

## The polyamide membranes functionalized by nanoparticles for biofouling control

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Received 13 April 2018; Accepted 3 July 2018

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### ABSTRACT

This paper presents the results on the modification of polyamide (PA) membranes using nanostructures such as titanium dioxide nanoparticles (TiO<sub>2</sub> NPs) and zinc oxide nanotubes (ZnO NTs) used to provide the antibiofouling properties. Plasma treatments with argon (Ar) and mixture of argon (Ar) and oxygen (O<sub>2</sub>) were used to activate the surface of flat-sheet membrane in order to facilitate the attachment of TiO<sub>2</sub> NPs and ZnO NTs. As a consequence, TiO<sub>2</sub> NPs and ZnO NTs were enabled to be attached to the membrane surface. Scanning electron microscopy and X-ray photoelectron spectroscopy were used to characterize the particles deposited on the treated membranes and the strength of the nanostructures fixation to the membrane surface. It was found that the plasma activation with Ar-O<sub>2</sub> enabled more stable deposition and fixation of NPs on a membrane surface compared with Ar plasma treatment. It was also found that the filtration properties of both modified membranes were higher compared with the native one. The microbiological experiments showed that ZnO-modified membranes had stronger antibacterial properties than TiO<sub>2</sub>-modified membrane.

*Keywords:* Polyamide membranes; Plasma; TiO<sub>2</sub> NPs; ZnO NTs; Antibacterial properties

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### 1. Introduction

Constantly growing human population and its living standards as well as progressive development of the industry and the agriculture result in growing demand for water. However, this demand is not covered by the limited water resources. Therefore, a lot of efforts have been made to recover water from wastewater or process effluents and recycling, preferably in a closed loop [1]. Due to the low production costs, wide range of products fulfilling diverse requirements, high quality, ease of up-scaling, low energy consumption and environmental friendliness, and the polymer membranes gain growing popularity in water treatment processes [2]. However, the effectiveness of the membrane filtration is

limited by *biofouling* – colonization of membrane surface and pores by microorganisms [3]. *Biofouling* causes decrease of the filtration efficiency over time, increase of transmembrane pressure and deterioration of its selectivity [4]. Bacteria – the major group of microorganisms – contribute to the biofilm formation and its development is associated with the assimilation of nutrients and secretion of extracellular polymeric substances (EPSs) strengthening the biofilm structure [5]. The biofilm layer facilitates adsorption of the inorganic matter and forms irreversible deposits on the polymer membrane surface. Moreover, the presence of biofilm leads to the membrane polarity, the increase in hydrodynamic pressure and – in a consequence – the higher operational costs [6]. Since *biofouling* is considered as one of the major issues hampering the application of membrane techniques [7], the additional

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pretreatment processes are applied to reduce bacterial levels in feed streams. Even so, some living bacteria remain and still can proliferate. Thus, biofouling consists of not only biotic organic compounds but also abiotic matter that originate during the decay processes [8].

The problem of *biofouling* is nowadays believed to be the most important topic of polymer filters and membranes, particularly, in the processes of washing and sanitizing of food processing plants. Filtration materials used to treat wastewaters rich in nutrients are inevitably associated with the biofilm formation. Hence, the issue of the development of excellent antimicrobial filtration units is highly important to address.

One of the most promising approaches to cope with biofouling is a surface modification of filtration materials to impart the antimicrobial properties [9]. So far, a lot of trials have been undertaken to modify a membrane surface, and they are oriented to change membranes hydrophilicity and antibacterial properties that can be useful in membranes' operation [10–11]. The emerge of nanotechnology has provided enormous possibilities in improving functional properties of filtration materials. Nanostructures are currently most often applied onto materials dedicated to cope with bacteria. The implementation of metal oxide nanoparticles (NPs), for example, by means of grafting onto argon plasma preactivated membranes, results in the considerable reduction of living microflora on the material [3]. Among metal oxide NPs, the most promising features such as physical and chemical stability, high catalytic activity and antibacterial efficiency are revealed by zinc oxide nanoparticles (ZnO NPs) [12]. The other commonly known materials are silver nanoparticles (Ag NPs) and three possible mechanisms of their antimicrobial activity are as follows: (1) the disruption of cells' membrane integrity and oxidation stress, (2) the intercalation with intracellular biomolecules leading to deeper metabolic malfunctions, and (3) the release of silver ions. The deposition of Ag NPs is performed, among others, by means of plasma reactor, resulting in a very uniform grafting yield of NPs [13]. Recently, the use of composite filtration materials containing graphene (Gr) or graphene oxide (GO) has been reported, which may interact with cell components, for example, membranes, proteins or DNA, and trigger the activation of bio-chemo-physical interactions between bacteria and functionalized material [14].

There are two major nanostructure dispersion methods described in literature, concerning the modification of membranes: in situ method based on mixing with membrane raw material and ex-situ technique, in which a modifier is immobilized onto a membrane surface. It was observed that membranes modified according to ex-situ approach revealed more dense yield of nanostructures bigger in size. Instead, the membranes modified in-situ had less dense, smaller, and homogeneously deposited nanostructures. The lower density of nanostructures is considered to have limited availability to their growth under conditions of the increasing porosity in membrane structure [15]. It was observed that biocidal activity of the membrane was considerably greater along with the greater yield of nanostructures, but of a smaller size. The antibacterial activity is also dependent on the crystallinity of the particle as well as the proper wavelength of used UV radiation. Titanium dioxide nanoparticles (TiO<sub>2</sub> NPs) in the form of anatase are more stable than rutile or brookite.

Their antimicrobial activity as well as ability to degrade organic compounds are based on the continuous generation and release of free radicals. To obtain the highest possible bactericidal efficiency, the UV radiation should be included in the wavelength corresponding to the energy gap of the applied active material. Then, TiO<sub>2</sub> NPs cause disturbances of cells' membrane integrity, whereas released ions may bind to the negatively charged biomolecules and interfere the cell metabolism [16–18]. Despite the benefits, modification with TiO<sub>2</sub> NPs in membrane matrix is burdened with the possible pore blocking and losses in the filtration efficiency [17,18].

