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THE POLYAMIDE MEMBRANES MODIFIED BY COPPER OXIDE USING PVD TECHNIQUES

Key words: polyamide membranes, PVD techniques, copper oxide, leaching, antibacterial properties.

Abstract: The aim of this research was to examine the influence of process parameters of low-temperature plasma treatment on the permeability, stability, and antibacterial properties of polyamide membranes. As a result of the work, the process conditions were selected for plasma deposition of copper oxide, which enable the high stability of the copper oxide coatings on the filtration materials characterized by efficient permeability and antimicrobial activity. Further work is necessary to examine new generation filtration materials in real process conditions for industrial post-consumer liquids. This can contribute to the implementation of the new generation filtration materials proposed in this work.

Membrany poliamidowe modyfikowane tlenkiem miedzi przy użyciu technik PVD

Słowa kluczowe: membrany poliamidowe, techniki PVD, tlenek miedzi, stabilność, właściwości antybakteryjne.

Streszczenie: W pracy przedstawiono wyniki badań dotyczące wpływu parametrów procesowych niskotemperaturowej plazmowej obróbki powierzchni membran poliamidowych na przepuszczalność, stabilność i właściwości antybakteryjne wytworzonych materiałów filtracyjnych. W rezultacie przeprowadzonych eksperymentów dobrano warunki procesowe plazmowej obróbki tlenkiem miedzi, które umożliwiają wytworzenie stabilnych materiałów filtracyjnych charakteryzujących się wysoką przepuszczalnością i właściwościami antybakteryjnymi. Konieczne są dalsze prace umożliwiające zbadanie zachowania wytworzonych materiałów filtracyjnych w rzeczywistych warunkach procesowych przy użyciu ścieków przemysłowych. Dopiero takie działania mogą przyczynić się do udanej komercjalizacji rozwiązania materiałowego zaproponowanego w niniejszej pracy.

Introduction

Membrane filtration plays a significant role in many processes in food, pharmacy, medicine, and environmental engineering [1–4]. Due to their unquestionable advantages, such as simplicity, application flexibility, efficiency, and economy, these techniques can find many applications in a variety of technological processes. The rapid development of membrane filtration has been influenced by the progress in the field of chemical engineering and material engineering. In the production of membranes, mainly polymers have been used, such as polyamide, polypropylene, and polysulfone, which enable the formation of porous structures [5,6]. They are also characterized by very good physical and chemical properties, such as inactivity and processing simplicity. A serious limitation of the polymer membranes is biofouling phenomena consisting of microorganisms settling on the membrane's surface and in the pores of a membrane [7–9]. The growth of biological matter on the filter materials is a complex process, which is usually slow covering several key steps (Fig. 1). This process can be reversible or irreversible. The first step of biofouling formation is relatively fast and concerns the adsorption of nutrients on the material's surface. It can occur within even two hours. Organic substances in the filtration medium and retained on the filter surface can be the source of the growth for microorganisms and contribute to their adhesion on the surface of the membranes. The mechanism of biofouling involve the proliferation of the microbial cells as a result of permanent access to the organic matter and biofilm formation as a result of the excretion of extracellular polymeric substance (EPS) by microbial cells. The resulting structure, called biofilm, is a specific transport barrier for potential biocidal agents. It is extremely compact and difficult to eliminate by the external factors [9,10]. Biofouling leads to a significant decrease in the efficiency of membrane filtration and alters the selectivity of membranes and energy consumption as a result of the changes in process parameters, e.g. transmembrane pressure [1–3].

