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Opinions on the Development of Ultrahigh Permeation Membranes

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ABSTRACT

In this work, recent progresses made in the development of membranes with ultrahigh permeation rate for reverse osmosis (RO) and membrane distillation (MD) are briefly summarized and the future prospect of those membranes is discussed. In fabrication of ultrahigh permeation RO membranes, carbon nanotube, aquaporin, graphene and fluorous oligoamide nanorings were used and in all of them several orders of magnitude higher fluxes than the conventional commercial membranes were achieved. Ultrahigh MD membranes were fabricated mostly from carbonaceous materials also with several orders of magnitude higher fluxes than conventional commercial membranes, except for those made of ultrathin polymeric material, which demonstrated a high flux at a low transmembrane temperature difference. Despite these remarkable achievements, it was concluded that many challenges would be encountered to produce a sufficient amount of water by the so-called membrane chips.

Keywords: Ultrahigh permeation membranes, Reverse osmosis, Membrane distillation, Membrane chips, Future prospect

1.0 RO MEMBRANES

The first commercial RO membrane was developed by Loeb and Sourirajan using cellulose acetate as the membrane material in nineteen sixties. Later in nineteen seventies, Cadotte developed thin film composite polyamide membranes based on interfacial polymerization and now these membranes are dominant in the commercial market. However, since the fluxes of the membranes are limited for polymeric materials due to the flux-selectivity trade-off rule, attempts have been made to increase the flux of RO membranes by orders of magnitude using non-polymeric materials.

1.1 Membranes based on Carbon Nanotube

Hummer *et al.* [1] and Kalra *et al.* [2] made molecular dynamics simulations (MDS) of water transport in single-walled carbon nanotubes (SWCNTs) in 2001 and 2003, respectively. The simulation predicted permeation rate of 5.8 water molecules per ns per CNT [2]. Inspired by these results, Holt *et al.* in 2006 made micro-fabricated membranes to show that the water permeation rate was 3 orders magnitude higher than the value predicted by the Hagen-Poiseuille equation [3]. The measurement of water flow rate through CNT was also made via the stopped-flow technique by Li *et al.* in 2020 [4]. The obtained flow rate was slightly higher than Tunuguntla *et al.*'s data [5].

Since the Science paper of Holt *et al.* was published, many attempts have been made to fabricate industrially viable carbon CNT-based membranes [3]. Because of difficulty to make membranes of large sizes employing

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CNTs alone, those attempts were made by the development of nanocomposite (TNC) membranes, in which carbon nanotubes (CNTs) were embedded in aromatic polyamide thin-film composite (TFC) membranes.

Examples are the works of Cruz-Silva *et al*. [6], Lee *et al*. [7], Kim *et al*. [8], Zhang *et al*. [9], Inukai *et al*. [10], Kim *et al*. [11] and Zhao *et al*. [12]. All of them have reported improvement of RO membrane performance, in terms of durability, antifouling capacity, flux and mechanical strength. For example, Inukai *et al*. [10] reported that the flux could be almost doubled by incorporating MWCNTs in polyamide membrane while maintaining selectivity for NaCl. The more recent development of CNT-related membranes is summarized in the review paper of Kumar *et al*. [13].

1.2 Biomimetic Membrane

MDS revealed that the water permeability through an aquaporin pore is 10^8-10^9 water molecules/s [14]. The water permeability of aquaporin was then measured by the stop-flow method by Hovijitra *et al*., resulting in good agreement with MDS [15]. Kumar *et al*. [16] and Tang *et al*. [17] postulated that AqpZ-based biomimetic membranes can potentially achieve a water permeability as high as 601 L/m^2.h.bar (or LMH/bar), which is 2 orders of magnitude higher than the currently available commercial membranes. Zhao *et al*. [18] fabricated an aquaporin-based biomimetic membrane via the interfacial polymerization method. The membrane with an area greater than 200 cm^2 had good mechanical stability and the performance was better than commercially available membranes. A typical example of experimental data obtained by a laboratory made membrane is water permeability (~4 LMH/bar) with comparable NaCl rejection (~97%) at an applied pressure of 5bar. Its permeability was ~40% higher compared to a commercial brackish water RO membrane (BW30) and an order of magnitude higher compared to a seawater RO membrane (SW30HR). Li *et al*. [19] also fabricated aquaporin incorporated TFC membrane. The membrane exhibited a stable water flux around 20 LMH and 99% NaCl rejection at a constant pressure of 55 bar using 32,000 mg/L NaCl solution. The flux was 80 % higher than the commercial SW30RT membrane. A Danish company known as Aquaporin is manufacturing flat sheet and hollow fiber membranes for RO and forward osmosis (FO) based on their technology called Aquaporin Inside [20].

