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Fakulta mechatroniky, informatiky
a mezioborových studií

EFEKT NANOVLÁKENNÉ STRUKTURY NA PROUDĚNÍ FILTRAČNÍCH MÉDIÍ

Autoreferát disertační práce

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Abstrakt

V této disertační práci spojuji formou sebraných publikací všechny zásadní oblasti týkající se vývoje nových membrán, od literární rešerše, přes vývoj metodiky hodnocení, k výrobě membrán, jejich testování a v neposlední řadě jejich použití při zpracování průmyslové odpadní vody.

Vývoj vhodné a ekonomicky proveditelné technologie pro zpracování průmyslových odpadních vod až do nulového odtoku kapaliny je nezbytný, zvláště v době stále se zpřísňující odpadové legislativy, která prosté vypouštění prakticky vylučuje.

Membránová destilace se v této situaci jeví jako vhodné řešení, neboť může být poháněna alternativními zdroji energie, případně odpadním teplem. Navíc umožňuje zahuštění nástřiku až k mezi nasycení bez zásadního poklesu intensity toku skrz membránu. Především z důvodu nedostatku vhodných membrán je v současnoti jejich využití v průmyslu minimální.

Kombinací nanotechnologie a membránového výzkumu jsem dokázal úspěšně vyvinout a otestovat nové nanovlákenné membrány specificky určené pro membránovou destilaci. Tyto materiály mají výrazně lepší intensity toku než současné komerční produkty. Proto mohou výsledky této disertační práce významně podpořit uplatnění membránové destilace při zpracování odpadních vod i ochraně životního prostředí.

Abstract

Based on a collection of recent publications, this PhD thesis covers all fundamental areas of new membrane development, including theoretical background research, assessment of methodology, membrane fabrication and testing, and even an industrial application.

There is an urgent need to develop of appropriate and economically feasible technologies to treat industrial waste waters at up to zero liquid discharge, particularly as ever more stringent European legislation leads to a situation where simple discharge is no longer an option.

Membrane distillation can provide a solution as it can achieve feed saturation levels without any significant flux decline, while being driven by alternative energy sources or even waste heat. Unfortunately, large-scale application has been held back by inefficient membranes.

Today, the combination of nanotechnology and membrane science had lead to the development of novel nanofiber membranes for membrane distillation that have unrivalled trans-membrane flux and show a promising future for application in the protection of our environment.

Keywords: membrane distillation, zero liquid discharge, industrial waste water

Objectives and Contributions

The primary objective of my PhD thesis was to study media flow across nanofiber structures, aiming at flux improvement in two areas of waste water treatment:

1. Nanofiber deposits with silver nanoparticles. Improving long term performance of ultrafiltration membranes by inhibiting bacterial growth on their surface.
2. Development of completely new nanofiber membranes specifically for membrane distillation, with better performance than current commercial products.

In both cases, a continuous loop of testing and subsequent membrane optimisation was necessary to finally obtain competitive materials of my own original design. Moreover, membrane distillation was tested with real industrial waste water and a feasibility calculation carried out to assess its economical potential. The contributions of this work consist of

- development of a testing methodology for the use of nanomaterials in membrane separation
- design and construction of experimental testing units
- design, testing and optimization of new membranes
- significant publication results
- transfer and cooperation with MemBrain, s.r.o. in the area of membrane distillation
- contribution to several research projects under TUL, most notably
    - NANOBIOWAT: Environmental friendly nanotechnologies and biotechnologies in water and soil treatment (TE01020218). TAČR, WP4 – Nano- and bio-modified filters and membranes for water treatment.

  - NAMETECH: FP7 – Development of intensified water treatment concepts by integrating nano and membrane technologies.

The main benefit of this approach consists in the integrated sequence of steps that led me from testing of ultrafiltration membranes to development of my own membrane distillation membranes from my original conceptual idea and first prototypes, over building testing units and membrane optimization, to final pilot-scale testing of membrane distillation on a real industrial effluent stream, the whole process being covered by scientific publications.

Contents

1. Introduction

One of the most urgent challenges in the world today is the rising demand for clean drinking water combined with the need to treat the ever increasing production of industrial and municipal waster water. To meet these increasing needs, there is an urgent need for the development of innovative new technologies and materials. While novel approaches for cheap and self-sustained processes that are as durable as existing technologies are being continuously examined, we have not yet seen a break-through technological advance to rival the global spread of reverse osmosis (RO). Nanotechnology may play a key role in resolving many of current and future problems with water purification, however, as it offers novel materials with truly remarkable properties for water desalination, reuse or recycling.

Today, membrane processes play a crucial role in water purification, from removal of suspended particles and micro-organisms by microfiltration (MF), removal of larger organic molecules by ultrafiltration (UF), to waste water softening by nanofiltration (NF) and complete desalination by membrane distillation (MD) or RO. Polymer membranes, crucial components of the membrane process, can be fabricated by a range of methods, from phase inversion techniques, such as immersion precipitation or evaporation induced phase separation, to stretching, track-etching or electrospinning [1].

Electrospinning is a very flexible technique that creates nanofiber layers from a range of polymers. In this process, thin filaments are formed from polymer solutions using an electrostatic field as the main drawing force. Thanks to their very high specific surface area and very fine pore size, these non-woven webs are very suitable for use as membranes. This PhD thesis covers two parts related to the development of novel membranes, both deriving from diverse properties of the layers:

1. The possibility to combine additives with electrospun fibres by mixing them with the spinning solution was the main motivation for the investigation into bio-fouling during UF, which negatively affects trans-membrane flux. In this work polyurethane (PUR) and polyethersulphone (PES) coating with immobilized biocide

nanoparticles of silver were fixed onto the surface of commercial UF membranes in order to avoid the formation of bio-film on the feed side of the membranes.

2. The very high porosity resulting from the interconnected structure between nanofibres, which allows for the efficient transfer of molecules [2], drove research into media flow across nanofiber structures into the realm of MD, where evaporated molecules are driven through the membrane's pores from a hot feed to a cold distillate by a difference in vapour pressure. MD sorely lacks suitable membranes and it is believed that this is the root cause preventing MD from becoming a mainstream desalination technology [3].

Materials research on new membranes, whether UF or MD, should be clearly focused on industrial application. Hence, novel materials must provide clear benefits over conventional and established technologies. Industry in general is quite rightly sceptical of new break-through technologies promising unrivalled performance; therefore the potential risk must be worth it.

This PhD thesis is unambiguously focused on applied research and was initiated with the quite attractive topic of improving flux in UF through mitigation of microbial growth on the membrane's surface. Over time, however, other techniques proved to be more effective and, along with unresolved environmental issues and the ever falling price of new membranes, this method of UF flux maximisation became a blind route. Nevertheless, all the acquired knowledge on the advantages and drawbacks of nanofibers in a pressure driven process helped me to identify a unique application potential in another membrane separation process, and I came up with the tedious idea to develop a nanofiber membrane for temperature driven MD.

MD has always needed high-flux membranes by nature as the flux cannot be increased simply by higher feed pressure and temperature gradients also have their practical limits. Nanofiber membranes proved highly suitable for this application and the first attempts resulted in positive findings [4].

