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Development of a bio-mimetic membrane module for desalination of sea-water through forward osmosis (FO) (NST-404-00073)

Concluding report
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Development of a biomimetic membrane module for desalination of sea-water through forward osmosis (FO) (NST-404-00073)

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I dette projekt identificeres de primære teknologiske barrierer, der på nuværende tidspunkt forhindrer brug af en aquaporin-baseret flydende væskemembran til kommerciel afsaltning af havvand gennem direkte osmose. Aquaporin er et protein, der findes naturligt i levende celler. I cellerne anvendes proteinet til at filtrere vand i alt fra bakterier til menneskers nyrer. Den direkte osmose foregår uden at påføre tryk udefra og kan således være en energibesparende metode.

I projektet er det lykkedes at finde frem til egnede membranformuleringer og forbedrede metoder til indkapsling af de flydende membraner. Der er produceret og testet membranprøver og både ydelsen og levetiden for membranerne er øget betydeligt gennem projektperioden.

Membranprøverne er blevet testet med meget gode resultater til brug for NASAs ønske om at kunne genanvende "yellow water" i rummet.

Membranerne er endnu for kostbare til at kunne anvendes i stor skala til afsaltning. I det videre forløb vil der være fokus på denne opskalering.

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Jörg Vogel & Mark Perry
Aquaporin A/S
01.02.2012

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Danish summary

Vi har færdiggjort arbejdspakke 2 i projektet “Udvikling af et biomimetisk membranmodul til afsaltning af havvand gennem direkte osmose (NST-404-00073)”. Afslutningen af arbejdspakke 2 markerer enden på NST-404-00073, hvorfor resten af denne opsummering vil fokusere på de hovedresultater vi har opnået gennem hele projektforløbet.
Vi startede projektet med målet om først at identificere de teknologiske barrierer vedrørende brug af en aquaporin-baseret flydende væskemembran til afsaltning af havvand, og derefter udarbejde en kort liste af flydende membranformuleringer og moduler med potentiale for at bryde førnævnte teknologiske barrierer.
Gennem projektforløbet lykkedes det os ikke alene at udarbejde en kort liste af flydende membranformuleringer og moduler, men også at udvikle en forbedret metode til indkapsling af flydende membraner. Denne metode har løftet vores membranteknologi til et punkt, hvor vi har kunnet producere og teste membranprøver til en rumapplikation i samarbejde med NASA Ames, Moffett Field, CA (US).
Projektets resultater er primært blevet formidlet gennem følgegruppen bestående af vigtige spillere indenfor vandindustrien I Danmark (se kapitel 6). Desuden har Aquaporin A/S deltaget I Singapore Water Week 4-8 juli 2011, hvor teknologien og udviklingen af en membran til afsaltning af havvand blev præsenteret. Vores deltagelse i Singapore Water Week 2011 har resulteret I en indbydelse til at deltage I Singapore Water Week TechXchange workshoppen 2012 I en gruppe af top 6 udvalgte firmaer med muligheden for at præsentere deres teknologi for interessenter indenfor området.

English summary

We have finished work package 2 in the project “Development of a biomimetic membrane module for desalination of sea-water through forward osmosis (FO) (NST-404-00073)”. Work package 2 concludes the scheduled work in NST-404-00073, and the remainder of this summary will therefore focus on our main achievements throughout the entire course of the project.

We set out to first identify the technological barriers for using an aquaporin-containing liquid membrane formulation for desalination of seawater and once identified, come up with a short-list of liquid membrane formulation and modules with the potential to breach said technological barriers.

During the course of this project we succeeded in not only coming up with a short-list of liquid membrane formulations and modules, but also developed an improved method for liquid membrane encapsulation, which lifted our membrane technology to the point where we were able to produce and successfully field test membrane samples for a space application at NASA Ames, Moffett Field, CA (US).

The project’s results have primarily been communicated through the follow group, which contains important players within the water sector in Denmark (see chapter 6). Furthermore Aquaporin A/S participated in the Singapore Water Week from the 4th of July to the 8th of July 2011. Here we presented our technology and our development work towards a biomimetic membrane for desalination. Following our participation in the 2011 Singapore Water Week Aquaporin A/S has been invited to participate in the 2012 Singapore Water Week TechXchange Workshop in the group of top 6 selected companies with the opportunity to present their technology to interested parties within the field.

1 Introduction

The overall goals of this project's first two work packages have been on one hand to identify possible solutions for overcoming the technological barriers in developing a biomimetic membrane module for desalination of seawater (primary goal of work package 1) and on the other hand identify a combination / combinations of available in-house membrane technologies in Aquaporin A/S, which have the potential to solve the previously identified technological barriers (primary goal of work package 2). In this concluding report we summarize the work done in both work package 1 and 2 and give an outlook to what will be investigated in our next ECOINNOVATION project (NST-404-00100), which was recently granted and will run in the period 1st of February 2012 to the 1st of February 2013. In our work package 1 report we included detailed background information on the concepts of forward osmosis, aquaporin-mediated water transport, biological and biomimetic membranes, the Aquaporin inside™ liquid membrane technology, draw solution design and concentration polarization. We therefore refer readers to the work package 1 report for background information, as it will not be repeated in this concluding report.

2 Summary of work done in work package 1

2.1 Main Achievements

When we first started our work in work package 1, Aquaporin A/S had just developed a prototype liquid membrane formulation but as such not started to deal with the technological barriers hindering the use of the liquid membrane formulation for desalination. In short, these barriers boil down to the following:

1. Forward osmosis liquid membrane design
2. Draw solution design
3. System design

The following subchapters summarize the main conclusions and findings from our work in work package 1.

2.1.1 Improved understanding of coupling between liquid membrane components and macroscopic properties

The shelf-life and overall stability of liquid membrane formulations has been improved through variations in the 4 major liquid membrane components.

The aquaporin inside™ liquid membrane consists mainly of 4 components:

1. Aquaporin proteins
2. Biomimetic membrane components
3. A hydrophobic oily phase

4. Aqueous buffer solutions

Depending on the specific nature of these 4 components, different microscopic and macroscopic properties of the resulting liquid membrane emerge. The macroscopic properties include viscosity, stability towards mechanical stimuli, shelf life and interactions between the liquid membrane and the encapsulation membranes. A significant amount of work has been performed in work package 1 toward increasing the shelf-life and overall stability of liquid membrane formulations through variations in the 4 major components. Unfortunately, we cannot disclose the exact nature of the components in the optimized liquid membrane formulation since this is proprietary information.

2.1.2 Improved fabrication method of liquid membranes

We have developed a simple fabrication method, which combined with specific choices of the 4 main liquid membrane components, has increased liquid membrane yield by a factor 10.

The Aquaporin Inside™ liquid membrane is essentially a water-in-oil emulsion. The process of formulating stable high-yield water-in-oil emulsions is well described in literature and by drawing from this knowledge; we have refined our choices of the 4 main liquid membrane components to increase the yield[1] by a factor 10.

2.1.3 Identifying draw solution candidates from an extensive literature study

When dissolved in water, $KHCO_3$, $MgSO_4$, $NaHCO_3$ and produce draw solutions that fulfill the necessary criteria for industry applicability. $MgSO_4$ is currently being used in FO desalination test facilities run by the company Modern Water.

The draw solution constitutes the driving force in the forward osmosis process and as such is critical for the overall technical and economical feasibility of FO for desalination. Table 1 summarizes the main criteria a draw solution needs to fulfil in order to be applicable in industrial processes. The table illustrates the trade-offs involved when choosing a suitable draw solution osmolyte. In some criteria a larger molecular size is desirable whereas the opposite is true in other criteria.

For more detailed information please refer to chapter 3 in the work package 1 report (Appendix 1)

[1]Yield refers to the ratio between the volume of final liquid membrane and the combined volume of the starting ingredients.

Table 1: Main draw solution criteria

Criterion	Supporting information
High osmotic pressure	The osmotic pressure in the draw solution is what drives the FO process. The osmotic pressure of a solution is linearly related to the molar solubility (mole/L) of the osmolyte in question.
Low reverse diffusion	The liquid membrane is not a complete barrier towards osmolyte diffusion from draw to feed. Osmolyte that enters the feed no longer contributes to the osmotic driving force. In addition – depending on the application – osmolytes could pose a source of pollution in the feed. Reverse diffusion can be minimized by choosing osmolytes with a larger molecular size and/or different charge.
Low concentration polarization (CP)	Concentration polarization covers any membrane related process by which the effective osmotic driving force is reduced. In FO processes the reduction of osmotic driving force can take place both inside and outside the membrane on the draw side when the flow of permeate (i.e. separated water) locally dilutes the draw solution. Concentration polarization can be reduced by choosing osmolytes with a high diffusion rate in the draw. Usually this implies choosing draw osmolytes with a small molecular size.
Low/no toxicity	Since reverse diffusion is very difficult to eliminate completely, it is important to choose draw osmolytes with low or preferably no toxicity.
Stability	Solutes unable to maintain their osmotic effect in the solution will lower the overall flux. Solutes that degas, precipitate or react with the membranes used can damage or block the FO-system.
Inexpensive	In desalination prices vary from 0.5 -5$ per m^3 produced water. Draw osmolyte price must be matched to this price-range.
Recyclable	If draw osmolytes can be cost-effectively recycled, the initial price of the osmolyte can be higher.
Easy and cheap to separate from permeate	In desalination the end product is potable water, hence an additional processing step is needed where the draw osmolyte is removed from the permeate. The larger the draw osmolyte, the easier it is to separate from the permeate.

2.1.4 Developing test systems for liquid membrane encapsulation and initial testing of said systems

We have developed a lab scale system for liquid membrane performance evaluation under FO operation. The company Modern Water is already operating FO desalination test facilities, so we do not expect large-scale FO system design to constitute a technological barrier in the future.

A liquid membrane needs to be encapsulated and its volume must be restrained to function as a FO membrane. We have developed a flat sheet module for liquid membrane testing, which restrains the volume of the liquid membrane between two encapsulation membranes, as well as the surrounding system needed to test liquid membrane performance under FO operation.

For more detailed information please refer to chapter 4 in the work package 1 report (Appendix 1)

2.2 Remaining challenges

During our work in work package 1 it became clear to us, that we would face two main challenges in our future work towards a functioning FO membrane prototype for desalination of sea-water. These challenges are described in more detail in the following two chapters.

2.2.1 From flat sheet configuration to hollow fibre modules

Moving from a flat sheet module to a hollow fibre module for liquid membrane encapsulation is a technological challenge.

We have observed that commercially available flat sheet membranes bulge during FO operation when used as encapsulation membranes for liquid membranes. Bulging means that the volume of the liquid membrane could be less restrained during operation, which could somewhat compromise the overall membrane performance. In a hollow fibre module, the total volume of the liquid membrane used to surround each hollow fibre will be fixed per default. Therefore we expect better membrane performance when moving to a hollow fibre module. This transition, however, is not without challenges:
In a flat sheet module it is straightforward to fill liquid membrane between the encapsulation membranes. In a hollow fibre module it's another story altogether. Individual hollow fibres are typically anywhere from 200-1000 µm in diameter and there are thousands of fibres in industrial size modules. In a hollow fibre module containing liquid membrane as an enabler for forward osmosis, each individual fibre needs to be completely surrounded by liquid membrane and the distance between neighbouring fibres has to be as small as possible (<500 µm) while ensuring no fibres come into physical contact with each other (physical contact between fibres can result in leakage of draw osmolytes from draw to feed). When taking into account the flexibility of hollow fibres, the sheer number of them in industrial modules and the relatively high viscosity of the liquid membrane used in flat sheet membranes, filling of a hollow fibre module needs further technological development.
For more information about liquid membrane volume restriction please refer to chapter 1.5 of the work package 1 report (Appendix 1).

