COMPARISON OF THE CHARACTERISTICS OF MEMBRANES WITH AND WITHOUT EXTERNAL MODIFICATION WITH NANOPARTICLES OF SILVER

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Abstract

The aim of this study was to monitor antimicrobial abilities of filtration materials with and without the addition of silver. Microfiltering material SPURTEX with nanoparticles of silver, from SPUR a.s. Zlín was modified in Palacký University Olomouc - Regional Centre of Advanced Technologies and Materials. The modifications of membranes consisted of covalent bounding of Ag nanoparticles on the surface of the membrane through a polymeric linker. The advantages of this method are low service expenses and absence of potentially dangerous chemicals, which may be released into the water. Dimensions of membrane pores are ranged between 0,30 μm ± 0,12 μm, meaning that the selected membrane should be able to catch most of the microorganisms. Escherichia coli was selected for the simulation of microbiological contamination. This bacterium is an indicator of fecal contamination and its occurrence in water is very strictly monitored. The spreading of this bacterium in a human being is the cause of a range of digestive and urogynaecological diseases. 100 ml of contaminated water was filtrated at a pressure of 0,5 bar through a filtration device, which is made from anticorrosive steel and was sterilised before the experiment. For every sample, parameters of filtration were determined (filtration time, amount of bacteria before and after filtration, efficiency of filtration, etc.). In the samples, *Escherichia coli* on VRBL agar (Biokar Diagnostics, France) was determined using the plate cultivation method during 24 h at a temperature of 37 ˚C. The results of laboratory experiments shows materials with surface modification of Ag have a better microbiological characteristic. A more detailed description and results are in the experimental and methodological part of this submission.

Keywords: Nanomaterials, filtration, bacteria, silver

1. INTRODUCTION

Membrane technologies are often used for water treatment, because it is a very good process for removing particles, turbidity and microorganisms. However, natural organic substances cause reduction of the permeability of the membrane. Organic pollution is a serious problem for membrane processes and is usually caused by inactivity of pores or involvement of organic substances on the surface of the membrane [1].

The quality of the membrane is also lowered by biological contamination which involve microorganisms causing biofouling [2]. Biofouling can be defined as a closed matrix of bacterial populations bonding to each other and/or to the surface [3]. One of the possible variants of preventing biofouling can be the usage of nanotextiles. Nanotextiles are non-woven textiles formed by fibres with an average length of 50-300 nm. The size of pores ranges 0,30 μm ± 0,12 μm, which means the membrane should be able to capture all of the microorganisms[4].

Anorganic nanoparticles with their unique physical and chemical attributes represent an important material in the development of nanocomponents, which can be used in physical, technical, biomedical or chemical applications [5] [6]. Nowadays, great attention is given to the incorporation of silver (Ag) to membrane materials for its antimicrobial attributes, known since the Middle Ages [7]. These conclusions are confirmed by a lot of scientific papers [8] [9]. Iones of Ag (Ag^+) show bactericide effects on 12 bacterial species, including *E.coli* [10]. Mechanism of activity of Ag^+, is in inhibition of income and output of phosphates, mannitol, succinate and proline [11], more precisely, displacing native metal ions from bonding places in enzymes [12]. Other studies show the influence of Ag^+ on DNA replication or structural changes in the cell wall [13]. The disadvantage of materials with addition of this metal is the washing out of Ag from membrane and the reduction of antimicrobial abilities [14] [15].

This paper deals with the usage of nanofibrous structures modified with nanoparticles of Ag. The paper follows previous experiments with nanofibrous structures, designed for the filtration of water. With Ag modification we wish to increase the removal of microorganisms, like it was attempted by Decostere et al. (2009) [16], who was able to improve filtration by two orders.

2. MATERIALS AND METHODS

In the experiment, selected materials were used (see Table 1), which were drenched in distilled water before the experiment. For the simulation of microbial pollution, the bacterium *Escherichia coli* were selected. Distilled water with addition of *E. coli* was poured into a filtration device in the upper part of the apparatus. Pressure was applied through the filling valve and during the experiment was rectified by manometer. Filtration material was anchored to the filtration head. The sample of water was transported through the filter and after 100 ml of water was added, the filling valve closed. During the experiment, the time of flow of the filtrate was measured. In the sample, coliform bacteria were established by plate cultivation method on VRBL agar (Biokar Diagnostics, France) for 24 h at 37 ºC.

