Antifouling properties of membranes containing Metal-organic frameworks (MOFs)

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Introduction

Membrane technologies have been used for the production of drinking water and wastewater treatment in order to meet the stringent regulatory requirements for drinking water and the discharge limits related to nutrient discharge. In spite of their widespread use, the industrial application of membrane processes is hindered by the control of membrane fouling [1].

Fouling is caused by the accumulation of organic and inorganic substances, as well as biofilm formation due to the deposition or growth of microorganisms. Some recent works has been oriented to the inclusion of antimicrobial substances to prevent biofilm growth [2-3].

This work presents a new approach to prepare composite polymeric membranes for water filtration that include metal–organic frameworks (MOFs), an important class of hybrid organic-inorganic crystalline porous materials [4]. Two cobalt imidazolate MOFs and one Ag coordination polymer (AgTAZ) as comparison were evaluated as a bactericidal material before being introduced in the spun membranes. The control of release of metal gives excellent antibacterial activities and durability against gram negative bacteria and yeast.

Evidence of high antimicrobial activity on bacterial growth on membranes loaded with different MOFs will be presented. Our data show that MOFs produced with simple, cheap and commercially accessible linkers are suitable for use in membrane technology for cleaning water with reduced biofilm formation.

Keywords: fouling; membranes; metal-organic frameworks

1. MATERIALS AND METHODS

AgTAZ is prepared with a polyazaheteroaromatic compounds, 1, 2, 4-triazole. ZIF-67 ($Co(Hmim)_2$) is isostructural to ZIF-8,[17]. Co-SIM-1 (cobalt-based Substituted Imidazolate Material) is a novel analogue of its zinc-based parent SIM-1; they were synthesized by solvothermal procedure.

Electrospun was prepared with transparent PLA (trade name: 'PLA Polymer 2002D') from NatureWorks LLC, UK, molecular weight of ∼121,400 g/mol and a melting temperature of 160◦C. A NANON-01A electrospinning unit was used for this purpose. The morphology of porous nanofibers after sputter coating was examined using a scanning electron microscope (SEM) from Carl Zeiss (EVO MA15). A fluorometer/luminometer Fluoroskan Ascent FL was used for recorder the fluorescence emitted for bacterias over all membrane surface and grown culture. To evaluate the bacterial activity of MOFs, two commercially available strains of gram negative bacteria *E. coli* CECT 4102 and *P. putida* CECT 4584, gram positive bacteria *S.aureus* CECT 240 and the yeast *Saccharomyces cerevisiae* CECT 1170 were used as model microorganisms.

2. RESULTS AND DISCUSSION

The as-prepared microorganisms were subjected to an antibacterial experiment using a diffusion method. On an agar plate inoculated with different the strains, we place approximately 1 mg of the materials to be evaluated. Both MOFs based on cobalt ions show a significant antibacterial activity, with an inhibition diameter of around 15 mm. Surprisingly, AgTAZ appears to be the weakest to inhibit the growth of the bacterial strains (inhibition diameter of 2 mm). This initial experiment shows that both ZIF-67 and Co-SIM-1 are able to diffuse in this medium and to inhibit the growth of all microorganisms used. We also performed tests to determine the biocidal effect of the tested materials in suspension as well as the release of free metals to the solution. These experiments were carried out after 20 h of incubation, when the bacteria are in their exponential growth phase. As shown in Figure 1, MOFs displayed interesting antimicrobial properties against bacteria and yeast.

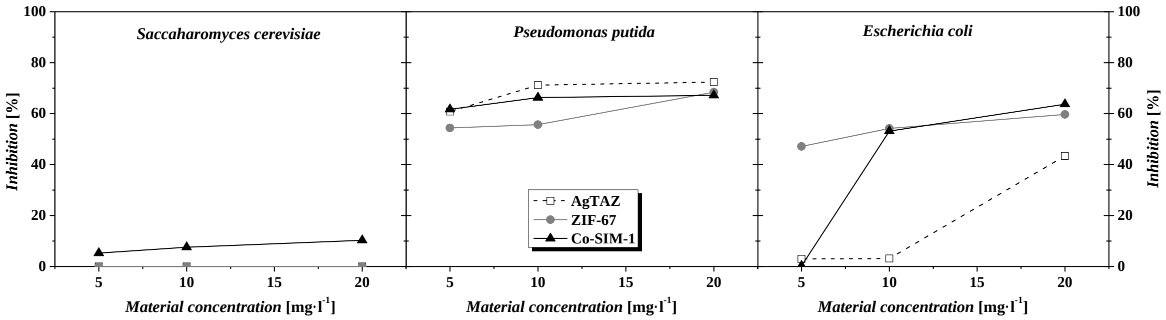

Fig. 1 Bactericidal performance of of AgTAZ, ZIF-67 and Co-SIM-1 against *S. cerevisiae*, *P. putida* and *E. coli*.

After these results we took the appropriate MOF for realize the electrospun (Co-SIM-1) according bacterial performance and showed better properties for the process of electrospinning. SEM micrographs of electrospun fibers with MOFs are shown in Figure 2. As expected, monodispersed Co-SIM-1 nanoparticles were located on the fibers. Fibers were mostly bead-less and homogeneity in diameters.

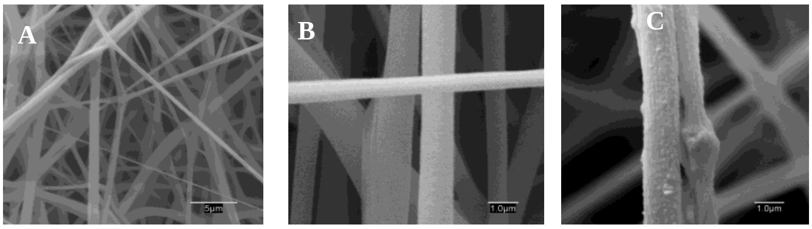

Fig. 2 SEM micrographs of (A and B) unloaded neat PLA, (C, D and E) PLA/CoSIM-1 fibers

On membranes different test were made, after 24 hours of contact with grown medium the membranes were placed in contact with agar plates and incubated approximately 20 hours. It shows less growing of bacteria the ones in contact with CoSIM-1 fibers. A process of dehydration and drying with acetone and ethanol was then carried out to analyze the membranes by SEM. The membranes without CoSIM-1 shown strong biofilms in different parts of sample, especially for *S.aureus,* reduction of biofilms was remarkable with MOF fibers. Another tests for quantify the biocidal effect was made by LIVE/DEAD, bacterial viability kit, and fluorescein diacetate (FDA). Two different measures were realized, solid and liquid phase, in solid phase were present the membranes after 20 hours contact with grown culture, a lecture over all surface of membrane was taken. We determinate the optimum integration time where the bacterium was in the high point of exponential growing phase in contact with blank membrane. Liquid phase was made with supernatant from the contact between bacteria and membranes. Abiotic blank was made with the objective to know if in the absence of bacteria there were fluorescence emission that is not related to the activity of the organism and a negative blank to know optimal growth conditions.

3. CONCLUSIONS

In summary, our work demonstrates that it is possible to use metal organic frameworks based on cobalt as antibacterial materials. The materials exhibit remarkable antibacterial activities and durability, due to the control of the release of cobalt ions in biocidal solutions. The incorporation of these MOFs within the polymer matrix of a fiber was successful and it shows bactericidal properties.

4. REFERENCES

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