2.2.2 Improving liquid membrane performance under FO operation

It should be possible to improve liquid membrane performance with regards to water flux by up to a factor 10 or more in order to obtain commercially competitive desalination modules.

At the end of work package 1, liquid membrane performance with regards to water flux was <5 L/m^{2}h. Our calculations have shown that a water flux of 50 L/m^{2}hmay be necessary for a liquid membrane module to be commercially viable. This means that the water flux has to improve by a factor 10 or more before a commercially viable liquid membrane module is a reality. We have identified several tracks to achieve this higher water flux:

- Decrease the distance between encapsulation membranes in the flat sheet module. The shorter the distance water molecules have to travel through the liquid membrane, the less resistance they will have and the higher the flux will be
- Make the transition to hollow fibre modules
- Optimizing the draw solution for a higher osmotic gradient
- Further optimize the liquid membrane formulation – e.g. implementing a higher aquaporin concentration.

3 Summary of work done in work package 2

The overall goal of work package 2 has been to identify combinations of liquid membrane formulations and liquid membrane modules, which solve the technological challenges described and encountered in work package 1. The main take-home message from work package 1 with regards to technological challenges is that the water flux performance of our liquid membrane formulations in combination with liquid membrane modules needs to be significantly improved.
Based on forward osmosis literature and our own research into the topic, water flux performance can potentially be improved in several different ways (see chapter 2.2.2).
At the beginning of work package 2 we decided to focus our efforts on decreasing the distance between encapsulation membranes in the flat sheet module. This turned out to be a good choice; the result being a technology leap, which enabled us to not only identify combinations of liquid membrane formulations and liquid membrane modules to solve the water flux problem, but actually produce these combinations and successfully field test them for a manned space flight application at NASA Ames, Moffett Field CA, US.

3.1 Main Achievements

The technology leap and NASA field test along with other achievements in work package 2 are summarized in the following chapters.

3.1.1 Technology leap: Substantive reduction in liquid membrane thickness

> We have significantly improved membrane performance as well as membrane performance reproducibility by developing a method (patent pending) by which our liquid membrane formulation can be encapsulated in a very thin encapsulation membrane.

In work package 1 we encapsulated a 500 µm thick liquid membrane layer between two encapsulation membranes; the resulting sandwich had a water flux <5 L/m^2h when tested under FO operating conditions. In work package 2 we have developed a method[2] for encapsulating and stabilizing a liquid membrane inside a single encapsulation membrane. This technology leap in effect means that we have reduced the thickness of the active liquid membrane layer and as a result obtained significant improvements in membrane performance, membrane reproducibility and membrane lifetime (

[2]The method is proprietary and as such cannot be disclosed here.

Table 2) to a point where we have been able to produce and field test membranes at NASA Ames Research Centre in Moffett Field, CA, US.

Table 2: Membrane performance in work package 1 and work package 2

	Work package 1 Technology	Work package 2 technology
J_w (water flux)	< 5 L/m^{2}h	~ 20 L/m^{2}h
Reproducibility (rate of successful experiments)	< 5%	> 80%
Membrane lifetime	Hours	Days to weeks

Our calculations (not shown here) have shown that the prototype scale FO membrane technology developed in work package 2 can extract water at price of 0.1USD per litre. In large-scale desalination facilities today, the cost of treating water varies from 0.5 USD/m^3 (lowest reported price to date – HyFlux Singapore) to above 5 USD/m^3 (depending on the location of the facility; see work package 1 chapter 1.5 for more information). Hence our current technology is improving, but will not yet be feasible for large-scale desalination, and as a result we are also investigating niche applications where our prototype scale membrane technology makes sense from an economical point of view. One such application is separation of water from bodily fluids (yellow water) in space.

3.1.2 Field testing of membranes at NASA Ames, Moffett Field CA, US

We successfully field-tested our membranes at NASA AMES laboratories in California, USA. We achieved the highest performance of urea rejection they have seen so far with a forward osmosis membrane. The cooperation will be continued in 2012 with increased active area membranes.

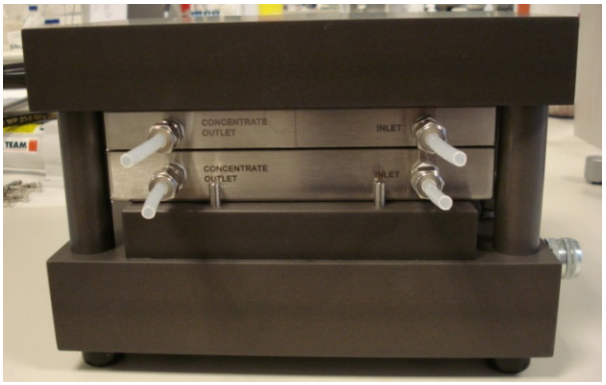
In October 2011, we field-tested our membranes at NASA AMES laboratories in California, USA. We transported 10 readily prepared membranes in special plastic containers to the US and tested them in a homemade setup that was similar to one in our lab. The difference is that NASA is interested in water recovery from body fluids and thus feed was changed from seawater to a urine mimicking solution. The results were promising with a water flux of 15 L/m^{2}h and a reverse salt of 3.5 g/m^{2}h. In addition, our membrane showed a promising urea rejection, which, according to NASA, is the best they have seen so far. In comparison, the only commercially available forward osmosis membrane from HTI (Hydration Technologies, USA) only had arejection of around 50% or less combined with a water flux of around 10 L/m^{2}h.
On the basis of these promising first results NASA invited us to come back to test flat sheet membranes with a bigger active area. The first experiments were carried out with membranes with an active area of 4.5 cm^2 and the next ones to be tested at NASA AMES should have an area of 140 cm^2.

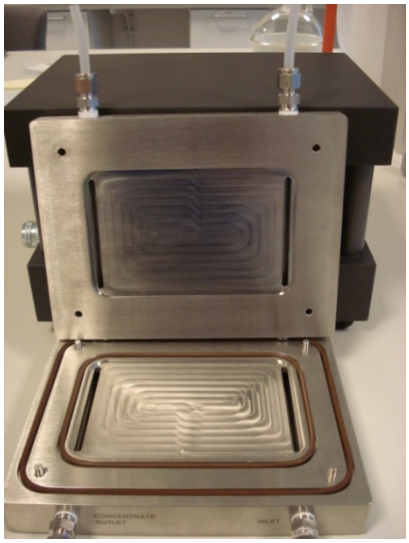
The official announcement of Aquaporin's successful tests at NASA AMES can be found at: http://aquaporin.dk/156/News/44/aquaporin-completes-first-successful-field-test-at-nasa.aspx

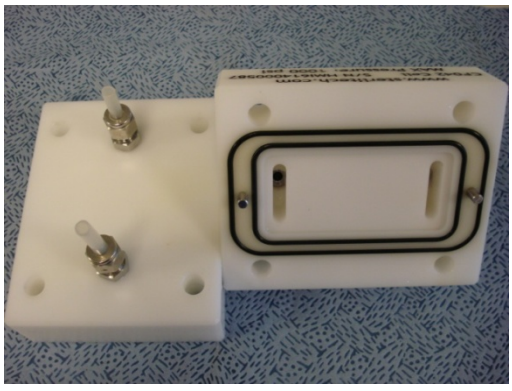
3.1.3 Up scaling active membrane area from 4,5 cm^2 to 140 cm^2

With our new portfolio of test chambers with 3 different sizes of up to 140 cm^2 we are well equipped to further improve and upscale our membrane production and testing.

The up-scaling of our production process and test setups to bigger active areas has always been a priority but became more defined with our cooperation with NASA AMES. Our standard experiments were carried out using a small homemade chamber where membranes with a diameter of 47 mm and an active area of 4.5 cm^2 could be tested. This setup enabled us to run a variety of experiments, testing support membranes and fabrication protocols in a fast, easy and inexpensive way, especially with regards to the availability of aquaporin proteins. After securing a steady delivery of aquaporin protein we are now able to apply our techniques to bigger membrane areas. Therefore, we acquired two additional chambers with 33 cm^2 and 140 cm^2 respectively (Figure 1).







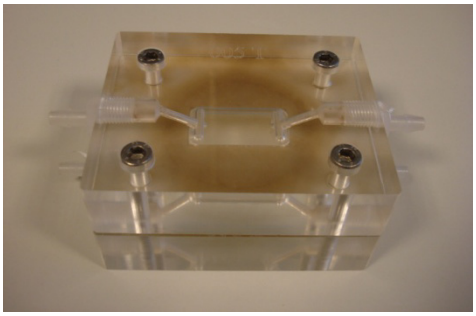


Figure 1: Portfolio of test chambers for membrane performance characterization experiments at Aquaporin A/S. The top row shows our biggest chamber with an active membrane area of 138 cm^2. Bottom row left is the next smaller one with an area of 33 cm^2 and on the bottom right our work-horse so far with a active area of 4.5 cm^2.

First experiments with bigger membrane area have also been successfully performed already. Figure 2 shows an example of an experiment with the biggest active area tested by Aquaporin A/S so far.

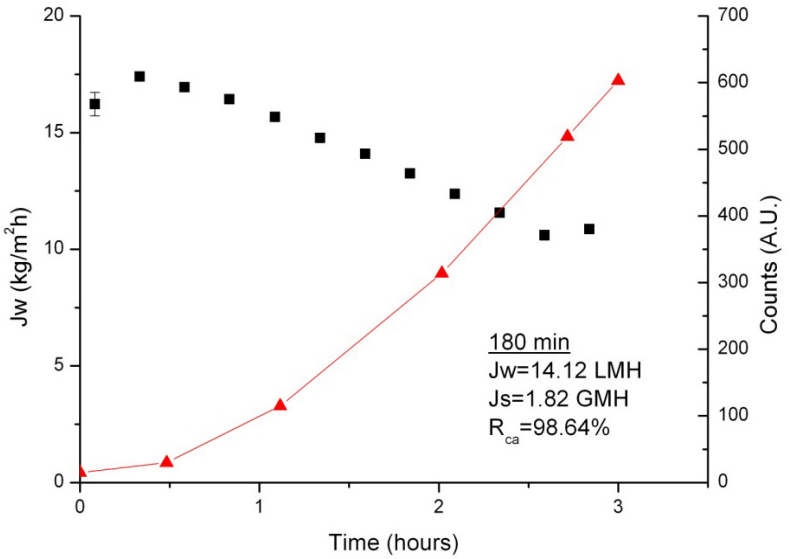


Figure 2: Example of a membrane experiment with a membrane with an active area of 140 m^2. The water flux of 14 L/m^2h paired with a salt flux of 1.82 g/m^2h results in an efficiency of 0.12 g/L. The decrease in water flux over time is due to continuous dilution of the draw solution during FO operation.

