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## Antimicrobial foam-filter based on commercial support coated with polydopamine and silver nanoparticles for water treatment

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#### ABSTRACT

Fresh water is a critical resource on the planet and the treatment techniques employed worldwide are often insufficient at removing contaminants, leading to their release in the environment. This work displays the development of a foam-filter based on open-cell polyurethane foams coated with polydopamine and an antimicrobial metal for water treatment processes. A simple coating method is proposed and the resulting tool is characterized. Its antimicrobial activity is assessed on pure water-based cultures of Staphylococcus aureus, Escherichia coli, Legionella pneumophila and Candida albicans in optimal growth conditions. This study also investigates the stability and reusability of the foam-filter. The results show that silver grafting via this one-step original approach (namely OCPUF@PDA/Ag) exhibits a good antimicrobial activity on the selected microorganisms, with a complete microbicidal effect against C. albicans and E. coli after 3 h of contact time (5 and 6 Log decrease, respectively), and after 24 h of contact time for S. aureus. The foam-filter shows great stability and recyclability as it can be reused at least 4 times with the same overall activity, as well as significant antifouling properties. The mechanism of action was partially investigated and shows that reactive oxygen species are generated inside the bacterial cells after contact with the foam. This study gives a starting framework for the development of a bio-inspired polydopamine material with interesting physical, antifouling and antimicrobial properties applicable in water treatment processes.

#### 1. Introduction

The worldwide phenomenon of urbanization, characterized by a concentration of populations in the same areas (cities) and an increase of polluting activities, leads to rising levels of microbiological and chemical pollutants in water (Chaudhry and Malik, 2017; Some et al., 2021; Yuan et al., 2019; Bastaraud et al., 2020). Water quality is a major issue in both developing and developed countries,

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particularly with the occurrence of waterborne diseases outbreaks in drinking water (Hrudey et al., 2003). Waterborne diseases encompass a range of afflictions, including gastrointestinal diseases (diarrheas, cryptosporidiosis), respiratory infections (legionellosis), neurological infections (meningoencephalitis) and skin infections (Craun et al., 2010). On a larger scale, contaminated wastewater is released into the environment, leading to the deterioration of aquatic life and ecosystems, the contamination of soils and water sources, as well as providing a favorable environment for horizontal gene transfer, which leads to the appearance of multi-drug resistant microorganisms (Yadav and Rao, 2019; Mukherjee et al., 2021; Barancheshme and Munir, 2018). The emergence of such microorganisms, which remain unaffected by multiple antimicrobial compounds, is a major health concern as the treatment of these infections remains complex. *Escherichia coli (E. coli)* and *Staphylococcus aureus (S. aureus)* are two of the main pathogenic bacteria involved in deaths associated with drug resistance. The World Health Organization (WHO) even estimates that the number of deaths due to antibiotic resistance could reach 10 million by 2050 if no actions are taken, such as the development of new effective therapies (Tacconelli et al., 2017; Bonetta et al., 2016, 2022).

Studies have shown that conventional wastewater treatment plants (WWTP) often lack effectiveness in removing microbiological contamination from water, and could even be a source of proliferation and infection to nearby populations through the bioaerosolization of pathogens, such as fungi, viruses and bacteria, particularly *S. aureus* and *E. coli* (Vítězová et al., 2012; Kataki et al., 2022). According to the WHO, 2 billion people live in water-stressed regions, which is expected to increase drastically due to climate change. Moreover, fecal contamination has been detected in drinking water sources of 2 billion people and is estimated to cause 485, 000 diarrheal deaths each year (Drinking-water, 2022).

In this context, it is necessary to develop simple, efficient and eco-friendly processes in order to effectively reduce the risk of human and environmental contamination with pathogenic microorganisms from wastewater. Zero oxidation state metals (Ag, Au, Cu.) and metal-oxide nanoparticles (CuO, ZnO.) formulations have been used as sanitizers for centuries (Mittapally et al., 2018; Gharpure et al., 2020). Studies have shown that the antibacterial properties of free nanoparticles mainly come from two mechanisms: (i) the direct interaction between the active phase and the bacterium resulting in the disruption of the bacterial cell wall integrity, thereby causing its death (Yadav and Rao, 2019; Gharpure et al., 2020; Santo et al., 2012; Hong et al., 2012) and (ii), the release of metal ions (especially for silver or copper particles), initiating the generation of reactive oxygen species (ROS) that promptly inhibit cellular respiration, causing DNA degradation and ultimately causing the death of the bacterium (Gharpure et al., 2020; Santo et al., 2008; Warnes and Keevil, 2011). These particles are thus serious candidates to be used as water treatment agents. However, for future process designs, the direct use of free particles in water for treatment applications is not suited because of their negative environmental impact and uneasy step of separation from the treated water. Therefore, it is necessary to support these antibacterial agents on structured supports (e.g., filters) for future efficient and environmentally friendly designs of water remediation processes. Some studies have shown the grafting of silver-based active phases on various materials such as zeolites, carbon fibers or graphene oxides (Rivera-Garza et al., 2000; Park and Jang, 2003; De Faria et al., 2014), however such supports are not ideal for water treatment processes. Among potential supports, foam-filters or commercial open-cell polyurethane foams (OCPUFs) seem to be a much more suited approach for applications in water process. In fact, the open-cell foam (Fig. 1) allows an important surface over volume ratio, a small pressure loss (even at high flow) (Edouard et al., 2008; Huu et al., 2009), efficient mass transfers, an intimate mixing of the reagents (Richardson et al., 2000; Giani et al., 2005), an easy separation from the solution (e.g., stock, load or recyclability operations) and presents a high recyclability potential. In other words, a filtration step is not necessary as opposed to processes using nano-powders of antimicrobial agents. Moreover, OCPUFs are lightweight structures, commercially available at low cost due to the large variety of applications (e.g., insulation, filters for aquariums, cars or domestic appliances) involving their physical and mechanical properties (Engels et al., 2013).