1.3 Membranes based on Graphene and Graphene Oxide

Cohen-Tanugi and Grossman made a MDS of the water and NaCl transport through nanopores of graphene [21] and showed that graphene membrane allows the permeability of as high as 2000 LMH/bar with perfect NaCl rejection, which is several orders of magnitude higher than the conventional RO membrane. Membranes with a graphene domain of 5 μm diameter were then fabricated by oxygen plasma etching of graphene grown by chemical vapor deposition [22]. The membrane with the lowest defect exhibited 100% salt rejection with very high fluxes at both RO and FO conditions. The area of single-layer graphene was increased to cm-scale by O'Hern *et al*. [23]. The membrane demonstrated nanofiltration (NF) capacity when the experiments were conducted by FO.

According to the latest news [24], Clean TeQ Water (ASX:CNQ) subsidiary, NematiQ, is now able to fabricate 1000 m of 1000 mm wide flat sheet graphene membrane by roll-to-roll coating. The membrane is called nanofiltration membrane but seems more like ultrafiltration membrane. Akbari *et al*. [25] cast liquid crystals of graphene oxide (GO) on a nylon sheet using a casting blade. The membrane area was as large as 13 x 14 cm^2. The membranes showed nanofiltration performance with flux 10 times as large as commercial NF 270 membrane. Zhang *et al*. [26] exfoliated GO nanosheet by sonication, which was then functionalized by sulfonation and mild reduction. The membrane also showed nanofiltration capacity.

1.4 Membranes based on Fluorous Oligoamide Nanorings ($^{Fm}NR_n s$)

Itoh *et al*. [27] synthesized a series of fluorous oligoamide nanorings that underwent supramolecular polymerization in phospholipid bilayer membranes to yield nanochannels with different interior diameters and the interior walls which are densely covered with fluorine atoms. The water permeation rate was also calculated by MDS and experimentally determined by the stopped-flow fluorescence method. Flow rate per channel was said to be higher than those of aquaporin and carbon nanotube.

2.0 MEMBRANE DISTILLATION (MD) MEMBRANE

Recently a number of papers have been published on the ultrahigh flux MD membranes. Most of them were made of carbonaceous materials such as carbon nanotubes, graphene and graphene oxide. Examples are the reports of Chen *et al*. [28] on a layer of porous carbon structures, Gon *et al*. [29] on graphene composite membrane, Sun *et al*. [30] on carbon nanotube network membrane, Lu *et al*. [31] on nanoporous graphene membrane and Chen *et al*. [32] on GO nanosheet. All of them were with vacuum membrane distillation (VMD), except for Lu *et al*. [31] who worked with direct contact membrane distillation (DCMD).

Most recently, Chen *et al*. [33] prepared the submicrometer-thick and nanopore-structured graphdiyne membranes on porous Cu hollow fbres. They claimed that their membranes were better than graphitic membranes that had been fabricated before them.They also reported ultrahigh DCMD flux. It should be noted that all of these membranes are made of carboneceous materials with nano-sized pores to take advantage of slippery pore wall, but the sizes are too large for RO membranes.

On the other hand, Qtaishat *et al*. [34] reported ultrahigh flux membranes for DCMD using non-carbonaceous materials. According to their method, a thin layer formed by the reaction of 1H,1H,2H,2H perfluorododecyltrichlorosilane (FTCS) and m-phenylenediamine was transferred to an anodic substrate. Due to the enhanced vapor pressure of water in nanosized capillaries, the membrane showed a high water flux (ca 40 LMH) even when the feed and permeate temperaute were 25 and 20°C, respectively.

3.0 OPINIONS

The development of ultrahigh flux membranes for RO and MD is summarized in Table 1.

