

Anna KOWALIK-KLIMCZAK^{a,*}, Ewa STANISŁAWEK^a, Joanna KACPRZYŃSKA-GOŁACKA^a,
Monika ŁOŻYŃSKA^a, Marta BOJARSKA^b, Wojciech PIĄTKIEWICZ^a, Piotr WIECIŃSKI^c

^a Institute for Sustainable Technologies – National Research Institute, Radom, Poland

^b GVC Filter Technology, Bologna, Italy

^c Faculty of Materials Science and Engineering, Warsaw University of Technology, Poland

* Corresponding author: anna.kowalik-klimczak@itee.radom.pl

PLASMA TREATMENT OF MEMBRANE SURFACES USING COPPER OXIDES

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Key words: plasma treatment, polymeric membranes, copper oxide, leaching, antibacterial properties.

Abstract: The novel technique that will be introduced for modifying surfaces is plasma treatment, which creates a great potential in the development of a variety of functional properties of polymeric membranes. Application of this technique in the processes of membrane modification allows functionalization by the manufacturing metal oxides such as copper oxide, silver oxide, or titanium dioxide on the surface. In this work, the polymeric membranes were activated with low-temperature plasma of different gases (Ar and Ar-O₂) and subjected to copper oxide deposition. The leaching of copper from the surface of plasma-modified membranes and its permeability and antimicrobial activity were examined. It was found that CuO-modified membranes pre-activated in an Ar or Ar-O₂ mixture are characterized by much lower stability than ones without pre-activation. Moreover, the filtration properties of CuO-modified membranes were unchanged compared to native ones, and these filtration materials are characterized by antibacterial properties.

Plazmowa modyfikacja powierzchni membran polimerowych przy użyciu tlenku miedzi

Słowa kluczowe: plazmowa modyfikacja powierzchni, membrany polimerowe, tlenek miedzi, stabilność, właściwości antybakteryjne.

Streszczenie: Techniki plazmowe to nowatorskie metody modyfikacji powierzchni, które umożliwiają nadanie różnorodnych właściwości funkcjonalnych membran polimerowych. Zastosowanie technik plazmowych podczas modyfikacji membran polimerowych umożliwia ich funkcjonalizację poprzez wytwarzanie tlenków metali, takich jak tlenek miedzi, tlenek srebra lub dwutlenek tytanu na ich powierzchniach. W ramach przeprowadzonych prac membrany polimerowe aktywowano niskotemperaturową plazmą w mieszaninie w różnych gazów (Ar i Ar-O₂), które następnie poddawano modyfikacji przy użyciu tlenku miedzi. Zbadano stabilność związania tlenku miedzi z powierzchnią membran modyfikowanych plazmą i jej przepuszczalność oraz aktywność przeciwdrobnoustrojową. Stwierdzono, że membrany modyfikowane CuO wstępnie aktywowane w Ar lub mieszaninie Ar-O₂ charakteryzują się znacznie mniejszą stabilnością niż te bez wstępnej aktywacji. Ponadto właściwości filtracyjne membran modyfikowanych CuO były niezmiennione w porównaniu z materiałami natywnymi, a wytworzone materiały filtracyjne charakteryzowały się właściwościami antybakteryjnymi.

Introduction

Pressure driven membrane processes are considered as one of the best solutions to the problem of water scarcity [1–3]. However, the key problem of the widespread use of membrane processes in large-scale wastewater treatment is the cost of the recovery of reusable water. During the process of water recovery from wastewater in membrane systems, the permeate

flux may decrease over time due to the deposition of filtrated liquid components on the surface or the internal structure of the membrane [4–11]. This phenomenon is particularly in the dead-end filtration systems where the feed solution is introduced in a direction perpendicular to the membrane surface until concentration is achieved. Consequently, it leads to a reduction in the filtration efficiency, necessitating chemical cleaning of the membranes and, in extreme cases, replacing them. Due

to the high intensity of membrane contamination during operation and the inability to effectively clean them, their lifespan significantly shortens. In addition, due to the decrease in efficiency, it is necessary to use a larger surface area of membranes and/or higher transmembrane pressure, which results in higher energy consumption and an increase in both investment and operating costs.