Some works have shown the use of OCPUFs as antibacterial catalytic support for water remediation by direct grafting of silver nanoparticles on the material (Phuong Phong et al., 2009; Jain and Pradeep, 2005; Nadafan et al., 2016), which demonstrates good antibacterial activities on *Escherichia coli*. Nanoparticles seem to interact with the nitrogen atoms of the polyurethane, fixing them to the support but no studies concerning their mechanical resistance was carried out. In previous works, we have shown that these foams are easily functionalized with a mussel-inspired polydopamine (PDA) coating (Pardieu et al., 2016; Edouard et al., 2016; Lefebvre et al., 2017). PDA possesses biocompatible and adhesive properties (i.e., nontoxic and no hazardous effect on the environment), and is



Fig. 1. a) Commercial foam-filter (polyurethane open-cell foam) used in this work; b) magnified 30 times under digital microscope.

therefore an excellent bio-inspired polymer candidate for biomedical applications (Liu et al., 2014; Yeroslavsky et al., 2015; Fullenkamp et al., 2012; van der Westen et al., 2012; Lee et al., 2007). Thus, encouraged by the remarkable properties of both the OCPUF and the PDA coatings, we propose in this work a simple and robust method for commercial polyurethane foams coating with silver particles. It has been demonstrated that PDA exhibits only a moderate antibacterial effect (Yeroslavsky et al., 2015; Lu et al., 2015; Su et al., 2016). Therefore, PDA is generally used as an adhesive coating agent on the surfaces of materials, which allows to further graft external antimicrobial agents on them (Yeroslavsky et al., 2015; Fullenkamp et al., 2012; Jiang et al., 2013; Sileika et al., 2011; Liu et al., 2016). Generally, in open literature, two steps are required (referred to as indirect route), *(i)* PDA coating, followed by *(ii)* grafting of the active phase or particles on the support (Lefebvre et al., 2017). The foam-filter obtained by a direct route (one-step only) coating method and presented in this work are named OCPUF@PDA/Ag. The direct-route coating method consists in a simple dip-coating of an OCPUF in a solution of dopamine, facilitated by the addition of a chemical oxidant containing the metal of interest (e. g., Ag).

Finally, the antimicrobial performances of the functionalized foam are evaluated in batch conditions in liquid media against environmentally relevant pathogenic bacteria, such as *Legionella pneumophila* (*L. pneumophila*), *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*), as well as *Candida albicans* (*C. albicans*), a pathogenic fungus. An attempt to understand the mechanism of action of the developed foam-filter towards bacteria was also conducted. The performances, mechanism of action, "run-life", and applications in water treatment processes of this new antimicrobial tool is evaluated and discussed.

#### 2. Materials and methods

#### 2.1. Materials and characterizations

Commercial compounds were used as received. Polyurethane open-cell foams (20ppi - Fig. 1) were purchased from FoamPartner. Their characteristics are as follows: mean strut size:  $277 \mu m$ ; mean window size:  $1218 \mu m$ ; mean cell size:  $3457 \mu m$ ; density: 0.027–0.033, porosity: 0.94–0.97. Cylindrical samples of 8 cm<sup>3</sup> ( $200 mg \pm 1 mg$ ) were used without prior treatment. Dopamine hydrochloride 99% was purchased from Alfa Aesar. Tris base buffer and iron (III) pyrophosphate were purchased from Sigma-Aldrich. Silver nitrate 99.5% was purchased from Acros organics. Luria's Broth was purchased from Conda, D-glucose and Agar from Euromedex, Peptone from BD, Plate Count Agar (PCA) medium from Merck, and L-cystein and ACES from Roth. Dichlorodihydrofluorescein diacetate (H2DCFDA), Bacto Yeast Extract, and Phosphate Buffer Saline (PBS) were purchased from Thermo Fisher Scientific.

