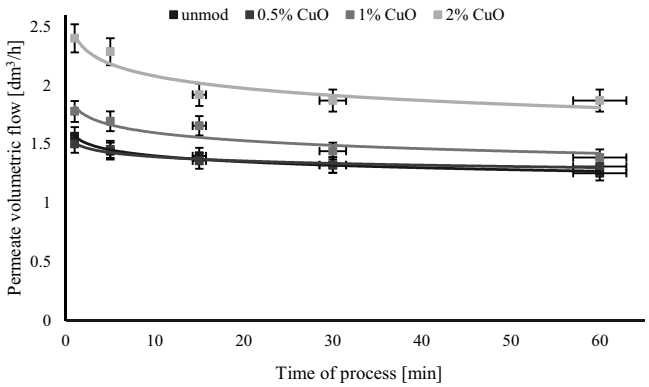

Fig. 9. Change of permeate volumetric flow during the process for different types of membranes.

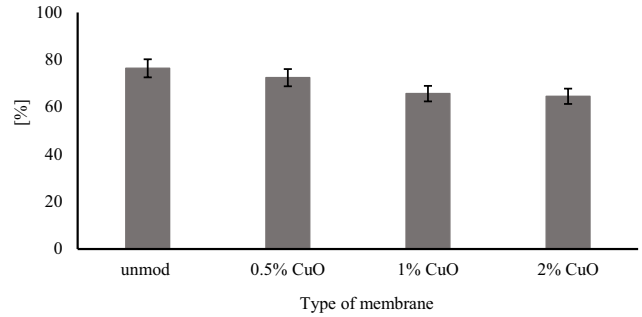

Fig. 10. Retention of BSA for different types of membranes.

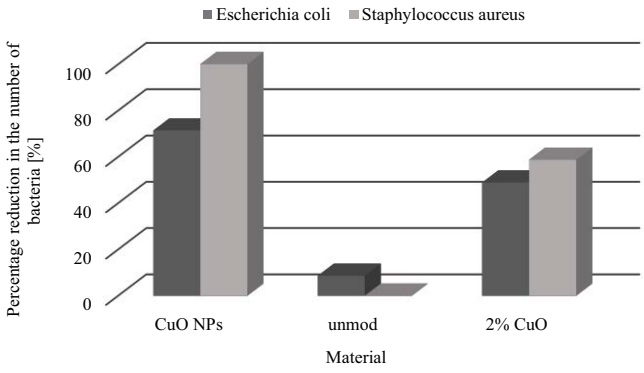

Fig. 11. Reduction of the number of bacteria in contact with the tested material (CuO-NPs – nanoparticles, unmodified material – membrane without nanoparticles, 2% CuO – membrane with 2% of CuO-NPs).

the ability of the membrane to remove BSA from water decreases with the increase of CuO-NPs concentration. The decrease in the retention results from the increase in the porosity and pore diameter of the CuO-NPs-containing membranes.

3.5. Antibacterial properties

Based on the results of bacteriostatic tests (Fig. 11) of the CuO-NPs used and the membranes containing CuO-NPs it can be concluded that both materials (nanoparticles and

membranes with nanoparticles) have antibacterial properties against both Gram-negative and Gram-positive bacteria. The results shown in Fig. 11 confirm that the antibacterial properties of the modified membrane are much greater than those of the unmodified one. It can be concluded that the presence of CuO-NPs on the surface of the membrane is responsible for these properties.

4. Summary

Based on the conducted research, it should be concluded that the modification of membranes with CuO-NPs allows for the improvement of the antibacterial properties of the membrane. In addition, the production of membranes using the wet phase inversion method enables the production of CuO-modified membranes with better permeability and slightly worse separation properties.

The presence of CuO-NPs affects the porosity and pore diameter of the produced membranes. Both of these parameters increase with the concentration of CuO-NPs. It should be emphasized that there is a certain concentration limit of using CuO-NPs without deteriorating the properties of the membrane. Above this concentration, the mechanical and selective properties of the membrane deteriorate significantly.

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