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# ARTIFICIAL WATER CHANNELS – TOWARD BIOMIMETIC MEMBRANES FOR DESALINATION

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**Abstract** - Natural systems have evolved for millions of years to transport metabolites across the cell membranes. Among them, Aquaporins (AQPs) are biological channels known for fast water transport with ion exclusion. AQPs can be mimicked using simpler artificial water channels-AWCs to explore the naturally evolved water transport in artificial systems and to assess the basis for biomimetic desalination processes. Selective water translocation has been shown to depend on water-wires spanning the pore that induce dipolar orientation. Toward this objective, AWCs combining a particularly broad range of self-assembling features: H-bonding, water recognition, hydrophobic effects, etc. This might play an important role in the ability to finely control the hydrophilic or hydrophobic the constitutional domains of the channel responsible, for selective recognition and high-water translocation, respectively. Densely packed AWCs incorporated within TFC polyamide membranes will lead to a greater fundamental understanding on how selective pores can be optimized at the nanoscale to facilitate ultrafast and highly selective transport of water for the treatment of saline feed streams. Future routes to robust desalination membranes including AWCs will solve pressing challenges, such as the stability, scalability and fabrication of membrane for water desalination, ultrapure water production and the storage of clean energy applications

Universal access to safe drinking water is a fundamental need and human right. [1] Competition over increasingly contaminated freshwater during the last decades has made the availability of this resource a serious global challenge for the 21st century. Water scarcity and the problems associated with the lack of the clean water are well known. Because oceans hold 97.5% of the total water in our planet, [2] desalination is considered as one of important solutions to problem of freshwater scarcity, along with environmental remediation technologies and conservation policies. Currently, about 100 million m<sup>3</sup>/day of desalinated water is being produced, with an annual increase of more than 10% [3].

To address the increasing demand for water supply, several cutting-edge technologies have been explored during the last decades.[4] Current technologies are based on thermal processes (Multi Effect Desalination – MED or Multi Stage Flash- MSF) and membrane processes (Reverse Osmosis-RO, Electrodialysis-ED, Membrane Distillation-MD and Forward Osmosis-FO), with RO being the dominant process used for seawater or brackish water desalination. [5] Most of the RO membranes relies on an anisotropic polymerized thin-film composite (TFC) polyamide-PA layer produced by interfacial polymerization on an underlying porous support layer, commercially available polysulfone, all integrated into spiral wound modules for fitting in pressure vessels [6]. Current Reverse Osmosis-RO desalination can produce water at < \$ 1/m<sup>3</sup>, which is about 5 times the cost of treated surface water. Energy use has dropped but is still about twice the thermodynamic minimum required when operating at 60% recovery, is around 1.2 kWh/m<sup>3</sup> and this value increase above 1.5 kWh/m<sup>3</sup> at 80% recovery. [6] Closed-circuit RO will soon allow operating at these high recovery regimes but with higher minimum energy requirements. There is need for membrane innovation. The target of the future membrane is to increase both the water permeability while achieving high salt rejection. As pointed out recently, in many cases selectivity matters as much if not more than permeability. Efficiency may increase in the coming years by changing the process conditions, or by changing the membranes. [7]

The RO desalination, using thin-film composite-TFC membranes, has evolved over the years bringing down the costs significantly. [8] But, the desalination is still relatively expensive. More than half of a century has passed since the first functional RO membrane was designed. [9] New materials bearing promise for higher productivity in desalination have been developed in recent years, consequentially leading to the emerging research fields of thin-film nanocomposites-TFN [10] and biomimetic

membranes [11]. Recent research propose to find an easily scalable Artificial Water Channels AWC approach that could be immediately applied to desalination systems to increase their energy efficiency.