Modifications to create stable bonds of biocidal agents with the polymer membrane, as well as to give the same antibacterial properties still remain a challenge of the membrane technology. In many cases, the most effective method of membranes modification using nanostructures of metals and their oxides is the dispersion in the mass of the polymer, but their presence in the deeper structures of the membrane causes a slight antibacterial property. That is why the manufacture of polymer composite membranes modified with hybrid materials based on GO with the addition of silver NPs (Ag) has become more and more popular [19,20]. However, there are still a few reports on the combination of a plasma treatment for the activation of functional groups of the membrane surface, with chemical methods of the surface modification of polymer membranes to impart the antibiofouling properties. The modifications of the membrane surface are considered more promising than those made in the membrane matrix, since they are more cost effective due to the reduced modifier amount.

The aim of this work was to develop a method of a surface modification of polymeric membranes based on the low-temperature gas plasma of argon (Ar) and argon-oxygen (Ar-O<sub>2</sub>). This could allow for the stable fixation of nanostructures of TiO<sub>2</sub> and ZnO on the surface. Such modified membranes were tested in terms of the structure of the deposited nanolayers, filtration performance, and antibiofouling properties toward two representative bacterial groups, Gram-positive (*Bacillus subtilis*), and Gram-negative (*Escherichia coli*).

## 2. Experimental

### 2.1. The activation and modification techniques

A low-temperature plasma obtained by the low-pressure glow discharge technique, was used to activate the polymeric membranes. The activation processes were carried out in the WU-2M plasma reactor produced by the Institute for Sustainable Technologies – National Research Institute in Radom [21]. The activation processes of the membrane surface were carried out using two working atmospheres: Ar (100%) and a mixture of both Ar (90%) and O<sub>2</sub> (10%). The time and the pressure of the plasma activation were 2.0 min and 1 mbar, respectively. The process conditions used to activate the polyamide (PA) membrane surface were presented in the work [22]. The membranes activated with gas plasma were coated with nanostructures of metal oxides suspended in aqueous solutions. The concentration of the metal oxides suspension was 0.1%. Then, the membranes covered with nanolayers were rinsed several times with deionized water, centrifuged, and dried. The membranes used in the study

were the MAGNA membrane filters made of PA characterized by a 0.22  $\mu\text{m}$  pore size. NPs which were used for the experiments were titanium (IV) oxide –  $\text{TiO}_2$  from Alfa Aesar (anatase, 32 nm) and nanotubes (NTs) of zinc (II) oxide – ZnO (100 nm) generated by the hydrothermal method at the Institute for Sustainable Technologies – National Research Institute in Radom. In the further experimental steps, the microstructure and the chemical composition as well as the permeate flux and antibacterial properties of membranes modified with  $\text{TiO}_2$  NPs and ZnO NTs were examined.

## 2.2. Membrane surface characterization

The microstructure of the membranes surface was characterized via images recorded with two scanning electron microscopes: Hitachi TM 3000 TM table-top series equipped with BSE and Hitachi electron back-scatter detector with field emission with SU-70 Schottky. The analysis was carried out in vacuum conditions ( $1 \cdot 10^{-8}$  Pa) at an accelerating voltage of 15 kV and a secondary electron (SE) reception angle of  $30.4^\circ$ , using the SE detector.

The chemical composition of the tested membranes and the chemical environment of identified elements were analyzed by X-ray photoelectron spectrometer for chemical analysis (XPS/ESCA) spectrometer from PREVAC equipped with hemispherical energy analyzer VG Scienta R3000. Data acquisition was performed in SWEPT mode, at the pass energy of 200 eV and step size of 200 and 50 meV for survey scans and detailed spectra, respectively. XPS spectra demonstrated the number of counts (counts per second) of photoelectrons with a specific binding energy (BE), which were ejected from the surface and measured by the analyzer. The analyzes were performed with an achromatic soft X-ray source of aluminum (Al) anode and in ultra-high vacuum ( $3 \cdot 10^{-12}$  bar). The relative composition of each element was determined according to the intensities of their main characteristic peaks. After recording the survey spectra of the photoelectrons, detailed spectra were recorded for elements identified in the survey scans. The BE calibration was performed with the C 1s line (284.8 eV) from the adventitious carbon layer. In order to identify chemical composition of detected elements, the detailed spectra were deconvoluted with CasaXPS (Gaussian–Lorentzian shape line, Shirley background) [23].

## 2.3. Filtration performance

The permeate flux was determined by measuring the time required to filter deionized water ( $100 \text{ cm}^3$ ) through the membrane ( $8 \text{ cm}^2$ ) under defined transmembrane pressure (500 mbar). The deionized water characterized with the conductivity and pH of  $5.3 \mu\text{S}/\text{cm}$  and 6.5, respectively. For this purpose, the laboratory “dead end” filtration set-up was used.

## 2.4. Microbiological experiments

Model microorganisms of Gram-positive *B. subtilis* (ATCC 6633) and Gram-negative *E. coli* (ATCC 25922) bacteria were first cultured in a flask containing 20 mL of Luria Bretani (LB) broth at  $37^\circ\text{C}$  in shaking incubator (Innova) for

24 h. The following day, the suspensions of bacteria were diluted with PBS to reach the concentration of approximately  $100 \text{ CFU}/\text{cm}^3$ . Before testing the antibacterial properties, the membranes were sterilized for 30 min with UV-C lamp in a laminar cabinet. Using a vacuum filtration kit at 500 mbar, the volume of  $10 \text{ cm}^3$  of a bacterial suspension in PBS was filtered through the membranes. Then, the membranes were placed on LB agar plates and left in the incubator overnight at  $37^\circ\text{C}$ . The number of viable bacteria on a membrane was evaluated by colony counts and expressed as  $\log(\text{CFU}/\text{cm}^3)$ .