The solution to these problems may be the modification of the surface of the membranes (Fig. 1), which will effectively reduce the deposition of contaminants on the surface of the membranes. Modification of the surface of polymer membranes involves physical methods using gas or metal plasma and a chemical with appropriate solutions or a combination of both methods [12–16]. Plasma modification is performed by the treatment of the surface of the polymer with a variety of ionized gases, e.g., Ar, CF_4 , Ar- CH_4 , CH_4-N_2 [17–21] or the deposition of thin layers of metals, such as silver (Ag) [13], titanium (Ti) [17], or copper oxide (CuO) [22, 23].

Plasma processing techniques are also commonly used to activate the surface of a polymer prior to

chemical modification with the grafting of hydrophilic macromolecules, e.g., polyethyleneimine, polyacrylic acid, or polyethylene oxide [24]. This creates functional groups whose charge depends on the pH of the solution [12]. Nanostructures with antibacterial or photocatalytic properties, e.g., zinc oxide (ZnO), silver oxide (AgO), copper oxide (CuO), and titanium dioxide (TiO_2) [14, 21, 25–27], are also used to modify the surface of polymeric membranes. In recent years, there has also been an increase in interest in the production of polymeric membranes modified by graphene and graphene oxide (GO) [28–30].

The huge number of available modifiers and the variety of modification techniques (Fig. 1) allow the development of research standards for modified membranes that are no less important than the development of the modification technologies themselves. The high stability of the modifying layer on the membrane is set by the limited leaching to the water, which is a particularly crucial issue that determines the admission of the developed filter material for the use in the industry [27].

