# A novel and simple fabrication method for a biomimetic-inspired lath-structured ceramic microfiltration membrane for the treatment of oil-in-water emulsions

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Water contaminated with oil is recognized as a major source of pollution worldwide [1]. The separation of O/W emulsions using microfiltration (MF) has been widely recognized because of its ease of operation, high separation efficiency, and low energy consumption [2]. Ceramic membranes have been widely explored as competent alternatives to traditional polymeric membranes for treating oily wastewater [3]. Despite the exceptionally high rejection rate (>90%) of oil-water (O/W) emulsions, membrane fouling is an inevitable phenomenon that limits the separation efficiency of ceramic membranes [4]. Biomimetic technology, known as the lotus effect, has attracted attention as a groundbreaking method for reducing membrane fouling [5]. However, it is difficult to control the nanostructured surfaces of ceramics, while polymer fabrication is facile.

The main aim of this research is to fabricate a ceramic membrane with a novel morphology that intrinsically increases the surface roughness and oleophobicity for the separation of O/W emulsions. We adapted a colloidal sol-gel method to synthesize a Nepenthes pitcher plant-inspired $\alpha$-$Al_2O_3$ membrane by controlling the solution pH using acetic acid as a peptizing agent. Three different peptizing conditions (pH 5.0, 4.5, and 3.5) were chosen referred to as S5, S4, and S3, respectively. For comparison, conventional $Al_2O_3$ membrane was also developed, referred to as P7. Filtration experiments with multiple cycles were conducted to determine flux recovery rate and fouling ratios.

The fabrication of an $\alpha$-$Al_2O_3$ membrane by a sol-gel method proved to be effective in improving the surface properties. Fig. 1a shows the SEM micrograph of the membrane S3 with uniform lath-like microstructure. The morphology of the membrane particles resembles that of the Nepenthes pitcher plant. It exhibited a surface roughness (root mean square deviation, $R_q$) of 286 nm (Fig. 1b), greater than that of all the other membranes. The surface wetting ability is a key factor in a highly efficient O/W separation system. Membrane S3 exhibited the hydrophilic contact angle of 10.52° (Fig. 1c) with corresponding oleophobic contact angle of 128.51° (Fig. 1d), highest among all the membranes.

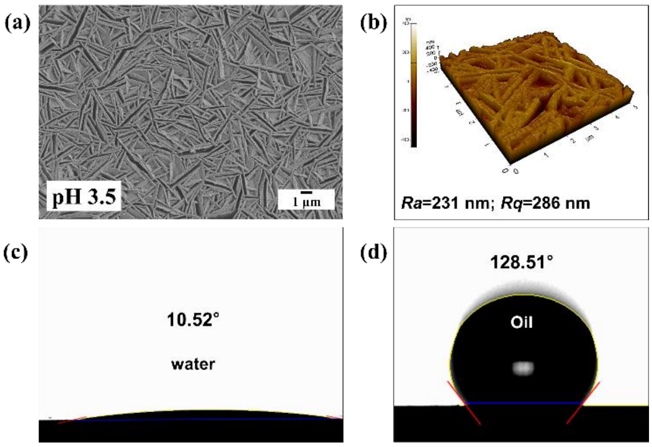


Fig. 1. (a) Surface microstructure, (b) surface roughness, (c) water contact angle and (d) underwater oil contact angle of sol-gel synthesized MF membrane (S3).

The separation performance of the synthetic oil emulsion (1000 mg·L$^{-1}$) was investigated using a conventional MF membrane (P7) and three sol-gel-synthesized membranes (S5, S4, and S3) during a 4-cycle filtration. Membrane S3 exhibited the highest steady permeability of 44.1 L·m$^{-2}$·h$^{-1}$·bar$^{-1}$, as shown in Fig. 2a. It featured a flux recovery rate of 90.9% (Fig. 2b) with minimal irreversible fouling ratio (Fig. 2c) and rejection rate as high as ~99% (Fig. 2d).