I have further evolved the first membrane concept by testing various polymers (first polyvinylidene fluoride (PVDF) and then PUR) with different thermal-pressure lamination parameters to finally obtain materials that surpass commercial products. I have even designed and built a testing unit for direct-contact MD that I used to evaluate the MD performance under a range of conditions. Based on my design ideas and detailed instructions and/or suggestions regarding material and structural parameters, membranes were fabricated by my colleagues from the Laboratory of Nanomaterial Application (CxI) and the Department of Non-wovens and Nanofibrous Materials (TUL). As this PhD thesis is based on scientific publications that were a joint collective work, the relative contribution of the authors is given in Table 1.1 [1], covering all the development stages, from background research and membrane assessment methodology, to membrane fabrication, design of experiments, testing, and industrial application.

The study of trans-membrane flux through nanofiber structures is divided into two separate sections following the two basic approaches: (i) adding nanofibers to existing membranes (Section 2 and 3), and (ii) creating a stand-alone nanofiber membrane (Section 4 and 5). The commentaries on the collected publications appear after the theoretical parts, in order to clearly explain my approach to the concerns discussed.

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[1] Publication [5] has been accepted by Desalination and Water Treatment. Publication [6] is currently under review by Journal of Nanotechnology.

Area	**Stage**	**My Contribution**	**Co-Authors**
MD [7]	Background research	**Review paper**	Proof-reading
UF [8]	Membrane assessment methodology	DOE Permeability Ag stability Proof-reading	Electrospinning Lamination **Paper**
MD [9]	Experimental setup	Unit design Repeatability **Full-text, poster**	Construction
MD [10]	Laminated PVDF (large module)	Membrane design Experiments **Paper**	Electrospinning Lamination SEM
MD [5]	Laminated PVDF (small module)	Membrane design Experiments **Paper**	Electrospinning Lamination SEM
MD [6]	Self supporting PUR (small module)	Membrane design Experiments **Paper**	Electrospinning SEM
MD [11]	Industrial application	Experiments **Paper**	Feasibility SEM
MD [12]	Industrial application	Experiments (IEX) Proof-reading	Experiments (Zn) **Paper**

Table 1.1: Relative contribution of co-authors to each publication. Note: DOE = design of experiments, Ag = silver, Zn = zinc, SEM = scanning electron microscopy, IEX = ion exchange.

2. Mass Transport in Membrane Separation Processes

The common thread to all the publications in this thesis is the study of flux through porous structures and membranes. Membrane processes are a key part of many industrial separation processes; hence, the results obtained have a wide application potential. In order to set the established terminology used throughout this work, the following chapter contains a brief overview from the principal handbooks [13, 14, 15, 16, 17] addressing the basics of mass transport in *pressure* driven membrane processes. The transport of heat and mass in *temperature* driven processes is addressed separately in Section 4.

The core component of the separation process is a selective semipermeable membrane barrier that allows components to pass from the feed into permeate (also known as the filtrate, diluate, or distillate), while others are retained in the retentate or concentrate. A volumetric flux (J) from the bulk solution across the membrane is induced by a driving force, which may be a difference in pressure, concentration, voltage or temperature. Separation is then achieved by using a membrane that is permeable to components that differ from the bulk in physical or chemical properties, such as size, charge, or volatility. Typical pressure driven processes are summarized in Table 2.1, including the characteristic membrane pore sizes and approximate pressures.

Process	Pore Size	Pressure	Application
MF	10 to 0.05 μm	0.1 to 2 bar	Colloid removal
UF	0.05 to 0.002 μm	1 to 10 bar	Bacteria removal
NF	0.002 to 0.001 μm	5 to 50 bar	Water softening
RO	<0.001 μm	10 to 100 bar	Sea water desalination

Table 2.1: Pressure-driven membrane processes

While the transition between processes is not sharp, as pore size decreases applied pressure increases, from relatively small hydrostatic pressures in MF to large pressures in RO, in order to provide sufficient flux across the membrane.

Flux and the driving force are proportional and can expressed by *Darcy's law*

$$J = C_m \cdot \triangle p \tag{2.1}$$

where C_m is a permeability coefficient that also incorporates the thickness of the membrane selective layer. In order to assure high permeability, therefore, very thin skin layers are often used. Asymmetric membranes are made by attaching this thin layer (1 μm) to an open porous structure.

2.1 Operation Modes

There are two fundamentally different ways of running pressure driven membrane processes: dead-end and cross-flow. In *dead-end filtration* the bulk is pumped through the membrane and pressure is constant over the membrane surface. In *cross-flow filtration*, the bulk is pumped tangentially to the membrane and there is a pressure drop along the membrane surface. The feed comes in at one end, permeate passes through the membrane and retentate leaves at the other and recirculates. In dead-end filtration, the retentate in not removed continuously.

2.2 Membrane Retention

Retention can be defined as:

$$R_m = 1 - \frac{c_p}{c_f} \tag{2.2}$$

where c_p is permeate concentration and c_f is the feed concentration [15]. As the retained components are transported towards the membrane by convection, the surface concentration is often larger than that in the bulk solution. This enhanced surface concentration, known as *concentration polarization* (CP), can lead to an increased permeate concentration. Because concentration on the membrane surface is greater than that in the bulk, the true retention is often higher than the observed retention.

2.3 Osmotic Pressure

Hydrostatic pressure may build up between the two sides of a semi-permeable membrane where each has a different solute concentration, resulting in osmotic flow towards the more concentrated solution. Obviously, if hydrostatic pressure on the side with higher concentration equals the osmotic pressure, osmotic flux is prevented. Osmotic flow ceases at equilibrium, when the concentrations are the same and osmotic pressure is zero.

The whole phenomenon is induced by the chemical potential of the solvent, defined as

$$\mu_s = \mu_s^0 + R \cdot T \cdot \ln(a_s) + V_s \cdot p \tag{2.3}$$

where μ_s is the chemical potential of the solvent, μ_s^0 is the standard chemical potential of the solvent, R is the universal gas constant, T is the thermodynamic temperature, a_s is the activity of the solvent, V_s is solvent volume and p is the hydrostatic pressure. As a result, solvent concentration (activity) is higher on the more dilute side. Since the system wants to reach equilibrium, solvent will flow from the higher solvent potential to the lower solvent potential, and this flow will be proportional to the solvent chemical potential gradient over the membrane.

To obtain flux through the membrane, the applied hydrostatic pressure on the bulk side must be greater than the osmotic pressure difference between the permeate and bulk side. By adding this term to Darcy's Law we gain the *osmotic pressure model*:

$$J = C_m \cdot (\triangle p - \triangle \pi) \tag{2.4}$$

where $\triangle \pi$ is the osmotic pressure difference. Typically, the bulk is often recirculated and permeate continually removed, thus the equilibrium is never reached and flux is maintained. For instance, as the osmotic pressure of sea water is around 30 bar, a hydrostatic pressure of at least the same amount is required to induce flow through a typical RO membrane. Osmotic pressure can also be significant in MF and UF processes as large molecules diffuse slowly and a relatively high concentration on the membrane surface is maintained.

2.3.1 Calculation of Osmotic Pressure

For low molecular weight molecules at low concentration, the osmotic pressure π can be calculated using the van't Hoff equation:

$$\pi = i c_i R T \tag{2.5}$$

where i is the van't Hoff factor of the solute, $c_i = n_i V^{-1}$ is the solute molar concentration, R is the universal gas constant and T is the thermodynamic temperature. The number of dissociated ions is included in the experimentally determined value of van't Hoff factor i, which has to be looked up in the literature.