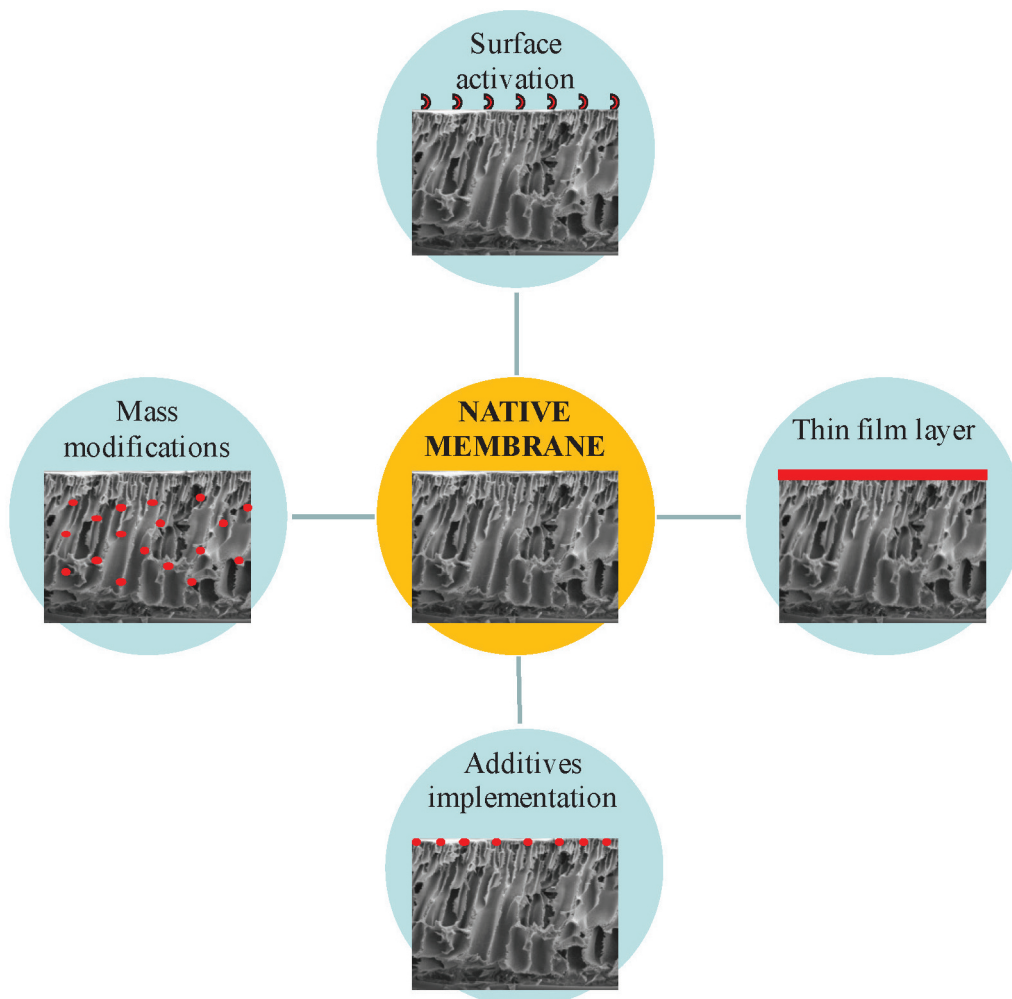


Fig. 1. Methods of modification of polymeric filtration membranes

The aim of this study was to investigate the stability of copper oxide (CuO) deposited with plasma on a polyamide membrane and to evaluate their filtration and antibacterial properties.

1. Experimental

In the study, the influence of copper oxide (CuO) plasma treatment of polyamide membranes on permeate flux during filtration of demineralized water was examined. The membranes were also tested in terms of antibacterial properties and the stability of CuO coatings. Filtration materials used in the experiments were MAGNA polyamide membranes (GVS Filter Technology), which have a 0.22 μm pore size and a permeate flux of 1.0 $\text{dm}^3/(\text{m}^2\text{s})$ during the filtration of demineralized water at a pressure of 0.5 bar.

Plasma treatment with CuO was carried out on native membranes and the membranes pre-activated with gas plasma using working atmospheres consisting of argon (100%) and a mixture of argon (90%) with oxygen (10%). The time of treatment in non-metallic plasma was 120s. The selection of appropriate treatment time was based on previous works [22]. The modification in metal-gas plasma included the formation of CuO coatings on the surface of the membranes (without activation and pre-activated with Ar or Ar-O₂ mixture) using the magnetron sputtering method (MS-PVD). Plasma modification times of membranes using CuO were 30 s and 120 s. In turn, the current during plasma treatment of polyamide membranes was 0.2 A and was selected during previous tests [22]. For the plasma treatment of membranes, the Standard 3 chamber was used, which was discussed in a previous paper [22].

The stability of the CuO coatings on the membrane surfaces during plasma treatment conducted under different process conditions was tested during the filtration of demineralized water at a pressure of 0.5 bar. The filtration tests were performed in a dead-end laboratory set-up consisting of a pump and a membrane placed in the housing. The demineralized water was characterized by a conductivity of 5.3 $\mu\text{S}/\text{cm}$ and a pH of 6.5. Leaching of copper (Cu) from the surface of the membranes after plasma treatment with CuO was examined on the filtrates of the demineralized water by the measurement of concentration of Cu using inductively coupled plasma mass spectrometry (ICP-MS) (iCAP Q by ThermoFisher Scientific). The operational parameters of ICP-MS used during the measurement of Cu concentration were discussed in [22]. Prior to the determination of the Cu concentration, the samples were mineralized for 90 minutes at 120°C using the DigiPrep Mini device (SCP Science).

The permeate flux was determined by measuring the time required for the filtration of demineralized

water (100 cm^3) through the active surface of polyamide membranes (8 cm^2) at a pressure of 0.5 bar.

The antibacterial properties of surface-modified membranes were tested against representative microorganisms for Gram-positive bacteria (*Bacillus subtilis*). Prior to microbiological tests, the membranes were sterilized with UV-C in a laminar cabinet for 30 minutes. Then, the suspension of appropriately diluted bacteria in physiological saline buffer was filtered through the membranes, which then were placed on LB with agar plates and incubated at 37°C for 24 h. After this time, bacterial colonies that had grown on the membranes were counted. The results of bacterial viability on membranes were expressed as log CFU/ cm^3 .

