Macro-patterning of micro-crumpled nanofiltration membranes by spacer imprinting for low-scaling desalination

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SUMMARY (12-POINT ARIAL BOLD CAPITAL LETTERS)

Surface patterns provide a chemical-free approach to reduce fouling by mimicking nature, and are yet limited by their complicated fabrication procedures. Here we develop readily scalable methods to create sub-micrometer- and millimeter-scale patterns on membrane surfaces for low-scaling desalination, with a focus on the anti-scaling mechanism. Specifically, a robust polyethylene (PE) lithium battery separator prepared from melt casting and stretching has been used as the support for nanofiltration (NF), giving micrometer-scale crumples on the surface. Then the PENF membrane is imprinted by permeate spacer during tests, leading to millimeter-scale patterns. A comparison of the impact of different feature sizes on scaling, ranging from smooth-, nm-, µm- and mm-levels, was given through no-stirring dead-end and crossflow tests. Results indicate that µm-scale patterns are resistant to scaling through both spatial and hydrodynamic effects, and mm-scale patterns are also effective in reducing scaling solely due to hydrodynamic effects.

KEYWORDS (12-POINT ARIAL BOLD CAPITAL LETTERS)

Surface pattern, scaling, nanofiltration, feature size

INTRODUCTION (12-POINT ARIAL BOLD CAPITAL LETTERS)

Billions of years' evolution endows creatures with microstructured surface to combat the attachment of ubiquitous microorganisms and other foulants in their living environments.[1] Inspiration from nature have driven the development of patterned membranes for improved fouling resistance. For example, soft-lithographic phase inversion[5] and nanoimprint lithography (NIL)[3] have been widely developed to fabricate patterned membranes, where silicon molds fabricated through light lithography was served as a mold. However, the high cost of silicon wafer and complexity of lithography technology largely limit the wide application of this method in industry.

Here, we present facile method to create µm- and mm-level patterns on the surface of NF membranes for excellent scaling resistance in desalination, and reveal the underlying mechanism. The micro-features are inherited from the PE support made by melt casting and stretching, and macro-features are formed via in-situ imprinting against commonly used permeate spacers. Besides, a comparison of different feature sizes on scaling, ranging from smooth-, nm-, µm- and mm-levels, will be given. Carefully designed experiment will be conducted to clearly identify the role of spatial and hydrodynamic effects of different pattern sizes on scaling, with the aid of CFD simulations.

METHODS (12-POINT ARIAL BOLD CAPITAL LETTERS)

Membrane preparation

NF membranes including DF304i, DF304 and PENF as kindly provided by Beijing OriginWater Technology Co., Ltd. were used. All are poly(piperazine-amide)-based thin-film composite (TFC) membranes. DF304i and DF304 were based on traditional non-woven-supported polysulfone (PSF) support, and PENF was based on polyethylene made from melt casting. A permeate spacer was put beneath the membranes according to common practices, unless otherwise specified.

NF scaling tests

The membranes were evaluated in pressure-driven processes for their scaling performances. Both dead-end and crossflow modes were employed to study membrane scaling and fouling. No mechanical stirring was introduced to dead-end tests, and the linear flow rate was 5 cm/s for crossflow tests. Nonwoven or permeate spacer was placed in the permeate side for PENF and denoted as 'PENF nonwoven' or 'PENF spacer'. The membranes were stabilized with deionized water under the testing pressure for three hours. An unsaturated feed solution containing 25 mM $CaCl_2$ and 10 mM Na_2SO_4 was used in dead-end tests. Saturated $CaSO_4$ solution with 35 mM $CaCl_2$ and 20 mM Na2SO4 was applied in crossflow tests. The initial flux for dead-end and crossflow tests were 35 L m^{-2} h^{-1} and 60 L m^{-2} h^{-1}, respectively.

RESULTS AND DISCUSSION (12-POINT ARIAL BOLD CAPITAL LETTERS)

As is captured in the SEM images in Figures. 1a-c, three distinctly different types of structures are seen on the surfaces of the NF membranes employed in this study, including a smooth surface on DF304i, nm-level Turing structure on DF304, and micro-crumpled surface on PENF with μm-level strip-like features.