3.1.4 Development of standardized system for membrane performance evaluation

An in-house automated benchmarking system for membrane performance characterization has been developed and implemented, where a fluorescent marker determines forward rejection of molecules. In addition, a suitable commercially available support membrane has been identified.

Experimental setup

In the WP1 we introduced our first setup-prototype. During WP2 this preliminary setup was further refined to the one shown in Figure 3. The arrangement of components is flexible and can be used for different chambers with the exception that the size of the reservoirs needs to be adjusted. The basic structure contains a scale for water flux determination, a conductivity meter and conductivity flow cell for reverse salt flux measurements and a pump to drive the liquids on a counter-cross-flow path across the membrane. All measurement data is recorded by a computer, which enables us to run experiments fully automated.

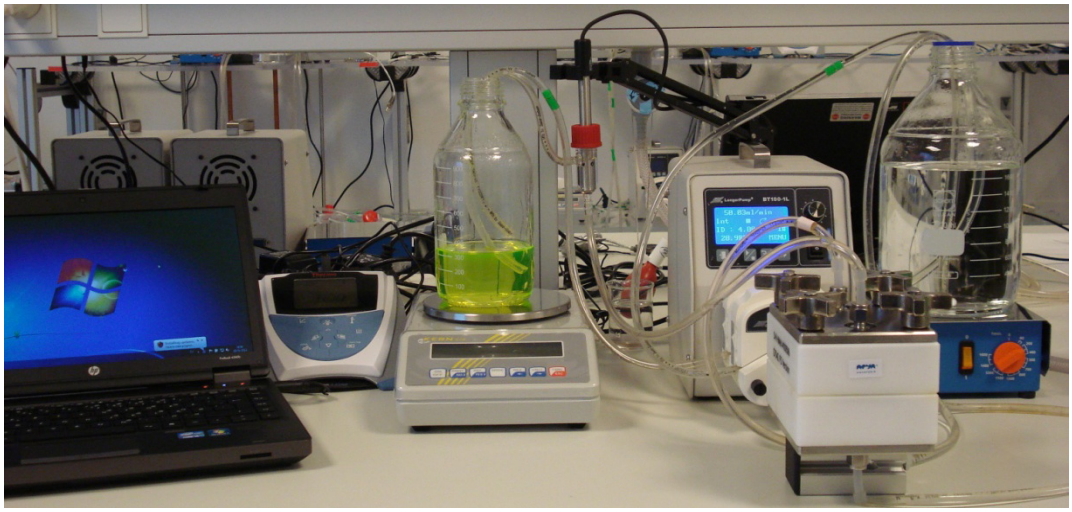


Figure 3: Aquaporin A/S standard test setup for membrane characterization; Components are: a computer for data acquisition, conductivity meter, scale with feed reservoir, conductivity flow cell, pump, chamber and magnetic stirrer and draw reservoir (left to right).

Our standard draw solution is a NaCl solution. The use of NaCl as draw was decided after the draw solution analysis done in WP1. This draw solution is the standard throughout literature and by using it we can compare the performance results of our membrane directly to the results of state of the art FO systems. Furthermore, NaCl is a cheap commercially available component that helps us to run multiple experiments at a reasonable price. However, the downside of using NaCl as draw and deionized water as feed is that the forward molecule rejection properties of our membrane cannot be determined. To be able to measure a forward rejection of molecules we needed to introduce a reporter molecule into our feed solution. Here, an easy and fast way would be to measure the concentration of a substance by fluorescence. Therefore, we concentrated on the investigation of fluorescent markers.

Reporter molecule

In general, the Rejection rate is calculated according to:

$$\mathbb{R} = 1 - \frac{c_P}{c_f} \qquad \text{(I)}$$

c_P …… solute concentration in permeate
c_f …… solute concentration in feed

The concentration of solute in feed is known as we work with defined feed solutions. The solute concentration of permeate has to be calculated from the increase of reads (e.g. fluorescence counts) in the draw solution over time.
Our starting point for this calculation is the relationship of diluting concentrations:

$$c_1 * V_1 = c_2 * V_2 \qquad \text{(II)}$$

If we now relate (II) to our tests assuming that $c_{start}=0$ in draw we get:

$$c_p * V_p = c_{draw} * V_{draw} \qquad \text{(III)}$$

In general, the concentration of solutes in draw (c_{draw}) might not be 0 to begin with so we have to take the increase in concentration to calculate our permeate concentration.

$$c_p * V_p = c_{draw,final} * V_{draw,final} - c_{draw,start} * V_{draw,start} \quad \text{(IV)}$$

$$c_p = \frac{c_{draw,final} * V_{draw,final} - c_{draw,start} * V_{draw,start}}{V_p} \quad \text{(V)}$$

Combining (V) and (I) we get:

$$\mathbb{R} = 1 - \left[\frac{V_{draw,final} * c_{draw,final} - V_{draw,start} * c_{draw,start})}{V_{permeate} * c_{feed}}\right] \quad \text{(VI)}$$

To simplify the calculation we assume a constant feed concentration, which in reality is untrue. Due to the fact that water is extracted and solute rejected, the concentration of solutes in feed increases. However, by neglecting this fact we underestimate the rejection value of the membrane, which means that we calculate the lower limit of the rejection spectrum of our membrane.
The conversion of fluorescence counts, measured with a handheld fluorometer, to an actual concentration can be done with the help of standard curves that were prepared beforehand. In our tests, we concentrated on 3 different fluorescent markers. All of them accumulated in the membrane, which was clearly visible when disassembling the chamber after an experiment. The colouring was most intense in the active area. The intensity of the coloration depended on the reporter molecule used. One of the candidates accumulated in the membrane to such an extent that it clogged it, which resulted in a dramatic decrease in water flux. Another two of the markers accumulated not only in the membrane but also in the tubes and reservoirs and could not be removed entirely without greater effort when cleaning the system. This means leftovers could influence the measurement in the next experiment. However, one of the markers could be easily measured in the draw solution and did not leave any visible or measurable traces in the system. It thus makes a good reporter for membrane performance and thus was selected as a reporter molecule for further membrane experiments. Details of the marker are reserved for patent protection.

Support Membrane
With the refined setup and the performance characterization in place, the next step was to screen commercially available membranes to find suitable supports or encapsulation membranes for our liquid membrane. A support membrane should be open enough not to hinder any water flux but not too open so that the liquid membrane will be contained and not just flow through. Furthermore, the support should be thin so to minimize concentration polarization effects. In an extensive test series of over 200 experiments we tested 20 different commercially available membranes. As a result, we could identify 2 candidates that fulfilled our criteria and showed promising performance values in connection with our encapsulated liquid membrane.

In the end we can conclude that we were able to identify all necessary parameters that are needed to have an optimized setup for membrane characterisation. Figure 4 shows a typical result of a membrane test with all data that is needed to compare our membranes among each other and also to our competitors. The data that is most important for us

when looking at membrane performance are water flux (J_w), reverse salt flux (J_s), efficiency parameter (J_s/J_w) and fluorescent marker rejection (R_{ca}). The water flux describes how many litres of water pass 1 m^2 of membrane over the course of 1 hour. The reverse salt flux is a similar value that describes how many grams of salt pass the membrane. By dividing both factors we get the so called efficiency factor which tells us how many grams of salt are needed to transport 1 L of water across the membrane. The last value we look at is the marker rejection, which we calculate from the amount of marker that passes over into draw over time. As described before, this value gives us an idea of the forward rejection properties of our membrane which means, how big is the retention of molecules going into the direction of the water flux.

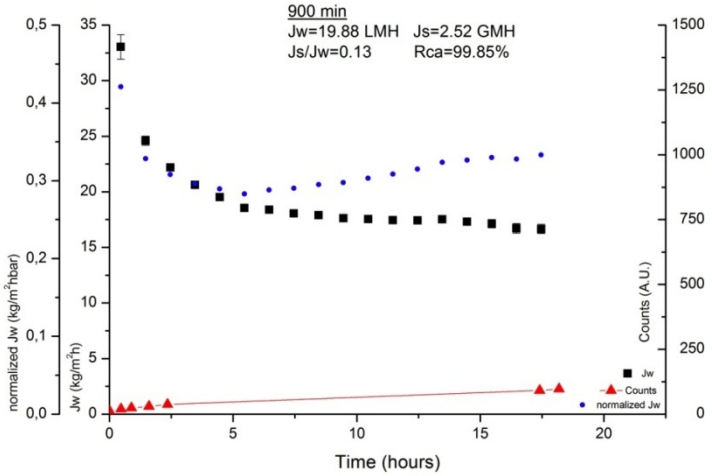


Figure 4: example of an analysis graph for a membrane characterization experiment; The red line indicates the increase in fluorescent marker reads over time (basis for marker rejection calculation), the black points are the water flux where each point is the flux averaged over 1 hour, the blue points are the normalized flux which is the water flux per bar osmotic pressure; in addition the reverse salt flux and the efficiency parameter are added to the graph.

3.2 Remaining challenges

Two primary technological challenges remain to be solved before the FO membrane technology developed in work package 2 can be commercialized, namely reproducibility in membrane performance (e.g. J_w, J_s, RCA etc – see chapter 3.1.4 for more details) and in house knowhow regarding up-scaling of membrane area from cm^2 to m^2. These challenges will be described in more detail in the following two chapters.

3.2.1 Reproducibility in membrane performance

Our aim is to achieve >95% reproducibility in membrane performance based on the following benchmark values: J_w> 15 L/m^2h / J_s< 5 g/m^2h / RCA > 98%.

Our current membrane performance reproducibility is around 80% when using the following benchmark values, which have been determined through in-house testing of commercially available FO membranes from HTI[3]:

- J_w> 15 L/m^2h
- J_s< 5 g/m^2h
- RCA > 98%

(all values are calculated averages over 15h runtime in our in-house setup)

For our first product we aim to have >95% reproducibility. Increasing the reproducibility to >95% will require optimization of the membrane production protocol. So far we have identified around 10 key parameters, which we believe need to be simultaneously controlled during membrane production to achieve high reproducibility.

3.2.2 Up-scaling membrane area from 140cm^2 to m^2 scale

Our aim is to develop and implement a pilot production line capable of producing flat sheet membrane at a rate of 2 m^2 per day. Membrane performance should fulfill the reproducibility requirements described in chapter 3.2.1

Up-scaling membrane area from cm^2 to m^2 will require a transition from “hand-made” membrane production to automated roll-to-roll membrane production. The challenge here will be to implement our current membrane production protocols in an automated system while maintaining membrane performance and membrane performance reproducibility. We have recently hired a process engineer to gain in-house expertise in setting up pilot production lines.

[3]Hydration Technology Innovations is a US-based company producing and selling the only commercially available FO membrane today.

4 Concluding remarks

We have successfully developed and field-tested a biomimetic flat sheet membrane technology based on aquaporins capable of separating water from various aqueous solutions through forward osmosis. Currently though the initially developed 1st generation membrane technology is too expensive per litre water separated to be used competitively in large scale or community desalination applications. As a result, in addition to our continued work on the up-scaling of the Aquaporin Inside™ technology we are also looking into identifying different market segments where our current 1st generation membrane technology is commercially viable. This is one of the main topics at hand in our new ECOINNOVATION project (NST-404-00100), which will run from the 1st of February 2012 to the 1st of February 2013.