2. Results and discussion

The first step of the work involved the examination of the stability of CuO on native and both Ar and Ar-O₂ activated membranes (Figs. 2 and 3). It was found that the concentration of Cu leached from the surface of the membranes treated by plasma for 30 s was maintained at a much lower level than for 120 s. Regardless of the time of CuO plasma treatment of the membranes, it was found that the membranes pre-activated in Ar or Ar-O₂ mixture were characterized by much lower stability than the native membranes (without pre-activation). In addition, it was observed that the concentration of Cu leached from the surfaces of membranes activated in Ar or Ar-O₂ decreases with the increasing volume of filtered water. This means that, in the first phase of the filtration process, unbound Cu ions were washed out from the membrane.

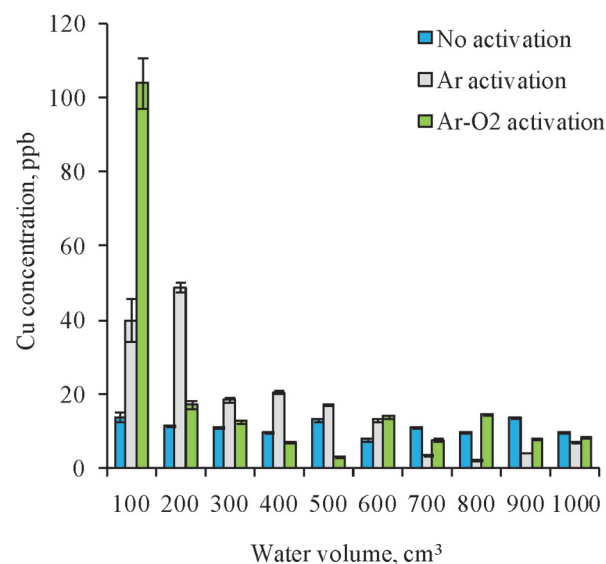


Fig. 2. The stability of CuO coatings during filtration of demineralized water through the membranes treated with plasma for 30 seconds

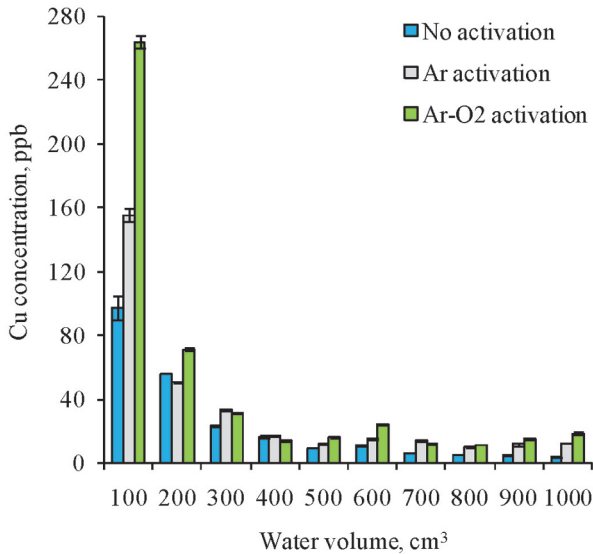


Fig. 3. The stability of CuO coatings during filtration of demineralized water through the membranes treated with plasma for 120 seconds

Filtration properties of membranes after CuO plasma treatment were analysed during experiments conducted on demineralized water (Fig. 4). Based on the analyses, it was found that the plasma treatment of membranes using CuO slightly changes the permeate flux of demineralized water compared to the unmodified (native) membrane. The most favourable results were obtained for the native membranes treated with CuO plasma for 30 s (yet without pre-activation). These membranes were characterized by a high permeate flux, which was identical to that obtained when testing unmodified native membranes. The extension of the plasma treatment time of the membranes without pre-activation to 120 s turned out to result in a decrease