18 M $\Omega$  deionized water (Q20 Millipore filtration system) was used for solution and culture medium preparation, as well as for the washing procedure. Foam-filters were tested on *Legionella pneumophila paris*, *Staphylococcus aureus* (CIP 4.83), *Escherichia coli* (CIP 54.127) and *Candida albicans* (ATCC 90028).

Pictures of the foam-filters were realized with a VHX-6000 digital microscope. Scanning electron microscopy (SEM) was performed with a FEI Quanta 250 FEG microscope at the "Centre Technologique des Microstructures" ( $CT\mu$ ) at the University of Lyon (Villeurbanne, France). Samples were deposited on a flat steel holder and coated under vacuum by cathodic sputtering with carbon. The samples were observed by SEM under an accelerating voltage of 15 kV. Elemental analysis was performed with an EDS-SDD detector (SAMx) with an active area of 30 mm<sup>2</sup>. Fluorescence microscopy images were obtained with an EVOS FL Cell Imaging System from Thermo Fisher Scientific.

FT-IR analyses were realized on a Nicolet iS50 spectrometer from Thermo scientific.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed at the Institut Pluridisciplinaire Hubert Curien of the University of Strasbourg, France. Foam-filter samples were collected after test, briefly rinsed in 70% ethanol and dried at 70  $^{\circ}$ C before dissolution in H<sub>2</sub>SO<sub>4</sub> and analysis.

Inductively coupled plasma optical emission spectrometry (ICP-OES) and X-ray photoelectron spectroscopy (XPS) were realized at the Institut de Recherche sur la Catalyse et l'Environnement of Lyon (Villeurbanne, France).

#### 2.2. Methods

#### 2.2.1. Polydopamine coating on OCPUF

Polydopamine coating on OCPUF was realized by dip-coating according to the procedure described by Lee *et al.*, (2007) and adapted by Lefebvre *et al.*, (2017). Briefly, an 8 cm<sup>3</sup> foam sample was dipped into a solution of dopamine at 2 mg/mL, buffered with Tris base at pH 8.5 and was left in the solution under magnetic stirring and visible light for 24 h. The foam was then dried under vacuum and washed several times in deionized water.

#### 2.2.2. One-pot PDA/Ag coating on OCPUF

Fig. S1 displays the one-step original approach used in this work for antimicrobial coating preparation on open-cell foam-filters. The simple and versatile procedure consists in the addition of a chemical oxidant containing a metal of interest (e.g., Ag) in the solution during dopamine oxidation. A 50 mM aqueous solution of silver nitrate was prepared and dopamine hydrochloride was added to the solution at a concentration of 2 mg/mL. The OCPUF sample was dipped in the solution for 24 h under magnetic stirring without prior pH control. The sample was then dried under vacuum and thoroughly washed in deionized water before final drying. The resulting foam-filter is named OCPUF@PDA/Ag.

#### 2.2.3. Antibacterial activity evaluation on E. coli and S. aureus

The activated foam-filter presented above was evaluated on the selected microorganisms with the procedure described on Fig. S2. For the antibacterial activity evaluation, a sub-culture of bacteria was realized in Luria-Bertani broth (LB) at 37 °C and shaken overnight at 180 rpm. The bacterial suspension was then adjusted to  $1.10^6$  Colony Forming Unit per milliliter (CFU/mL). 40 mL of adjusted suspension were then placed in a 50 mL Falcon tube with a foam-filter and incubated at 37 °C on a rotating wheel at 9 rpm for 24 h. 1 mL aliquots of the culture medium were collected after 0, 1, 3, 5, 7 and 24 h of contact time and serially diluted in 9 mL of sterile 0.9% NaCl aqueous solutions. 100 µL aliquots of each dilution were plated in triplicate on Plate Count Agar (PCA) and incubated overnight at 37 °C before enumeration of viable colonies. Each experiment was carried out in triplicate. To ensure ideal growth conditions, adjusted suspensions of the bacterium without foam-filters were used as control for each experiment.

#### 2.2.4. Antibacterial activity evaluation on L. pneumophila

For the elimination kinetics studies of *L. pneumophila*, the procedure described in *2.2.3* was followed with slight adjustments of culture conditions to ensure ideal growth of the bacterium. The bacteria were cultured and plated on Charcoaled ACES buffer agar, the liquid cultures were realized in AYE broth and serial dilutions were performed in PBS. The bacteria were sub-cultured for 15 h at 37 °C starting from a suspension at O. D. = 0.1 and was diluted to 1/100 before addition of the foam. Incubation time was extended to 4 days before enumeration of viable colonies.