**Natural water channels –toward bio-assisted Aquaporins-embedded membranes.** Natural systems have evolved for millions of years to accept functional biostructures to transport metabolites across the cell membranes. Most of natural physiological processes depend on selective exchanges between a cell and its environment and water is playing an important role. The natural water channels, the Aquaporins (AQP) are known for their fast transport rates ( $\sim 10^8$ - $10^9$  water molecules/s/channel) and the perfect rejection of ions. [12] Due to its energy efficiency, membrane technologies start to adapt the AQP water purification technologies. [13] The high permeability / selectivity of AQPs inspired their incorporation into membranes for water-purification applications. This way, a new branch of membrane technologies for water purification called AQP bioassisted membranes was developed. As so it was an attractive option to combine the potential of the AQPs with the current existing technology in membrane-based water filtration. As soon as the functions of the AQPs became know, it seems logical that in order to make use of its high selectivity and water transport, the protein need to be used in conjunction with a membrane barrier. Their large-scale applications it is of interest, owing to the high costs of the AQPs production, low stability and practical synthetic constraints of membrane fabrication processes. In the simplest fashion these membranes consisted of three main components: i) AQP proteins ii) amphiphilic molecules as building blocks for the construction of protecting liposomes in which the AQPs are embedded and iii) a polymeric support for mechanical resistance. The choice for the amphiphilic molecules is argued for by the fact that the AQPs are transmembrane proteins and their native environment is partly the hydrophobic region of the lipids found in cellular membranes, meanwhile keeping the “mouths” of the protein exposed to the water from the cytosol. As such, a first reasonable strategy was to fabricate membranes having an active barrier a lipid bilayer containing AQP for the enhanced water permeation. It was shown showed that the supported lipid bilayer (SLBs) membranes are suitable impermeable platforms for incorporation of AQPs for water filtration. However, no reliable results have been obtained with such AQPs/ bilayers. In a compromise to obtain high stability and relatively good performance bio-assisted membranes a different synthetic strategy was applied by using a mix-matrix approach, when bilayer vesicles incorporating AQPs has been incorporated into traditional polyamide thin films [14]. This way the AQPs can maintain their efficiency having a basically native lipid membrane environment and at the same time, having minimal defect influences on the composite membrane in interaction with the polyamide matrix (Figure 3). The hybrid AQP-PA based membranes proved to be 40% permeable than their simple thin film composites (TFC) counterparts, meanwhile being stable for periods relevant for industrial applications at a lower energy consumption and operating cost. [15]

Most of the current designs for AQP membranes involve polymeric host materials, which can make it viable for upscaling and use in industry. Active high flux AQP membranes, became the commercially available products. Production of AQP proteins is a feasible task since biological protocols and reagents are used, but the purification setup still represents an expensive and time-consuming obstacle. The question ‘how the natural proteins /artificial host matrix systems can be efficiently used together’ has been thus partially answered. [26-28] However, no clear strategies converge to the easy synthetic development of robust AQP *bio-assisted reverse osmosis (RO) or Forward osmosis (FO) membranes*, working at high pressure and high salt concentrations, incompatibles with biological AQPs. Most importantly, today not readily usable AQP-based membrane exists for desalination.

They are many challenges to use the AQP as selective transporters related to their:

- a) Long term stability when embedded in artificial membranes;
- b) Bio-stability and unconventional processing requirements: high pressure and salinity;
- c) Production - membrane proteins are challenging to mass produce;
- d) AQPs present an important flux, but not an acceptable permeability per active area, the selectivity is not reaching more than 97%, a critical problem for desalination.

A possible way forward is to replace AQPs with synthetic channels. Recent advancements have made it possible to synthesize artificial water channels-AWCs that feature efficient, yet selective transport of water based on size exclusion and H-bond clustering at the molecular level. [16] Another of the current disadvantages of biomimetic AQPs membranes is the low density of water channels per unit area of  $\sim 40$  channels/ $\mu\text{m}^2$ .

**Why are Artificial Water Channels important?** Biomimetics or biomimicry is the science behind mimicking the well-tuned natural processes. Nature should provide answers for efficient desalination. A possible way forward is to replace AQPs with synthetic AWCs. Ion-rejecting, highly permeable artificial *biomimetic* channels may provide a route to producing highly efficient membranes for separations, particularly desalination. In practice, there is currently no economically viable RO membrane on the market! Therefore, there are incentives to further reduce cost and energy use for desalination as it becomes more widespread. Recent advancements have made it possible to synthesize AWCs that feature efficient transport of water. AWCs exhibit the following potential advantages: a) they are easily tunable and may be chemically optimized for desirable properties; b) they can be prepared on a large scale at low cost; c) Engineering processing without bio-related steps becomes simpler and more reproducible; d) they should also be robust with a longer lifetime into membranes.