## 3. Results and discussion

### 3.1. Structure of membranes

Prior to nanostructures embedding, the surface of PA membranes was activated in the inert gases such as argon (Ar) and both argon and oxygen ( $\text{Ar-O}_2$ ). The aim of the gas plasma treatment was to clean and activate the functional groups on the surface of the polymer membranes, mainly due to the oxidation. An appropriate selection of gases and process parameters allows to impart new structural and functional properties of polymer materials [22]. The plasma conditions applied in this work resulted in small changes in the structure of the tested membranes (Fig. 1). Similar results were obtained in another work [24].

Both, native and plasma treated membranes were modified with  $\text{TiO}_2$  NPs and ZnO NTs. These additives were implemented from an aqueous solution. It was found that the native membrane was covered with some  $\text{TiO}_2$  NPs agglomerates (Fig. 2(a)). Plasma treatment of the membrane increased the reactivity of the PA, and thus much more agglomerates of  $\text{TiO}_2$  NPs were observed in the membrane structure (Fig. 2(b)) than in the native membrane (Fig. 2(a)). The deposited layer of  $\text{TiO}_2$  NPs was denser on the membrane treated with  $\text{Ar-O}_2$  (Fig. 2(c)) than on the one treated with Ar (Fig. 2(b)). This was probably the result of a greater chemical reactivity of the PA due to the activation with the  $\text{Ar-O}_2$  plasma. Similar results were obtained for the membranes modified with ZnO NTs (Fig. 3).

The scanning electron microscopy (SEM) results of the microstructure of  $\text{TiO}_2$ -modified membranes showed that this compound was deposited densely and evenly on the membranes after plasma treatment with the  $\text{Ar-O}_2$  mixture (Fig. 4).

The SEM images of ZnO-modified membranes depicted that this compound was deposited on the membranes treated with  $\text{Ar-O}_2$ , both in the form of individual nanostructures and their agglomerates, predominantly in the form of nano-flowers (Fig. 5).

### 3.2. Chemical composition of membranes

The chemical composition of the membrane surface modified with  $\text{TiO}_2$  NPs and ZnO NTs was examined by XPS, which enabled elementary qualitative and quantitative analysis of the most outer layer of materials (1–10 nm depth). XPS spectra of modified membranes are shown in Figs. 6 and 7. The analysis of the spectra shows that the surface of tested membranes consisted of carbon (C 1s), oxygen (O 1s), nitrogen (N 1s), and titanium (Ti 2p) or zinc (Zn 2p), depending on the modification.

The quantitative analysis showed that the atomic concentrations of titanium (Table 1) and zinc (Table 2) were much

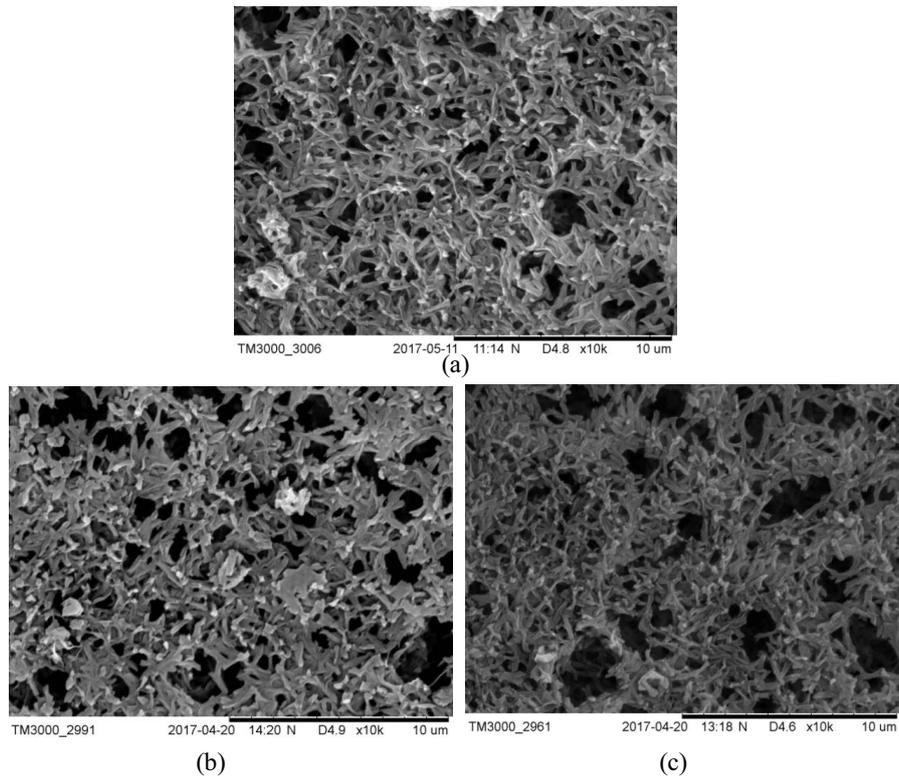


Fig. 1. The surface of membranes: native (a) and treated with Ar (b), and Ar-O<sub>2</sub> (c).