#### 2.2.5. Antifungal activity evaluation on C. albicans

To assess the antifungal activity of the foam-filter against *Candida albicans*, the procedure described in 2.2.3 was followed and slightly modified. The fungus was cultured on sabouraud agar. The liquid sub-culture was incubated for 35 h at 180 rpm in sabouraud broth and adjusted to  $1.10^5$  CFU/mL. The aliquots were plated on sabouraud agar plates and incubated for 48 h before enumeration of viable colonies.

#### 2.2.6. Evaluation of reactive oxygen species (ROS) generation

To investigate the mechanism of action of the foam-filter on bacteria the H2DCFDA green fluorescence probe was employed on cultures of *S. aureus* and *E. coli*. A kinetic study of ROS generation was performed on cultures of *S. aureus* and *E. coli* by following the procedure described in 2.2.3 and aliquoting of the culture medium at different time points. After 0, 90, and 150 min of contact with the foam-filter, 4 mL of culture medium were aliquoted and centrifuged. The supernatant was removed, and the pellet resuspended in PBS. Commercial H2DCFDA powder was diluted in DMSO and added to the suspension at a final concentration of 10  $\mu$ M before incubation of the mixture at 37 °C in the dark for 15 min. The suspension was then centrifuged and approximately 20  $\mu$ L of supernatant was left inside the tube to resuspend the pellet. 5  $\mu$ L of this bacterial suspension were transferred between a slide and a glass coverslip before



OCPUF@PDA/Ag

OCPUF@PDA/Ag

**Fig. 2.** Digital microscopy and SEM images of foam-filters coatings with a) OCPUF; b) OCPUF@PDA; c) OCPUF@PDA/Ag; and d) OCPUF@PDA/Ag under SEM at higher (x40000) magnification for particle diameter measurement.

observation under an epifluorescence microscope. A foam-free culture was used as negative control and subjected to the same procedure.

#### 3. Results

#### 3.1. Antimicrobial foam-filter characterizations

#### 3.1.1. Microscopy and EDX

The developed foam-filter was studied after functionalization under digital microscope (Fig. 2c) to assess successful surface modification and coating homogeneity. Scanning electron microscopy (SEM) was also carried out to study the structure of the surface of the coating, and is represented by the black and white images, as well as to assess the diameter of the particles (Fig. 2d). Fig. 2a shows the bare polyurethane foam-filter before coating, exhibiting a deep blue color with no roughness. A simple PDA coating was realized on OCPUF following the procedure described by Lee and coworkers (Lee et al., 2007). As can be seen on Fig. 2c and according to Pardieu *et al.*, (2016) and Lefebvre et al. (Pardieu et al., 2016; Lefebvre et al., 2017), this PDA coating produces a drastic change of color of the support, shifting from a blue to a dark brown/black color, with increased roughness due to PDA particles aggregated on the surface of a PDA film. Images of the developed direct route coating method, OCPUF@PDA/Ag, are shown on Fig. 2c and shows a green shaded coating with silver particles of small size ( $\simeq 200$  nm; Fig. 2d). The silver grafting also appears to happen by aggregation of particles, distributed across the entire surface of the foam-filter (Fig. S3).

Table S1 shows the mass gains, obtained by weighing of the sample, after coating (Eq. S1 and S2). A mass percentage of PDA + Ag of 24.3%wt OCPUF is reached when a solution of 50 mM of silver nitrate are used for the coating. This percentage drops to 14.5%wt OCPUF when the concentration of silver nitrate solution is at 20 mM, and reaches 11.8%wt OCPUF with a 100 mM solution of silver nitrate, with significative variability ( $\pm$  6.24%).

Energy dispersive X-ray spectroscopy (EDX) analysis is realized on the foam-filter to confirm the presence of the element of interest on the surface.

Fig. S4 shows the EDX analyses performed on the coatings and confirms the presence of silver on the surface of the OCPUF@PDA/ Ag foam-filter (Fig. S4c).

#### 3.1.2. ICP-AES, XPS and FTIR

Inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed to measure the metal content on the foamfilter (Table 1) and shows a silver content of 7.4  $\pm$  0.3 (% w/w).

X-ray photoelectron spectroscopy (XPS) analyses were realized on the foam-filter to determine the degree of oxidation of silver. Fig. S5 displays the XPS spectra of Ag 3d obtained on the sample after synthesis of the coating. Only one binding energy (BE) band of Ag 3d5/2 is detected, with a value of 368.3 eV. According to XPS tables, these values are attributed to metallic silver (Ag(0)).