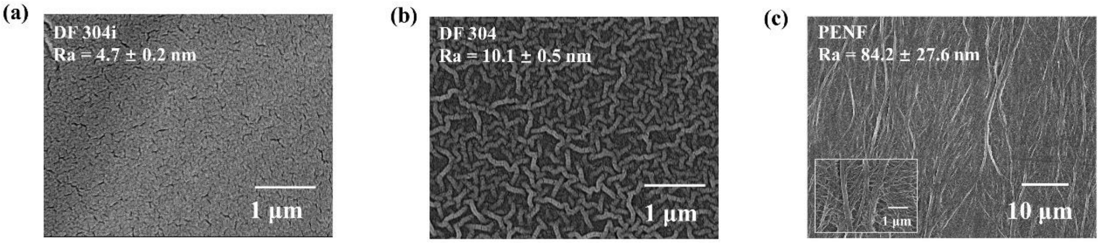

Figure 1. (a)-(c) FESEM images of (a) DF304i, (b) DF304 and (c) PENF;

Figure. 2a shows the scaling behaviors of three membranes in dead-end tests. Fast and comparable flux decline can be observed on DF304i and DF304. On the contrary, a much milder flux decline is experienced by PENF in both dead-end and crossflow modes (Figure. 2c). Since hydrophobic surface and relatively high negative charge on PENF are believed to result in more severe scaling,[2] the current low scaling behavior of PENF should be attributed to micro-crumpled structure. Results in unstirred dead-end tests suggests that surface features have a direct spatial effect in suppressing scaling. Supported by the SEM image in Figure. 2b, crystal growth is effectively inhibited to one direction by the spatial restrictions of the microscale features since micrometer-sized salt crystal is preferentially located in the spacing between two adjacent features. Besides, as a stable environment benefits crystal growth,[4] higher shear stress in the ridge regions and the secondary flow (Figure. 2d) may limit the growth rate of salt crystals, contributing to lower scaling rate.

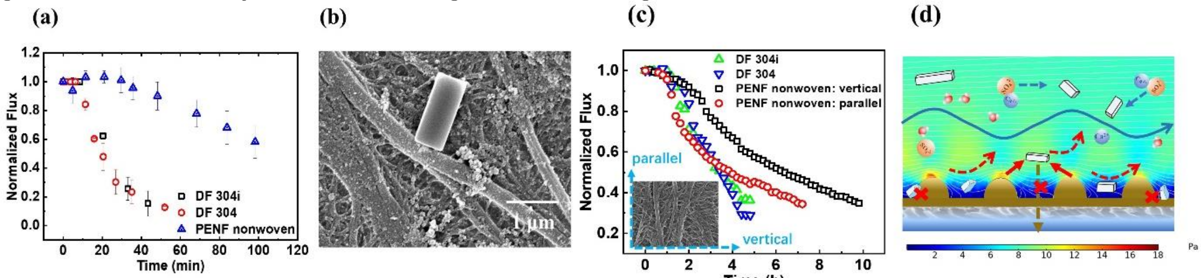

Figure 2. (a)-(b) Normalized Flux decline of three membranes in (a) dead-end scaling and (b) crossflow scaling. (c) SEM images of crystals formation under dead-end conditions after 15 min. (d) illustration of anti-scaling mechanisms on micro-crumpled PENF membrane with streamlines and shear stress.

A permeate spacer with mm-level continuous line features on the front and weaving features on the back is placed beneath the membrane in practice to imprint surface patterns onto PENF membranes (Figure. 3a-b). In comparison, conventional NF membrane supports are prepared by phase inversion on nonwoven fabrics to avoid membrane failure. Four configurations (spacer: vertical; spacer: parallel; reverse: vertical; and reverse: parallel) were adopted in crossflow tests, where spacer (or reverse) refers to the configuration where front (or back) side of spacer faces PENF, and vertical (or parallel) refers to the configuration where the main features are perpendicular to (or in parallel with) feed flow.

