



Research Paper

The Combination of Polyvinyl Alcohol and Silicone Rubber Enhances Pervaporation Membrane Performance

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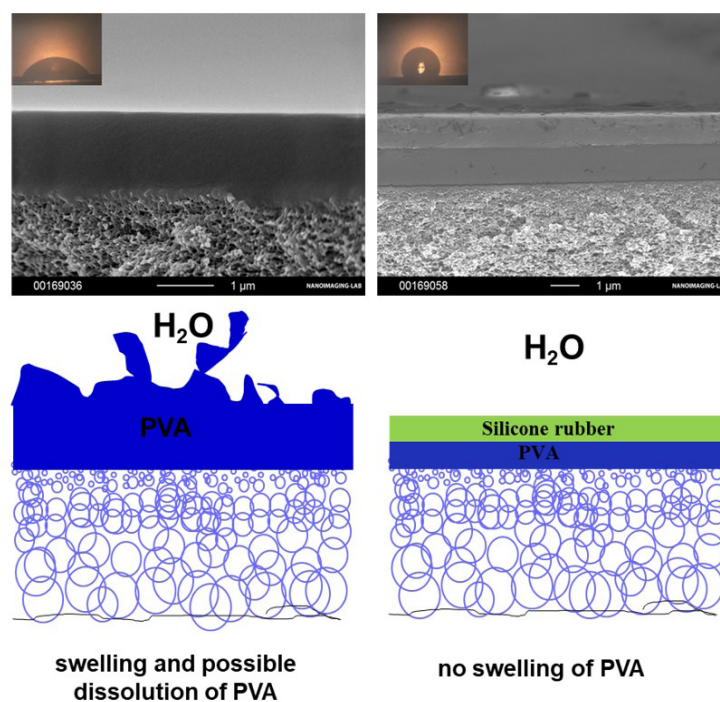
Keywords

Multilayer membrane
 Pervaporation
 Desalination
 Polyvinyl alcohol
 Silicone rubber

Highlights

- Silicone rubber enhances the performance of polyvinyl alcohol membrane
- A new multilayer membrane compatible with water and solvents is developed
- The multilayer membrane shows good performance for desalination by pervaporation

Graphical abstract



Abstract

Although research on silicone rubber membranes focuses on the removal of volatile organic compounds (VOC) from water, here we report the use of silicone rubber as a protective layer in the fabrication of hydrophilic membranes. By combining the high water vapor permeability of silicone rubber with the high water selectivity of polyvinyl alcohol (PVA), we have developed a new multilayer pervaporation membrane. Firstly, a thinner and less cross-linked PVA membrane with enhanced water flux was developed (without compromising dramatically the selectivity). Secondly, the thin PVA membrane was protected by a silicone layer to hinder the swelling and dissolution of the polymer in hot aqueous solutions. The aim of protecting the PVA membrane is to improve the stability and lifetime of the thinner and less cross-linked membrane. Pervaporation tests showed that the additional silicone (hydrophobic) layer does not reduce the water permeate flux or the selectivity of the thin PVA membrane and confirms its role in protecting the selective layer. Long-term stability tests with ethanol/water and glycol ether/water mixtures demonstrated that the new multilayer membrane is stable under different operating conditions (e.g., feed water concentration from 0.5 to 100 wt.% and operating temperature up to 110°C). The multilayer membrane also showed promising performance for the emerging application of desalination by pervaporation. Therefore, this new membrane formulation produces a robust pervaporation membrane with high water flux.

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1. Introduction

Commercial polyvinyl alcohol (PVA) membranes (e.g., PERVAPTM) are used in pervaporation and vapor permeation industrial plants for the dehydration of solvents like ethanol, isopropanol, tetrahydrofuran, sec-butanol, acetonitrile, methyl ethyl ketone, etc. as well as for methanol removal from other solvent mixtures [1, 2]. Recently, one of these membranes has been industrially applied for the dehydration of organic solvent/water azeotropic streams containing water up to 60 wt.% [3]. This new application shows great potential for pervaporation of streams containing even higher water concentrations (>90 wt.%). However, the excessive swelling of PVA membranes in aqueous media can lead to polymer dissolution (compromising the stability), especially at high temperatures [4-7]. PVA dissolution in aqueous solutions is generally hindered by applying high degrees of chemical cross-linking [6, 8-13]. Highly cross-linked membranes however exhibit low permeate fluxes, which results in industrial plants with large membrane areas [14]. Mainly, pervaporation is applied to the dehydration of solvents with low water content (<20 wt.%) and its application in streams with high water content is limited. To improve the competitiveness of PVA membranes and extend its application for streams with high water content (including desalination by pervaporation), the permeate flux and robustness of the membrane must be enhanced, while keeping the same selectivity.