Finally, the FT-IR spectrum of the OCPUF@PDA/Ag foam-filter is shown in light blue on Fig. S6, along with OCPUF in dark blue and OCPUF@PDA in red. Some distinctive peaks can be found such as N-H stretching at 3300 cm<sup>-1</sup> from urethane functions for OCPUF which broaden for OCPUF@PDA and OCPUF@PDA@Ag and can be associated to catechol groups (Dreyer et al., 2012), C-H stretching from alkyl groups at 2870 cm<sup>-1</sup>, C=O stretching at 1720 cm<sup>-1</sup>, C=C stretching from aromatic functions at 1530 cm<sup>-1</sup>, C-C stretching at 1215 cm<sup>-1</sup> and C-N stretching from indole groups at 1100 cm<sup>-1</sup>.

#### 3.2. Antimicrobial activity

Antibacterial and antifungal activities of the foam-filter were tested against *S. aureus* (Gram-positive bacterium), *E. coli* and *L. pneumophila* (Gram-negative bacteria) and *C. albicans* (Fungus). Fig. 3 shows the evolution of the bacterial concentration, measured in Log<sub>10</sub> CFU/mL (Colony-Forming Unit per milliliter), as a function of contact time (0; 1; 3; 5; 7 and 24 h) for the tested samples in liquid culture media. The standard deviation on the curves was determined by conducting three replicas per test. No antibacterial effect was observed against *S. aureus* and *E. coli* with OCPUF@PDA as the growth curves follow the control curves (Fig. 3a, b). However, no colonies could be enumerated (more than 6 Log decrease) with OCPUF@PDA/Ag after 24 h of contact against *S. aureus* and 3 h of contact against *E. coli*. Similar results are observed against *L. pneumophila* (Fig. 3c) after 5 h of contact (5 Log decrease). The antifungal activity of the foam filter was evaluated against a culture of *C. albicans* (Fig. 3d). The viable yeast concentration drops drastically during the first 3 h of experiment, with nearly no enumerable yeast cells after 3 h of contact time, which represents a 5 Log decrease in concentration (- 99.999%) in comparison to the initial population.

Table 1Silver quantification by ICP-AES on foam-filter.

Sample	Silver content (%w/w)
OCPUF@PDA/Ag	$\textbf{7.4} \pm \textbf{0.3}$



Fig. 3. Antimicrobial activities of OCPUF@PDA/Ag foam-filter VS Control, in triplicate, against a) S. aureus; b) E. coli; c) L. pneumophila, and d) C. albicans.



 $\checkmark$ 

Fig. 4. Comparison of transmitted VS green-filtered epifluorescence microscopy images of ROS generation inside bacterial cells after 0, 90, and 150 min of contact with the foam-filter against a) *S. aureus*; and b) *E. coli*.

#### 3.3. Evaluation of foam-filter mechanism of action on bacteria

The generation of ROS inside the bacterial cell following contact with the foam-filter was assessed on *S. aureus* and *E. coli*. Fig. 4 shows epifluorescence microscopy images of the bacterial cultures taken after 0, 90, and 150 min of contact with the foam. As can be seen on Fig. 4a, *S. aureus* is emitting only a very light fluorescence which indicates that no ROS are produced inside the cells before contact with the foam-filter. However, after 90 min of contact with OCPUF@PDA/Ag, all the bacteria present in the focal plane are exhibiting a strong green fluorescence, suggesting an intense production of ROS. The fluorescence seems to have increased after 150 min of contact with the foam-filter. The same observations can be made for *E. coli* (Fig. 4b).

#### 3.4. Stability and recyclability of foam-filter

For potential applications in water treatment processes, the stability and recyclability of the antimicrobial foam-filter are important features for the future design process, it was therefore reused several times. The study was carried out on *S. aureus* as it was the most resistant of the tested microbial models.

The procedure described in Section 2.2.3. was followed for 24 h (representing 1 run). Afterwards, the foam-filter was removed from the culture medium, quickly rinsed in sterile deionized water and immediately dipped in a fresh and adjusted liquid culture of *S. aureus* for 24 h (second run). The procedure was repeated 4 times (i.e., 4 consecutive runs), in triplicate (3 foam-filter samples and 3 bacterial cultures for each run). A foam-free culture was used as control each time. Fig. 5 shows the activity of the OCPUF@PDA/Ag foam-filter on 4 consecutive runs. The foam-filter kept the same overall activity after 24 h of contact for at least 4 runs, but the abatement rate decreases after Run 1 and stabilizes for Runs 2–4. In fact, as can be seen on Fig. 5a, there is a difference of approximately 4 Log after 5 h



Fig. 5. Reusability of OCPUF@PDA/Ag against S. aureus: a) elimination curves; b) percentage of bacterial elimination after 24 h of contact time.

of contact between the first run and the other runs. However, after 24 h of contact all the runs are close to zero, which demonstrates a slower elimination rate after the first run but a same overall efficiency on at least 4 runs.

The stability and quality of the foam-filter coating was assessed after test by microscopic techniques. The morphology of the coating before and after several runs seems to be identical as no particular damage can be seen on its structure (Fig. 6). SEM images showed on Fig. 6 were all realized on aggregates.