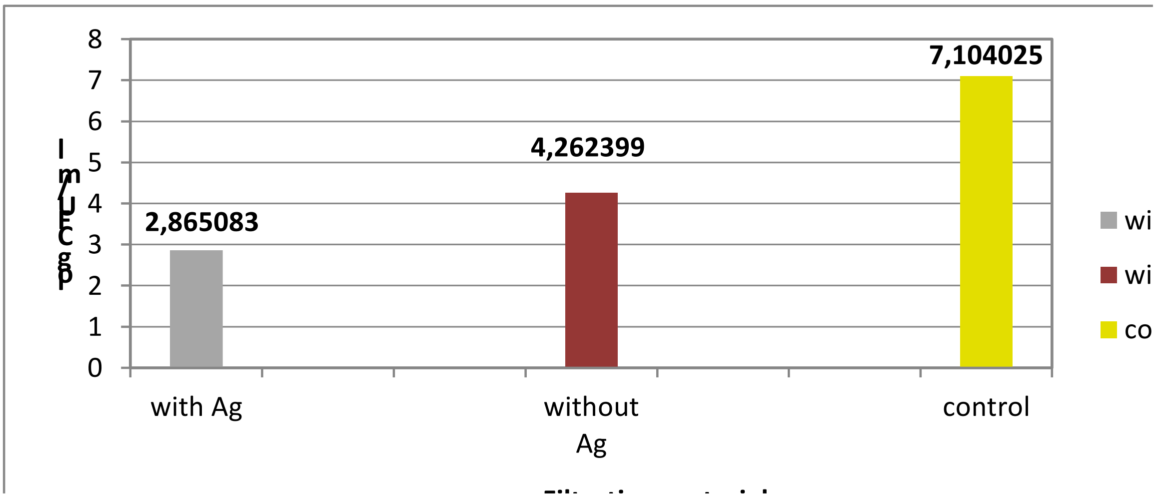
Table 1

membrane	material	middle size of pores [µm]	flow capacity after 1 h	pressure conditions [kPa]
with Ag	PU nNT 2g/m SPURTEX MF	0,3	150 $l/m.h^{-1}$	7,5
without Ag	PVDF	0,5	250 $l/m.h^{-1}$	7,5

3. RESULTS

In chart 1 is the comparison of selected membranes and their antimicrobial abilities.

Chart 1 Selected membranes and their antimicrobial abilities



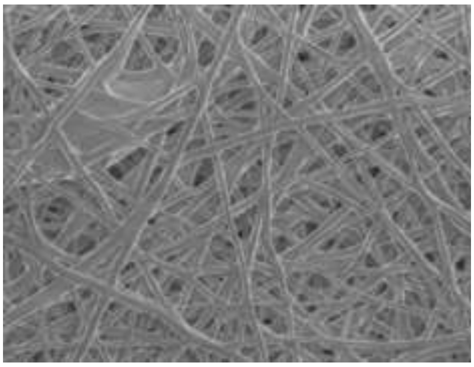


Fig.1

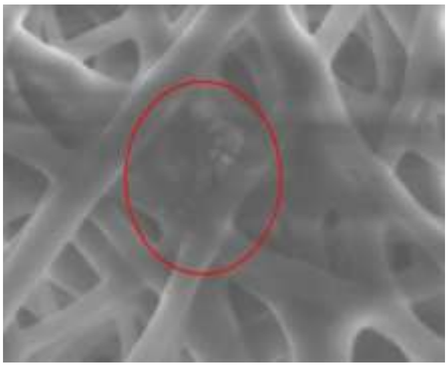


Fig.2

In Figs. 1 and 2 are SEM images of the modified membrane.

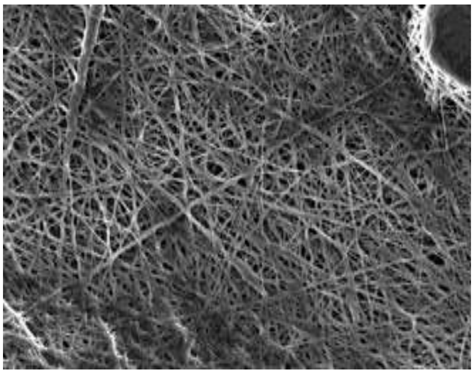


Fig.3

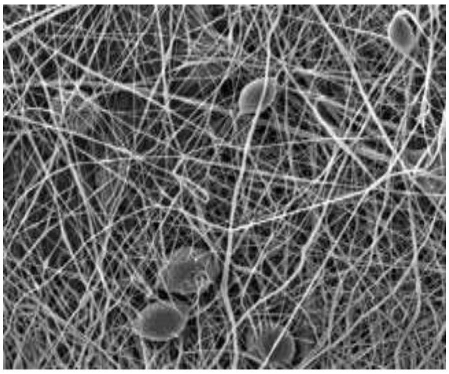


Fig.4

In Figs. 3 (without Ag) and 4 (with Ag) membranes under electron microscope are shown.

4. DISCUSSION

The results of our experiment did not confirm that the application of Ag to nanotextiles will increase antimicrobial efficiency. Pre-filtred water with addition of *E.coli,* contained this bacteria even after the microbiological analysis, because with microfiltration it is not possible to capture all the microorganisms [17]. The causes of unsatisfactory results can be the following: damage of filtration materials (in production, in transport, in manipulation, etc.), insufficient contact time of causes Ag, and inappropriate size of pores.

Study of Gómez et al. (2006) [18] suggests that microorganisms are deformable by mechanic strain, which leads to the reduction of their mass. We can assume that a similar mechanism worked on microorganisms during the filtration as well. The inhibition ability of Ag^+ depends on the size of particles, whereby particles are smaller with larger area, they have better antimicrobial effects [19]. According to Zodrov et al. (2009) [20] Ag^+ reacts better with gram-negative bacteria (thus *E.coli* also), because of negative charge of peptidoglycane in the cell wall. This conclusion is confirmed with Feng´s et al. (2000) study [21]. Not even a membrane made from polyethersulfone with addition of $AgNO_3$, which was sterilized before experiment, do not confirm a 100 % effectivity against *E.coli* [21]. Cao et al. (2010) [22] states, that the release of Ag^+ has a significantly better effect with NaCl than with deionized water. They justify this with the interaction of Ag^+ and Na^+ and Cl^- from the solution.

CONCLUSION

In this paper filtration materials with and without addition of silver were compared. We analysed their ability to capture, or more precisely, to leak *E.coli*, which is an indicator of faecal contamination in water. The results of microbial analysis show high filtration efficiency of selected materials. The next objectives of our papers will be to find an appropriate way of anchoring Ag particles and testing their durability and resistance to washout, the development and testing of membranes with functionalized surfaces and nanobiocides that could be a more effective alternative for cleaning and water treatment.

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