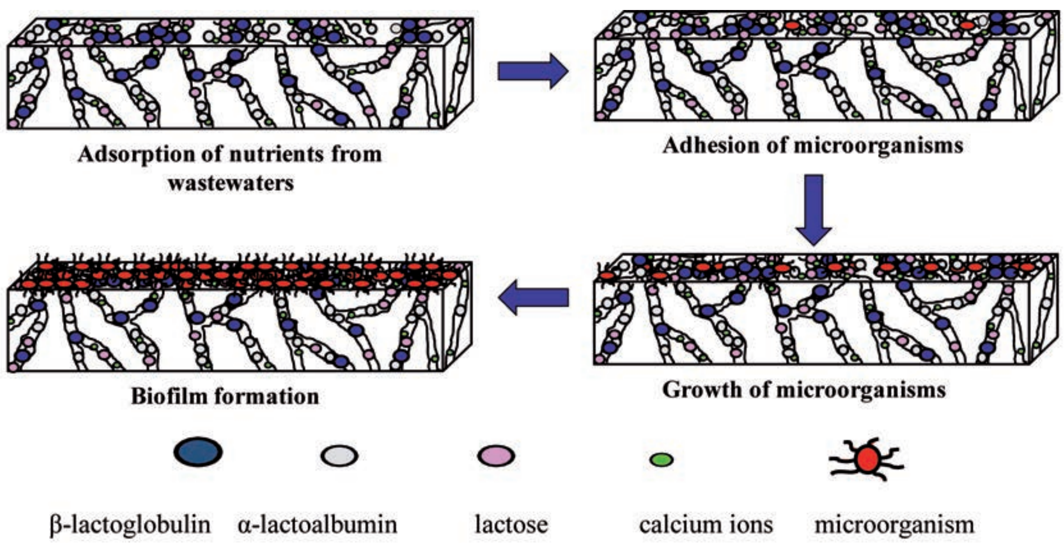

Fig. 1. Mechanism of biofouling formation on the polymer membranes

The biofouling on the membrane enforces more frequent cleaning or replacement of the membranes resulting in the lower efficiency and higher filtration costs. One of the most promising ways to overcome the problem is a membrane surface modification to impart the antimicrobial properties [11–28]. So far, many attempts have been made to modify the surface of the membranes that can help to control membrane contamination. It is still a problem to obtain the membrane with highly stable coatings during filtration processes carried out under real operating conditions [29–31].

The aim of the work was to develop appropriate process parameters for plasma surface deposition of copper oxide (CuO) on the polyamide membranes, which enables the generation of stable filtration materials with high permeability and antibacterial properties.

1. Experimental

For the surface modification of the membranes at low-temperature metallic (metallic-gas) plasma and non-metallic (gas) plasma of PVD (Physical Vapor Deposition) process were used. For gas plasma, the low-pressure glow discharge technique was used, while the gas-plasma was obtained using the magnetron sputtering technique. The activation processes using glow discharge in an inert gas as well as magnetron sputtering processes were carried out using a chamber (Fig. 2) that was designed and built at the Institute for Sustainable Technologies – NRI in Radom [32].

As a part of the experimental work, the influence of plasma process conditions (current and the exposure time) was examined on the permeate flux during the filtration of demineralised water. The stability of the CuO coating was examined with ICP-MS to measure the concentration of Cu in demineralised water filtered through the modified membranes. The antibacterial properties of the membranes were examined using a vacuum filtration system. Filtration materials used for the research involved MAGNA polyamide membranes (0.22 μm pore size). Permeate flux was 1.0 $dm^3/(m^2s)$ during filtration of demineralised water at a pressure of 0.5 bar.

Plasma treatment with CuO was carried out using both non-activated membranes (native) and membranes pre-activated in gas plasma using working atmospheres consisting of argon (100%) and argon (90%) with oxygen (10%). The activation time of membranes in non-metallic plasma was 120 s and selected based on previous works [27, 33, 34]. In turn, the processes of modification in the metal-gas plasma included the formation of CuO

Fig. 2. The chamber used for plasma treatment of polyamide membranes

coatings on the surface of the membranes (without prior activation and activation in Ar or Ar-O_2 mixture) using the magnetron sputtering method (MS-PVD). The time of plasma treatment of membranes using CuO was 30 and 120 s. The electric current during plasma treatment of polyamide membranes was changed in the range of 0.2-0.8 A. Substrate polarization during modification of the membranes with metal-gas plasma was avoided because of the sudden increase in temperature that could damage the polymer. The permeate flux was determined by measuring the time required for filtration of demineralized water (100 cm^3) through the active surface of polyamide membranes (8 cm^2) under the pressure of 0.5 bar at 25°C. Membrane filtration was carried out with a laboratory *dead-end* filtration system consisting of a pump and a membrane in the housing. The stability of CuO coatings deposited on the membrane surfaces was examined in the demineralized water filtered at a pressure of 0.5 bar. For the tests, demineralized water was chosen, which was characterized by specific conductance and pH of 5.3 μS/cm and 6.5, respectively. Concentrations of copper (Cu) ions in such obtained filtrates were determined with an ICP-MS (Inductively Coupled Plasma Mass Spectrometer – iCAP Q, ThermoFisher Scientific). The detailed operating parameters for ICP-MS measurements are summarized in Table 1. Prior to the determination of Cu concentration, the samples were mineralized for 90 minutes at 120°C using a DigiPrep Mini device (SCP Science).