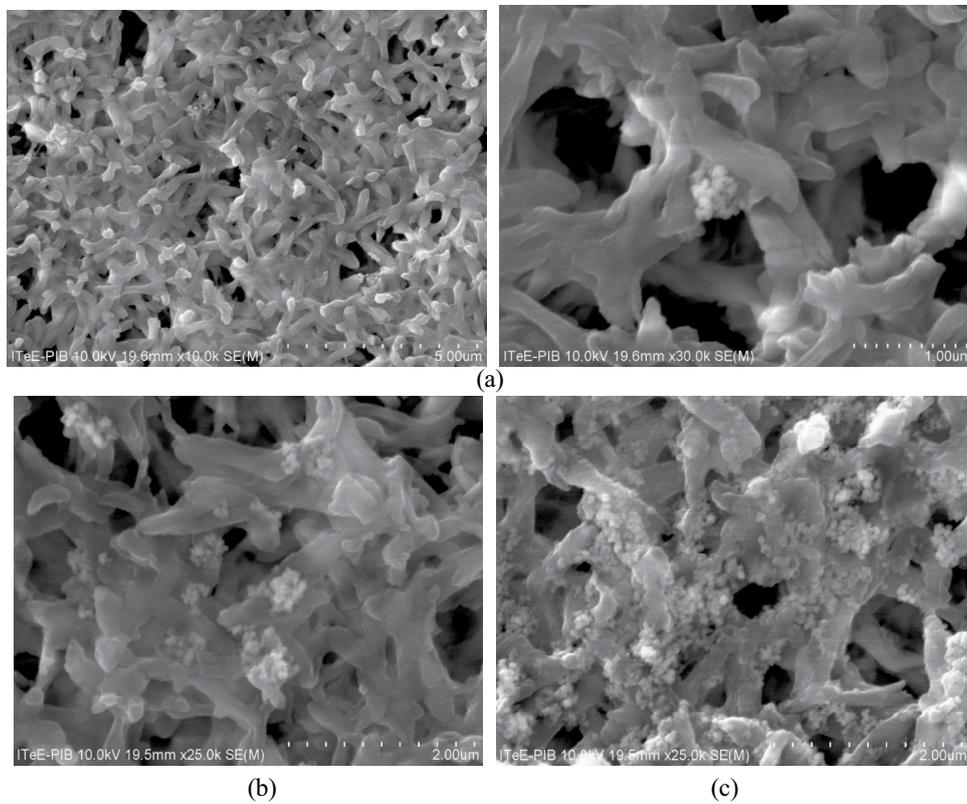


Fig. 2. The structure of the membranes modified with TiO<sub>2</sub> NPs: native membrane (a), membrane treated with Ar (b), and membrane treated with Ar-O<sub>2</sub> (c).

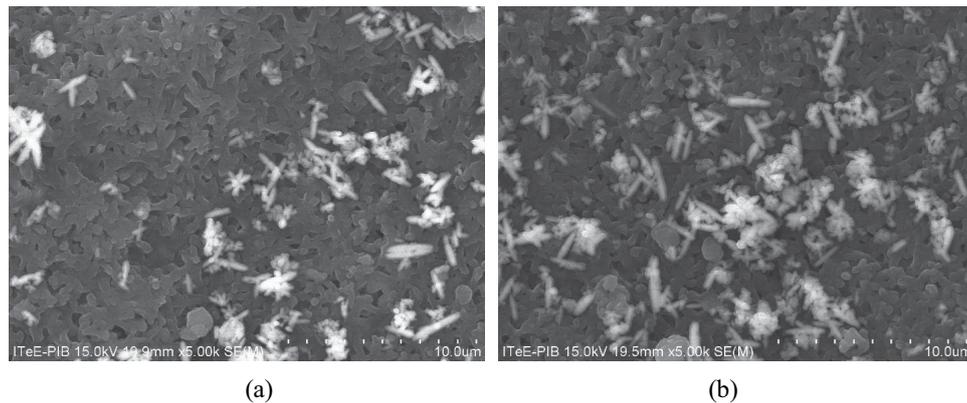


Fig. 3. The structure of the membranes modified with ZnO NTs: membrane treated with Ar (a) and membrane treated with Ar-O<sub>2</sub> (b).

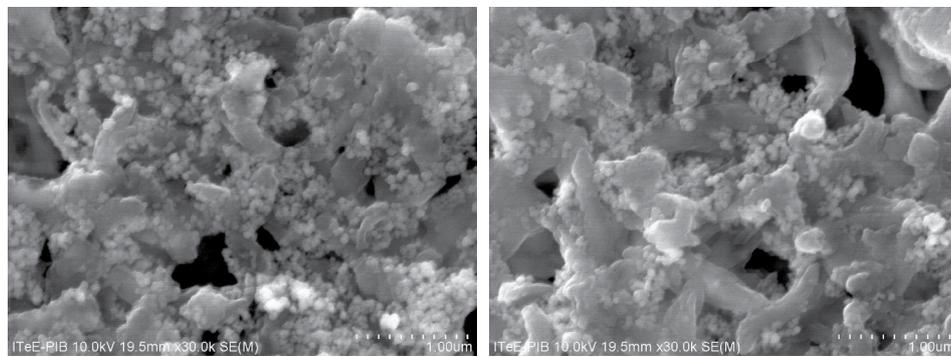


Fig. 4. The structure of the membrane modified with TiO<sub>2</sub> NPs after plasma treatment with Ar-O<sub>2</sub>.

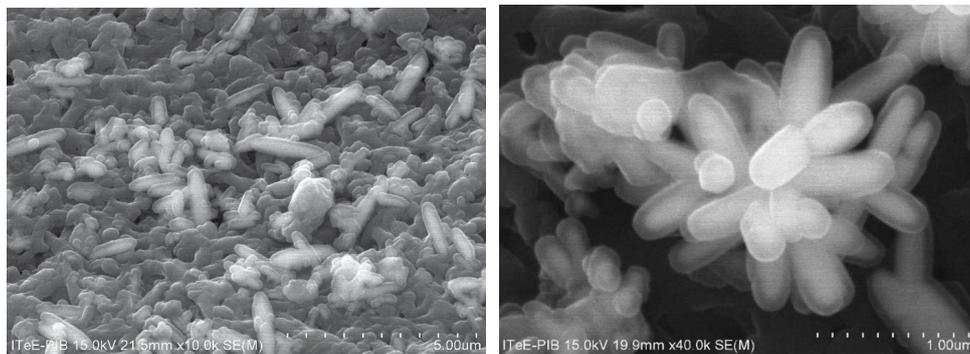


Fig. 5. The structure of membrane modified by ZnO NTs after plasma treatment with Ar-O<sub>2</sub>.

higher on the surface of the membrane treated with Ar-O<sub>2</sub> than with Ar only. However, the differences in the content of zinc were not as significant as for titanium for both Ar and Ar-O<sub>2</sub> treated membranes. The deposition of the nanostructures on the polymer surface was probably affected by the size of the nanostructures used for the modification. The activation of the membrane surface with both Ar and Ar-O<sub>2</sub> resulted in the higher content of the oxygen compared to the native membrane and a slight increase in the content of nitrogen (Table 1). The plasma treatment in Ar-O<sub>2</sub> and the implementation of TiO<sub>2</sub> led to the higher atomic concentration of both oxygen and titanium compared with Ar only treated membrane,

which was not observed for the membrane modified with ZnO. Plasma treatment in Ar-O<sub>2</sub> resulted in a small increase in Zn content compared to the activation with Ar only (Table 2).