5 Outlook to ECOINNOVATION NST-404-00100

The purpose of our next ECOINNOVATION project is to further develop the flat sheet FO membrane technology invented in work package 2. Our work will be focused on the following main issues:

- Identify market segments with environmental relevance where our 1st generation membrane technology is commercially viable
- Further improve membrane performance
- Improve membrane reproducibility performance from 80% to >95%
- Up-scale membrane area from cm^2 to m^2
- Investigate possibilities for applying our flat sheet membrane technology for reverse osmosis applications

6 Acknowledgements

We would like to thankThe Danish Ministry of the Environment for co-funding this project under the ECOINNOVATION framework. We are also grateful for the feedback and discussions provided by the members of this project's follow-group:

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APPENDIX 1 – workpackage 1 report

Development of a biomimetic membrane module for desalination of sea-water through forward osmosis (FO) (NST-404-00073)

Work-package 1 report

Jörg Vogel & Mark Perry
Aquaporin A/S
01/06/2011

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Danish summary

Vi har færdiggjort arbejdspakke 1 i projektet "Udvikling af et biomimetisk membranmodul til afsaltning af havvand gennem direkte osmose (NST-404-00073)". Arbejdet har været fokuseret på at identificere løsninger på de primære teknologibarrierer i udviklingen af et biomimetisk membransystem til afsaltning af havvand. Disse barrierer er: designet af det biomimetiske membransystem, designet af den osmostisk drivende opløsning ("draw"-opløsninger) og designet af et komplet system til afsaltning af havvand baseret på direkte osmose.

Gennem vores arbejde har vi udviklet et omkostningseffektivt flydende membran design baseret på en vand-i-olie emulsion. Vores flydende membran har vist sig at have større tilbageholdelsesgrad for salt end den kommercielle direkte osmosemembran fra HTI (Hydration Technology Innovations). Desuden kan den opbevares i flere uger ved stuetemperatur uden at tage skade. Vores fremtidige arbejde på designet af den flydende membran vil blive fokuseret på at øge dens vandtransporterende egenskaber, så den bliver konkurrencedygtig indenfor afsaltning af havvand.

Vi har lavet et udtømmende litteraturstudie mht. design af "draw"-opløsning og identificeret flere mulige kandidater, som kan anvendes til direkte osmose processer. En af disse kandidater ($MgSO_4$) bruges efter alt at dømme allerede i direkte osmose pilotanlæg i Oman og Gibraltar[4]. Vores fremtidige arbejde på "draw"-opløsning design bliver at teste de identificerede kandidater sammen med vores flydende direkte osmose membran.

Tilsidst har vi mht. systemdesign udviklet flere testmoduler til flydende membran, som vil blive anvendt til fremtidig karakterisering af deres ydeevne i direkte osmose processer. Vi er endvidere overbeviste om at det arbejde, der allerede nu finder sted inden for direkte osmose anlæg til afsaltning af havvand, vil løse mange af de udfordringer, der på nuværende tidspunkt begrænser det kommercielle potentiale af direkte osmose teknologier.

[4] Pilotanlæggene drives af firmaet Modern Water, et globalt firma som specialiserer sig i at levere patenterede vandteknologier såsom "manipulated osmosis (MO)", hvilket er deres version af en direkte osmose teknologi.

English summary

We have finished work package 1 in the project “Development of a biomimetic membrane module for desalination of sea-water through forward osmosis (FO) (NST-404-00073)”. The work has been focused on identifying solutions to overcome the main technology barriers in developing a biomimetic membrane for desalination of seawater, namely forward osmosis liquid membrane design, draw solution design, and system design. During our work we have developed a cost effective liquid membrane design based on a water in oil emulsion, which shows superior rejection rates as compared to the commercial FO membrane from HTI (Hydration Technology Innovations) and has a long shelf life (several weeks). Our future work on the liquid membrane design will be to increase its water extraction capabilities in order to make it commercially competitive for desalination purposes.

Regarding the draw solution design, we have performed an extensive literature study and identified several candidates for FO operation, one of which ($MgSO_4$) is most likely already being used in FO pilot plants in Oman and Gibraltar[5]. Our future work on draw solution design will be focused on testing the identified candidates together with our liquid membrane design.

Regarding the system design, we have developed several liquid membrane test modules, which will be used for further membrane performance characterization. In addition, we are assured that current work already taking place in implementing FO pilot plans will solve many of the challenges, which need to be overcome in order to make FO a competitive alternative to RO (reverse osmosis) when it comes to desalination of seawater.

[5] The pilot plants are run by Modern water, a global company specializing in providing patented water technologies such as manipulated osmosis (MO), which it their version of an FO water extraction technology.

1 Introduction

The overall goal of this project - within The Danish Ministry of the Environment's ECOINNOVATION framework 2010 - is to develop a biomimetic membrane system with embedded aquaporin proteins to be used for desalination of seawater through forward osmosis. In the following chapters we will give a brief introduction to the concepts and technology involved in forward osmosis, the aquaporin protein, biological and biomimetic membranes, and liquid membranes. We then move on to summarize the progress and findings we have made in work-package 1. Finally we give an outlook to the work currently going on in work-package 2.

1.1 The project in short

Budget	Timeframe	Deadlines
• 2.062.200 DKK • 25% funding (515000 DKK) from The Danish Ministry of the Environment's ECOINNOVATION frame work	• 1 calendar year; - start 01.02.2011 - end 01.02.2012 • 50 man months work in total	• Work package 1 report: 01.06.2011 • Work package 2 report and final report: 01.02.2012

1.2 Osmosis, reverse osmosis, and forward osmosis

The process of osmosis can be defined as:

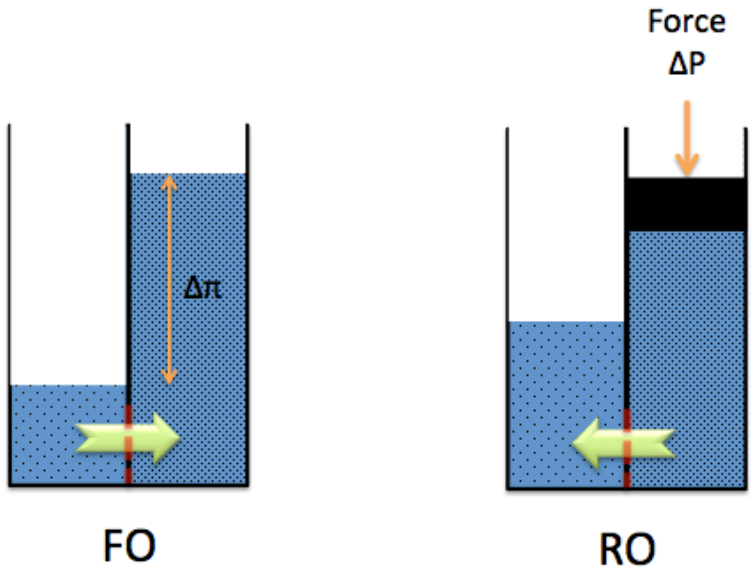
The movement of solvent[6] molecules through a selectively permeable membrane into a region of higher solute concentration, aiming to equalize the solute concentrations on the two sides.

As a result of osmosis, it requires energy to force water through a selectively permeable membrane from a region of high solute concentration to a region of low solute concentration (reverse osmosis (RO)). Oppositely water flows freely through a selectively permeable membrane from a region of low solute concentration to a region of high solute concentration (forward osmosis (FO)). This is illustrated in Figure 1, where ΔP in the RO process is the hydraulic pressure needed to overcome the osmotic pressure $\Delta\pi$. In the FO process, the osmotic pressure $\Delta\pi$ is the driving force for the flow of water from the low solute region to the high solvent region. The osmotic pressure of dilute solution can be approximated by the Morse equation:

[6] A solvent in this respect is a liquid, gas or solid which dissolves another substance (the solute) to form a solution. An example of a solution is salt water in which the solvent water dissolves the solute salt.

$\Delta\pi = iMRT$ [7]

Where “i” is the van’t Hoff factor, “M” is the molarity of the solution, “R” is the gas constant,



and “T” is the temperature.

Figure 1: The principles of reverse osmosis (RO) and forward osmosis (FO). In desalination of seawater the semipermeable membrane should be permeable to water and not the solutes being removed.

In summary, RO processes for desalination of seawater require large amounts of energy to create the hydraulic pressures needed to overcome the osmotic pressure of seawater. Typically RO operating pressures range from 50-70 bar [1]. In FO processes, the water is extracted all by itself from regions of low solute concentration (the “feed”) to high solute concentration (the “draw”). In other words, if seawater is separated by a water selective FO membrane from a region with higher solute concentration, water molecules will automatically be extracted from the seawater. No energy input is needed for the extraction. Obviously energy is needed in a later stage to separate the extracted water molecules from the high concentration solution. In chapter 4 we will discuss how this extraction process can be designed in order to keep the overall energy consumption of FO desalination below RO desalination. It is the lower energy consumption per treated unit of water, which is our main driving force for developing an FO membrane for desalination of seawater.

1.3The aquaporin protein

The aquaporin protein is Nature’s own highly selective and highly effective water channel. Discovered in 1992 by prof. Peter Agre, aquaporins are responsible for transporting water in almost all living cells from simple bacteria to the human kidney, where they are responsible for a daily water uptake of 150-200 L. Given the single channel osmotic permeability constant of aquaporin, the size of an aquaporin molecule, the membrane

[7] As an example, the osmotic pressure of sea-water is roughly 27atm

area, the osmotic driving force, the operating temperature, and the aquaporin coverage of the membrane one can calculate the theoretical water flow through the membrane (Appendix 2). Aquaporin single channel osmotic permeability constants have been measured in the range of 10^{-14} cm^3/s to 10^{-13} cm^3/s [2][2], which result in a possible water flow through $1m^2$ membrane (50% aquaporin coverage, 293 K, 45 bar osmotic driving force)[8] of 14 L/hour to 140 L/hour. The only commercially available FO membrane from Hydration Technology Innovations (LLC, Scottsdale, AZ) has a water flow under identical working conditions of around 10 L/hour*m^2 (average value from numerous measurements in our lab). In addition to a higher water transport potential compared to the current FO membrane, aquaporin based FO membranes also promise a higher quality of filtered water due to the inherently high selectivity of the aquaporin protein[9].

1.4Biological and biomimetic membranes

Biologic membranes are a complex mix of different membrane components, membrane-spanning proteins, and membrane-associated proteins. Common to most biological membranes is their thickness of around 4nm and their building blocks of amphiphilic molecules such as lipids. An amphiphilic molecule has a water loving (hydrophilic) and a water hating (hydrophobic) part. It is this combination of hydrophilic and hydrophobic regions that causes amphiphilic molecules to self assemble into membrane sheets as the one shown below (Figure 2), where the hydrophobic regions are organized towards the central part of the sheet and the hydrophilic regions are organized toward the aqueous surroundings. Although biological membranes are the natural home for aquaporins, they contain a wide range of membrane spanning pores and transporters, which render them unsuitable for a semi-permeable water filtration membrane where only water molecules are supposed to pass through. On the other hand, since membranes in nature exhibit mechanical and chemical stability to a wide range of different external stresses they have been a primary source of inspiration for artificial biomimetic membrane systems containing only a subset of membrane spanning proteins to yield specific functionalities (in the case of aquaporins, a highly selective and effective water filtration membrane). The main challenges when creating biomimetic membranes for industrial purposes such as water filtration are:

1. Protein compatibility
2. Mechanical and chemical stability
3. Highly impermeable to the solutes that are to be removed
4. Up scalable to large membrane areas at low cost

In traditional biomimetic membrane research, membranes usually fall short in stability and scalability [3][3].