Fig. 7 shows SEM images of the foam-filter after 72 h of incubation in the liquid culture of *S. aureus* in the same conditions as for the activity tests described in Section 2.2.3. (Fig. 7b) versus a fresh foam-filter (Fig. 7a) (i.e. no contact with bacteria). As opposed to the control, only a few bacterial cells are visible (white spheres of  $\simeq 1 \mu m$  indicated by white arrows) on Fig. 7b. According to Wijesinghe et al. (Wijesinghe et al., 2019), this result demonstrates that no biofilm has formed after 72 h of contact with the concentrated bacterial culture.

ICP-AES and ICP-OES analyses were also performed on the foam-filter before and after tests to quantify silver content and on the liquid culture medium after test to quantify silver leaching (Table 2). As can be seen, the silver content drops from  $7.4 \pm 0.3$  (%w/w) before test to  $5.04 \pm 0.1$  (%w/w) after 1 run, with 3.56 mg/L of silver detected in the solution after the first run. The silver content seems to remain constant after the first run and only very small quantities of leached silver are detected in solution after the following runs.

XPS analyses were performed after test to detect any potential shift in silver oxidation degree. Fig. S7 shows the XPS spectra of Ag 3d obtained for the foam-filter after 4 runs. In comparison with Fig. S5, two BE bands are now detected for 3d5/2 with values of 367.2 eV and 368.4 eV, indicating a change in the oxidation degree of silver grafted on the foam-filter during the test.

#### 4. Discussion

The polydopamine-based foam-filter exhibits enhanced contact-active antimicrobial activities against gram-negative *E. coli* and *L. pneumophila* bacteria, gram-positive *S. aureus* bacterium, and *C. albicans* fungus.

As opposed to other PDA-coated substrates (Su et al., 2016), OCPUF@PDA did not show any antibacterial effect (Fig. 3a, b). It is possible that the extremely favorable growth conditions used in this work (i.e., high bacterial concentration and incubation at 37 °C with agitation on a rotating wheel in nutrient broth) do not allow to observe the effect of the PDA coating alone. However, even under these favorable conditions for bacterial growth, the developed foam-filter functionalized with this direct-route method (OCPUF@P-DA/Ag) shows the complete elimination of the initial population of all the tested microbial models, with a good reproducibility.

The solubility of the chemical oxidant (AgNO<sub>3</sub>), the pH of the solution and the nature of the buffer are key features for an efficient coating. For this direct-route coating, not adding any buffer to fix the pH turned out to be a good solution to limit silver precipitation due to the presence of anions and allowed the synthesis of small particles (Fig. S8). Moreover, the important pH variations (3 pH units) to acidic conditions do not seem to prevent dopamine from polymerizing into PDA (Zheng et al., 2015; Bernsmann et al., 2011). Several



Fig. 6. Digital and SEM images of OCPUF@PDA/Ag: a) before test; b) after 1 run; c) after 4 runs.



Fig. 7. Biofilm formation study through SEM imaging of a) Control OCPUF@PDA/Ag and b) OCPUF@PDA/Ag after 72 h of contact with a concentrated *S. aureus* liquid culture.

#### Table 2

Silver content quantification by ICP-AES on foam-filter and by ICP-OES on culture medium before and after test.

	Before test	After 1 run	After 4 runs
OCPUF@PDA/Ag Liquid culture medium	7.4 ± 0.3 (%w/w) ø	$\begin{array}{l} 5.04 \pm 0.1 \; (\% \text{w/w}) \\ 3.56 \; \text{mg/L} \end{array}$	$5.0\pm0.2$ (%w/w) 0.70 mg/L

concentrations of  $AgNO_3$  were tested for the coating and 50 mM gave the best mass gains (Tab. S1) as well as the best antibacterial activity (Fig. S9).

The size of the particles can decrease considerably depending on the conditions of the coating and could play a non-negligible role on the antimicrobial activity. The addition of AgNO<sub>3</sub> provided particles of small diameter ( $\simeq 200$  nm). FT-IR analyses (Fig. S6) do not allow to confirm silver grafting and the similarity of the spectrum do not show any strong difference in coating composition.

Regarding the difference in activity of the foam-filter on the gram-positive bacteria and the gram-negative bacteria, our results are consistent with the literature and can be explained by their differences in cell wall composition (Beveridge, 2001; Durán et al., 2016).

