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Towards integrated anti-microbial capabilities: Novel bio-fouling resistant membranes by high velocity embedment of silver particles

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ABSTRACT

Biofilm formation on membranes during water desalination operation and pre-treatments limits performance and causes premature membrane degradation. Here, we apply a novel surface modification technique to incorporate anti-microbial metal particles into the outer layer of four types of commercial polymeric membranes by cold spray. The particles are anchored on the membrane surface by partial embedment within the polymer matrix. Although clear differences in particle surface loadings and response to the cold spray were shown by SEM, the hybrid micro-filtration and ultra-filtration membranes were found to exhibit excellent anti-bacterial properties. Poly(sulfone) ultra-filtration membranes were used as for cross-flow filtration of *Escherichia coli* bacteria solutions to investigate the impact of the cold spray on the material's integrity. The membranes were characterized by SEM–EDS, FT-IR and TGA and challenged in filtration tests. No bacteria passed through the membrane and filtrate water quality was good, indicating the membranes remained intact. No intact bacteria were found on hybrid membranes, loaded with up to 15 wt% silver, indicating the treatment was lysing bacteria on contact. However, permeation of the hybrid membranes was found to be reduced compared to control non-modified poly(sulfone) membranes due to the presence of the particles across the membrane material. The implementation of cold spray technology for the modification of commercial membrane products could lead to significant operational savings in the field of desalination and water pre-treatments.

1. Introduction

Premature failure of filtration membrane systems due to fouling caused by biological compounds [1–3] increases both the operating and capital costs associated with desalination and water treatment by millions of dollars every year in the European Union alone [4,5]. Strong surface adsorption of organic carbons suspended in feedwaters is used as a food source by bacteria and algae, leading to biofilm formation which strongly impacts on membrane performance [6]. Biofilm growth induces degradation of membrane polymeric materials [7] through redox reactions, blocking pores and sharply reducing membrane performance [8]. Fouling of membranes is defined operationally as the reduction in water flux caused by an increased resistance to water transport across the fouling cake formed on the membrane surface and/or across the membrane pores [9–11]. Although costly and detrimental to the environment, chemical treatments are available to restore flux, although these induce further premature degradation of the membranes, modules and facilities [12]. The uniqueness of each water stream renders the design of a universal anti-biofouling technique difficult and often water composition analysis [13–15] and membrane autopsies are required to understand fouling sources and mechanisms [16,17]. No conventional anti-fouling coatings have been found that are suitable due to poor adhesion of the anti-fouling layer or partial obstruction of the membrane pores. Developing new routes to reduce bio-fouling of water filtration membranes is a major challenge that needs to be overcome in order to satisfy the increasing global demands for freshwater and for urban wastewater purification [18].

Recently developed strategies to reduce bio-fouling include the decoration or surface patterning of the membrane surface to induce catalytic degradation of both carbon feed-stocks and bio-foulants prior to their surface adhesion [19–21]. Routes to incorporate

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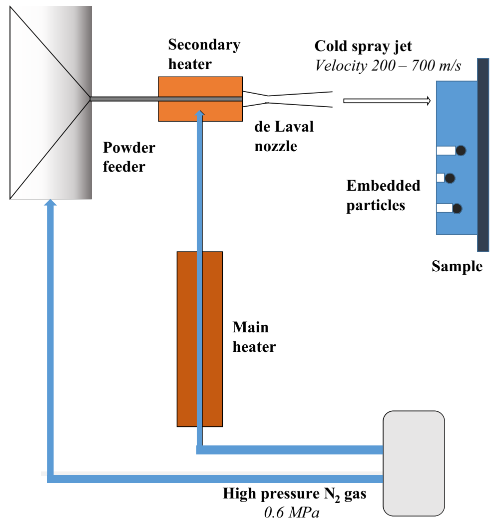

Fig. 1. Schematic of the cold-spray embedding of Ag particles across the polymeric membranes.

catalytic materials include nano-particle impregnation [22], chemical anchoring [23], mixing within the polymer matrix during membrane synthesis [24] or growth from metal salts in solution [25]. However, low surface coverage, occlusion of incorporated particles by the polymer, poor particle adhesion, premature ageing of the polymer matrix, as well as low effective metal decoration yield leading to expensive material waste, have limited their scope of industrial application.