[8] Standard working conditions in our lab
[9] Aquaporin proteins are more than 99,9999% selective for water, meaning that in effect no solutes pass through.

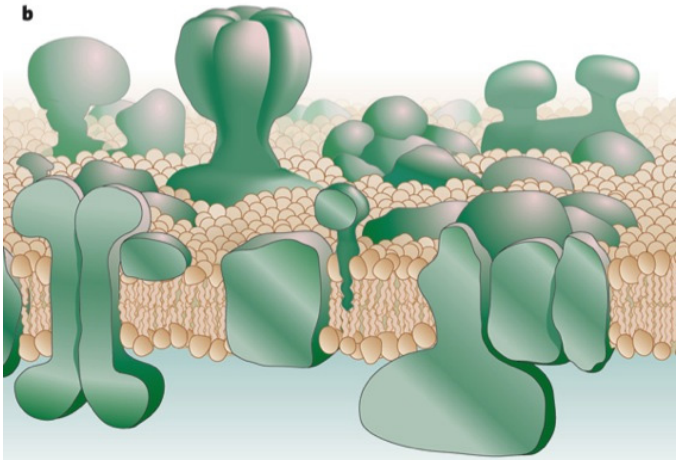


Figure 2: Schematic representation of a biologic membrane. The membrane itself is composed of a double layer of lipid molecules (yellow). Membrane associated and membrane-spanning proteins (green) constitute a large part of the membrane.

1.5Liquid membranes – principle and economical feasibility

A liquid membrane has the purpose to build up a thin gaseous or liquid barrier between two miscible liquids or gases and thus regulate the mass transfer between both phases. The membrane strips one phase (feed phase) of a component or solute and transports it across to the other phase (stripping phase) where it releases the transported component again. The development of liquid membranes for filtration purposes has experienced a significant increase in interest over the last two decades. This is due to the great potential these membranes exhibit - high selectivity combined with a high permeability and an efficient use of energy [4], [5]. The high selectivity can be reached with the help of the components that are in the liquid membrane. These can be more selective than the openings in a polymeric membrane. Since diffusion in liquid is orders of magnitude higher than diffusion through solid polymers [4][4] also permeability can be improved by using liquid membranes.

The main reasons for developing a liquid membrane design for aquaporin based biomimetic membranes for industrial uses are to address the issues of stability and scalability. Planar biomimetic membranes are inherently fragile due to their thickness of only 4 nm. Hence up-scaling a planar biomimetic membrane platform to square meter sized areas and beyond is a formidable challenge. On the other hand spherical biomimetic membrane shells, which resemble living cells in Nature, are remarkably stable.

By taking the cue from Nature we have developed the liquid membrane design shown in Figure 3. The design is based on a water-in-oil emulsion in which the aquaporin proteins are loaded into the biomimetic membranes constituting the shells of the water filled compartments. The oil ensures that water transport only takes place through the water filled compartments. A liquid membrane must be encapsulated (i.e. held in place) in order to be able to function as a forward osmosis membrane (Figure 4). Figure 5 shows a microscopy image of an actual liquid membrane sample. More details on our progress with liquid membrane systems are presented in chapter 2 and 4.

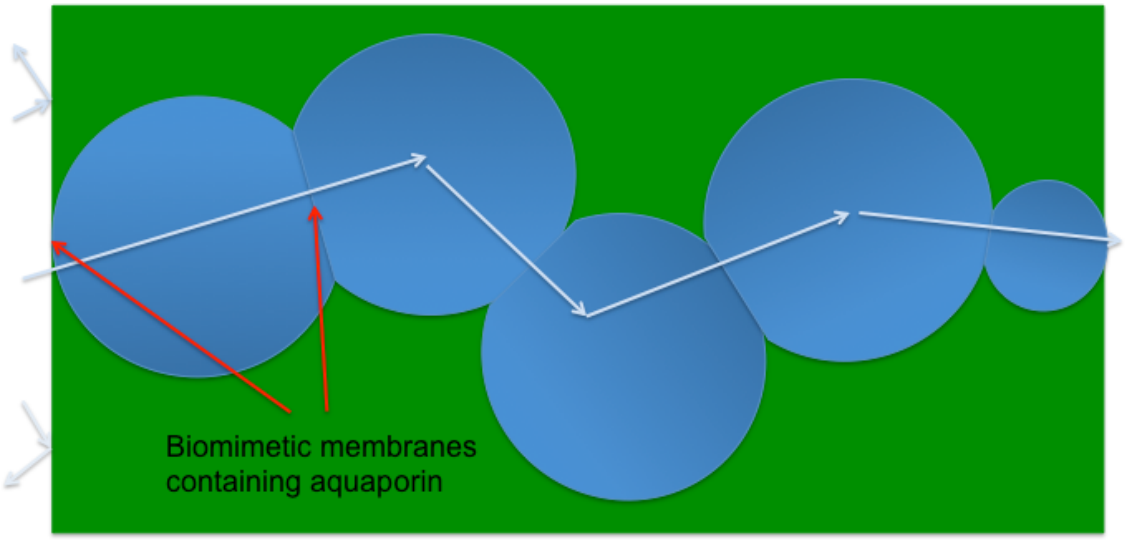


Figure 3: Working principle of a biomimetic liquid membrane containing aquaporins for forward osmosis applications. The water filled shells consist of biomimetic membranes loaded with aquaporins. The selectivity of the liquid membrane is achieved by surrounding the water filled shells with an oil, which ensures that water transport only takes place through the water filled compartments. In this schematic water is extracted from left to right.

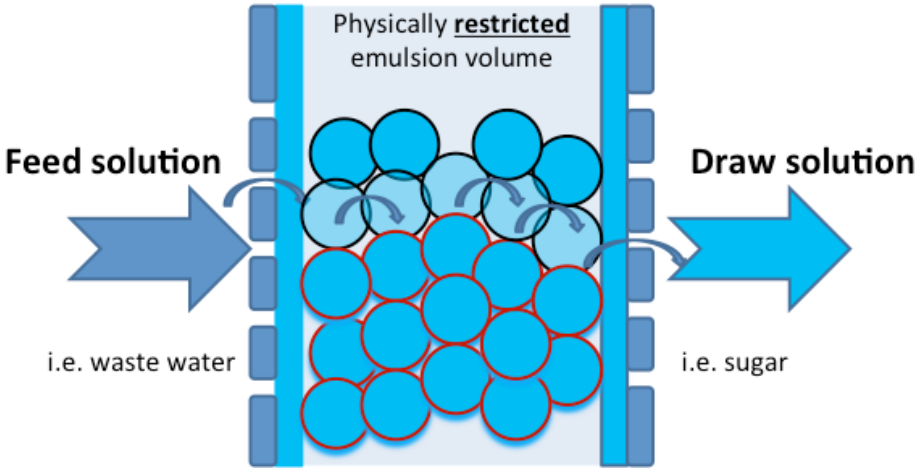


Figure 4: Schematic of a liquid membrane encapsulated by two encapsulation membranes, one on either side facing the feed and draw solutions. The presence of encapsulation membranes is needed to physically restrict the liquid membrane volume and prevent it from leaking into the feed and draw solutions. Without a physically restricted emulsion volume, the liquid membrane would simply swell and lose its integrity when subjected to a high osmolarity draw solution.

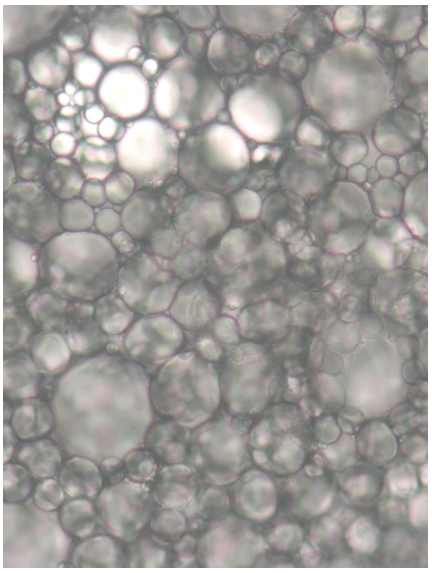


Figure 5: Bright field microscopy image of an actual liquid membrane sample. The shells are loaded with aquaporins. Image acquired at 40x magnification.

The following tables provide an overview of the economical feasibility studies we have made on liquid membranes with aquaporins for water extraction applications through forward osmosis:

Table 3: Overview of liquid membrane costs

	Liquid membrane cost[10]	Cost of aquaporin	Cost of remaining liquid membrane components
Small scale production (10000 USD/kg aquaporin)	40 USD/litre 4-20 USD/m^2	30 USD/litre	10 USD/litre
Large scale production (1000 USD/kg aquaporin)	13 USD/litre 1.3 – 6.5 USD/m^2	3 USD/litre	10 USD/litre

For desalination of seawater today by RO, the cost of treating water varies from 0.5 USD/m^3 (lowest reported price to date – HyFlux Singapore) to above 5 USD/m^3 (depending on the location of the facility. Global Water Market 2011 [6]). In the following calculations we use an estimated average price of 1.4 USD/m^3. 20% of this cost is estimated to be due to the actual RO membranes. Thus in order to be a cost reducing alternative to conventional RO membranes, in locations where the cost of treating water is 1.4 USD/m^3, the price of treating water with an aquaporin based liquid membrane has to be below 0,28 USD/m^3.

For large-scale production and an active membrane surface area of 10m^2/litre of liquid membrane, the liquid membrane cost is 1.3 USD/m^2. In this case we aim for a minimum sales price of 3 USD/m^2, corresponding to a gross margin of 56%.

From a business perspective, this means that 1 litre of liquid membrane has to be able to treat more than 11 m^3 of water in order to be competitive. Our current goal is 35 m^3 of treated water per litre liquid membrane, which places us at a cost of 0.1 USD/m^3 treated water.

Along with the current limits for remaining salt content in the treated water, this puts the following requirements on liquid membrane performance:

Table 4: Necessary liquid membrane performance for competitive FO

	Water flux	Salt flux	Operational lifetime
Liquid membrane performance	50 litre/m^2/hour	<200 mg/m^2/hour	1 month

These are tough requirements to meet, however markets also exist where the price of treating water is significantly higher compared to desalination. Providing a complete

[10] Liquid membrane cost is calculated per litre membrane and per square meter active membrane surface area; depending on the thickness of the liquid membrane layer, 1 litre of liquid membrane results in 2-10 m^2 active membrane surface area.

market analysis is beyond the scope of this report. Here it suffices to say that we have identified markets where liquid membrane performance can be lower while still providing a competitive product.

1.6 Work-package 1

The goal of work-package 1 is:

"To identify possible solutions for overcoming the technology barriers in developing an aquaporin-based biomimetic hollow fibre contactor module for desalination of seawater"

These technology barriers can be boiled down to 3 categories, which will be described in more detail in chapters 2, 3 and 4:

1. Forward osmosis liquid membrane design
2. Draw solution design
3. System design

In 1.5 we calculated the liquid membrane performance needed for a competitive product

Table 5: Necessary liquid membrane performance for competitive FO

	Water flux	Salt flux	Operational lifetime
Liquid membrane performance	50 litre/m^2/hour	<200 mg/m^2/hour	1 month

When evaluating the technology barriers listed above, it is important that the end goals for the liquid membrane performance enter into our considerations.