Antimicrobial activity of CuO-modified membranes was examined against a reference for microorganisms for Gram-negative bacteria (*Escherichia coli*). Microbiological tests were carried out using a vacuum

Table 1. Operating parameters of ICP-MS

Parameters	Values
Forward power, W	1548.6
Cool gas flow, dm^3/min	13.956
Auxiliary gas flow, dm^3/min	0.8021
Nebulizer gas flow, dm^3/min	1.02464
Dwell time, s	0.005
Number of replicates	3

filtration kit. Membranes were sterilised for 30 minutes with UV-C lamp in a laminar cabinet. In a saline buffer, *E. coli* inoculum from a 24-hour culture was prepared according to measurements of absorbance, which was about 0.3 at 475 nm (according to the ASTM E2149-13a method). The resulting suspension was diluted using the serial dilution method. From the 10-2 dilution, 35 μl was suspended in 1000 ml of physiological saline buffer obtaining an approximate concentration of 7*103 CFU/ml. The amount of 10 ml of the prepared solution was filtered through membranes, which were then placed in agar Luria Bretani media (LB) and incubated in a heating oven at 37°C. After 24 hours, the amount of colonies grown on the membranes was calculated with colony-forming unit (CFU) counting, which is a conventional indirect method for assessing viability. The results are expressed as a percentage (%) of cell viability, which was calculated based on CFU counting on the membranes. The number of colonies grown on the native membrane (control) was treated as 100% cell viability.

2. Results and discussion

The first step of the research was to examine the influence of electric current and the time of CuO-plasma treatment of polyamide native membranes on the permeate flux of demineralized water (Fig. 3). It was found that the increase in electric current and the extension of time of plasma treatment contributes to the reduction of permeate flux determined during the filtration of demineralised water compared to unmodified membrane. The permeate flux was more favourable for the membranes treated with plasma for 30 s at the current higher than 0.2 A. It was observed that permeate flux diminished by 7% compared to the unmodified membrane.

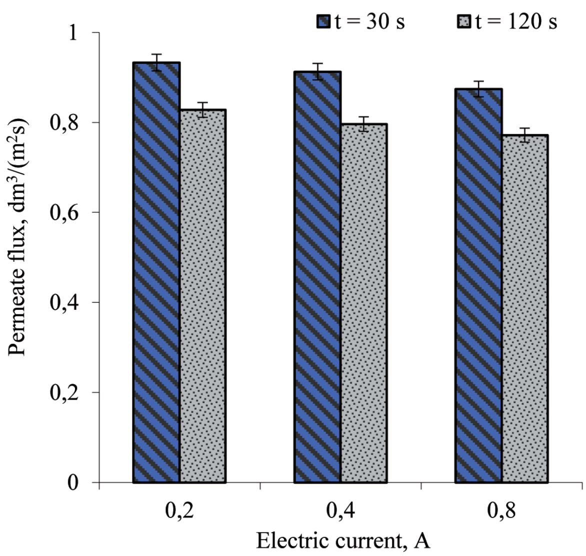

Fig. 3. Influence of electric current and plasma treatment of polyamide membrane (without pre-activation) using CuO on permeate flux determined during filtration of demineralised water

In the next step, the tests were carried out on the membranes pre-activated in Ar (Fig. 4) or Ar-O_2 (Fig. 5). Both ways of activation resulted in permeate flux similar to that obtained for untreated membranes (Fig. 3). This means that, regardless of the pre-treatment modification step, but along with the increase in electric charge and the extending of the time of CuO plasma treatment, a decrease in the membrane performance was observed. It was found that it is most beneficial to pre-activate membranes with both Ar and O_2 and conduct plasma treatment with CuO for 30 s at 0.2 A in order to maintain high permeability, as the decrease in permeate flux was 3% (Fig. 5).

The stability of the modifier on the membrane was determined by measuring the Cu concentration in the filtrates of demineralised water that passed through the modified membranes (Fig. 6). It is expected that the

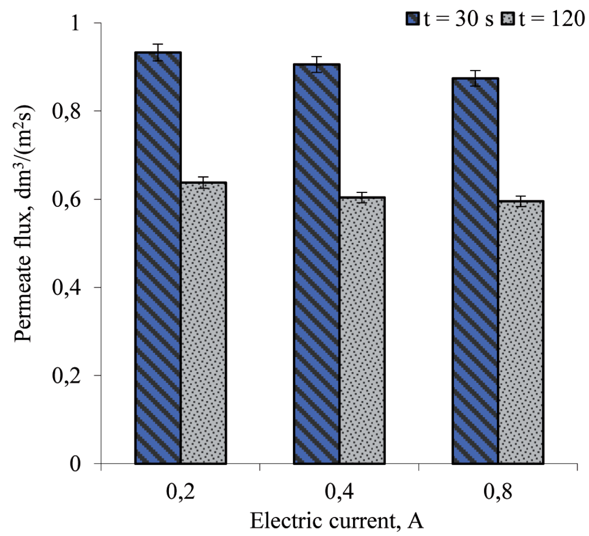

Fig. 4. Influence of electric current and time of CuO plasma treatment of polyamide membrane (pre-activated with Ar) on permeate flux during filtration of demineralised water