The chemical bondings of the elements were determined based on the analysis of detailed XPS spectra of specific elements recorded in high resolution. XPS detailed spectra of titanium, oxygen, carbon, and nitrogen present on PA membranes: modified with TiO<sub>2</sub> NPs after plasma treatment with Ar and Ar-O<sub>2</sub> are shown in Fig. 8. The titanium peak (Ti 2p) after TiO<sub>2</sub> NPs modifications consisted of two peaks due to its doublet nature (Fig. 8). The doublet with Ti 2p<sub>3/2</sub> peak at 458.36 eV corresponded to Ti<sup>4+</sup> in TiO<sub>2</sub>, but only for

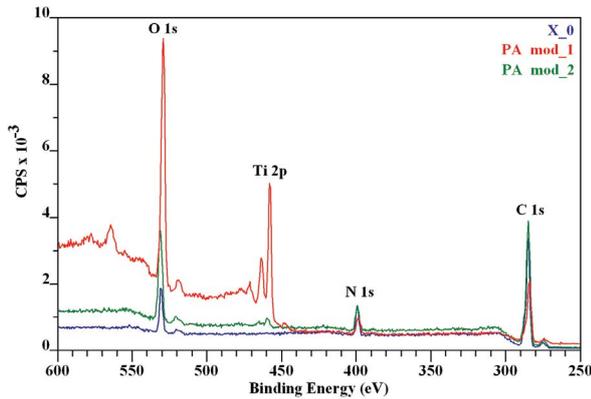


Fig. 6. XPS survey spectrum of membranes: native (X<sub>0</sub>), modified with TiO<sub>2</sub> NPs after Ar plasma (PA mod<sub>2</sub>), and modified with TiO<sub>2</sub> NPs after Ar-O<sub>2</sub> plasma mixture (PA mod<sub>1</sub>).

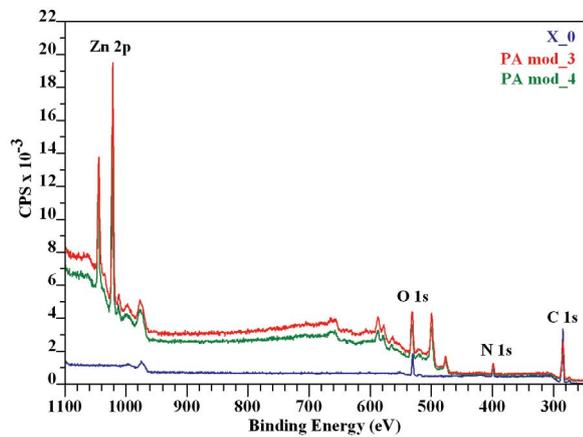


Fig. 7. XPS survey spectrum of membranes: native (X<sub>0</sub>), modified with ZnO NTs after Ar plasma (PA mod<sub>4</sub>), and modified with ZnO NTs after Ar-O<sub>2</sub> plasma mixture (PA mod<sub>3</sub>).

Table 1

The composition (relative atomic concentration of elements) of the surface of native membrane and treated with Ar and Ar-O<sub>2</sub>

Characteristic peak	Native membrane	Membrane treated with Ar	Membrane treated with Ar-O <sub>2</sub>
C 1s	79.66	71.51	67.30
O 1s	9.61	15.69	21.49
N 1s	10.73	12.80	11.21

Table 2

The composition (relative atomic concentration of elements) of the membrane surface modified with TiO<sub>2</sub> NPs and ZnO NTs

Characteristic peak	Membrane treated with Ar and TiO <sub>2</sub>	Membrane treated with Ar-O <sub>2</sub> and TiO <sub>2</sub>	Membrane treated with Ar and ZnO	Membrane treated with Ar-O <sub>2</sub> and ZnO
C 1s	73.37	37.81	54.90	55.40
O 1s	18.93	45.69	24.20	23.80
N 1s	7.32	5.26	7.90	6.80
Ti 2p	0.97	11.23	–	–
Zn 2p	–	–	13.00	14.00

the membrane modified with TiO<sub>2</sub> NPs after Ar-O<sub>2</sub> plasma treatment. The O 1s spectrum of the same sample showed two deconvoluted peaks at 529.44 and 530.85 eV. The two peaks could correspond to TiO<sub>2</sub> and C=O, respectively. The deconvolution of C 1s spectra for both samples indicated on the presence of the adventitious carbon and C–C/C–H bondings at 284.74 eV (PA mod<sub>1</sub>) and 284.72 eV (PA mod<sub>2</sub>), and 287.63 eV (PA mod<sub>1</sub>) and 287.24 eV (PA mod<sub>2</sub>), which could be attributed to C=O. The binding energy (BE) of N 1s peak (399.26 eV) from both tested membranes corresponded to the presence of the amide bonding, characteristic to the basic material of the samples, that is, PA.

XPS detailed spectra of zinc, oxygen, carbon, and nitrogen detected on PA membranes modified with ZnO NTs after plasma treatment with Ar and a mixture of Ar and O<sub>2</sub> are presented in Fig. 9.