2 Status: FO liquid membrane design

Take home messages:

- Easy to produce – easy to modify
- Long shelf life – several weeks
- Initial rejection rates exceeds commercial FO membrane
- Optimization is on-going to improve water flux – achieving a sufficiently high water flux is currently seen as the main technology barrier.

Our current liquid membrane formulations consist of off-the-shelf (i.e. cheap) components within the component categories:

- Oil
- Biomimetic membrane components
- Aqueous buffer solutions

In addition to the aforementioned components, our liquid membrane formulations also contain aquaporin protein. During the course of work package 1 we have improved the liquid membrane fabrication method as well as gained a comprehensive understanding of how changes in membrane components and protein content affect macroscopic properties of liquid membranes, such as overall stability (shelf life) and viscosity.
We have started testing liquid membrane formulations in FO set-ups (see for example figure 6 in chapter 4 and appendix 2) and initial experiments show that our liquid membranes have a higher rejection of both salt and larger fluorescent markers (for example calcein) as compared to the commercially available membrane from HTI.
As stated in the take home messages, the water flow through our current liquid membranes in combination with encapsulation membranes and liquid membrane housings (see chapter 4) is still too low (<5 l/m^2h) compared to the necessary liquid membrane performance values listed in table 2. This could be due to concentration polarization (see appendix 2) taking place in the current encapsulation membranes used, the thickness of the liquid membrane layer itself, too much oil in the liquid membrane formulation, deactivation of aquaporins due to denaturing, or a combination of all of the above factors. In work package 2 we will address these issues further in order to achieve a sufficiently high water flux.

3 Status: Draw solution design

Take home messages:

- We have identified all the necessary criteria, which must be met in order to have a draw solution applicable to industrial processes.
- According to literature, $KHCO_3$, $MgSO_4$, $NaHCO_3$ and $MgCl_2$ fulfil these criteria to an acceptable level[11]. These draw solutes will be tested in more detail in work package 2
- We feel confident that Modern Water[12] is currently using $MgSO_4$ as a draw solute in their FO desalination test facilities in Gibraltar and Oman.
- Other possibilities for draw solution design include high concentration sugar solutions, such as 5M fructose, or ACD[8] (a solution of highly dissolvable thermolytic ammonia salts which upon heating decompose into ammonia and carbon dioxide gasses). Fructose (figure 7) and ACD (appendix 3) have been tested in our lab with limited success.

As mentioned before, a carefully designed draw solution is another factor in making FO a viable alternative to existing technologies. Different factors have to be considered when choosing a draw solution for a given process. In general it can be said that an optimal draw solution should fulfil following parameters:

- **High osmotic pressure**
  This criterion is crucial since a high osmotic pressure in draw solution always improves the flux of permeate water. The criterion is related to high solubility (g/l), but by using small molecules/ions, a high osmotic pressure can still be obtained at low concentrations.
- **Low reverse diffusion**
  Due to the membrane not being a perfect barrier molecules from the draw solution will diffuse against the water flow into the feed. This diffusion is driven by the large solute concentration difference between feed and draw. The leakage of molecules from draw into feed can cause a decrease in the water flux driving force and furthermore, can contaminate the feed. This contamination has to be taken into account because it has an impact on how the feed will be processed further.
- **Low CP**
  This criterion is related to the osmotic pressure since most of the osmotic driving force is lost to CP (Concentration Polarization). When the permeate passes through the membrane and dilutes the draw it is important to have a high diffusion rate of

[11] Refer to appendix 3 for more information
[12] Modern water is a global company specializing in providing patented water technologies such as manipulated osmosis (MO), which is their version of an FO water extraction technology.

the solutes in the draw. Otherwise the osmotic difference across the membrane (the driving force) is decreased and thereby the flux.

- **Low/no toxicity**
  Residual amounts of draw solution are always difficult to avoid in the final product water – especially when the final separation process has to be cost-effective. Therefore it is important to use non-toxic solutes. Here, to help identify suitable candidates the Hazardous Materials Identification System (HIMS) can be used.
- **Stable**
  Solutes unable to maintain their osmotic effect in the solution will lower the overall flux. Solutes that degas, precipitate or react with the membranes used can damage or block the FO-system.
- **Inexpensive**
  When choosing between two nearly identical systems the cheapest is always preferred. A 10% improvement in flux will not justify a 50% increase in price. The current price for desalination of 1 m^3 of seawater can lie anywhere in between 0.5 and 5 $ depending on where and of which size the plant is [6]. Therefore, draw solutions; membranes and pumps should not exceed that price at any point.
- **Recycle**
  Related to price, and ease of separation. If the solutes in draw can be recycled the price will be drastically lowered.
- **Easy and cheap to separate from permeate**
  The better the separation of draw and permeate is, the better the osmotic pressure is kept (less dilution), the price reduced (less loss of solutes and need of further cleaning of permeate) and the toxicity lowered (if any). Here, the extraction of the filtered water from the draw solution is crucial. Suitable techniques could be a slight heating to evaporate the dissolved draw compounds or a Nano filtration (NF) step. This criterion is often the Achilles heel (Figure 6) of any FO process since using another filtration step lowers the production of final product water and increases cost and energy consumption. Therefore, draw molecules should be chosen so that they are easily separable from the filtered water.

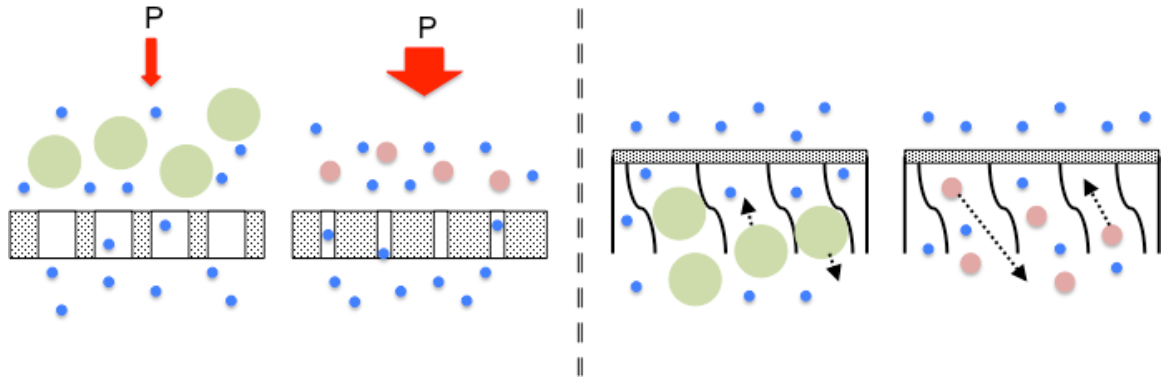


Figure 6: The Achilles heel of selecting draw solutes. Left: Larger draw solutes require less energy to be separated from permeate. Right: Larger draw solutes have a lower diffusion rate towards the active layer of the FO membrane in question. This results in dilutive concentration polarization and hence a lower flux performance.

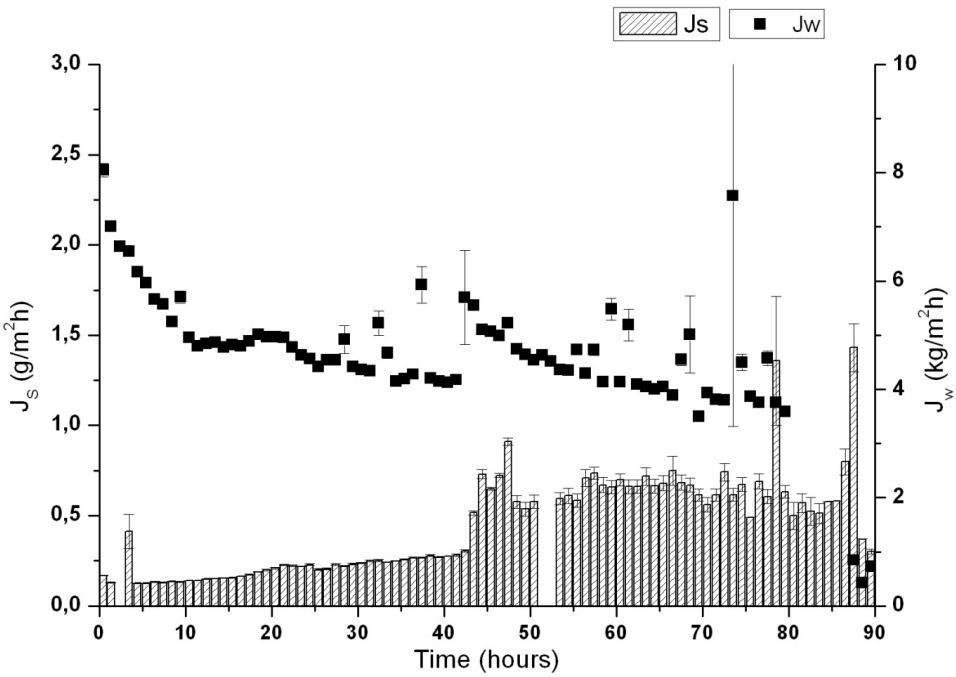


Figure 7: Desalination of seawater (Øresund) using the commercial HTI membrane and 5 M fructose as draw. High osmolarity fructose solutions have a high viscosity, which due to concentration polarization effects reduce the water flow to around 4 l/m^{2}h. In addition the leakage of salt from feed to draw is above the 200 mg/m^{2}h limit needed to produce potable water.

4 Status: System design

Take home messages:

- An in-house FO test set-up has been developed (Figure 8)
- A flat sheet module has been developed for testing liquid membrane formulations under FO operating conditions (Figure 9)
- Hollow fibre contactor modules for liquid membrane formulations are currently being developed through external partnerships (Figure 10)
- Modern Water has implemented FO desalination test facilities, using a commercially available FO membrane, in Oman and Gibraltar (Figure 11). The fact that large-scale systems already exist for FO desalination means that this most likely will not be a technology barrier for our FO membrane design in the future.