Like gas separation membranes [15-17], the permeate flux of pervaporation composite membranes can be improved by reducing the thickness of the selective layer [18]. Decreasing the membrane thickness to the nanometer scale, the permeate flux can be increased by one or more orders of magnitude [15, 16]. However, the risk of getting pinholes or defects during membrane fabrication is high, because thin polymeric membranes are produced by using very diluted polymer solutions, so defects are formed due to the dewetting processes and polymer solution penetration into the pores of the porous support [19, 20].

Wijmans et al reported that porous support with controlled pore size at the surface could produce optimal thinner defect-free membranes with improved gas permeances [21, 22], but despite optimal manufacturing of the porous support, further reduction of the selective layer cannot prevent the risk of having pinholes or defects. Thus, a trade-off between membrane thickness and pinholes/defects is observed during membrane manufacture.

A way to avoid the pinholes/defects and improve the permeate flux of PVA membranes is not only to reduce the thickness but also to reduce the degree of cross-linking. So, the simultaneous reduction of thickness and degree of cross-linking up to a certain extent would result in membranes with better performance. However, because of the reduced thickness and lower degree of cross-linking, the stability and lifetime of PVA membranes could be compromised.

For a long time, multilayer membranes have been proposed and developed to produce high-performance and stable thin-film membranes [23, 24], especially by applying an additional gutter and/or protective layer [16, 20, 24-31]. Following that strategy, Huang et al [30, 32] developed a pervaporation multilayer membrane with hydrophobic coatings. By using hydrophobic perfluoro-polymers as a protective layer, they demonstrated that the swelling of hydrophilic membranes can be effectively prevented when the feed streams contain a high water concentration. Their results showed that the selectivity of the multilayer membrane slightly increased compared with the uncoated hydrophilic membrane (only for high feed water concentrations), but the membrane permeance decreased threefold.

Silicones are alternative materials to perfluoro-polymers, they show unique properties in terms of permeability, processability, and cost. In fact, for gas separation membranes, silicone rubber plays an important role as a gutter and protective layer due to its high permeability, and good thermal and chemical properties [16, 20, 23-26]. Silicones are versatile due to their chemical structure; this feature enables the formation of fascinating materials with tailored properties [33]. Silicones have a unique property as a repellent of liquid water [33, 34], but at the same time, they have high permeance of water vapor [34, 35]. This intriguing property of water permeation through silicones has drawn attention for many years by some researchers [36-39]. However, only in recent years, the research group of Prof. McCarthy [34] investigated the anomalous water vapor permeability through silicone membranes, offered a mechanism of water permeation, and suggested its use as a membrane for water purification.

In this work, we have investigated the use of silicone rubber in the production of hydrophilic thin membranes. By reducing the PVA membrane thickness and the degree of cross-linking, and by protecting it with a silicone rubber layer, a robust hydrophilic/hydrophobic multilayer membrane was

developed. Although the principle is like that of Huang et al's approach, here we use the silicone rubber that repels liquid water but has very high vapor permeability. Because of this unique property of silicone rubber, we demonstrate that the permeance of thin and less cross-linked hydrophilic membrane does not drop like those protected by perfluoro-polymers. In addition, silicone rubber is cheaper and easier to process than perfluoro-polymers, so, it is more suitable for membrane fabrication at a large scale and commercialization. The development of this new multilayer membrane took more than five years, and now, it is intensively being tested for dehydration of different organic solvents by pervaporation and the emerging application of desalination. Long-term stability tests at a laboratory scale confirm that this multilayer membrane has reliable performance over time for a broad feed water concentration range.

2. Materials and Methods

2.1. Materials

PVA, maleic acid, sodium chloride, sulfuric and chlorohydric acid, and hexane were purchased from Sigma-Aldrich. Sylgard® 184 silicone elastomer and polyacrylonitrile (PAN) porous membrane are supplied by Dow Corning and DeltaMem AG, respectively. Ethanol A15 and glycol ether were purchased from Thommen-Furler AG, Switzerland. The water used in the experiments was demineralized.

2.2. Membrane preparation

The PVA membrane is prepared according to the proprietary formulation of DeltaMem membranes, which is reported elsewhere [6, 11, 40, 41]. Briefly, the membranes consist of a non-woven polyester fabric support, porous PAN support with asymmetric pore structure, and a selective layer from PVA and/or a hydrophilic copolymer.

The PVA solution together with the cross-linker and the acid catalyst is first prepared in water and cast on the PAN porous support, then it is partially dried in an oven (70-120°C). Subsequently, a silicone rubber protective layer is deposited onto the thin PVA membrane. Finally, the obtained multilayer membrane is cross-linked and dried in an oven at a defined temperature (140-190°C).

The silicone solution is prepared according to Sylgard® preparation specification, however, the final formulation of the coating solution is optimized by DeltaMem and cannot be disclosed because it is a trade secret. Nevertheless, any other formulation for the silicone rubber membrane preparation could be applied.