At higher concentrations, the simplifying assumptions that solute molar fraction $x_i \approx n_i n_s^{-1}$ and that $\ln x_s$ may be replaced by $\ln(1 - x_i) \approx -x_i$ are invalid and Eq. 2.5 has to be rewritten as:

$$\pi = \frac{\ln x_{solvent}}{V_m} R T \tag{2.6}$$

where V_m is the solvent molar volume and x_s is the solvent molar fraction.

2.4 Resistance to Mass Transport

In Darcy's Law and the osmotic pressure model, the flux through the membrane was dependent on the applied hydrostatic pressure and the osmotic pressure difference.

In practice, the flux can decrease even to as low as 5 % of the initial flux. This can be caused by the build-up of a concentration gradient in the laminar film covering the membrane surface (CP), by formation of a macromolecular gel layer on the membrane surface, or other types of fouling. Thus, a term representing total resistance in the form of a series of resistances is added to the Darcy's Law and osmotic pressure models:

$$J = \frac{\triangle p - \triangle \pi}{\eta \cdot (R_{memb} + R_{CP} + R_{foul})} \tag{2.7}$$

where η is the dynamic viscosity, R_{memb} is the membrane resistance, R_{CP} is the resistance by CP, and R_{foul} is the fouling resistance. As the total resistance increases with time, flux declines, provided that constant pressure is applied.

2.5 Concentration Polarization

(CP is the effect where retained macro-solutes accumulate on the membrane and form a second membrane. This results in restriction of flow through the filter and changes in selectivity, with the result that normally permeating species may by rejected. Typically, permeate flux increases with pressure. With CP, however, there is no response to pressure at all. There is a concentration gradient between concentrated solutes on the membrane surface and the bulk fluid, which generates a diffusive flow back to the bulk until steady–state conditions are reached and the convection of the solute to the membrane is equal to the diffusion from the membrane.

Convective transport of solutes to the membrane leads to a concentration increase in the boundary layer on the membrane surface. This convection of the solute to the membrane is balanced by diffusion back to the bulk solution and that part of the solute that goes to the permeate side.

$$J \cdot c = D \cdot \frac{dc}{dx} + J \cdot c_{perm} \tag{2.8}$$

where D is diffusivity, J is intensity of volumetric flux, c is concentration of solute, and x is distance normal to the membrane.

3. Mitigation of biofilm formation on ultrafiltration membranes

UF is a new and increasingly used variation of membrane filtration where pressure pushes a liquid against a semi-permeable membrane in a continuous system. One of the most significant complications in the UF process is *membrane fouling* caused by adsorption onto internal structure or the build up a layer of retentate on the membrane surface. This leads to CP which is the major cause of decreasing permeate flux through the membrane. Industrial applications range from waste-water treatment and whey production to virus removal and enzyme production in the pharmaceutical industry. Principle design considerations include high retention, hydrolytic stability and very good process flux.

3.1 Membrane Fouling

Fouling is a major concern in ultrafiltration. Process fluid changes the membrane properties, either chemically or physically, which results in decrease of flux through the membrane. Both fouling and CP reduce throughput, resulting in a significant additive resistance, with a process flux potentially ten times lower levels than that with pure water. Hence, the inclusion of anti-fouling measures is very important when designing the process. Proper selection of membranes, operating conditions, feed pretreatment, start-up techniques and cleaning type and frequency can make a major difference in fouling. The most popular method for reducing fouling is to recirculate the feed and maintain a high cross–flow velocity parallel to the filter. Note, however, that while the feed continuously removes the cake from the membrane surface, the remaining retentate thickens as more filtrate is removed.

In Eq. 2.7, CP gives contributes constantly (R_{CP}) to the total resistance of mass transport through the membrane. Flux should be constant with constant hydrostatic pressure; however, whereas CP contributes with constant resistance to mass transport, fouling contribution increases continuously, resulting in a continually decreasing flux.

This complex phenomenon is affected by many factors, including temperature, concentration, pH, ion strength and hydrophylic/hydrophobic interactions, typically resulting in adsorption of different molecules or colloids on the membrane surface, pore blocking by different cells, bacteria or aggregated macromolecules, or the build-up of a cake layer. Fouling is a complex phenomenon and its nature depends on the filtered medium and hydrodynamic conditions.

3.1.1 Biofouling

When filtering surface water with microbiological contamination, a resistant bio-film is formed on the membrane surface, deteriorating flux and membrane selectivity. Modern UF membranes tackle the problem by having the feed side extremely smooth, optimized for tangential or cross-flow operation. In this arrangement, feed is moved along the membrane, washing away most sediments in a recirculation mode. Micro-organisms, however, actively adhere onto the membrane surface and replicate, causing undesirable bio-film formation.

Membrane bio-fouling or bio-film formation is one of the biggest challenges in membrane separation processes [18]. Even after chlorine treatment, some bacteria survive and continue to multiply on the membrane surface [19], not to mention the potential to degrade the active membrane layer by the inevitable chlorine oxidation.

3.2 Silver Nanoparticles

Silver ions and silver-based compounds have long been known for their excellent biocide properties [20] and, consequently, have also been used to improve bio-fouling resistance. Despite only being dispersed throughout the membrane matrix, they showed very little resistance to washing [21]. In our paper **Membrane modification with nanofiber structures containing silver** [8], we provide details on our efforts to discover more effective methods of silver immobilization.

In this work, we modified commercial PES NADIR® UP150 UF membranes made with various forms of nano silver (silver nitrate, benzoate and behenate), by placing a nanofiber layer with nano silver onto the membrane surface, either by thermal–pressure lamination or by free deposition. Two polymers were used in this study:

1. PUR – the most abrasion-resistant elastomer, with good chemical and mechanical stability, and long-term heat resistance.
2. PES – heat-resistant, high performance engineering thermoplastic with excellent dimensional stability and chemical resistance.

As the silver precursors added alter the spinning solution viscosity, a key parameter for successful for fiber formation, an important part of recent work undertaken by J. Dolina, has consisted of the optimization of electrospinning conditions. Following from this, I tested the modified membranes for any changes in permeability, antimicrobial properties and silver leaching, and gave my feedback to adjust the membrane fabrication process. Concurrent characterisation of nano-modified and blank Nadir UP150 membranes enabled a direct assessment of the effect of nanofiber structure and its post-treatment on membrane permeability and nanosilver stability.

I found that all modified membranes displayed excellent antimicrobial properties, though at the expense of reduced permeability. The temperature of lamination needed to be optimized such that it was high enough for good adhesion of the nanofibers, and low enough to preserve good transport properties of the resulting composite. I found that free deposition, which eliminated the thermal–pressure lamination step, resulted it higher permeabilities, as confirmed by both Millipore/Amicon dead-end cell and an Alfa Laval M10 cross-flow unit.

The long chain and low solubility silver behenate showed better stability compared to the more soluble silver nitrate and benzoate, but silver leaching was still considered excessive and more work is needed to avoid this. Such work should also consider all the environmental aspects of potential nano-toxicity. There are two principal drawbacks related to improving UF membrane performance in this way:

1. One of the biggest selling features of nanofibers, their extreme surface density, has not been fully exploited as it is best applied in applications where the filtrate passes *through* the nanofiber layer. Unfortunately, the industrial standard is cross-flow filtration. Moreover, dead-end depth filtration, where the particles (or bacteria) are trapped inside the membrane pores, makes cleaning difficult, if not unworkable, considering how fine and brittle the nanofibers are.

2. Fixation of nanofibers onto the glossy surface of UF membranes eliminates this smoothness and, in practical applications, would not only increase the pressure drop along the module but also help the particles to attach better to membrane surface.