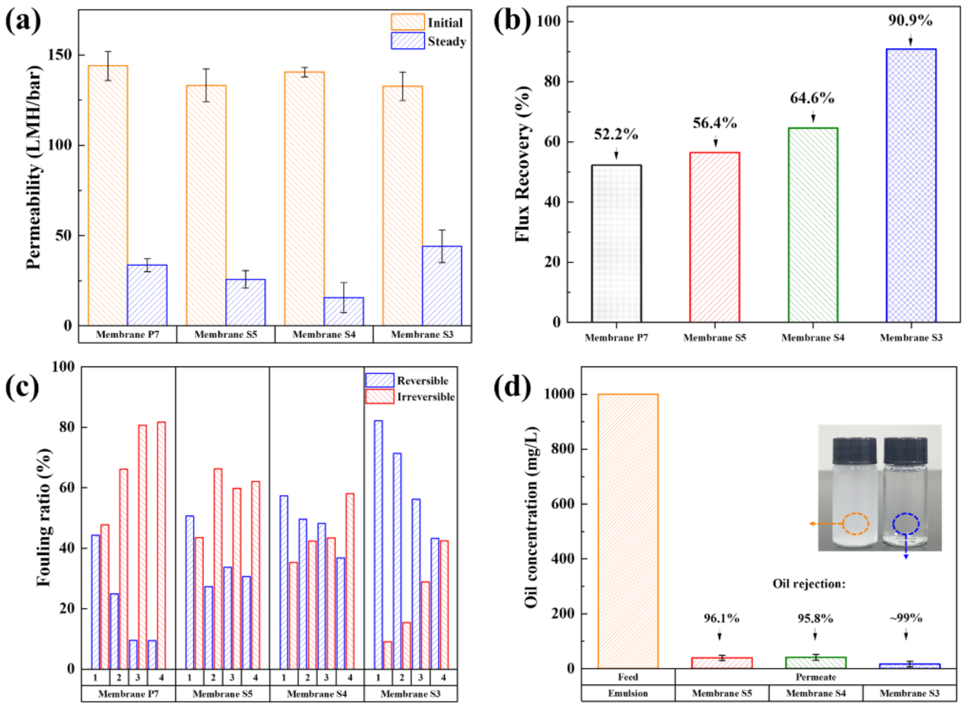


Fig. 2. Separation performance of conventional alumina MF membrane and sol-gel synthesized membranes. (a) Comparison of initial permeability and steady permeability. (b) Flux recovery rates of the different MF membranes after O/W separation. (c) Fouling ratios of the different MF membranes during a 4-cycle O/W filtration. (d) Oil concentration of the feed and permeate (the inset shows the appearance of the feed and permeate solutions).

The performances of all the membranes under the four-cycle filtration are summarized in Table 1. Based on these results, it was concluded that S3 exhibited a better flux recovery rate and irreversible fouling resistance than the other membranes.

Table 1. Comparison of the separation performance of membranes P7, S5, S4, and S3 after a four-cycle O/W filtration.

| Membrane | Pore size | Permeability ($J_p$) | Surface roughness | Contact angle | Permeability ($J_1$) | | Flux recovery | Rejection |
|---|---|---|---|---|---|---|---|---|
| | | | | | Initial | Steady | | |
| | µm | $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ | $R_q$, nm | ° | $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ | | % | % |
| P7 | 0.26 ± 0.03 | 381.1±8.1 | 145.8 | 88.84 | 144.1 | 33.6 | 52.27 | ~99 |
| S5 | 0.29 ± 0.03 | 352.6±9.1 | 24 | 81.51 | 133.2 | 25.7 | 56.46 | 96.1 |
| S4 | 0.29 ± 0.03 | 375.8±2.6 | 44.1 | 89.11 | 140.5 | 15.6 | 64.64 | 95.8 |
| S3 | 0.28 ± 0.03 | 364.4±7.8 | 286 | 128.51 | 132.7 | 44.1 | 90.91 | ~99 |

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