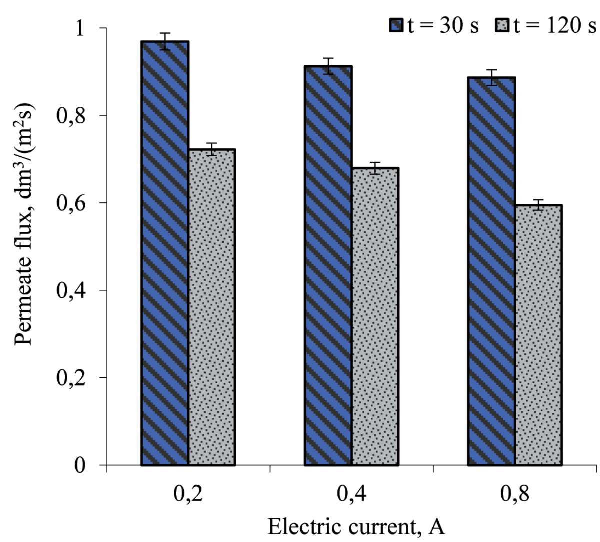

Fig. 5. Influence of electric current and time of CuO plasma treatment of polyamide membrane (pre-activated with both Ar and O_2) on permeate flux during filtration of demineralised water

coating is strongly attached and not leached from the membrane surface. Leaching is as much important issue to be considered as permeability performance of the filtration membranes. It was found that the pre-activation of the membrane in the Ar-O_2 mixture contributes to the greater release of Cu from the CuO plasma treated polyamide membrane (Fig. 6). In the case of the membranes treated for 30 s, this was already visible at a current of 0.2 A (Fig. 6a). For membranes treated for 120 s, it is particularly noticeable at a current ≥ 0.4 A (Fig. 6b). Although plasma treatment of polyamide membranes using CuO carried out at 0.2 A for no longer than 30 s allows one to obtain membranes with a stable coating during filtration of demineralised water in a dead-end system, additional research on Cu leaching from the surface of the membranes in a cross-flow system is still needed with model post-consumer liquids. High stability in the actual operating conditions enables application in the industry for the wastewater treatment.

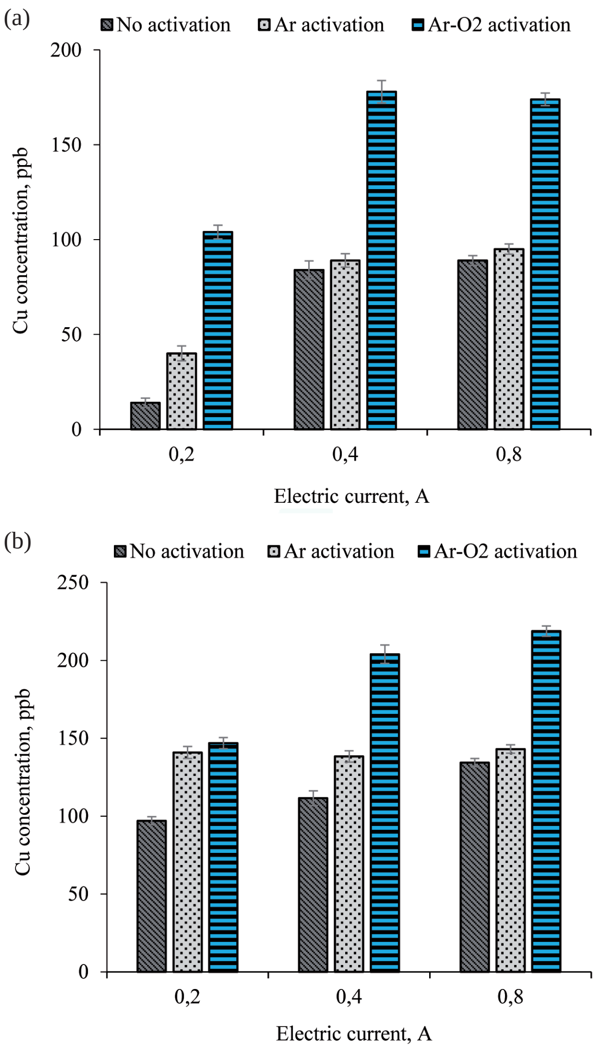

Fig. 6. Influence of electric current applied during plasma treatment carried out for 30 (a) and 120 (b) seconds on polyamide membranes (native and pre-activated with Ar or Ar-O_2 on the concentration of Cu leached during filtration of demineralised water