These shortcoming were to be solved in cooperation with Palacký University Olomouc (UPOL), where antimicrobial modification of dead-end micro-filters was first developed, based on their patent for covalent immobilization of silver nanoparticles by the polymer linker polyethylenimine (PEI) [22].

The findings were very promising and biocidal properties were excellent. Two different methods were used to test biocidal properties:

1. Cultivation tests based on Czech technical norm ČSN EN ISO 20645, using bromthymoline blue as indicator. Live bacteria that ferment lactose to produce acids, change its colour to yellow (Figure 3.1 a).

2. Fluorescent marking of micro-organisms using the Live/Dead method (http://www.lifetechnologies.com), in which dead broken cells colour red, while live cells remain green and filter fibers blue (Figure 3.1 b).

Tests of long-term permeability and silver stability were undertaken using an MS-1 unit designed by myself and constructed by MEGA a.s. Covalent silver was very stable without negatively affecting the flux. Unfortunately, the prepared paper called **Universal Approach to Covalent Immobilisation of Silver NPS on a Variety of Solid Substrates with Antibacterial and Antifouling Effect** was never submitted for publication.

At this point, given all the compromises and unsolved environmental problems with silver nanoparticles, I left for a six-month internship with Flemish Institute for Technological Research in Belgium (VITO) to study the process of membrane distillation and its application on waste water treatment.

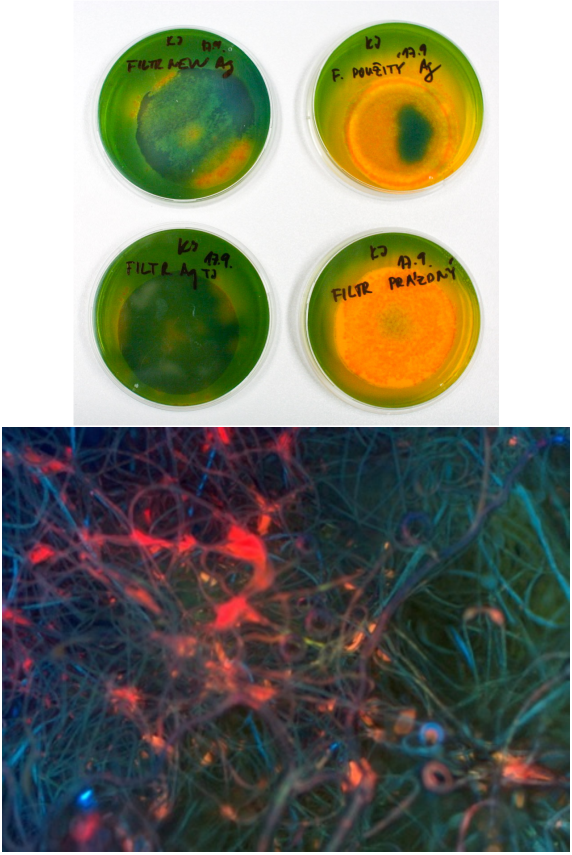

Figure 3.1: a) Cultivation tests, b) Live/Dead fluorescence

4. Membrane Distillation

MD is a thermally driven process that uses hydrophobic microporous membranes to separate vapours from aqueous streams. An induced vapour-pressure difference drives evaporated molecules through the membrane's pores from a hot feed to a cold distillate. While MD was originally designed for sea-water desalination, it can be used to separate a range of non-volatile substances from solvents. MD has many attractive features compared to 'traditional' desalination techniques, with lower operating temperatures than distillation and lower operating pressures than RO. Moreover, temperature-driven MD is not limited by osmotic pressure and can concentrate feed to saturation levels, theoretically retaining 100 % of non-volatiles.

Despite its potential, MD still needs large-scale application above 1000 m^3 per day in order to gain serious industrial recognition. Unfortunately, present performance simply cannot match that of RO, mainly due to a lack of suitable membranes, developed specifically for MD [3]. At present, hydrophobic MF membranes are used, despite suffering from pore wetting and poor thermal efficiency. This is mainly as they have been structurally optimized for removal of bacteria and suspended particles from water rather than temperature driven liquid vapour separation. In MD, the membrane simply acts as a barrier or contactor between two phases with different vapour pressures and displays no selectivity for any particular species. Membrane contactors naturally have different structural requirements than MF membranes; indeed, nanofiber layers appear to be quite extraordinary in this regard.

In order to establish the relevant terminology and relations used during nanofiber membrane development, the following section gives a brief excerpt from a chapter on membrane distillation that I wrote in Czech for the monography **Membránové dělení plynů a par** [7].

4.1 Module Design

An appropriate trans-membrane vapour pressure difference can be achieved using several different designs. In direct contact membrane distillation (DCMD), the hot feed solution is in direct contact with the cold permeate solution across the membrane. This configuration can produce reasonably high fluxes and is best suited for applications such as desalination and concentration of aqueous solutions [23, 24]. This configuration was also used to test all the membranes in this work. Other designs make use of an air-gap (AGMD), sweeping gas (SGMD) or vacuum (VMD) to achieve better energy efficiency, dislocated condensation of volatiles [25] or enhanced vapour pressure difference, respectively, but for the purpose of simple laboratory testing, DCMD has proved adequate.

Most MD installations are either tubular modules or plate and frame modules [26]. Hollow fiber tubular modules have a large active surface area of over 3000 m^{-1}, giving them great potential for commercial applications [27]. Simple plate and frame modules, however, have the significant advantage of easy replacement of damaged membranes, particularly advisable when new membranes are developed and tested.

4.2 Membranes

4.2.1 Membrane Characterization

In MD, the membrane is just a non selective liquid-vapour interface. Among the principal design considerations, the following are key attributes of suitable MD membranes:

1. Low resistance to mass transfer to provide high fluxes,
2. high liquid entry pressure p_{LEP} to keep the pores dry,
3. low thermal conductivity to prevent heat losses, and
4. good thermal stability to sustain high feed temperatures.

The permeate flux is proportional to porosity, and inversely proportional to membrane thickness and tortuosity. To obtain high permeability, the membrane should be as thin as possible but also thick enough to maintain good heat efficiency. High membrane porosity results in high permeate fluxes and low heat losses through conduction as the heat transfer coefficient of gasses in the pores is much smaller than that of the polymer [23, 28]. It is true that permeate flux increases with pore size, which is in conflict with the requirement that the pores be as small as possible to avoid wetting. These requirements are so demanding that, as yet, there have been no commercial membranes developed specifically for MD.

One of the most important MD performance indicators is membrane hydrophobicity, quantified by either p_{LEP} or bubble point pressure. Although the optimum value should be determined for each application based on the feed solution, the general relationship can be expressed by as:

$$p_{LEP} = \frac{-2B\gamma_l}{r_{max}} \cdot \cos\theta < p_{process} - p_{pore} \tag{4.1}$$

where B is a geometric factor, γ_l is the surface tension of the solution, θ is the contact angle between the solution and the membrane surface (depends on the hydrophobicity of the membrane), r_{max} is the largest pore size, $p_{process}$ is the liquid pressure on either side of the membrane, and p_{pore} is the air pressure in the membrane pores [29].

4.2.2 Construction Materials

Hydrophobic membranes can be made of polypropylene (PP), polyethylene (PE), polytetrafluoroethylene (PTFE) or PVDF [30]. MD is mainly suited for applications where water is removed as this assures because that can assure that trans-membrane hydrostatic pressure does not exceed the p_{LEP}. The porosity of the membranes typically ranges from 0.60 to 0.95, pore size between 0.2 and 1.0 μm [29], and thermal conductivity is typically around 0.2 W m^{-2} K^{-1} [3, 27, 31].