The Zn 2p<sub>3/2-1/2</sub> XPS data was fitted into doublets that corresponded to different components. The BE of 1,022.05–1,044.89 eV for PA membrane modified with ZnO NTs after Ar plasma treatment, and the BE of 1,021.67–1,044.61 eV for PA membrane modified with ZnO NTs after Ar-O<sub>2</sub> plasma treatment could both be attributed to ZnO, but also to Zn and Zn(OH)<sub>2</sub>.

The deconvolution of O 1s XPS data for both samples supported the conclusion from previous results. The oxygen peaks of PA membrane modified with ZnO NTs after Ar plasma treatment were identified at BE of 530.34 and 532.21 eV, which could be attributed to Zn–O–Zn and Zn–O–H, respectively. However, the oxygen peaks of PA membrane modified with ZnO NTs after plasma treatment with a mixture of Ar and O<sub>2</sub> were identified at BE of 531.23 and 533.16 eV, which could be attributed to Zn–O–Zn and H–O–H, respectively.

The deconvolution of C 1s and N 1s peaks resulted in similar results as for membranes modified with TiO<sub>2</sub> NPs, which are C–C/C–H, C=O, and –NH.

### 3.3. Membranes filtration properties

It was found that the implementation of TiO<sub>2</sub> NPs or ZnO NTs from the aqueous solution onto the surface structure of the PA membrane increased the permeate flux determined during the filtration of deionized water compared with the native membrane (Fig. 10).

In the case of membranes modified with TiO<sub>2</sub> NPs, an increase in the permeate flux of 8% and 14% was observed for Ar and Ar-O<sub>2</sub> plasma-activated membranes (Fig. 10), respectively. The permeate flux for the membranes modified with ZnO NT of both treated with Ar and Ar-O<sub>2</sub> increased by

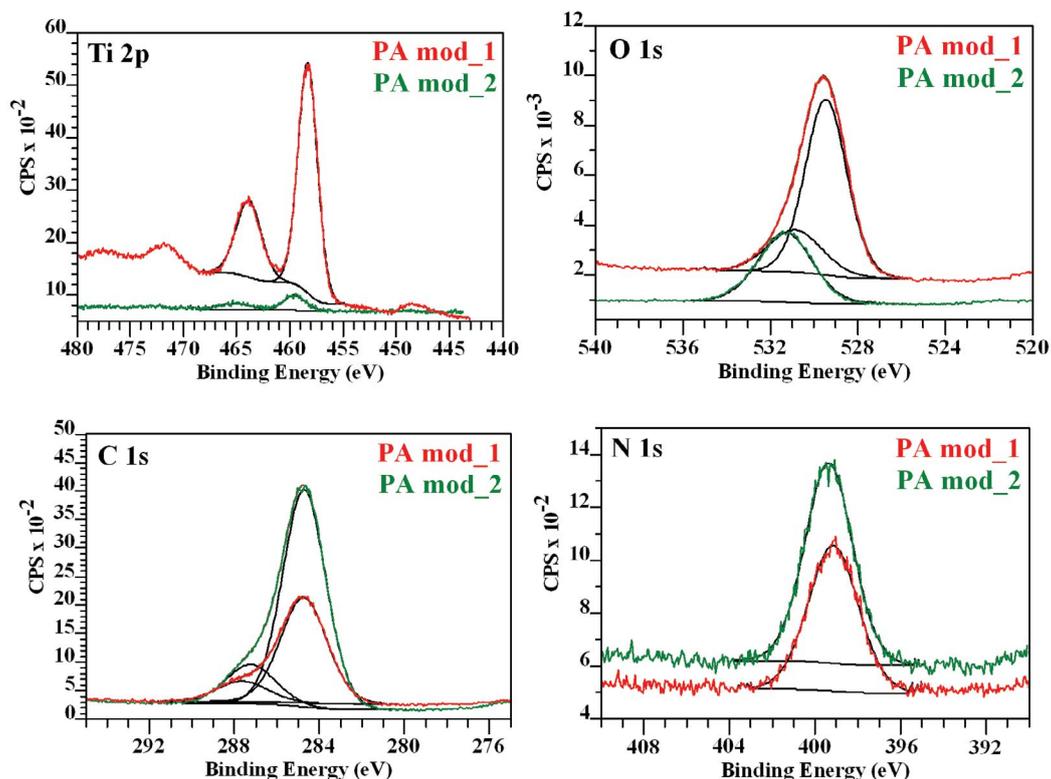


Fig. 8. XPS detailed spectra of membranes: modified with  $\text{TiO}_2$  NPs after plasma treatment with Ar (PA mod\_2) and modified with  $\text{TiO}_2$  NPs after plasma treatment with a mixture of Ar and  $\text{O}_2$  (PA mod\_1).

