POLITECNICO DI TORINO

College of Chemical and Materials Engineering
Master's Degree Course in Materials Engineering

Summary of the Master's Thesis (October 2022 Session)

"Nanostructured coatings to impart antibacterial properties to membranes for water filtration "

Candidate: Michela Toppan s277758

University speaker: Cristina Balagna
Company speaker: Alessandro Calogero (CRAB Medicina Ambiente)

SUMMARY
Potability and water purification, also in industrial processes, are fundamental treatments for purifying water and satisfying specific limits of the concentration of contaminants, such as heavy metal ions, dyes, pharmaceutical waste, bacteria, etc.
The removal of these pollutants is critical in wastewater treatment because they can contaminate the entire water supply chain. For this purpose, to obtain high quality water, polymeric-based microfiltration filters or membranes can be used, which remove microorganisms including bacteria.

The activity of this thesis involved the development of a nanostructured coating with antibacterial effect, deposited via co-sputtering on polymeric membranes for microfiltration.
The aim was to evaluate the effect of the coating on the microfiltration capacity of the membranes, both in terms of duration, filtration and bacterial contamination.
The activity was carried out thanks to a collaboration between the Glance - DISAT Group of the Politecnico di Torino and the company CRAB Medicina Ambiente (Biella). The coating is a thin composite layer composed of a zirconia matrix with embedded Ag nanoclusters. The membranes, used as substrate, are polymeric membranes of PCL and PAN/PCL, obtained through the electrospinning technique and kindly provided for study by the Nanofaber company (Rome). Since the substrates are thermal-sensitive, the parameters of the sputtering process have been optimized. In particular, the depositions were performed for short times of 10 and 20 min. The so-obtained samples were characterized by means of the morphological observation at the field emission scanning electron microscope (FE-SEM) and compositional analysis through energy dispersion spectroscopy (EDS).

The antibacterial effect of the coating was tested by means of qualitative inhibition halo tests towards two bacterial strains, *S. Epidermidis* and *E. Coli*.

Subsequently, an experimental set-up was developed (Figure 1) consisting of a filtration funnel, an underlying collection container with a sterile Pyrex bottle inside, a clamp to close and fix the filter between the collection container and the filtration funnel and a vacuum pump. This experimental set up, assembled at the chemical and microbiological laboratory of CRAB Medicina Ambiente, was used for evaluating the effect of the coating on membrane filtration in terms of bacterial proliferation on the membrane surface and the presence of bacteria in the filtered solution. In this case, the used bacteria were *Bacillus Subtilis Subsp. Spizizenii* (Gram positive), *Listeria Monocytogenes* (Gram positive), *E. Coli* (Gram negative).

Figure 1 - Experimental set up

The potential bacterial proliferation on the filter surface was control placing the filter placed on an agar after the filtration test. After 24 h incubation at 37 ° C, bacterial growth on the membrane was evaluated. The filtered solution was analysed by inductively coupled plasma mass spectrometry (ICP-MS) to evaluate the possible release of silver ions from the coated membrane.
To test the hydrophilic / hydrophobic nature of the sample and the coating on the substrate, an analysis of the calculation of the contact angle was carried out.

RESULTS

The polymeric membranes composed of PAN and PAN/PCL were coated with a composite nanostructured coating of zirconia matrix with silver nanoclusters embedded inside. The co-sputtering technique allows the deposition of coatings even on heat-sensitive materials such as polymeric membranes, optimizing the process parameters.
The depositions were carried out for short times (10 and 20 min) in order to avoid deterioration of the substrate due to the vacuum in the chamber and the overheating of the substrate itself during the process. The membrane of PAN/PCL appears to be more resistant to the deposition process than the other.

The membranes are realized by fibers with diameters of the order of few µm (Figure 2) with an interconnected porosity. PAN/PCL membranes are characterized by open pores greater than the size of the bacteria present in solution. The coating is uniformly distributed on the fibers of the membranes. The porosity of the PAN/PCL substrate does not change after the coating deposition process. On the other hand, the crystallinity of the polymer for the PCL membranes seemed to be altered due to the cooling of the substrate. In fact, only these samples changed colour also on the uncoated side.
Through the EDS analysis, the peaks of Ag and Zr post deposition are detected (the uncoated samples contained only carbon and oxygen).

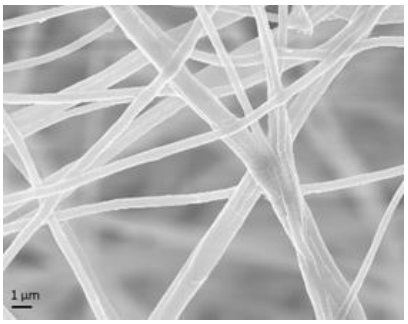

Figure 2 - PCL sample seen at FE-SEM

The membranes deposited at longer times (20 min) demonstrated a better antibacterial effect both towards *S. Epidermidis* and *E. Coli* than the samples deposited with a 10-minute process.
Filtration tests of bacterial solutions showed different behaviour depending on the used substrate. In fact, it was not possible to filter the bacterial solution through the PCL membrane. Probably the variation in crystallinity of the membrane led to a variation of the surface hydrophilicity/hydrophobicity, property also evaluated with the contact angle test (Figure 3).


Figure 3 - Hydrophobicity on PCL

The PAN/PCL samples with 10- or 20-minute deposition were instead effective for the process, with any type of bacterium and tested solution, in fact a good bacterial reduction was obtained and a post-incubation bacterial colony-free filter (Figure 4, 5, 6).

By ICP-MS analysis, there was a slight release of silver ions from the coated PAN/PCL sample obtained in the process at 10 min, while Zr ions were not released and detected in solution.

The greatest percentage of bacterial reduction, comparing the solution before filtration and after filtration, occurred for the sample in PAN/PCL with deposition of 20 min, while the other samples tested underwent a more intense proliferation.

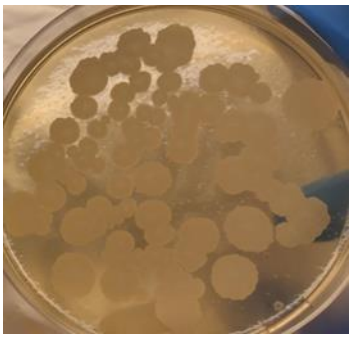

Figure 4 - Agar plate with contaminated solution on PAN/PCL with 20 min deposition

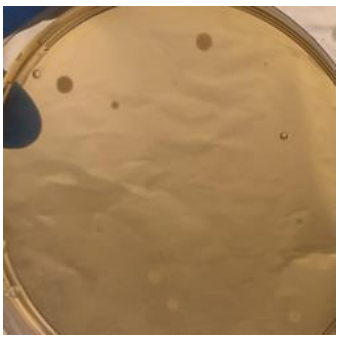

Figure 5 - Agar plate with decontaminated solution (post filtration) on PAN / PCL with 20 min deposition

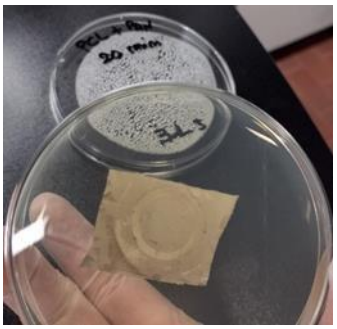

Figure 6 – Agar plate with PAN / PCL sample with 20 min deposition after 24h incubation