In this work, we could not discriminate the antibacterial activity of silver nanoparticles (AgNPs) over the activity of the released silver ions as these two phenomena occur simultaneously (Mikhailova, 2020). According to other works (Durán et al., 2016; Niyonshuti et al., 2020), the antibacterial mechanism of action of AgNPs is not fully understood yet. However, a few main mechanisms seem to garner consensus. Amongst them is the direct contact between the AgNPs and the bacterial cell wall, which is due to attractive forces, that causes the disruption of the membrane by forming holes, leading to proteins disruption and leakage of cellular content (Gharpure et al., 2020; Elbasuney and El-Sayyad, 2022; Agnihotri et al., 2013). Another mechanism is the release of silver ions (Ag<sup>+</sup>) from the NP through its oxidation  $Ag(0) \rightarrow Ag(I)$ , leading to the disruption of the bacterial outer membrane, the generation of reactive oxygen species (ROS), the destabilization of biomolecules such as respiratory enzymes, and impairment of DNA which strongly affects the transcriptional response (Gharpure et al., 2020; Durán et al., 2016; Bruna et al., 2021). According to Xiu et al., (2012) (Xiu et al., 2012), AgNPs would rather act as a carrier, allowing Ag<sup>+</sup> ions to be directly delivered to the bacterial cell, which would prevent them from being neutralized by natural ligands in the bacterium environment. The oxidative stress produced by AgNPs and silver ions induces the generation of ROS inside the bacterial cell, which causes damages to its components, such as DNA (Durán et al., 2016; Quinteros et al., 2016). As confirmed by Fig. 4 we can observe the production of a strong fluorescence with increasing intensity through time for both gram-positive and gram-negative bacteria. Reactive oxygen species are therefore generated when the bacteria are exposed to a prolonged contact with the foam-filter, which can explain their elimination. Controls are provided on Fig. S10 and S11 for both tested strains. Fig. S10a shows that not autofluorescence is produced by the bacteria as they are not exhibiting any green fluorescence in the absence of the dye. Fig. S10b demonstrates that the foam-filter is responsible for the observed fluorescence as it is not produced in foam-free conditions. Fig. S10c shows that green fluorescence from the dye is ROS-dependent as all the bacteria from the control culture are exhibiting a strong green fluorescence when exposed to  $H_2O_2$ , a source of ROS.

Another mechanism of action investigated in several works involve the impact of AgNPs binding to the bacterial cell wall, thus increasing the kinetic reorganization of histone-like nucleoid structuring proteins, and thereby impeding the expression of some essential genes for the survival of the bacterium (Niyonshuti et al., 2020; Sadoon et al., 2020; Alqahtany et al., 2019).

It is unclear whether a PDA surface can synergize the antimicrobial activity of AgNPs and the mechanisms underlying such a synergistic effect. However, according to Niyonshuti *et al.*, (2020) (Niyonshuti *et al.*, 2020), a plausible coordination between Ag and the catechol groups of the PDA coating can be responsible for this synergistic effect. In fact, heavy metals such as Ag(0) and Ag<sup>+</sup> ions from AgNPs can catalyze the redox cycling of the catechol/quinone couple in the PDA coating. Silver can promote the electron transfer from the catechol/quinone redox cycle to dioxygen, resulting in the generation of  $O_2^-$  superoxides (Niyonshuti *et al.*, 2020). The PDA/Ag interaction increases ROS generation, which causes significant damage to the bacterial cell wall, resulting in the death of the bacterium (Stark, 2005).

While the formation mechanism and the structure of PDA remain uncertain (Ding et al., 2016), the observed differences in mass

gains can be attributed to variations in reaction conditions induced by the addition of these oxidative species. The reactivity of the reduction/oxidation couples formed by the Catechol/Quinone groups, the  $H_2O/O_2$  groups and the Ag/Ag<sup>+</sup> groups is impacted by pH changes. An acidic reaction medium favors the formation of catechol groups in PDA, which can reduce more Ag<sup>+</sup> ions into Ag particles, hence increasing the mass of grafted silver on PDA. However, a high density of silver in the medium (100 mM) seem to negatively impact the formation of PDA which tends to form on suspended particles and not on the support.

XPS measurements were carried out to compare the oxidation degree of silver before and after test. The results remain not completely clear but show that the oxidation state of silver on the surface of the coating changes during the antimicrobial test. The single BE band of Ag 3d 5/2 of 368.3 eV detected after the coating of the foam (Fig. S5), is attributed to Ag(0) (NIST X-ray Photoelectron Spectroscopy Database, 2000). After test (Fig. S7), two BE bands of 367.2 eV and 368.4 eV are detected, suggesting a change in the oxidation degree of silver, making it more oxidized (NIST X-ray Photoelectron Spectroscopy Database, 2000; Kaushik, 1991). In other words, silver is in the form of chelated Ag(0) after coating of the foam and it is oxidized during the antimicrobial activity test.

