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Research Highlight

Air-infused superwetting membrane for solute separation

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Membranes, including those that are based on nanofiltration and reverse osmosis (RO), have become important components of systems used for efficient removal of ions and small molecules from water. Nanopore containing nanofiltration membranes are employed to separate divalent ions and >200 g mol^{-1} molecules utilizing size- and charge-exclusion mechanisms. In contrast, RO membranes, which possess transient pores and allow pressure gradient driven water passage, retain even monovalent ions [1]. However, both membrane types are severely limited by a trade-off between high water permeability and separation efficiency.

Surface wettability, which depends on interactions between a solid surface and liquid or gas phase, has been widely explored as a factor governing membrane separation performance in terms of water permeability, selectivity and antifouling [2]. Hydrophilic modification of membrane surfaces has been shown to increase water permeability owing to an enhancement in the affinity of channel walls to flowing water. Because the stable water layer formed on channel walls efficiently inhibits adhesion of hydrophobic contaminants, these modified membranes have an excellent antifouling capability [3]. However, the intrinsic properties of these membranes, such as pore structures, still govern rejection levels toward various solutes. Thus, using thinner membranes or applying high pressures results in poor water-solute selectivity.

Membranes integrated with a strongly interacting trapping phase that is not miscible with the species being separated have been designed to more selectively control mass transfer [4–7]. For example, introducing a low-surface-energy liquid like perfluoropolyether into pores of a hydrophobic membrane, such as polytetrafluoroethylene (0.2–20 μm pores), gives rise to a gated transport system [4]. Specifically, in systems of this type, liquid-gated pores can open and close in response to pressure, thereby enabling control over selective transport and retention of species. Moreover, these liquid-infused membranes have the capability to separate three-phase air–water-oil mixtures while sustaining their antifouling properties. Also, they can serve as selective barriers to isolate aqueous donor and acceptor phases, separate analytes from a complex system, and control unidirectional solute transfer through an asymmetric superwetting interface [6]. Hydrophilic polypyrrole-coated metallic mesh infiltrated with $LiClO_4$ aqueous solution for air purification can separate particulate matter and pollutant molecules from air [7]. Obviously, these new membrane-based separation systems, which do not function using a size-sieving mechanism, no longer suffer from the limitation caused by the permeability-selectivity trade-off.

The strategy based on liquid-infusion can be extended to the design of air-infused membranes for water purification. In systems of this type, a stable air layer trapped in micro- or nano-hierarchical structures on superhydrophobic surfaces efficiently blocks permeability of solute-containing water. In a recent work [8], Straub and colleagues reported that pressure-driven distillation occurs in air-infused membranes through a pathway involving sequential evaporation, gas-phase diffusion and condensation (Fig. 1). These membranes nearly completely block passage of salts and small neutral molecules, while they have high water permeabilities by decreasing the air layer. Owing to protection by the air layer serving as the separation barrier, excellent desalination performance is ensured even when the system is exposed to oxidants like chlorine and ozone.

The air-infused membranes prepared by Straub and colleagues are composed of a porous anodic aluminum oxide (AAO) substrate and a superhydrophobic coating confined to a submicrometer layer on the top channels of the membrane. Precise positioning of the coating is accomplished by using a sequence involving masking, metal sputtering and surface modification with a fluorinated alkylsilane. The results of spectroscopy and microscopy studies demonstrate that the new membranes contain the low-surface-energy modifier and uniform pore diameters that duplicate those of the initial AAO substrate. Importantly, the superhydrophobic coating on the surfaces of the membranes completely resists water wetting and enables formation of a highly stable air layer, while the bottom superhydrophilic channels readily capture water molecules.

The sub-100 nm pore size air-infused membrane has a liquid entry pressure of 12.1 bar, at which water replaces the air layer infused in the channels. Below this pressure, water flux increases in a manner proportional to the hydraulic pressure and reaches 88.0 kg m^{-2} h^{-1}, indicating that pressure-driven water vapor flow is taking place. Owing to the occurrence of a liquid-to-gas phase