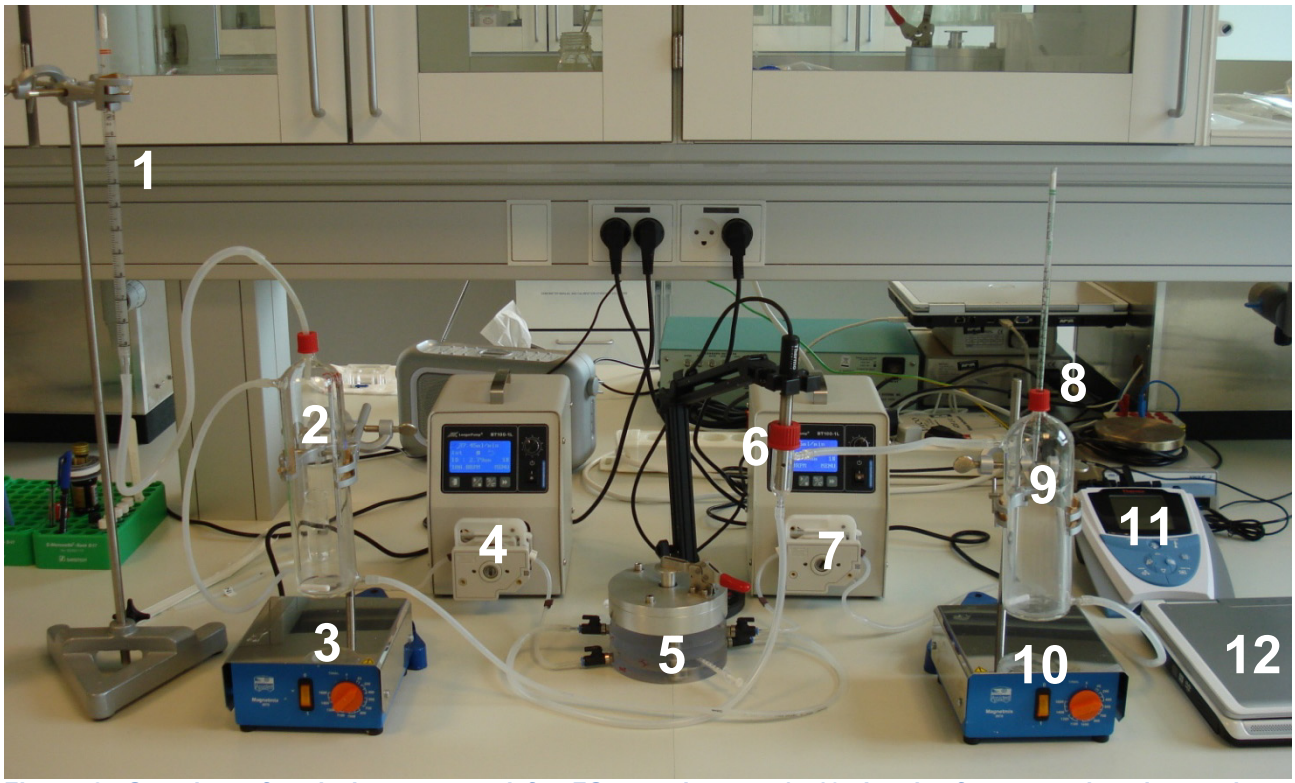


Figure 8: Overview of typical set-up used for FO experiments. 1: 10mL tube for measuring draw volume increase. 2: Draw reservoir. 3: Stirrer for draw reservoir. 4: Draw loop pump. 5: FO chamber. 6: Conductivity meter probe. 7: Feed loop pump. 8: 2ml tube for measuring feed volume decrease. 9: Feed reservoir. 10: Stirrer for feed reservoir. 11: Conductivity meter. 12: PC for data logging.

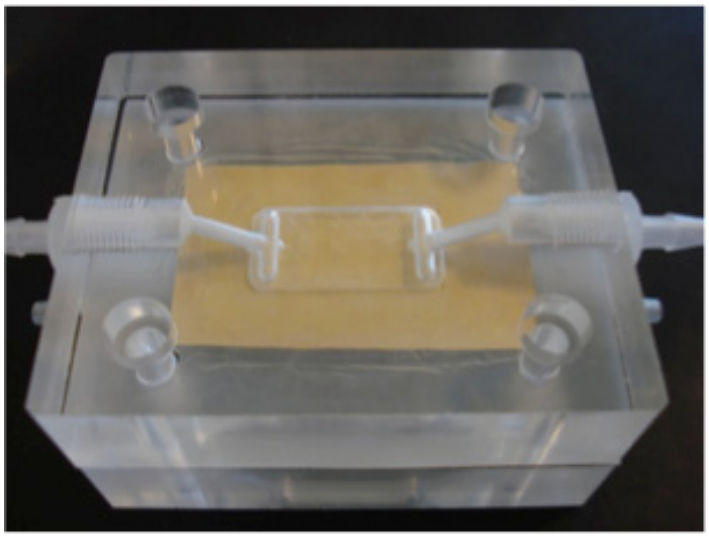


Figure 9: Flat sheet module for liquid membrane testing under FO conditions. The liquid membrane is sandwiched between two encapsulation membranes. Feed and draw solutions are connected through the tube connections. This module fits directly into position number 5 in figure 8.

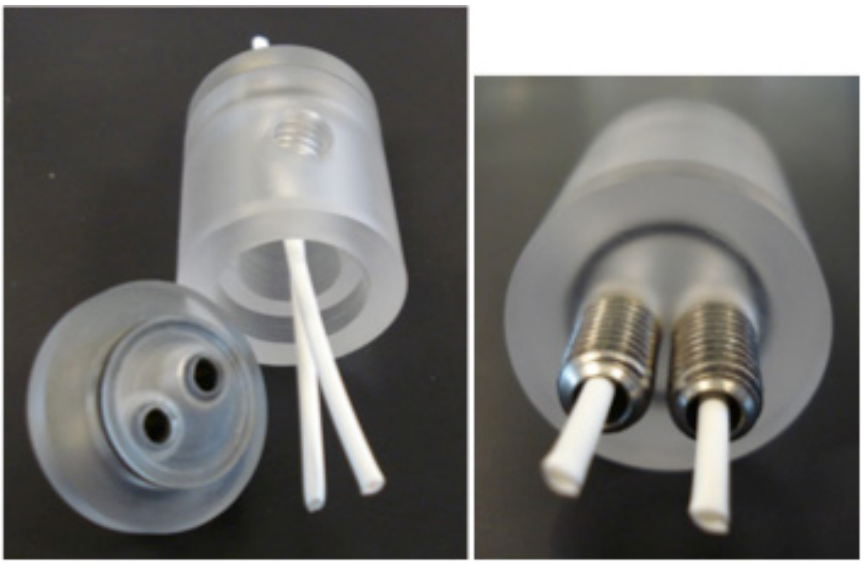


Figure 10: A crude example of a hollow fibre contactor module. Feed and draw solutions are connected to the internal volume of the hollow fibres and liquid membrane is filled in between. One of the advantages of a hollow fibre module is that the physical restriction of liquid membrane volume is easier to achieve as compared to a flat sheet module. Additional advantages include reduction of the mechanical stress imposed on a liquid membrane in the flat sheet module.

FO system design

The overall system design of a biomimetic desalination plant has to be chosen according to the placement and the environment around the site. In general a desalination plant based on biomimetic hollow fibre modules could be designed like the schematic in Figure 11 depicts. The saltwater intake has to be cleaned from organic material and bigger particles. The so pre-cleaned saltwater is then transferred via a pump (P1) to the hollow fibre contactor module where our liquid biomimetic membrane will facilitate water transport out of this saltwater and into the draw solution that is applied to the hollow fiber module via a second pump (P2). The so up-concentrated feed can now be mixed with fresh intake and used again or just disposed into the sea. On the other side of the circuit the now diluted draw solution has to be separated from the water that was extracted from feed. This can be done via a reverse osmosis step. This step is crucial for the overall energy balance of the system and the draw solution has to be chosen in such a way that easy separation is possible. After this separation step the desalinated water can now be further processed (e.g. addition of minerals). The fully recovered draw solution, in contrast, is transferred to the draw reservoir and can so be re-used for further desalination.

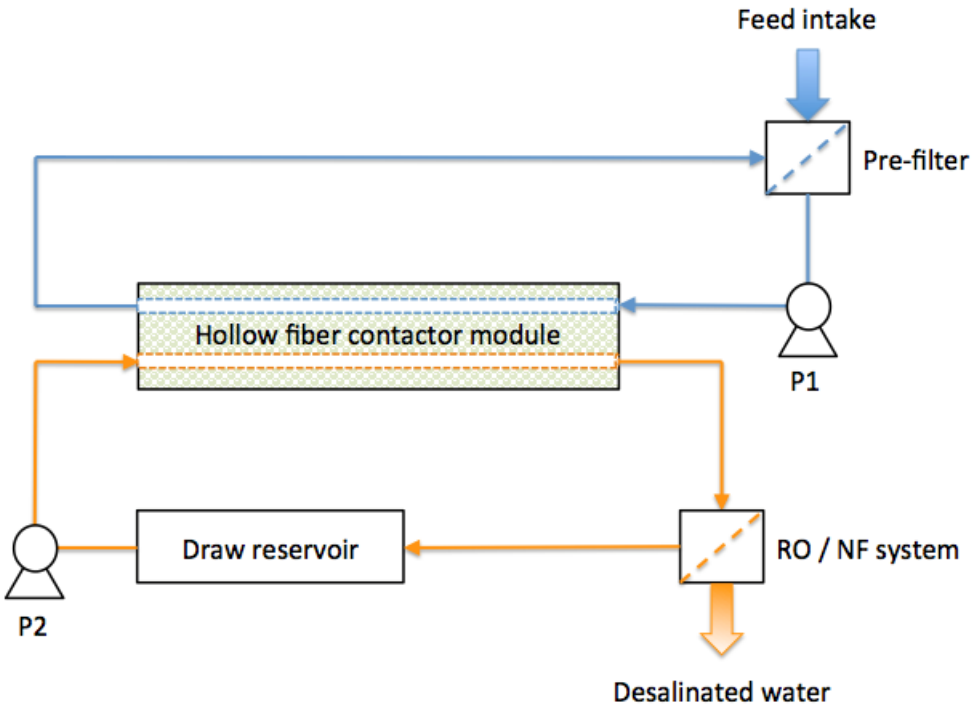


Figure 11: schematic of desalination plant (Figure adapted from [7]). In the Modern Water FO pilot plants, the energy consumption for treating water has been reduced by 30% compared to traditional RO plants.

5 Outlook to work package 2

The overall goal of work package 2 is to find a combination / combinations of liquid membrane modules and liquid membrane formulations, which have the potential of solving the technological challenges described in work package 1. In order to do so, we need to develop assays and test systems to monitor liquid membrane performance as well as give us feedback to what we can change if a given formulation does not perform well under FO operating conditions. So far we have initiated the development of the following assays and test systems:

- Operational FO system for testing of liquid membrane performance under different operating conditions, such as osmotic driving force, draw solution composition, encapsulation membranes and cross flow speed.
- Assays to detect the movement of fluorescent tracer molecules from the feed solution through the liquid membrane formulation and into the draw solution. These tracer molecules allow us to infer knowledge about the rejection properties (i.e. tightness) of liquid membrane formulations
- Assay to detect the immediate environment surrounding the aquaporins in situ in liquid membrane formulations. This assay is needed to assess whether different liquid membrane formulations are compatible to the aquaporin proteins, and whether this compatibility changes during the course of FO operation.

At the end of work package 2 we aim to have a narrowed-down selection of liquid membrane formulation candidates together with liquid membrane encapsulation membranes and housings, which are to be integrated in a lab-scale demonstration model showing proof-of-principle. This integration work will take place in a subsequent work package 3 provided we are able to secure funding for this work.

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Appendix 1: Water flow calculations

The water flow J_V from region 1 to region 2 through a membrane area S with a given membrane permeability constant P_F due to a hydrostatic driving force

P_1-P_2

and/or an osmotic driving force

$$\sum \sigma_i(\pi_{2i} - \pi_{1i})$$

is calculated as

$$J_V = \frac{P_F \cdot S \cdot V_w}{R \cdot T}((P_1 - P_2) + \sum \sigma_i(\pi_{2i} - \pi_{1i}))$$

where V_w is the molar volume of water, T is the temperature in Kelvin and R is the gas constant.