MD membranes can be prepared either by sintering (PTFE), stretching (PP, PTFE), phase inversion (PVDF) or, most recently, by electrostatic spinning [1, 32].

4.3 Heat and Mass Transfer

In MD heat and mass transfer are closely coupled together and occur in the same direction. In DCMD, the hot feed temperature (T_f) drops through the feed boundary layer to the membrane surface temperature (T_1), water evaporates and is transported through the membrane pores to the cold permeate side (T_2), where it then condenses. The flow temperature then drops through the permeate boundary layer to the cold permeate temperature (T_p). This effect is called *temperature polarization* (TP) and has been defined [28] as

$$TP = \frac{T_1 - T_2}{T_f - T_p} \tag{4.2}$$

By lowering the effective temperature difference, TP creates a resistance to mass transfer and is considered to be the main reason for low fluxes in MD [33]. When feed temperature is increased it has the following effects:

1. Decrease of the latent heat of vaporization ΔH
2. Increase in the feed vapour pressure p
3. Increase of turbulence by decreasing of dynamic viscosity η

There are three forms of heat losses that decrease the efficiency of MD: by TP, air trapped within the pores resisting mass transfer, and conduction through the membrane [34]. On the other hand, enhanced heat and mass transfer can be achieved by inducing turbulent flow, either with mesh spacers or by increasing the cross-flow velocity along the membrane. Heat transfer plays a significant role in MD efficiency. Four main steps are involved:

1. Heat transferred from the feed bulk to the membrane surface across the thermal boundary layer (TP)
2. Conduction through the membrane (heat loss)
3. Latent heat of vaporization (efficient heat)
4. Heat transferred from the membrane surface to the permeate solution across a thermal boundary layer (TP)

4.3.1 Vapour Pressure Difference

The mass flux (J) in DCMD is proportional to the vapour pressure difference across the membrane:

$$J = C_m \cdot (p_f - p_p) \tag{4.3}$$

where C_m is the membrane permeability and p_f and p_p are the vapour pressures at the feed and permeate sides. Vapour pressure increases exponentially with temperature and for low concentration solutions, where vapour pressure is assumed to be a function of temperature only, can be described by Antoine equation (4.4), where p is partial vapour pressure, T is thermodynamic temperature ranging from 284 to 441 K and A, B and C are component specific constants.

$$\log p = A - \frac{B}{C + T} \tag{4.4}$$

Water activity should be considered from both feed and permeate sides as vapour pressure will drop as solution concentration increases, such that:

$$p(T, x) = p_0(T) \cdot a_w(T, x) \tag{4.5}$$

where $a_w(T, x)$ is water activity as a function of temperature and concentration, and $p_0(T)$ is vapour pressure of pure water at a given temperature.

4.3.2 Membrane Permeability

Mass transfer through the membrane can be described by three models that relate mass transport to collisions between molecules, and/or molecules within the membrane. The dominant mass transfer mechanism of vapour permeation through a micro-porous structure depends on the ratio of the mean free path of molecules l, the mean pore size d and the Knudsen number $K_n = ld^{-1}$.

1. At $K_n < 0.01$ *molecular diffusion* occurs under the influence of concentration gradients.
2. At $K_n > 1$ *Knudsen diffusion* takes place and the collisions between the molecules and the inside walls of the membrane limit the mass transport.

3. At $K_n < 1$ in *Poiseuille (viscous) flow* ensures that there is a continuous fluid driven by a pressure gradient.

At 60ºC, l equals $0.11\,\mu$m and d ranges from 0.2 to $1.0\,\mu$m, so K_n will be between 0.5 and 0.1[29], indicating that vapour permeation falls between Knudsen and viscous flow.

4.3.3 Concentration Polarization

CP in MD is based on the same principle as in UF, though the consequences differ. Here, the liquid can reach a supersaturated state that can result in precipitation and/or scaling on the membrane surface. In pressure driven processes like UF, CP is usually on of the main reasons for flux decline. In MD, moderate flow rates and high heat transfer coefficients reduce its impact [35], only TP having a significant influence [36].

4.4 Operating parameters

4.4.1 Temperature and Temperature Difference

Feed temperature has a strong effect on permeate flux. Working at higher temperatures will increase the mass transfer coefficient across the membrane [30]. TP also decreases with higher feed temperature [24], though the process is more complicated, see Section 4.3. As there is little variation in vapour pressure at low temperatures, the effect of cold side temperature change is less significant than on the hot side.

It was observed that the permeate flux increases linearly with temperature difference [23], but the slope of the flux increase depends on which stream temperature remains constant [37].

4.4.2 Feed Concentration

MD can be used for highly concentrated solutions without suffering the large drop in permeability that is typical for pressure driven processes [23]. Generally, a flux decline can be experienced when feed concentration increases as partial vapour pressure decreases. At the same time, increased viscosity decreases the heat transfer coefficient due to a reduction in Reynolds number. When dealing with solutions of extremely high salt concentration, it becomes necessary to take into account the activity of water and use Eq. 4.5 instead.

4.4.3 Circulation Velocity

High recirculation minimizes the boundary layer and maximizes the heat transfer coefficient and flux. High fluid velocity also reduces the effect of temperature and CP. This effect is more significant on the hot side, whereas on the cold side the enhanced flow does not improve the permeate flux as significantly [38].

4.4.4 Membrane Fouling

An additional resistance layer may be formed on the membrane surface. Luckily, fouling in MD is significantly lower than in pressure driven processes and depends mostly on the reaction between the membrane and the feed, module geometry and operating conditions [39, 40].

In MD, the situation differs from pressure driven processes as increased deposition of foulants at the surface will lead to an increased pressure drop to levels where the hydrostatic pressure exceeds the liquid entry pressure of the feed into the membrane pores, resulting in pore wetting [33]. Pore wetting can also be caused by the presence of organic content or surfactants, which can reduce the surface tension of the feed solution or affect the membrane hydrophobicity [41].

Crystallization Fouling

Scaling results from the growth of crystals on the membrane surfaces during the treatment of concentrated saline solutions. Scale formation may affect membrane hydrophobicity and cause water to enter the pores. Precipitation of salts such as $CaCO_3$ can result in a rapid flux decline. A significant flux decline has also been reported during concentration of NaCl solutions containing organic matter [42]. The membrane in this case was completely covered with a fouling layer of NaCl and protein. Usually, scale formation or crystallization fouling takes place with aqueous solutions in which salt solubility decreases with temperature [33].

4.4.5 Applications

MD has been studied for a wide range of applications, especially in situations where low grade waste heat is available and when final brine concentrations that surpass the operational range of conventional pressure driven membrane processes are required. Many possible applications have been studied at the laboratory scale, and even pilot scale trials have been completed for specific cases. This section provides a brief overview of the most promising MD applications and describes several important pilot projects.

Laboratory Testing

Different types of hydrophobic membranes and configurations have been studied for a wide range of applications [30]. DCMD is the most frequently encountered MD configuration for laboratory scale research due to its simplicity and relatively high fluxes.