The synergy between the redox properties of the catechol/quinone groups of PDA and the  $Ag/Ag^+$  couple can explain the good antimicrobial activity of the foam-filter. This is consistent with the literature, which has demonstrated that  $Ag^+$  ions from  $AgNO_3$  are reduced by PDA's catechol groups, resulting in the formation of Ag(0) nanoparticles and quinone groups (Niyonshuti et al., 2020; Elbasuney and El-Sayyad, 2022; Yang et al., 2016). During the test, the surface of AgNPs is oxidized and Ag ions are formed, passing through the bacterial membrane and causing major damages (Durán et al., 2016; Wang et al., 2021). However, the redox properties of PDA allow the protection of the grafted antibacterial agents from a fast oxidation, hence a slow dissolution of silver (Lefebvre et al., 2017) and therefore the good stability of the foam-filter through time. The FT-IR analysis realized on the foam-filter after several runs (Fig. S12) do not show any modification of the surface of the coating, which is in agreement with Fig. 6.

SEM imaging realized on the foam-filter to investigate the potential formation of biofilms (Fig. 7), shows that no evident presence of biofilm is detected. In fact, according to literature, 72 h are necessary for most *S. aureus* strains to form a biofilm on a support in a liquid culture media (Wijesinghe et al., 2019). A biofilm is a bacterial network of which the matrix allows the strong attachment of the colony on a support, faster communication between the cells and protection from external aggressions (Moormeier and Bayles, 2017). The structure of a biofilm of *S. aureus* can be investigated using SEM and appears as a large accumulation of bacteria tightly adhered to one another and surrounded by a sticky matrix mainly composed of proteins, carbohydrates and extracellular DNA (Moormeier and Bayles, 2017; Reddinger et al., 2016). Fig. 7b shows that such structures are not visible on OCPUF@PDA/Ag after 72 h of contact in a concentrated suspension of *S. aureus*, and only a few isolated bacteria can be seen (white spheres of 1 µm in diameter). These results are in agreement with the literature as no biofilm formation was observed on PDA/Ag surfaces (Tang et al., 2015; Sri Abirami Saraswathi et al., 2019; Park et al., 2021). The differences observed in surface morphology between Figs. 6, 7 and S8 are due to different SEM pre-treatment methods, magnifications, apparatus, and studied area.

The loss of antibacterial activity observed after the first run (Fig. 5) is essentially due to leaching of the active phase as confirmed by ICP measurements (Table 2). No clear guidelines are given concerning silver concentration in treated water, however it is estimated that for freshwater aquatic life, the total recoverable silver should not exceed 1.2 mg/L (Standard Methods Committee of the American Public Health Association), which is the case in this work from the second run and prior dilution in the receiving water body. A silver concentration of 0.1 mg/L in drinking-water has been established by the WHO as safe for human consumption and values of the same order of magnitude are observed in this work, starting after run 3 (W.H.O., Silver in Drinking-water, Guidelines for drinking-water quality, 2 (1996) 1–9.). This leaching is mainly due to attrition against the sides of the tube as the foam-filter moves during the test, as well as the long (24 h) and constant contact time with the culture medium in such harsh conditions. The transition to a more industrial scale will have to take these constrains into consideration but should limit silver leaching. In fact, a reactor filled with foam-filters should greatly restrict the attrition as the foam-filters will not move. According to Z. Liu et al., (2016) (Liu and Hu, 2016) regeneration of silver on PDA coatings is possible by a simple dip-coating method, which could be easily applied to the foam-filters to extend their lifespan.

#### 5. Conclusions

In this work, we demonstrate for the first time that a commercial polyurethane foam coupled to a bioinspired one-pot coating of PDA and Ag is an efficient support for the fast elimination of concentrated pathogenic microorganisms under ideal growth conditions in batch reactor. The results show that this direct-route coating method displays great efficacy as no colonies of *C. albicans, E. coli, L. pneumophila* and *S. aureus* could be enumerated after 3 h, 3 h, 5 h and 24 h of contact with the foam, respectively. This foam-filter was successfully reused several times with the same activity after 24 h of contact on the most resistant of the tested microorganisms: *S. aureus*. Our results obtained in the worst-case scenario (i.e., high bacterial concentration and optimal growth conditions), are very encouraging and more experimental data with a real wastewater treatment system are needed to give a better support to this new tool with great antifouling properties for general biological and environmental applications. Because the antimicrobial foam-filter developed in this work is based on a structured support with remarkable transport properties, a bio-inspired PDA material of industrial size could be used for the first time (to our knowledge) in a real water treatment process design.

#### **CRediT** authorship contribution statement

Larrieu Mathis: Data curation, Investigation, Methodology, Writing – original draft, Formal analysis, Visualization. Blaha Didier: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation. Edouard David: Conceptualization, Funding acquisition, Investigation, Supervision, Validation, Writing – review & editing. Agusti Gerladine: Formal analysis. Mouniee Delphine: Data curation, Formal analysis, Methodology.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### **Data Availability**

Data will be made available on request.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.eti.2023.103468.

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