The technology tested here is being developed for marine antifouling technology [26–28] whereby individual metal particles (typically 10–30 μm diameter) are permanently embedded into the surface of polymeric materials. The metal particle powders are accelerated within a supersonic compressed gas jet to velocities up to 1000 m/s using a process known as cold spray. The particles penetrate the surface of the polymer, which plastically deforms around the particle to physically hold it in place with no chemical bonding necessary [26,29]. The embedded particles remain in contact with the outer surface via the impact tunnel formed by the particle penetration (Fig. 1). The use of particles exhibiting anti-microbial properties, such as silver, has the potential to create discrete bio-film resistant surfaces able to prevent the build-up of biological organisms. As the particles are deposited discretely, they form a discontinuous layer which is expected to still allow flux across the membrane with only partial occlusion anticipated, and allows the membrane to retain its flexibility without major structural or morphological damage. The antifouling action of the technique is via slow and controlled dissolution of the particles and release of metal ions.

In this study the cold-spray technique was applied to modify the surface of water purification and pre-treatment desalination membranes to infer anti-microbial properties. The stability of the embedded particles across the porous matrix and their impact on the anti-biofouling properties have been assessed. We demonstrate, for the first time, a proof of concept for an up-scalable route to incorporate silver particles into commercial membrane materials. The stability of the silver particle embedment is related to the materials macro-structures and hardness, and shown to be key parameters in the cold-spraying process. The potential of the modified membranes embedded with silver particles for the effective prevention of model biological organisms deposition during membrane operation is also demonstrated with simple fouling experiments. This route has the potential to reduce costs associated with membrane degradation and cleaning treatments during desalination processes.

Table 1
Materials properties and structural parameters of the membranes used in this work. The structural data are referenced from the membrane manufacturer or from materials properties [25,26]. Density, hardness, tensile strength and abrasive resistance are properties for dense materials, while pore size and porosity are intrinsic to the membrane material.

Properties *Trade name*	**Unit**	**PA** *HNWP – Millipore*	**CA** *HAW – Millipore*	**PVDF** *HVLP – Millipore*	**PSf** *ER – GE*
Density	g cm^{-3}	1.13	1.3	1.78	1.37
Rockwell hardness		M82	99	R77–83	M88
Poisson ratio		0.39	0.36	0.34	0.4
Tensile strength	MPa	78	20–60	25–60	70–95
Abrasive resistance	mg/1000 cycles	5	65	24	6
Pore size	nm	450	450	450	10
Porosity	%	79	79	70	< 20
Thickness	μm	170	150	125	100

2. Materials and methods

2.1. Membrane, reagents and materials

The membranes used were purchased from Millipore and Sterlitech (Table 1). A series of commercial polymeric membranes, consisting of microfiltration (cellulose acetate (CA), poly(amide) (PA), poly(vinylidene difluoride) (PVDF)) and ultrafiltration (poly(sulfone) (PSf)) membranes were cold sprayed. Chemicals and reagents used for the bacterial testing and solution preparation were purchased from Sigma Aldrich and used as received. MilliQ water was used to prepare all the solutions throughout this work. Silver powder (99.99% silver powder, with a particle size distribution such as d10%=4.9 μm, d50%=10.9 μm, d90%=17.3 μm) was purchased from Technic, Inc. (Cranston, RI, USA) and used as received.

2.2. Cold spraying technology

The samples were cold sprayed using a CGT KinetiksTM 4000 system (Sulzer Metco, Winterthur, Switzerland). The cold spray process was performed following a procedure previously described [26–28]. The powder was oven dried and loaded into the feeder as illustrated in Fig. 1. Heated nitrogen gas was accelerated through a CGT 24TC converging-diverging nozzle. The gas temperature and pressure in the stagnation area at the entry point to the nozzle were maintained at a constant 150 °C and 0.6 MPa, respectively. Nitrogen gas (0.5 m^3/h) was diverted through the powder feeder to act as a carrier for the silver powder. The powder-containing flow rejoined the main gas flow in the stagnation area so that the silver particles were accelerated through the nozzle to high velocity. The cold spray nozzle was controlled by an ABB IRB 2600 robot and moved in a raster pattern with 2 mm spacing between passes in order to cover a 114 × 57 mm^2 area of the samples. By adjusting the robot traverse speed in the range of 1000–1500 mm/s and the rotational speed of the powder feeder disc within a range of 0.3–3 rpm, higher or lower particle loading densities (numbers of particles per area of membrane) were prepared. Although the geometry and flow dynamics of the commercial nozzle and spray system were optimized for metal parts forming and not for discrete particles distribution depositions this system at the CSIRO was previously used to successfully lead to the formation of low density coatings across dense polymers used in marine technology anti-fouling coatings.

2.3. Materials characterization

Scanning Electron Micrographs (SEMs) and Energy Dispersive Spectroscopy (EDS) results were obtained on a dual beam Gallium