Within this context, the next impact may be related to increase the incipient potential, imagining that high water conduction activity obtained *with* natural AQPs can be bio-mimicked using simpler compounds that can display functions *like* the natural ones, the *Artificial water channels-AWCs*, using synthetic biomimetic approaches. AWCs have been recently proposed as a biomimetic AQPs. [17,18] They are constructed from artificial molecules defining a water-pore superstructure, surrounded by a hydrophobic exterior accommodating the membrane environment. [17-23] Within this context, mimicking AQPs by using simple AWCs is an important endeavor from both a) the fundamental science perspective related to the deeper understanding of water structure and b) its transport function and applied science perspective as AWCs might have timely impact on increasing water filtration efficiency by using natural principles to change the desalination paradigms. *Artificial ion-channels* have been extensively developed for decades (thousands of papers in literature) with the hope to mimic the ionic conduction of natural proteins. Amazingly, there was no systematic and little progress in the area of *Artificial water channels* before 2011. [16]

**Where are we now? Where are we going in this newborn field?** The target of the future membrane is to increase both the water permeability by 3 to 5 folds of the currently best TFC membranes while achieving/maintaining 99,9% salt rejection. As pointed out recently in many cases selectivity matters as much if not more than permeability. Next research might provide answers to essential question related to: a) complicated interactional scenarios related to water transport through biomimetic pores; b) bio-inspired desalination with membranes that mimic mechanisms of natural desalinators. Simpler architectures encapsulating water may provide excellent and valuable models for understanding/ novel biomimetic water channel systems. Although there is a rich inventory when it comes to molecular encapsulation of water, in most cases the host systems are highly polar which prohibits them to be used in conditions similar to the one offered by the membrane to AQPs. As so, the development of the AWCs is highly important. The first synthetic water transporting systems have been reported in 2011 [17] and the term of *Artificial water channels* has been coined practically one year later [18]. The common features of the AWCs are the presence of a central pore, which is a confining hydrophilic or hydrophobic region that allows the passage of water, and a hydrophobic shell that permits the insertion into the lipid membranes and subsequent analysis for water transport. There are main approaches towards designing these systems:

- *Single molecular channels*, as one molecular entity that can span the length of the bilayer;
- *Self-assembled supramolecular channels* that can self-assemble from multiple molecular components into architectures spanning the bilayer.
- *Nanochannels* related to Carbon Nanotubes and GO materials and membranes

**Single Molecular Channels.** The pillar[5]arenes, PAPI are the first reported single molecular channels [24]. Intramolecular H-bonds between lateral hydrazide arms confer robustness, keeping the membrane spanning channels intact, when inserted into a lipid bilayer. PAPI have a relatively low water transport rate: up to 40 molecules of water/s/channel. Like in AQPs, PAPI display water selectivity against  $H^+$  and  $OH^-$  ions. The explanation for this is the impeded proton hopping through a broken, discontinuous water wire, while the cation transport can be attributed to carrier transport mechanism. Following up on these results a second generation of more hydrophobic pillar[5]arenes,

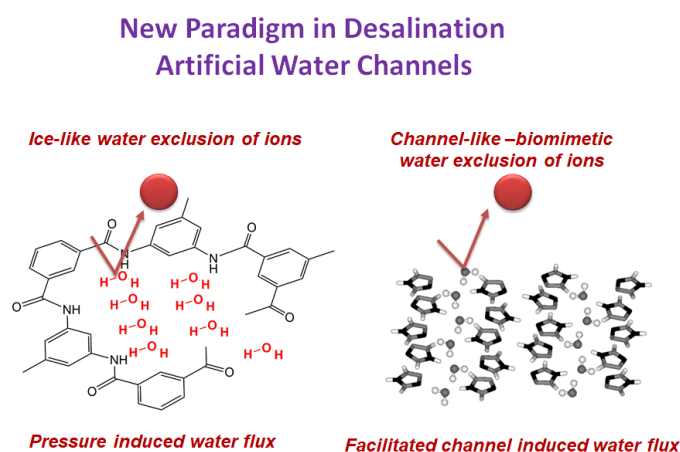
PAP2 containing poly-Phe arms showed a osmotic water permeability of  $3.5 \times 10^8$  water/s/channel [25], being in the range of AQPs and CTNs.

