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Limiting thickness of polyamide-polysulfone thin-film-composite nanofiltration membrane



DESALINATION

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HIGHLIGHTS

GRAPHICAL ABSTRACT

- A systematic study to explore limiting thickness of NF membrane.
- Membrane thickness and surface roughness increased with support of decreased pore size.
- High-flux membrane of 94 l·m⁻²·h⁻¹ with moderate 84% MgSO₄ rejection.
- High-selective membrane of 92% MgSO₄ rejection with moderate flux of $24 \text{ l} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$.

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1. Introduction



ABSTRACT

A systematic study was carried out to explore limiting thickness of the state-of-the-art nanofiltration membrane. The interfacial polymerization between aqueous solution of piperazine and organic solution of trimesoyl chloride over polysulfone ultrafiltration supports of average pore size 20, 100 and 200 nm, respectively had been performed to vary the membrane thickness and properties. The prepared membranes were designated as TFC-12, TFC-15 and TFC-24, respectively. Influence of the supports on membrane thickness, surface roughness and potential was observed by SEM, AFM, ATR-IR and zeta-potential measurements. The membrane thickness and surface roughness were found in increasing order of TFC-12 < TFC-15 < TFC-24. When tested for desalination of brackish water of 2000 ppm NaCl or 1000 ppm MgSO₄ at 150 psig, TFC-24 exhibited the highest salt rejection efficiency but the least flux of 26 $1 \cdot m^{-2} \cdot h^{-1}$ while the flux was enhanced to about 94 $1 \cdot m^{-2} \cdot h^{-1}$ but with lesser salt rejection for TFC-12 which was in agreement with the differences in membrane thickness and roughness. The results indicated a trade-off performance relationship for the nanofiltration membranes that the membranes of high-flux with moderate selectivity or high-selectivity with moderate flux could be prepared by varying supports from a same preparation condition.

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The pressure-driven separation processes based on polyamide– polysulfone thin-film-composite (TFC) membranes are already successful approaches for satisfying water demands required for domestic, agricultural and industrial uses throughout the world. It is economical, safe and an alternative to energy-intensive conventional processes. The present challenge is the preparation of the thin-film-composite membranes with a very thin active layer. This is of utmost importance as the fabrication of the membranes in the form of thin film as thin as possible over a porous support is highly desirable because the thin membrane film will allow optimal transport of molecules while the support will provide mechanical strength. A.P. Rao et al. [1] prepared several poly(*m*-phenylenediamine trimesamide)-polysulfone TFC membranes using semi-automatic casting and coating units in which the polyamide layer thickness could be varied from about 160 to 280 nm. It was observed on their study that dependence of water flux on polyamide film



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thickness as an inverse correlation trend, that, for the same salt rejection membranes, the permeate flux was more for those membranes which had a lesser film thickness. It was also observed from a detailed characterization studies performed on membranes of a large-scale preparation (1 m breadth \times 90 m length) [2], that the polyamide film structure might have a range of network structures with varied macromolecular structural units depending on the ratio of linear polymer chain network having – COOH groups and cross-linked networks of – CONH-linkages, and that this structural variance in macromolecular chains mainly resulted in salt rejection variance which was in consistent with zeta-potential of membrane surface which showed a higher negative potential for the higher performing membrane that had polyamide network structure with more of pendant COOH group.

The changes in the structure and composition of the polyamide film influenced the membrane performance both in terms of the salt rejection and water flux. While poly(*m*-phenylenediamine trimesamide)-

polysulfone TFC membranes are useful for RO process applications, the poly(piperazinetrimesamide)-polysulfone TFC membranes are useful for nanofilitration (NF) process applications. We reported earlier [3] that the different surface pore sizes (70 and 150 nm surface pore size average) of polysulfone support could affect the formation of the different types of TFC RO polyamide membranes. Similar studies of the porous polysulfone support effects on preparation of different TFC RO membrane types were also reported by others [4] in which the supports had average pore size in the range of 30-70 nm with different physicochemical properties. Further, it was reported [5] that the effect of supports of 40–90 nm pore size on preparation of different types of TFC NF membranes in which the top polyamide layer formed was about 1 μ m thick. It exhibited flux of $15-25 \text{ l}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ when tested for an aqueous feed of 1000 ppm Na₂SO₄ or MgSO₄ with only a slight change in the salt rejection efficiency (~95% Na₂SO₄ and ~87% MgSO₄ for all the membranes) even though there were differences in physical



Fig. 1. Top surface SEM images of the TFC membranes, TFC-24 (A), TFC-15 (B) and TFC-12 (C).

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