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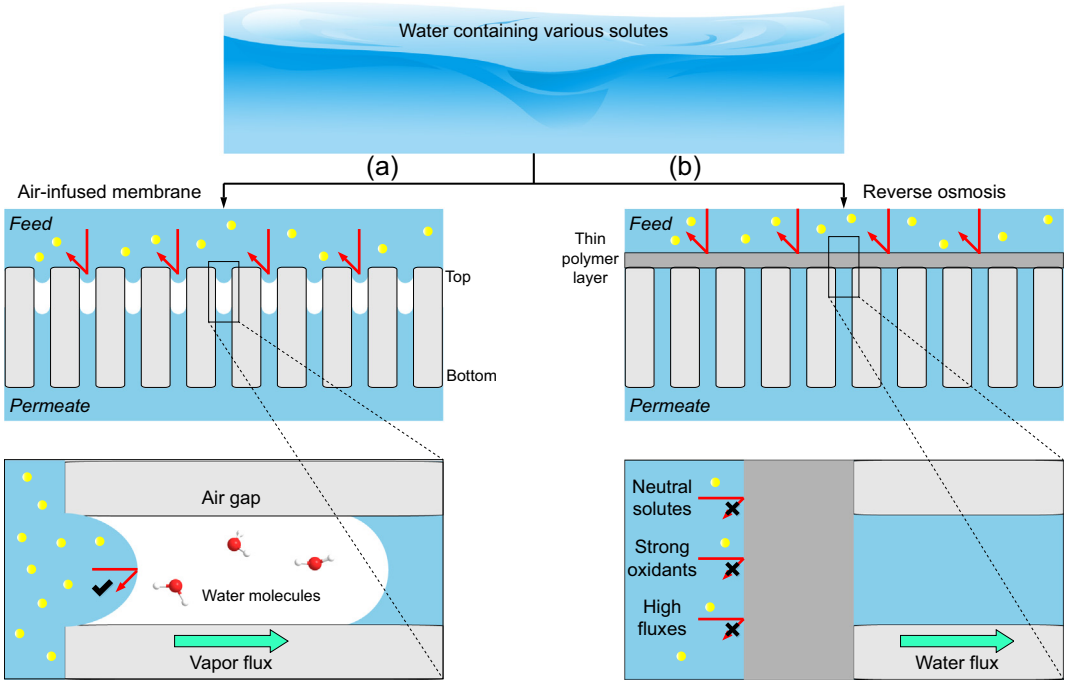

Fig. 1. (Color online) Illustration of possible pathways for separation of solutes from water. (a) Air-infused membranes operating via pressure-driven water vapor transport. (b) RO membranes are restricted by a permeability-selectivity trade-off.

change, the air-infused membrane nearly completely removes dyes such as allura red AC (Stokes diameter of ca. 1 nm). The level of salt retention by the membrane in a 50 mmol L^{-1} NaCl aqueous solution is higher than 99.8% after a 24 h separation period, which results in generation of permeates that have very low conductivities. Moreover, the membrane maintains high salt rejection and water flux over a 7 d separation period.

Both air-infused and conventional RO membranes display increased water permeability when their thicknesses are decreased. State-of-the-art RO membranes have decreased salt rejection levels with decreasing thickness as a consequence of a compromise between water permeability and salt rejection. In contrast, the air-infused counterpart experiences an increase in water permeability reaching 8.9 kg m^{-2} h^{-1} bar^{-1} while maintaining a high 99% salt rejection capacity. Moreover, Straub and colleagues found that latent heat transfer by water vapor flowing through the infused air layer has a negligible influence on water permeability. Also, the results of theoretical simulations show that these membranes function under near isothermal conditions. Finally, energy consumption by the air-infused membranes is comparable to that of a RO, although the origin of the pressure-driven distillation mechanism and importance of bottom superhydrophilic channels are unclear [6,9].

As selective barriers, air layer-based membranes display mass transfer behaviors that differ from those of thin polymer film-based RO membranes (Fig. 1). RO membranes typically do not separate small neutral molecules. This phenomenon is exemplified by a polyamide RO membrane which retains less than 50% of boric acid, urea and N-nitrosodimethylamine. In contrast, the new air-infused membranes almost completely (>95%) separate most of these small neutral molecules. Furthermore, upon exposure to high levels of chlorine and ozone, which are typically components of large-scale water treatment processes, RO membranes achieve less than 20% salt rejection and they display highly variable water flux levels. In contrast, owing to protection provided by the trapping air layer, the air-infused membranes maintain >99% salt rejection propensities and high-water flux levels when these strong oxidants are present.

Fabrication of air-infused membranes is greatly benefitted by the availability of porous AAO substrates that have controllable pore sizes and thicknesses, and well-developed surface modification techniques. The enhanced availability of superhydrophobic membranes, especially those constructed from one- and two-dimensional materials, as well as numerous state-of-the-art membrane-forming techniques should lead to increasing opportunities for development of the water purification membranes with tailored pore sizes and air layer thickness, as well as asymmetric superwettabilies. Challenges associated with implementation of air-infused membranes include the stability of the trapped air layer and current level of knowledge about the pressure-driven distillation mechanism. Water-air-membrane three-phase interfaces are vulnerable to low-surface-energy foulants in the water samples. *In situ* monitoring techniques are also required to probe the dynamic water evaporation process at the three-phase interfaces.

The seminal investigation by Straub and colleagues demonstrated that pressure-driven distillation, occurring in air-infused membranes, can facilitate separation of a variety of contaminants in water without suffering from limitations associated with the permeability-selectivity trade-off. It is anticipated that this finding as well as other observation made in the effort will stimulate future studies of interfacial mass transfer in phase-infused membrane systems. Trapping phases in systems of this type can be air, water, oil, and polar and nonpolar liquids. Surface energy matching between the trapping phases and membranes facilitates formation of a stable and selective barrier. Interaction between target molecules (or interferent) and the trapping phase can selectively control mass transfer. We believe that the interfacial optimization strategy can be used to design new separation systems for purification of air, and polar and nonpolar liquids.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

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