Extensive research has been undertaken on desalination of seawater at $\triangle T$ of 5°C to 25°C and fluxes typically between 5 and 30 kg $m^{-2}h^{-1}$, salt retention close to 100 % and distillate conductivity within the range 0.5 µS cm^{-1} to 10 µS cm^{-1} [3, 43]. DCMD has also been evaluated for the concentration of waste water from the textile and pharmaceuticals industries, on waters contaminated with metals and on waste water from an olive mill [23]). Due to its relative low feed temperature, MD can also be used for concentrating heat sensitive solutions in the food industry and has been widely tested for the concentration of fruit juices. MD has also been employed for selective extraction of volatile solutes and solvents, for the removal of ethanol from a fermenter and for the concentration of blood and plasma. A promising application of MD is the recuperation of spent acid from pickling baths in metallurgy. The VMD process can be used to shift the azeotrope of acid-water mixtures to a higher acid concentration. This has been previously shown for the hydrochloric acid-water azeotrope and the propionic acid-water system [29].

5. Development of Nanofiber Membranes for Membrane Distillation

While the assessment methodology [8] and theoretical background research [7] are covered in Section 3.2 and 4, this section contains a discussion on the fabrication and testing of MD membranes [5, 6, 9, 10], as well as their industrial application [11, 12]. Please note that one paper has been accepted by Desalination and Water Treatment [5], and one other is currently under review by Journal of Nanotechnology [6].

5.1 Membrane Fabrication and Testing

5.1.1 Initial Idea

My rather tedious efforts to fabricate and test new nanofiber membranes began after initial tests suggested that my idea of forming MD membranes from nanofiber layers may in fact haven been correct. Our one- and two-side laminated PVDF membranes were the thinnest of the array of PP, PE and PVDF commercial membranes tested, and had the highest fluxes [4], albeit only with pure water. Salt retention was relatively low, however, reaching only 98%, compared to over 99.9% for the other membranes. These results were attributed to minor ruptures in the super fine nanofiber layer which created a salt passage between retentate and distillate as indicated by an improvement in retention as recirculation velocity increased, ie. higher ratio of vapour flux relative to flow of salts through the membrane. One very positive finding was that the membranes did not suffer from irreversible pore wetting, pure water flux before and after the retention experiments remaining the same. Recirculation velocity had a positive effect on flux and our membranes appeared to be more susceptible to this effect, suggesting that TP was indeed more pronounced. One negative effect of thin membranes was a reduction in energy efficiency, which was about 30% in these first samples. Because the first results were positive and the issue of membrane thickness and performance has been left without a clear conclusion [32], I started pursuing the matter of very thin MD membranes further, with the aim of constructing membranes that were both highly efficient and permeable.

5.1.2 Experimental Setup

Testing the new membranes was initially conducted in cooperation with the department of Separation and Conversion Technology (SCT) of VITO; however, as the number of new membranes increased, I decided that it would be best to build my own experimental set-up, allowing me to have instant feedback on membrane performance under testing conditions that I considered important. This would allow me to retest suspicious results, confirm their repeatability and even share the equipment with other colleagues. As a first step, however, it was necessary to define the parameters to be evaluated and which equipment would be most suitable for obtaining repeatable and quality data.

Development of new MD membranes is clearly of great interest to many researchers today. Consequently, most MD manufacturers (e.g. MemSys – DE, Aquastill – BE, Solar Spring – DE, Convergence – NL) have lately acknowledged the potential of new laboratory testing equipment and have started to offer an array of suitable products. In 2013, however, the range on offer was more limited, not to mention the substantial cost involved. Hence, I decided to purchase just the module and connect it to the necessary peripherals myself.

The first set-up, with an effective membrane area of 500 cm^2, was built around a flat sheet module by Aquastill (NL). The resulting manual DCMD unit consisted of a peristaltic pump with a two-way rotational head that drove the feed and distillate through two heat exchangers connected to hot-baths, one for heating the feed and the other for cooling the distillate. A piping and instrumentation diagram of the unit is shown in an original research paper [10], in which the new PVDF nanofiber membranes were compared to commercial PE, PES and PTFE membranes that were provided by Aquastill along with the module. Regrettably, Aquastill requested that the manufacturers names remain undisclosed in both the research paper and this thesis. Flux was measured as a change in mass of feed and distillate on two weighing balances and was recorded on-line by a simple data-logging programme. Due to the limited accuracy (1.0 g) of these high capacity (10.0 kg) balances, which calculate the flux each minute and then take an average over a longer time period, more representative results were obtained by plotting volumetric flow intensity against time and taking its slope (Figure 5.1).

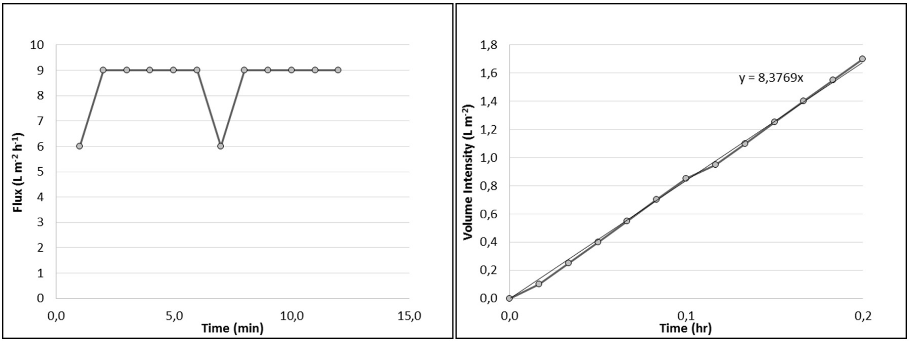

Figure 5.1: Two methods of flux calculation: a) One minute reading, b) Slope.

Temperature control, probably the most important aspect in MD, left a lot to be desired in the first design as permanent intervention was required. This was caused mainly by the cooling thermostat, which did not have sufficient power to remove all the heat coming across the membrane by both conduction and convection. First, I tried adding some stable cooling power by tap water, which was introduced by a T-joint right before the heat exchanger. Apart from not being very environmentally friendly, it was hard to control due to a permanent drop in water pressure. I even added an automatic valve that was controlled from the computer, but that did not help either, this time because the water throughput was not sufficient for the valve to operate correctly.

Consequently, I decided to design my own DCMD module and match its efficient heat exchange area to the available cooling power. So based on my drawing, T. Pluhař CNC-machined a 200 cm^2 membrane module from two thick transparent polycarbonate plates that were held together by a number of screws 2 cm apart. The membrane was surrounded on both sides by a standard 1 mm thick RO spacer. A photograph of the resulting set-up was displayed in a scientific poster entitled **Experimental investigation of membrane distillation** during the Prague PERMEA/MELPRO conference [9].

The driving force, the logarithmic mean temperature difference $\triangle T_{lm}$, comes from a heat exchanger analogy [16]. As the DCMD module is basically a heat exchanger itself, I preferred to used $\triangle T_{lm}$ instead of the $\triangle T$ of feed and distillate as by accounting for all four inlet and outlet temperatures, $\triangle T_{lm}$ gives better control, assuming that several assumptions (constant specific heat, constant heat transfer coefficient) hold true.

Consequently, the driving force is now controlled in a very straightforward way:

1. Set the *hot bath* so that the target inlet temperature is achieved (typically 60°C).
2. Set the *cold bath* so that the target $\triangle T_{lm}$ is achieved (typically 10°C).
3. Adjust slightly for enhanced precision.

One last advantage is the system's robustness when faced with shifts in recirculation velocity during tests on the effect of TP which then requires little to no adjustment in order to maintain an identical $\triangle T_{lm}$.