Interestingly, no distinguishable difference is found between spacer- and nonwoven-supported PENF membranes in their scaling resistance in unstirred dead-end filtration (Figure. 3c), which implies that mm-level pattern is not able to exert spatial limit on crystal growth or settlement. Nonetheless, patterned PENF imprinted on the front surface of spacer shows significantly reduced scaling in the vertical configuration, suggesting that mm-level patterns can still effectively impose hydrodynamic impacts on crystal growth. It is noticed that patterns formed by reverse side of the spacer (vertical configuration) does not show appreciable improvement compared to PENF on nonwoven, and parallel configurations lead to even more severe scaling (Figure 3d).

CFD simulations give more insights into the flow dynamics in the streams (Figure. 3e-f). In all cases, the average shear stress on the surface is lower than that on smooth membranes. Curved streamlines representative of secondary flow are again seen on vertical spacer configuration, accounting for the disturbed crystal growth and thus lower scaling. However, in the vertical, reverse spacer configuration, though similar streamlines also appear, more downward streamlines could be seen in the valley regions and the average shear stress is significantly lower than the vertical spacer configuration. Therefore, no significant benefit in scaling control is brought by this configuration. Similarly, in the parallel configuration, the low average shear stress coupled by insignificant gain in secondary flow results in even more severe scaling.

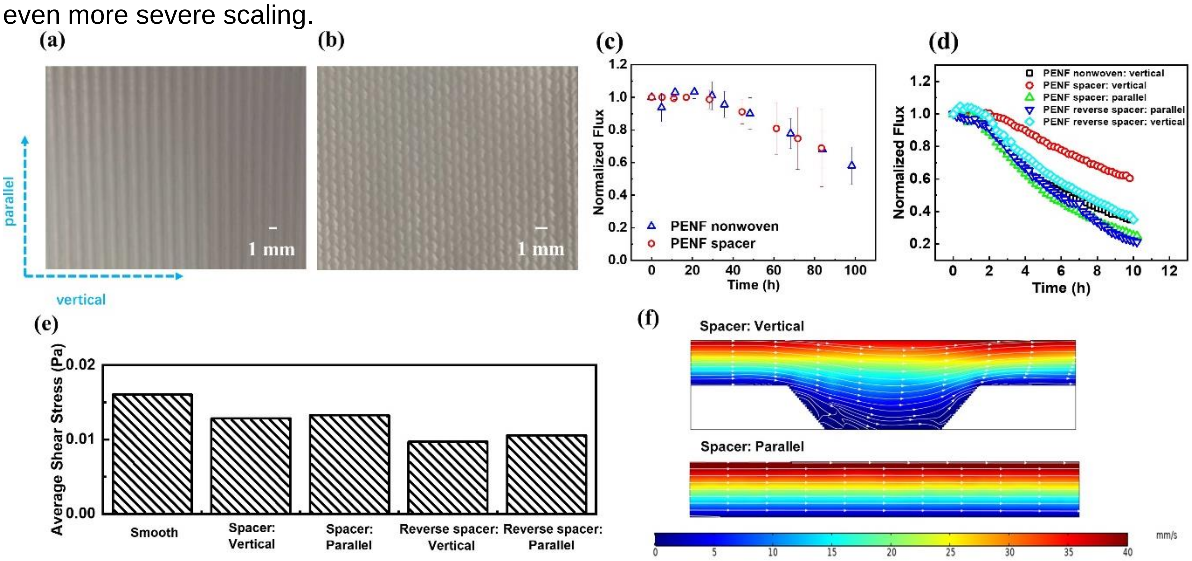

Figure 3. (a)-(b) photos of the surfaces of (a) spacer-imprinted PENF membrane; (b) reverse spacer-imprinted PENF membrane. (c)-(d) normalized flux of (c) dead-end scaling; (d) crossflow scaling. (e) Average shear stress on smooth surface and PENF on spacers of different configurations. (f) streamline profiles on PENF imprinted by permeate spacer.

CONCLUSION (12-POINT ARIAL BOLD CAPITAL LETTERS)

Our study has reported scalable methods to prepare membranes with sub-micrometer- and millimeter-scale patterns for low-scaling desalination. Scaling properties of smooth surfaces, and surfaces with nm-, µm- and mm-scale features have been studied. It is found that secondary flow generated by µm- and mm-level features can slow down the flux decline under crossflow conditions. Meanwhile, µm-level features can restrict the crystal growth on membrane surface due to the spatial effects.

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