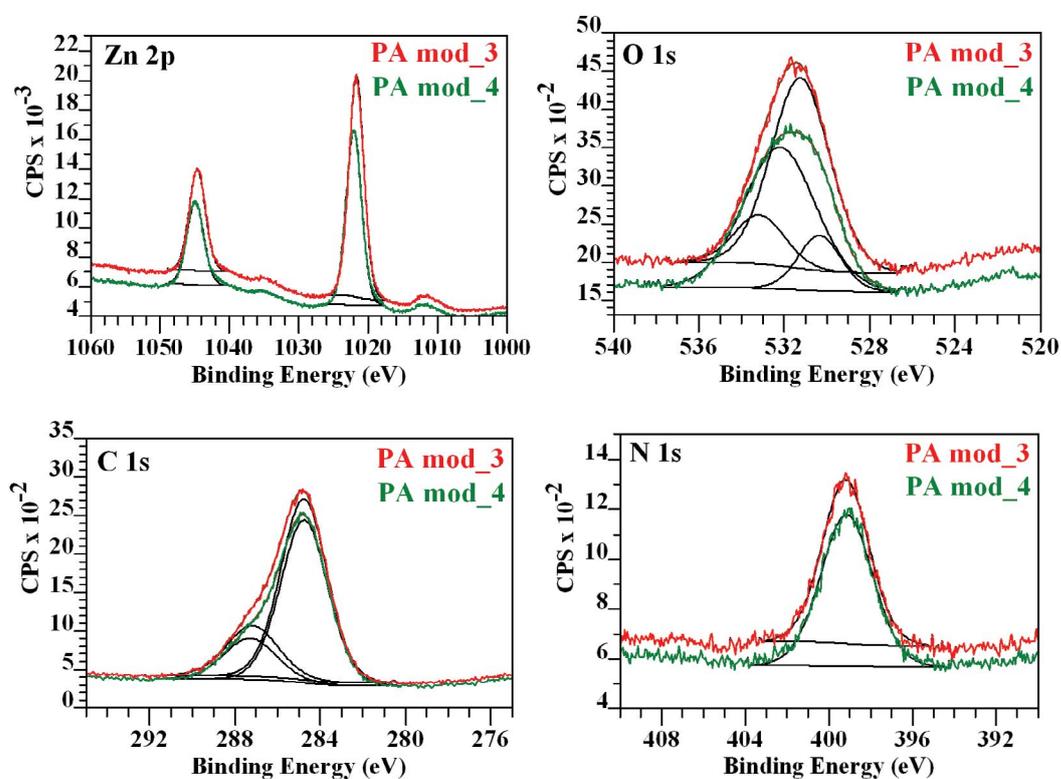


Fig. 9. XPS detailed spectra of membranes: modified with ZnO NTs after plasma treatment with Ar (PA mod\_4) and modified with ZnO NTs after plasma treatment with a mixture of Ar and  $\text{O}_2$  (PA mod\_3).

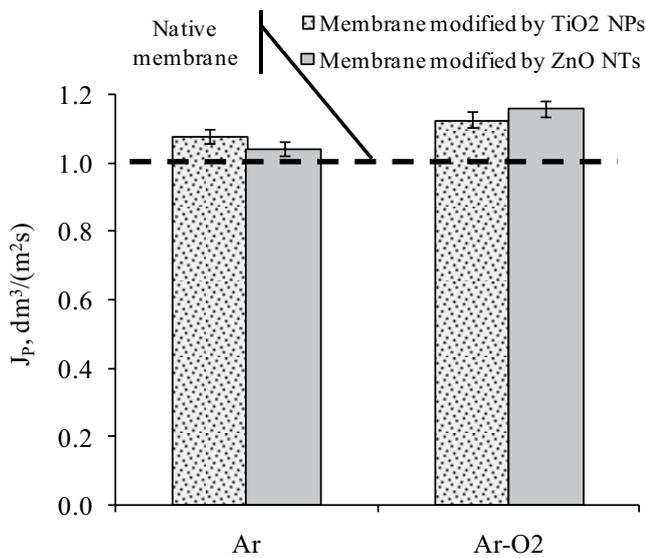


Fig. 10. The effect of the membrane modification with TiO<sub>2</sub> NPs and ZnO NTs on the permeate flux ( $J_p$ ) obtained during microfiltration of deionized water.

4% and 16%, respectively (Fig. 10). This was due to the fact, that the plasma treatment either with Ar or Ar-O<sub>2</sub> caused the PA structure to relax (Fig. 1), and consequently contributed to the increase in the permeate flux, which was determined during the filtration of deionized water compared with the results for the native membrane (Fig. 11).

### 3.4. Membranes antibacterial properties

The antimicrobial activity of the developed filtration materials was tested against two groups of representative

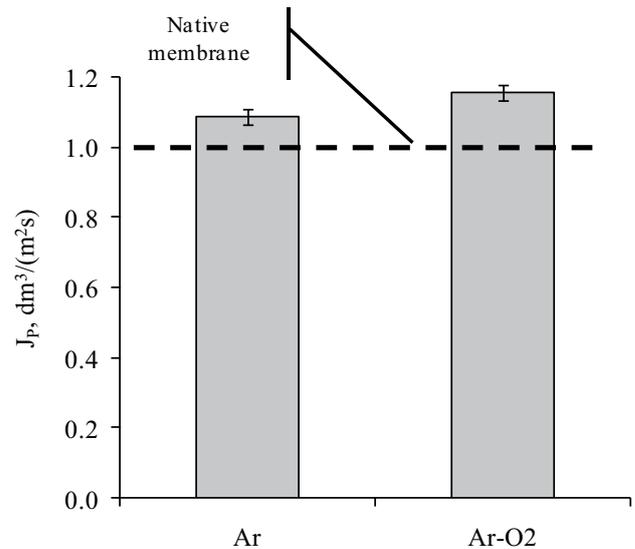


Fig. 11. The effect of plasma treatment of membranes with Ar and Ar-O<sub>2</sub> on permeate flux ( $J_p$ ) obtained during microfiltration of deionized water.

microorganisms such as Gram-positive (*B. subtilis*) and Gram-negative bacteria (*E. coli*). The results of the vacuum filtration of bacterial suspension (Fig. 12) showed that ZnO NTs modified membranes revealed stronger bactericidal effects against both *B. subtilis* and *E. coli* than the membranes modified with TiO<sub>2</sub> NPs. ZnO NTs embedded on the membranes resulted in 100% reduction of the CFU of both groups of microorganisms *B. subtilis* and *E. coli*. The number of viable bacterial colonies decreased by 84% and 17% for Gram-positive and -negative bacteria, respectively, for the membranes treated with TiO<sub>2</sub> NPs. Thus, the identified antibacterial effects allowed to assume that ZnO NTs deposited