The membrane permeability constant P_F for an aquaporin loaded membrane is calculated from the single aquaporin channel osmotic permeability constant p_F and the number of channels per unit area N_c as:

$$P_F = p_F \cdot N_c$$

Below are some relevant calculation examples (input values light grey shading, calculated values light green shading)

p_F	$1*10^{-13}$ cm^3/s	$1*10^{-14}$ cm^3/s
Area of 1 aquaporin channel	$4.225*10^{-13}$ cm^2	
P_F	0.24 cm/s	
S	1 m^2	
T	293K	
R	82.05746 (cm^3*atm)/(K*mole)	
V_w	18 cm^3/mole	
Membrane coverage of aquaporin	50%	
Driving force	45 atm	
J_V	144 l/hour	14 l/hour

Table 6: Calculated water flow for $p_F = 1*10^{-13}$ cm^3/s and $p_F = 1*10^{-14}$ cm^3/s

Appendix 2: FO operation and concentration polarization

FO operation

As mentioned in 1.2, FO solely uses the osmotic pressure to force water through the semi-permeable filtration membrane. No external hydrostatic pressure is used or needed. In basic words FO can be described as a process where water penetrates a semi-permeable membrane due to the differences in solute concentration between the two liquids on either side of the membrane – for example when water molecules are exchanged between the draw and the feed solution.
As in every other filtration process, the feed solution refers to the solution which enters the filtration system as the feed stream and which contains molecules that should be separated from the rest of the solution. The draw solution, which is also called osmotic agent or driving solution, generates the driving force for the FO separation process. It is a concentrated solution on the permeate side. Due to the difference in concentration between the permeate side and the feed stream, a high osmotic pressure is induced on the draw side which leads to a transport of molecules across the semi-permeable membrane. This means that the draw solution becomes diluted whereas the feed solution becomes more concentrated. The basic principle of FO can also be seen in Figure 12.

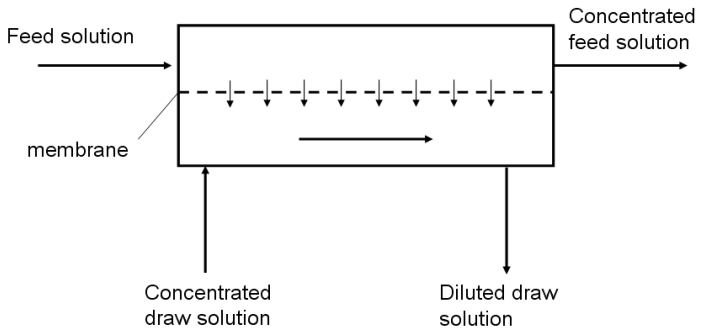

Figure 12: Principle of FO – a feed solution and a concentrated draw solution are separated by a dense, non-porous, selectively permeable membrane. Molecules from the feed are drawn in to the concentrated draw solution by the osmotic pressure caused by the concentration gradient between the two solutions. The output of a FO process is a concentrated feed and a diluted draw solution.

The main advantage of FO compared to other filtration/separation processes is that only minimal or no external hydrostatic pressure is required. This means that since the only pressure that is involved in the process is due to the flow resistance of the semi-permeable membrane the rest of the equipment can be rather simple. No-high pressure valves, fittings or tubing are needed and no additional components that pressurize the feed have to be installed. Furthermore, literature reports that FO may have a lower membrane fouling propensity than pressure-driven membrane processes [1], [2].

The most important factors to make FO an economically feasible alternative to present filtration techniques are high flux combined with a high rejection rate. Flux

defines the amount of permeate going through the membrane over time and the rejection rate tells us how many unwanted particles are rejected by the membrane. Both factors can be influenced by the draw solution and the membrane in itself. Cath [1] describes that a membrane optimized for FO should have a high density active layer, a thin support, that it should be hydrophilic and have a low affinity to fouling. Furthermore, it should minimize concentration polarization effects.

Concentration polarization

Concentration polarization (CP) influences the membranes' performance and results in what McCutcheon called a 'lower than expected flux' [3]. In general, CP is a build-up of concentration gradients on both sides of the membrane. Using the boundary layer film model Baker [4] calculates the concentration polarization modulus c_{t_0}/c_{t_b} as:

$$\frac{c_{t_0}}{c_{t_b}} = \frac{\exp\left(J_v\delta/D_i\right)}{1 + E_o\left[\exp\left(J_v\delta/D_i\right) - 1\right]} \qquad (1)$$

where J_v is the volume flux over the membrane, δ the boundary layer thickness, D_i the diffusion coefficient and E_o the membrane's intrinsic enrichment. This enrichment factor is defined as:

$$E_o = \frac{c_{i_p}}{c_{i_0}} \qquad (2)$$

with c_{i_p} as the concentration of salt in the permeate and c_{i_0} as the concentration of solute in feed at the membrane interphase.

In principle, there are two types of concentration polarization – internal and external. Gray [5] and McCutcheon [6] found that external concentration polarization as often observed in RO applications has minimal influence in FO applications. Here, several studies showed that the application of cross-flow and the use of spacers [7-13] minimize boundary layer and to such an extent that ECP can be neglected. As can be seen in (1), the magnitude of concentration polarization becomes exponentially smaller when decreasing the boundary layer thickness δ.

More important than external CP is the influence of internal CP. Internal concentration polarization can be further divided into dilutive ICP and concentrative ICP. If the active layer of the membrane faces the draw solution, as in PRO applications, solutes accumulate on the feed side inside the porous support and concentrative internal CP occurs. It is comparable with concentrative external CP but occurs inside the confined space of the membrane. In FO applications where the active layer faces feed, solutes in the draw have to diffuse through the porous membrane to the active layer. When now water permeates the active layer it dilutes the concentration of solutes at the active layer. This is called dilutive internal CP and causes the concentration at the inner active layer to be smaller than the concentration in the bulk which results in a smaller osmotic pressure and thus in a

smaller driving force. A schematic overview over concentration polarization effects in FO can be found in Figure 13. Limiting ICP is of outmost importance in the development of new forward osmosis membranes [14]. McCutcheon [6] proposed two ways to limit ICP – limiting the flux or increasing the diffusion coefficient. Looking at the purpose of FO like desalination a limited flux would be counterproductive. Therefore, increasing the diffusion coefficient of the solute in the osmotic agent would be the better option to choose. One way to do that is to change the draw solution. The other option is to tailor the membrane where the porous support should be made thinner or more porous which would increase diffusion of solute to and away from the membrane.
Therefore, the modification of current membranes is a viable option but also the introduction of new types of membranes should be considered. One example would be the introduction of a biomimetic liquid membrane containing aquaporins.

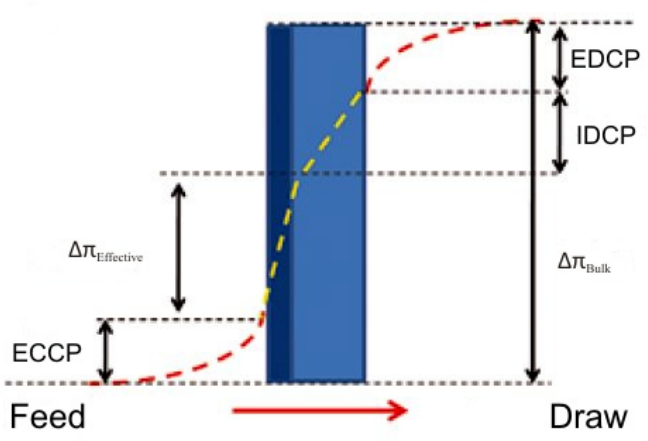

Figure 13: Schematic of polarization effects in FO; Instead of the bulk osmotic pressure $\Delta\pi_{Bulk}$ only the effective osmotic pressure defines the driving force for separation. The decrease in pressure is caused by concentration polarization effects in particular external concentrative CP (ECCP) at the active side of the membrane (dark blue) and internal dilutive CP (IDCP) inside the porous support (light blue) and external dilutive CP (EDCP) [15].

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Appendix 3: Literature study on possible draw solution candidates

Recently, Achilli, Cath and Childress published a paper where they screened inorganic materials in regards to their suitability as draw solution for forward osmosis applications [1]. Their initial criteria for finding suitable compounds were water solubility, if it is a solid phase at ambient temperatures, how hazardous it is, an minimum osmotic pressure of 1 MPa and the specific cost per L. Out of a total of 500 compounds they choose 14 for experimental investigation. Using the only commercially available and well-investigated FO membrane from HTI (Hydration Technology Innovations, LLC, Scottsdale, AZ) they investigated the draw solution's performance in regards to water flux and reverse solute flux. Draw solution re-concentration was then analysed using RO system design software. In the end of their extensive test series, Achillis et al. identified seven possible candidates that performed well in the before chosen two main categories of performance and replenishment costs. The often-used NaCl, for example, is well suited as a draw molecule because it is cheap and thus achieved a high score in replenishment costs. However, the performance is rather low and for the purpose of desalination it is unsuited. In contrast, $CaCl_2$ and $MgCl_2$ scored high in performance but suffer from high initial solute costs. Three compounds scored high in both categories – $KHCO_3$, $MgSO_4$ and $NaHCO_3$. However, due to mineral salt scaling at the membrane surface when concentrating the feed solution the authors suggest that '$MgCl_2$ may be the best draw solution for most water and wastewater applications ' [1].
Several of the in the study mentioned draw solutions are already under investigation by other research groups. In our lab we used an ammonia-carbon dioxide (ACD) solution as investigated by McCutcheon et al. [2] and fructose as possible draw solution candidates. In contrast to the inorganic compounds investigated in the before mentioned papers, fructose is an organic molecule. We found that the ACD system proved difficult to work with and especially the issue with premature degassing of the draw solution needs attention. Further attempts to use this draw system should be done with distillation column and re-injection of gas. Here, the fructose draw solution is the simplest method for obtaining high osmotic pressure, while still producing drinkable permeate from seawater in the form of diluted draw solution. However, when comparing economy of the two systems, the price for the ACD is almost 19 times lower making draw solutions of similar osmotic pressure (0.45 $\$/l_{Draw}$ vs. 0.024 $\$/l_{Draw}$). Using fructose as draw would therefore require a higher price for the final product and an option would be sell it as a sweet drink that could be charged at a higher price.
In an extensive study carried out as a PhD project Al-Zuhairi investigated the usability of $MgSO_4$ as a draw solution [3]. He used it in different concentrations and with different setups and compared his results with results obtained using NaCl as a draw tested under the same conditions. He could conclude that although $MgSO_4$ produces lower water fluxes than NaCl when using the same concentration it is suitable as a draw. Water flux in forward osmosis depends on difference of osmotic pressure and not just mere concentration, which he showed by having similar flux values when applying NaCl and $MgSO_4$ solutions with similar osmotic pressures.

Due to the fact that $MgSO_4$ has a high molecular weight it is easier to separate from the extracted water in an NF step. This means that a low energy process can be used for separation of draw and water, which makes $MgSO_4$ a suitable candidate for an efficient draw solution for desalination.
Due to the on-going research and the many different possibilities one ideal draw solution could not be identified yet. However, with the help of a scheme like the one developed by Achilli et al. several candidates can be identified and chosen depending on the later use of the final product.

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