**Self-assembled supramolecular channels.** The second category of AWCs use a non-covalent self-assembly strategy, that often confer the supramolecular channels properties that are not predictable and differ completely from that of their building blocks. Based on this concept it has been reported that AWCs that can self-assembly in tubular imidazole I-quartet channels, mutually stabilized by water wires [21]. They show similar structural features as found in the AQP pores, with a central pore size of  $\sim 2.6$  Å. The water molecules form a single molecular wire adopting a unique dipolar orientation inside the chiral I-quartets. The I-quartet channels are able to transport  $\sim 1.5 \times 10^6$  water/s/channel, which is within two orders of magnitude of AQPs' rates but most important, reject all ions except protons.[34] This ion-exclusion selectivity is important and unique for the AWCs. It is based on dimensional steric reasons, whereas hydrophobic and hydrodynamic effects appear to be less important. Recently, the research on water channels has been pushed a step further showing that a self-assembled "T-channel" is formed with morphological characteristics reminiscent to natural Gramicidin-A [19]. The formation of an aqua-lubricated channel is generated via H-bonding between water molecules and carbonyl groups identical to the carbonyl strings in AQPs.

**Nanochannels.** At the nanolevel, carbon nanotubes-CNTs offer an exciting source of inspiration to mimic natural channels. [26-27] The frictionless water flow is 4–5 orders of magnitude increasing over what would be seen in other conventional nanoporous or AQP structures. Important studies show ion-rejection at low salt concentrations which is promising for applications. In the past few years, membranes based on graphene and graphene oxide (GO) have gained considerable interest for their potential for desalination. [28] The swollen membrane allows any selectivity as water molecules are transported with ions. However, the spacing in a GO membrane can be controlled by physically restraining the membrane from swelling. When interlayer spacing is reduced to 7.0 Å, the ion permeation rate was reduced by two orders of magnitude while the water permeation was only halved.

**Outline beyond state of art:** All these examples studied must restore some balance to our understanding of the biomimicking of natural AQPs and remains an important exploring challenge. These findings show that natural channels can be bio-mimicked using simpler artificial compounds displaying constitutional functions like the natural ones (Table 1).The current research on AWCs is focused on their synthesis, molecular simulations and transport properties in lipid bilayer membranes. The osmotic water permeability of artificial systems ranges from several orders of magnitude lower than that of AQP1, with similar or even better values for Carbon Nanotubes CTNs (Table 1). The two main challenges for AWCs are i) to design tailored channels that reject salt

but allow the easy passage of water molecules and ii) the transfer of the AWCs from the nanomolecular level to that of large-scale membrane materials. Although this has been partly achieved using AQPs, no studies have been reported yet on integrating the AWCs within active layers casted onto membrane supports.



**Figure 1.** RO versus biomimetic artificial water channels for desalination strategies (image adapted with permissions from reference [3]).

Designing stable polymer matrixes capable of keeping AWCs in their active state will prove crucial for future hybrid membranes. The use of lipid bilayers or hydrophobic polymers as host matrixes, which certainly can be affected by the presence of organic solutes or surfactants in water, is not a necessary option. They have been used until now to compare the AWC with AQP One strategy to obtain active layer is to incorporate the AWC networks while forming the Polyamide PA layer of RO

membrane or to imagine new cross-linked polymers in order to obtain networks of AWC within the thin layers. If AWC are covalently attached to TFC, there is no degradation of layer, only temporary channel destabilization. This way the AWCs are dense and highly robust, would be encapsulated in the dense part of the membrane while the PA matrix should be responsible for the rejections of organics. To compete with polymeric reverse osmosis membranes, the current gold standard for desalinating seawater, water flux and rejection rates for artificial water channels need to be very close to that of AQPs. While having even higher flux values will not have a substantial impact on membrane filtration performances, highly water specific membranes will improve the quality of water produced as well as remove unnecessary pretreatment processes. Given the importance of developing even more efficient membranes for desalination, this will be an exciting and challenging project, potentially redefining the paradigms of desalination (Figure 1).