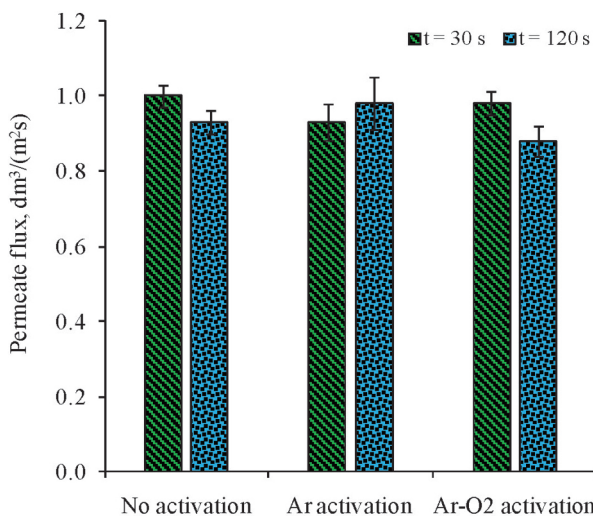


Fig. 4. Permeate flux obtained during the filtration of demineralized water through the membranes after CuO plasma treatment carried out for 30 (a) and 120 (b) seconds

of the permeate flux by about 7% with respect to the unmodified membrane.

The membranes characterized by the highest coating stability (Figs. 2–3) and permeability (Fig. 4) were selected for the determination of antibacterial activity against *Bacillus subtilis*, thus the membranes treated with CuO for both 30 s and 120 s but without initial activation. It was found that CuO modified membranes are characterized by high efficiency against *Bacillus subtilis*, which is a representative of Gram-positive bacteria (Fig. 5). The membrane treated with CuO for 30 s resulted in a 94% reduction of bacterial viability with respect to the unmodified membrane. In turn, the membrane after CuO plasma treatment carried out for 120 s was totally resistant to the growth of the bacteria, which may be associated with the higher content of CuO compound on the membrane surface.

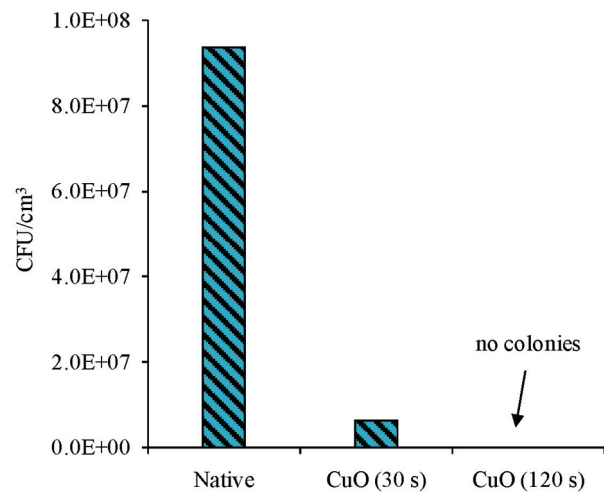


Fig. 5. Antibacterial properties of the membranes after plasma treatment with CuO

As a result of the experiments, it was found that the plasma treatment with CuO membrane surfaces without pre-activation carried out for no longer than 30 s allows one to obtain materials that work stably during filtration of demineralized water (Fig. 2). These membranes had good filtration properties compared to those initially activated (Fig. 4) and showed strong antibacterial properties (Fig. 5). However, it is necessary to carry out filtration tests using real wastewater, which will allow studying the antibiofouling and photocatalytic properties of the produced materials.

Conclusions

In this study, the leaching of copper from surface of plasma-modified membranes and its permeability and antimicrobial activity were examined. During the study, it was found that CuO-modified membranes pre-activated in Ar or Ar-O₂ mixtures were characterized by

much lower stability than ones without pre-activation. Moreover, the filtration properties of CuO-modified membranes were unchanged compared to native sample and these filtration materials were characterized by antibacterial properties *Bacillus subtilis*. Further work is necessary to examine the antibiofouling and photocatalytic properties of CuO-modified membranes in real process conditions for industrial wastewater.

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