5.1.3 Advances in Membrane Development

Based on my design ideas and detailed instructions and suggestions, all the membranes discussed here were electrospun by my colleagues from the Laboratory of Nanomaterial Application (CxI) and laminated by the Department of Non-wovens and Nanofibrous Materials (TUL). All particulars regarding membrane fabrication are described in detail in the attached papers [5, 6, 10].

Laminated PVDF Membranes on a Large Module

Even though I already knew that nanofiber membranes prepared by thermal pressure lamination show lower fluxes then free deposited nanofibers [8], the first successful MD membranes were made by laminating PVDF nanofibers onto a supporting spunbond layer. PVDF is quite sensitive to electrospinning and we wanted to be sure that the membrane would not break in operation. The resulting membranes, owing to their uniquely low thickness, had unrivalled permeability, but also suboptimal thermal efficiency. Compared to the inital testing on a small module in VITO [4], my first paper **Flux enhancement in membrane distillation**

using nanofiber membranes [10] was based on data from a large DCMD module of active membrane area of 500 cm^2. As this module is five time longer than its width, the recirculated solutions have sufficient space for the temperature profile to develop fully and, as a result, this module displays the best thermal efficiency. Nevertheless, I found that the energy efficiency of nanofibers cannot compete with that of commercial PTFE membranes, which sometimes surpassed the 100% treshold, probably due to a malfunction in one thermocouple. On the other hand, it has been shown that flux, energy efficiency and distillate purity are closely connected and one cannot be increased without sacrificing the other two.

The non-woven membranes produced significantly higher flux rates than commercially available MD membranes, thus tackling their biggest drawback. Several issues remain to be resolved, however, such as the unreliable temperature measurement and the long membrane envelope of the large module. While this provided high quality data, its long dimensions prevented me from testing some interesting membrane samples as it initially proved difficult to electrospin membranes to cover the 50x10 cm module.

Laminated PVDF Membranes on a Small Module

The second paper **Maximising flux in direct contact membrane distillation using nanofiber membranes** [5] is based on a presentation I gave on a conference in Rome in 2016 – *EDS Desalination for the Environment: Clean Water and Energy* – and basically confirms the older data on a new smaller module. This aspect was crucially important because I fixed the cross-flow velocity to keep TP under control when downscaling the original module to 200 cm^2, but I could not forecast the result. Based on repeated experiments, I decided there was a need to apply some sort of hydrophobic treatment to the membranes in order to tackle the lack of thermal efficiency, probably caused by water entering the membrane pores. A small circular CF_4 plasma was under development at the Laboratory of Nanomaterial Application (CxI) and its dimensions matched the new module area. Unfortunately, the first plasma treated membranes were deformed by the high temperatures and more development was needed to produce repeatable results.

Self-supporting PUR Membranes

I focused my work on improving thermal efficiency by developing thicker PUR layers, the results of which are presented in my third paper **Polyurethane nanofiber membranes for waste water treatment by membrane distillation** [6]. PUR is easier to form into multiple deposits and I had several membranes manufactured, both by varying conveyor speed and by overlay, and tested them for standard performance parameters, such as flux, energy efficiency and salt retention. These thicker membranes display both excellent flux and much better efficiency. Of course, their long–term performance in terms of hydrophobicity can never be comparable with that of polyfluorinated polymers such as PTFE or PVDF, and their thermal stability remains unverified, though I have yet to encounter any signs of structural deterioration.

In order to estimate the effect of hydrophobic treatment on thick PUR membrane performance, I tested the effect of a quick soak into commercial fabric impregnation on the thickest membrane (surface density 40,06 g m^{-2}). While flux was a little higher (non-significant) over a range of commonly tested cross-flow velocities (Figure 5.2 a), energy efficiency was greatly improved a lot over whole range (Figure 5.2 b).

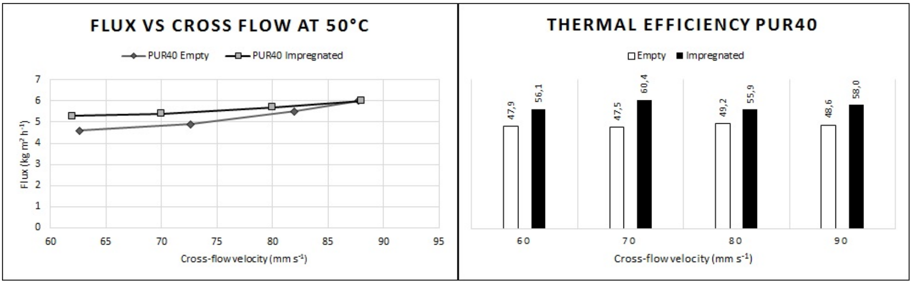

Figure 5.2: The effect of simple hydrophobic treatment: a) Flux remains similar, while b) Thermal efficiency is improved.

5.1.4 Industrial Application

An experimental investigation of the potential of MD for industrial waste water treatment was carried out during my six-month internship with VITO. DCMD was coupled with NF to treat effluents from ion-exchange

(IEX) regeneration streams and zinc ore refining. As the focus in this case was on development of a new technology rather than new membranes, validated commercial membranes were used throughout (MD – Donaldson, NF – KOCH, GE, DOW) for easy comparison.

As part of a project called *Blauwe Cirkel (Blue circle)* involving VITO and its industrial partners, we focused on inorganic concentrates resulting from industrial water reuse in order to solve the concentrate disposal problem through development of several valorisation schemes for the resulting salts. The goal was to combine traditional (NF) and emerging (MD) technologies and find an alternative to presently unsustainable practices in coastal regions, where brine is commonly neutralized and discharged to the sea. We needed to develop an economically feasible process train as, at that time, environmentally friendly alternatives were prohibitively expensive.

In the paper **Recovery of salts from ion-exchange regeneration streams by a coupled nanofiltration–membrane distillation process** [11], MD was tested by treating actual industrial waste water from ion-exchange regeneration. As the main goal was to recover NaCl, I investigated several scenarios of NF treatment aimed at retaining maximum NaCl content in the most concentrated stream, which was afterwards further concentrated by MD.

MD showed no significant flux decline, even though signs of scaling were observed on the membrane surface. The resulting salt composition was not sufficiently pure for reuse in the chemical industry, but was expected to qualify as road de-icing salt. Economically, the process was feasible only for larger plants above 200 $m^3 d^{-1}$, but only when discharge was prohibitively expensive or not allowed. The cost benefits of water reuse and salt recuperation were small when compared to the overall treatment cost. The main benefits of the process for this case study was the reduced discharge of chlorides to the environment.

At the IWA Verona conference in 2014, Wim De Schepper presented our work broadened by a study of treatment of zinc ore refinery effluents: **Recovering salts from industrial brines by NF-MD: Case studies on IEX regeneration waste-water and chloride rich wash water from a zinc ore refinery** [12]. In this case, the recovery of salts was also technically feasible but not economically interesting as long as discharge was allowed, the main driver being the upcoming discharge regulation. Despite this, the chloride content could still be lowered below the imposed discharge limit allowing for improved ambient environment quality and increased zinc production capacity.

Both these applications dealt with actual industrial waste water samples with very high total dissolved solids (TDS) content. Such effluents are extremely difficult to concentrate due to scaling, osmotic pressure, CP, increased viscosity and induced pressure drop in membrane modules. Hence, it was seen as a great achievement that MD was able to concentrate such waters almost to saturation levels. Since MD can maintain relatively high fluxes, even with high TDS, its logical use is in zero liquid discharge (ZLD) applications.