Table 1. Performance overview of artificial water channels (adapted with permission from [3]).

Water Channels	Net Permeability for water / Single channel permeability	Selectivity
Aquaporins – AQPs.	167 $\mu\text{m/s/bar}$ $4 \times 10^9$ water molecules/s/channel	High selectivity for water, perfect rejection of ions/ $\text{H}^+$
Carbon Nanotubes- CTNs Estimated diameter = 15 $\text{\AA}$	300 $\mu\text{m/s/bar}$ , $1.9 \times 10^9$ water molecules/s/channel	-
Carbon Nanotubes- CTNs Estimated diameter = 8 $\text{\AA}$	520 $\mu\text{m/s/bar}$ , $2.3 \times 10^{10}$ water molecules/s/channel	ion rejection in dilute solutions
Hydrophilic I-quartets, channel (2.6 $\text{\AA}$ )	3-4 $\mu\text{m/s/bar}$ $1.5 \times 10^6$ water molecules/s/channel	high selectivity for water, reject all ions except protons
Aquafoldamers, Hydrophilic channel (2.8 $\text{\AA}$ )	No permeability reported	high selectivity for water, reject all ions except protons
Hydropobic peptide tubular macrocyclic pores (6.4 $\text{\AA}$ )	51 $\mu\text{m/s/bar}$ $4.9 \times 10^7$ water molecules/s/channel	no selectivity for water, high conduction for $\text{K}^+$ and $\text{H}^+$
Hydrazide appended Pillar[5]arene, <b>PAP1</b> unimolecular channel (6.5 $\text{\AA}$ )	$8.6 \times 10^{-6}$ $\mu\text{m/s/bar}$ 40 molecules/s/channel	no selectivity for water conduction for alkali cations no conduction for $\text{H}^+$
Peptide appended Pillar[5]arenes, <b>PAP2</b> unimolecular channel (5 $\text{\AA}$ )	swelling: 30 $\mu\text{m/s/bar}$ or $3.5 \times 10^8$ shrinking: 1 $\mu\text{m/s/bar}$ or $3.7 \times 10^6$ molecules/s/channel	no selectivity for water, good conduction for alkali cations
Double helical water T-channels (~2.5-4 $\text{\AA}$ )	No permeability reported	Enhanced conduction states for cations and for $\text{H}^+$
RO membrane	2 $\mu\text{m/s/bar}$	99,8% rejection of salts versus water
FO membrane	2,5 $\mu\text{m/s}$	-
RO membrane	5,3 $\mu\text{m/s}$	-

## Conclusions

The *biomimetic water transport* can solve/improve the performances and life-time of the bio-assisted membrane systems in which highly selective, but labile AQPs are used. In terms of **economic gain** and the **economy of matter** the artificial systems, might represent an interesting alternative. This project, scientifically **challenging and of great fundamental interest**, is leading to pioneering scientific or applicative discoveries, as literature can attest. Biomimetic water transport, fundamental in nature, should allow not only to develop new knowledge and a greater understanding on bottom-up design of multifunctional systems, but also to address different societal challenges. The thin-layer polyamide membranes, used for water desalination since 1972 has improved dramatically over the last 60 years [29], however their low-resolution structure and the transport mechanism are still poorly understood. The ultimate performance of a membrane is usually determined by an increased flux (or permeance) due to the introduction of the defects in the membrane structure lowering the selectivity which is always decreasing. The first identification of Artificial water channels-AWCs, opened the door to new applicative desalination processes close to natural ones. We speculated at this time that biomimetic Artificial Water Channels - AWCs might have timely important influences to increase this driving force for the transport by using natural principles to change the water desalination paradigms.

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