Table 1 Summary of the development of ultrahigh flux membranes

Name	Year	Events	References
RO			
Carbon nanotube			
Hummer *et al.* and Kalra *et al.*	2001,2003	MDS, water transport in SWCNTs	[1,2]
Holt *et al.*	2006	Experiments with double-walled carbon nanotubes (DWCNTs) of sub-2-nm	[3]
Li *et al.*	2020	Experiments with stopped-flow technique	[4]
Cruz-Silva *et al.*	2016	Chlorine resistant nanocomposite membranes with MWCNTs	[6]
Lee *et al.*	2011	Review article on CNTs embedded membranes	[7]
Kim *et al.*	2014	Acidified CNTs embedded in TFC membrane	[8]
Zhang *et al.*	2011	Acidified MWCNTs embedded in TFC membrane	[9]
Inukai *et al*	2015	Anionic surfactant stabilized MWCNTs in TFC membrane	[10]
Kim *et al.*	2015	Nanocomposite membranes containing the mixture of carbon nanotubes and graphene oxides	[11]
Zhao *et al.*	2014	MWCNTs incorporated in polyamide RO membrane	[12]
Kumar *et al.*	2020	Review on nanocomposite membranes for desalination	[13]
Biomimetic membrane			
Jensen and Mouritsen	2006	MDS performed on water permeation in aquaporin	[14]
Hovijitra *et al.*	2009	Water permeability measured by stop-flow method	[15]
Kumar *et al.* and Tang *et al.*	2007, 2013	Prediction of high water permeation by aquaporin based biomimetic membranes and the future prospects	[16,17]
Zhao *et al.*	2012	Fabrication of aquaporin incorporated TFC membranes	[18]
Li *et al.*	2019	Fabrication of aquaporin incorporated TFC membranes	[19]
	2022	Information on commercial Aquaporin Inside	[20]
Graphene and graphene oxide			
Cohen-Tanugi and Grossman	2012	MDS on water and salt transport through graphene	[21]
Surwade *et al.*	2015	RO experiments with graphene size of 5 μm	[22]
O'Hern *et al.*	2015	Membrane size is increased to cm-size	[23]
	2022	News on commercial scale graphene membrane	[24]

Akbari *et al.*	2016	Graphene oxide (GO) membrane for NF	[25]
Zhang *et al.*	2016	GO nanosheet sulfonated and reduced for NF	[26]
Fluorous oligoamide nanorings			
Itoh *et al.*	2022	MDS and stop-flow experiment for water permeation	[27]
Membrane distillation			
Carbonaceous materials			
Chen *et al.*	2018	Report on MD by a layer of porous carbon structure	[28]
Gong *et al.*	2021	Graphene composite membrane with 2D nanochannels	[29]
Sun *et al.*	2022	Carbon nanotube network membranes	[30]
Lu *et al.*	2022	Nanoporous graphene membrane	[31]
Chen *et al.*	2021	Graphene oxide nanosheet	[32]
Chen *et al.*	2023	Fabrication of graphdiyne membranes	[33]
Non-carbonaceous materials			
Qtaishat *et al.*	2022	Thin layer of FTCS polymerized with MPDE with high flux at low temperature	[34]

3.1 RO Membranes

A common pattern is found in the development of ultrahigh flux RO membranes. All of them, except for fluorous oligoamide nanorings, begin with the discovery of the material by Nobel laureates. Then, the development is made by the following steps.

1) MDS of water transport is performed.
2) Water flow rate measurement through the nano-sized cylinder via the stopped-flow method.
3) Miniature-sized membrane is made and ultrahigh flow rate is confirmed.
4) Membranes of the cm-sized area are fabricated for filtration experiments.
5) Upon achieving successful results in 4), a module is constructed for the pilot scale experiments.
6) The membrane is commercialized.

Among those the results from step 1) to 3) are reported in high impact factor journals.

Even though there are some exceptions in sequence, the above steps are followed in most cases. Until now, only aquaporin and graphene reached Step 5. Aquaporin membrane has reached even step 6 but its application is mainly for FO. Considering the 17 years that have passed since the announcement of the CNT-based membrane in 2006, the progress is very slow.

Giwaa *et al.* [35] commented on the following challenges for the development of large-scale aquaporin membranes, which seem applicable to all other ultra-high flux membranes.

1) Production of a large quantity of aquaporin
2) Long-term stability of the aquaporin membrane
3) Good compatibility between aquaporin and the host membrane
4) Chemical cleaning of the membrane

In addition, there may be some other challenges such as,

1) Vertical alignment of nano-sized cylinders in the membrane
2) Reproducibility of filtration performance
3) Environmental issue of the release of nanoparticles into drinking water, even a very small amount

Hence, there are many risks to be taken into account, before ultra-high flux membranes enter into the commercial market.

1.3 MD Membranes

All of the works on MD membranes of ultrahigh flux were done with laboratory-scale filtration experiments. Therefore, the filtration data seem more realistic to be used for the fabrication of industrial scale membranes. However, growth of carbonaceous layer on a substrate is challenging. Besides, very high thermal conductivity of carbonaceous materials (few thousand W/m.K as compared to 0.1 to 0.3 W/m.K of polymeric material) will cause high conduction heat loss. To prevent the heat loss, VMD is applicable, which however is not necessarily an economical MD process. Moreover, even when the flux is very high, the process requires the supply of sensible and latent heat to produce a given amount of produced water and its recovery will be an issue, anyway. For the membrane operable at a low feed temperature, the recovery of the latent heat will also remain an issue.

Moreover, the membrane pore wetting has to be overcome before large scale MD application for seawater desalination becomes commercially successful. Thus, it looks extremely challenging to achieve such a dream as to produce a large amount of water by a membrane chip.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper.

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