While combining MD with crystallization has been proposed to remove precipitating salts and to increase MD concentration factors [43], these two studies unfortunately did not connect the MD concentrate to its final evaporation or crystallization stage. In such cases, special attention should be paid to salts that precipitate as they reach their solubility limit, and this should certainly be the next logical progress in the development of a feasible process train.

The experience gained with MD operation and process optimization from a technological point of view helped me to understand the peculiarities of the unique MD process, mostly in relation to the contradictory properties of membranes, some of which are both desirable and unfavourable. The VITO internship was clearly most influential in instigating the original idea to begin development of my own nanofiber membranes for MD.

Conclusion

At the beginning, the table was completely clean and I simply had an idea to develop nanofiber membranes for one process that has long been known for lacking suitable membranes. By the end, I had produced a novel application for nanofiber membranes that shows a commercial potential due to their unique properties compared to commonly available products. I never imagined the amount of work that would be involved, but now I am presenting a PhD thesis based on several publications relevant to the topic of membrane science, and to MD in particular. The publications include a thorough literature review, and cover membrane

Location	**Configuration**	**Company**	**Capacity**
Senoko – SG	VMD	MemSys	50 m^3d^{-1}
Abengoa – AE	VM	Aquaver	100 m^3d^{-1}
Torr-Coal – BE	AGMD	Aquastill	150 m^3d^{-1}

Table 5.1: Recent MD installations

development, evaluation and testing, and implementation of MD as a treatment of an industrial waste waters.

MD is an established concept that is still awaiting its first industrial application; and the development of appropriate MD membranes is the first step in that direction. Nowadays, there is an increasing trend for ZLD of industrial waste waters and their reuse and recirculation within the same facility. Even inland regions are being driven toward waste water valorisation and reuse. As such, ZLD technology could provide the added-value niche application that MD needs for commercial success, particularly as ever more stringent European legislation leads to a situation where simple discharge is no longer an option.

The economics of MD application can be significantly improved by an appropriate climate (autonomous solar powered MD units) or neighbouring infrastructure (power plants with excess waste heat presently eliminated via cooling towers in order to avoid thermal pollution) and most recent installations have been built near such structures (Table 5.1).

Traditional pressure-driven processes, such as seawater RO, have been optimized as regards membrane development and feed type for decades. Consequently, without such alternative energy sources, MD separation remains a costly process requiring a lot of power for the phase change to occur. I am convinced, however, that MD operation has as yet unrevealed potential for solving environmental problems, both now and in the future. As such, I will be carrying on the research started at TUL with MemBrain s.r.o. on an Aquastill two-spiral module pilot unit, focusing on the treatment of RO concentrates and industrial waste water with high TDS, quite possibly using an electrodialysis concentrate for the feed.

List of Symbols

A – Antoine equation constant in Eq. 4.4

a_w – Activity of water in Eq. 4.5

a_s – Activity of the solvent in Eq. 2.3

B – Geometric factor in Eq. 4.1

B – Antoine equation constant in Eq. 4.4

c – Concentration of solute in Eq. 2.8, mol m^{-3}

C – Antoine equation constant in Eq. 4.4

C_m – Proportionality constant, kg m^{-2} s^{-1} Pa^{-1}

c_f – Feed concentration in Eq. 2.2, mol m^{-3}

c_p – Permeate concentration in Eq. 2.2, mol m^{-3}

c_i – Molar concentration in Eq. 2.5, mol m^{-3}

c_{perm} – Permeate concentration in Eq. 2.8, mol m^{-3}

d – Mean pore size, m

D – Diffusivity in Eq. 2.8, m^2 s^{-1}

ΔH – Latent heat of vaporization, J kg^{-1}

i – Van't Hoff factor of the solute in Eq. 2.5

J – Intensity of volumetric flux in Eq. 2.4, 2.7 and 2.8, m s^{-1}

K_n – Knudsen number

l – Mean free path of molecules, m

$\triangle T_{lm}$ – Logarithmic mean temperature difference, K

M_i – Molecular weight in Eq. 2.5, g mol^{-1}

n_i – Number of moles of the solute, mol

$n_{solvent}$ – Numer of moles of the solvent, mol

p – Hydrostatic pressure in Eq. 2.3, Pa

p_0 – Vapour pressure of pure water in Eq. 4.5, Pa

$\triangle p$ – Hydrostatic pressure difference in Eq. 2.1, Pa

p_f – Vapour pressure of the feed in Eq. 4.3, Pa

p_{LEP} – Liquid entry pressure in Eq. 4.1, m

p_p – Vapour pressure of the permeate in Eq. 4.3, Pa

$p_{process}$ – Pressure at the membrane surface in Eq. 4.1, Pa

p_{pore} – Air pressure in pores in Eq. 4.1, Pa

R – Universal gas constant in Eq. 2.3 and 2.5, J mol^{-1} K^{-1}

R_m – Membrane retention in Eq. 2.2

r_{max} – Largest pore size in Eq. 4.1, m

R_{memb} – Membrane resistance in Eq. 2.7, m^{-1}

R_{CP} – Resistance by concentration polarization in Eq. 2.7, m^{-1}

R_{foul} – Fouling resistance in Eq. 2.7, m^{-1}

T – Thermodynamic temperature in Eq. 2.3 and 2.5, K

TP – Coefficient of temperature polarization in Eq. 4.2

T_1 – Membrane surface temperature in Eq. 4.2, K

T_2 – Membrane surface temperature in Eq. 4.2, K

T_f – Hot feed temperature in Eq. 4.2, K

T_p – Cold permeate temperature in Eq. 4.2, K

V_s – Volume of the solvent in Eq. 2.3, m^3

V_m - Molar volume of the solvent in Eq. 2.6, m^3 mol^{-1}

x – Distance normal to the membrane in Eq. 2.8, m

x_i – Solute molar fraction in in Eq. 2.6

x_s – Solvent molar fraction

γ_l – Surface tension in Eq. 4.1, N m^{-1}

η – Dynamic viscosity in Eq. 2.7, Pa s

μ_s – Chemical potential of the solvent in Eq. 2.3, J mol^{-1}

μ_s^0 – Standard chemical potential of the solvent in Eq. 2.3, J mol^{-1}

π – Osmotic pressure in Eq. 2.5, Pa

$\triangle\pi$ – Osmotic pressure difference in Eq. 2.4, Pa

θ – Contact angle in Eq. 4.1

Abbreviations

AE – United Arab Emirates

AGMD – air-gap membrane distillation

BE – Belgium

$CaCO_3$ – calcium carbonate

CP – Concentration Polarization

CxI – Institute for Nanomaterials, Advanced Technologies and Innovation

DCMD – direct-contact membrane distillation

DE – Germany

DOE – design of experiments

IEX – ion-exchange

MD – membrane distillation

MF – microfiltration

NaCl – sodium chloride

NF – nanofiltration

NL – The Netherlands

PEI – polyethylenimine

PES – polyethersulfone

P&ID – piping and instrumentation diagram

PP – polypropylene

PTFE – polytetrafluoroethylene

PUR – polyurethane

PVDF – polyvinylidene fluoride

RO – reverse osmosis

SG – Singapore

SGMD – sweeping gas membrane distillation

TDS – total dissolved solids

TUL – Technical University of Liberec

UF – Ultrafiltration

UPOL – Palacký University Olomouc

VITO – Flemish Institute for Technological Research

VMD – vacuum membrane distillation

ZLD – zero liquid discharge

Zn – Zinc

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