Microbiological activity of the developed filtration materials were carried out for the *Escherichia coli* bacteria, whose presence is a frequently used as an indicator of water pollution. The materials selected for the tests were CuO-treated membranes for 30 s at a current of 0.2 A, which were characterized by high permeability (Figs. 4–5) and stability (Fig. 6a) during the filtration of demineralised water. Photographs of the membranes after microbiological tests are presented in Fig. 7. The obtained results indicates that CuO modified membranes were highly efficient against *Escherichia coli*. It was observed that membranes pre-activated in argon exhibit the strongest bactericidal activity, which allowed eliminating 99% of microorganisms. Modification of membranes with CuO without prior activation resulted in a slightly weaker activity of 96%. The lowest antibacterial properties of 90% was observed for the membranes previously activated in Ar-O_2 mixture, which, at the same time, were characterized by the lowest stability of the CuO coating revealed by the leaching of Cu during filtration of demineralised water (Fig. 6a).

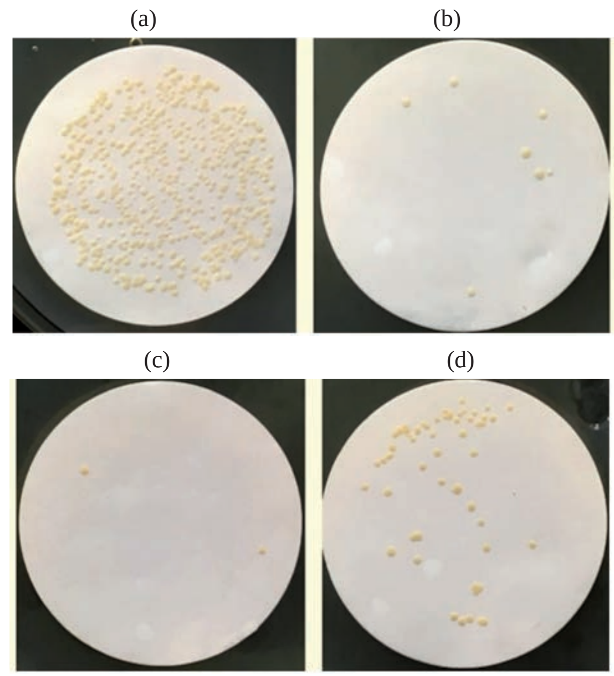

Fig. 7. Membranes after vacuum filtration of bacterial suspension: native membrane (a), CuO-modified membrane (b), CuO-modified membrane activated in Ar (c), CuO-modified membrane activated in Ar-O_2 (d)

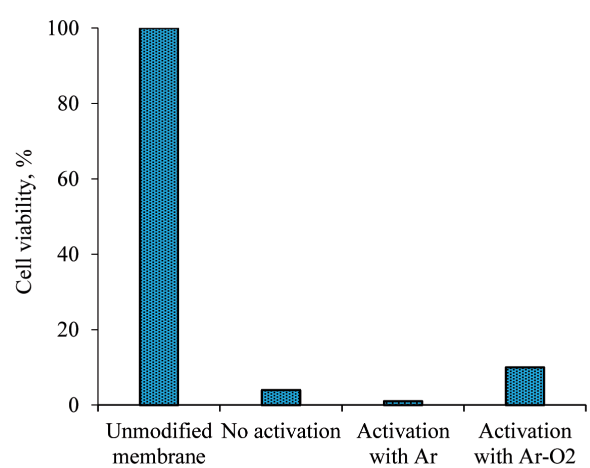

Fig. 8. Bacterial cells' viability on native and CuO plasma modified membranes

Conclusions

In this study, the process parameters of plasma treatment with CuO were selected for polyamide membranes in order to obtain a high performance of the filtration materials with a strong antibacterial activity against Gram-negative bacteria. During the study, it was found that the most efficient time of CuO plasma treatment was 30 s at a current of 0.2 A allowing one to produce the materials resistant to Cu leaching during filtration of demineralised water showing strong bactericidal activity to *Escherichia coli*. The obtained results are promising and have potential in the application of surface modified polyamide membranes with CuO. Nevertheless, such produced materials should be tested under the real operating conditions.

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