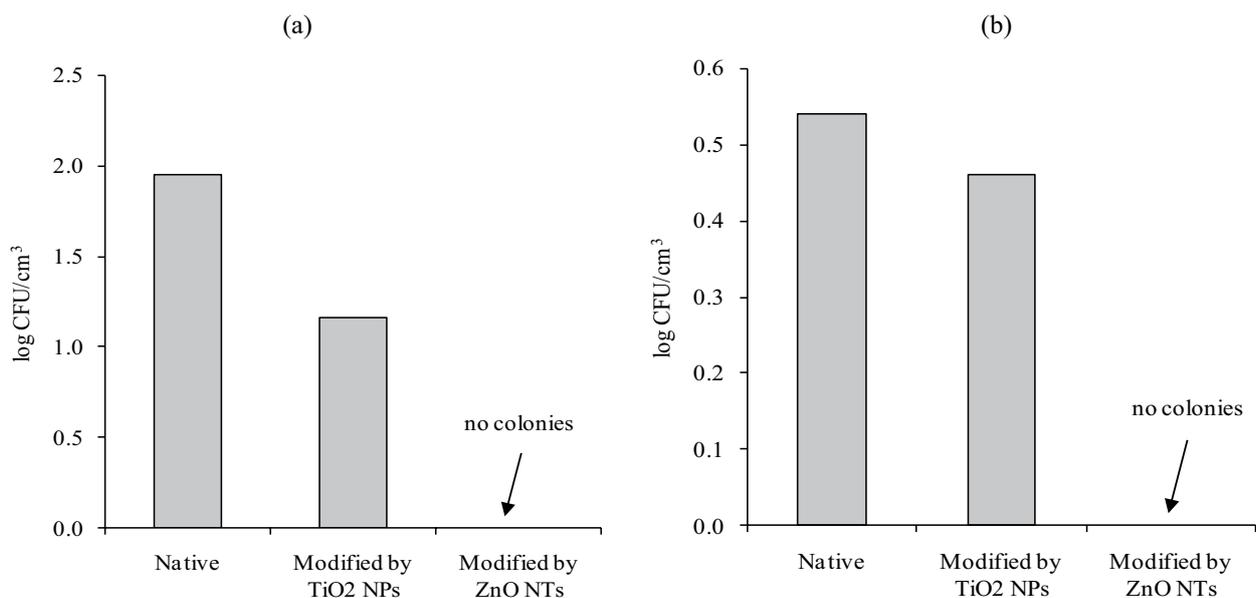


Fig. 12. Antibacterial effects of TiO<sub>2</sub> NPs and ZnO NTs modified membranes after prior plasma treatment with Ar-O<sub>2</sub> against *Bacillus subtilis* (a) and *Escherichia coli* (b).

on the surface of membrane were strongly attached due to prior plasma activation and prevented the biofilm development and the biofouling formation. Biofilm growth starts with bacterial cells adhesion to a membrane surface. Then, the cells divide and accumulate along with thick layers of the secreted EPS, which makes bacterial community resistant to unfavorable ambient conditions.

The efficiency of bacterial reduction by ZnO NTs coated membrane is very promising and have a great potential for the industrial application. Antimicrobial effects of the TiO<sub>2</sub> NPs modified membranes might be increased using UV radiation with a wavelength corresponding to the band gap energy of this compound. Several modes of actions of TiO<sub>2</sub> NPs have been proposed in regard to the toxicity to bacteria. Primarily, TiO<sub>2</sub> NPs cause oxidative stress to the bacterial cells due to the reactive oxygen species generated in photocatalysis and the disintegration of a cell membrane. The released ions from the cell combine with negatively charged biomolecules (including proteins, DNA, and RNA) interfering with the vital processes of microorganisms. However, it is essential to construct a suitable membrane module that allows for the uniform UV radiation to the membrane surface coated with photocatalytic nanostructures. This enables to examine the stability of the developed materials in the real-like conditions, including processing parameters (pressure, flow, temperature, and electromagnetic radiation), the composition of the feed and the chemical cleaning streams. Primarily, the most important issue is to examine appropriate conditions for surface-modified membranes before they are allowed to be implemented. The conditions to be evaluated involve: the stability of the modifying layer, the release of the modifying agent to the filtered liquid (*leaching*), and the impact of the modifying layer on the physicochemical parameters of the membranes surface, their filtration and separation properties. Taking into account the large number of potential modifiers and the variety of alteration techniques (chemical, physical, or physicochemical modifications), the development of research standards is no less important than the modification technologies themselves.

Another crucial point is the use of membranes modified with photocatalytic nanostructures to neutralize unpleasant odors resulting from the presence of volatile organic acids in water and wastewater. Due to the low molecular weight, they are able to easily pass through the commercial filtration membranes. For instance, in order to recover the water from wastewater in food industry, it is necessary to eliminate both, odors and other organic and inorganic pollutants. So far, solutions currently available on the market involve separate techniques to reduce the pollutant loads. Hence, it is necessary to continue the research toward the development of a membrane module that provides uniform UV radiation supply to the treated membrane surface, which is cost-effective and less time-consuming.

#### 4. Conclusions

In the study, the plasma treatment of the surface of PA membranes with argon (Ar) and a mixture of argon and oxygen (Ar-O<sub>2</sub>) was used to prepare the membrane to attach the metal oxide nanostructures, such as titanium dioxide nanoparticles (TiO<sub>2</sub> NPs) and zinc oxide nanotubes

(ZnO NTs). For both treated membranes, the filtration flux of deionized water was higher compared with the native membrane. The proposed method of the surface treatment resulted in the deposition of the uniform nanostructure layer of metal oxides, which increased the resistance of modified membranes to microbial activity. Primarily, the promising results were obtained for the membrane modified with ZnO NTs, which led to 100% reduction of viability for both Gram-positive (*B. subtilis*) and Gram-negative (*E. coli*) bacteria. Since, the UV light causes the oxidative stress to bacterial cells and it might enhance the biocidal effects of the TiO<sub>2</sub> NPs, it is necessary to develop a membrane module that enables uniform UV radiation supply to the surface of a membrane modified with nanostructures of photocatalytic properties. Such a membrane module would allow to verify the stability of the developed materials in the real-like conditions in terms of process parameters, composition of the feed and the chemical cleaning streams. This could also enable to evaluate the possibility of reducing volatile organic acids content that is mainly the source of unpleasant odors in water and wastewaters, particularly in food industry.

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