2.3. Membrane characterization

The thickness of multilayer membranes was characterized by scanning electron microscopy (SEM) using a Hitachi S-4800 scanning electron microscope (Hitachi High-Technologies Corporation, Japan) with a cold field emission electron source. The samples were immersed in ethanol and then frozen in liquid nitrogen for fracturing. Electrically conducting surfaces were achieved by sputtering the surface with a gold layer.

The water contact angle on the membrane surface was measured before and after pervaporation tests by using water and the sessile drop method in an AB Lorentzen & Wettre goniometer.

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) was used to confirm the presence of PVA and the silicone layer before and after the pervaporation tests. The spectra were recorded on a Bruker spectrophotometer in the range of 4000-400 cm⁻¹.

2.4. Pervaporation tests

Pervaporation tests were performed in laboratory equipment that operates as a batch system. The equipment includes three cells (each of 38 cm²). The solvent mixture (feed) is filled into the feed tank (three liters) and recirculated by a centrifugal pump (Speck) through the cells, the product from the cells is returned to the feed tank as retentate. Three heat exchangers maintain a constant feed temperature at the entrance of each cell (e.g., 95°C). On the permeate side, a pressure of 10 mbar is maintained by a vacuum pump (Edwards). A schematic diagram of the laboratory equipment is shown in Fig. 1.

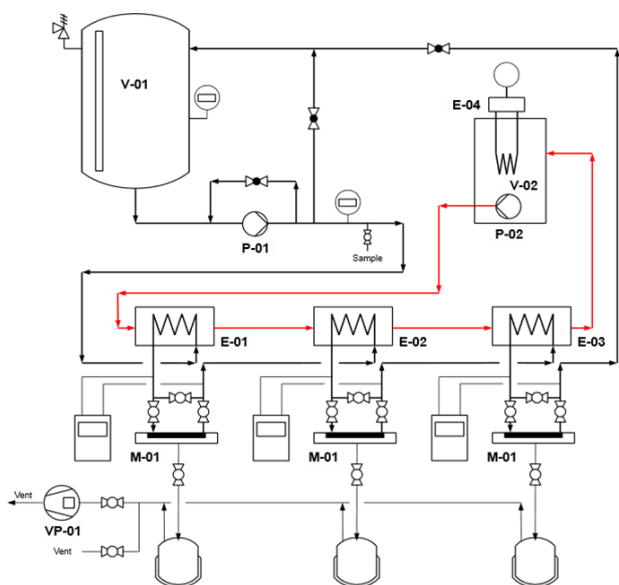


Fig. 1. Schematic diagram of the laboratory equipment for the pervaporation tests

Permeate samples are collected in cold traps with a mixture of dry ice and ethanol. For each measurement point, the amount of permeate, time, as well as the composition of feed/retentate and permeate samples are recorded

Pervaporation long-term stability tests (LTST) were continuously performed for more than 300h under the same operating conditions. However, in these tests, the membranes are contacted by the hot liquid mixture 24/7 (batch system). On weekends, processes of shutdown and startup are carried out to stress the membranes and to simulate the pervaporation plant operation. Every third day, the dehydrated solvent (batch) is replaced by a new mixture (new batch). To confirm the stability of the membrane, at least five different batches should be dehydrated, and the separation performance of the membrane must not change over time.

The retentate/feed compositions are monitored by Karl Fisher (KF) titration using a 737 KF Coulometer from Metrohm. The permeate composition is determined by gas chromatography (GC). The GC used is a 6890N from Agilent Technologies, which is equipped with a thermal conductivity detector (TCD) and autosampler.

The salt concentrations in the permeate during the pervaporation desalination tests are determined by measuring the conductivity with a Knick conductivity-meter 702. The conductivity meter was calibrated by using different NaCl solutions with concentrations ranging from 0 to 10 wt.% of NaCl.

3. Results and discussion

3.1. Membrane preparation and characterization

As described above, thinner defect-free composite membranes can be obtained by optimizing the pore size and porosity of the porous support [1,

21, 22]. Support with large pores and nonuniform pore size at the surface leads to defective membranes with the formation of pinholes. In addition, polymer solution penetration into the pores also occurs when larger pores are present at the surface of the porous support. Consequently, the polymer solution penetration into the pores increases the apparent total thickness of the separation layer [20].

The porous support used in this work is an optimized PAN porous membrane [1]. It has an average pore size of 20 nm at the surface, and its porous structure is asymmetric through the membrane thickness (Fig. 2). The pore size uniformity and the distribution of pores at the surface of the PAN membrane allowed us to produce defect-free thin selective layers.

On the PAN porous support, a diluted PVA solution containing the cross-linker and the acid catalyst is cast at room temperature. Then, the thin composite membrane is dried and cross-linked in a convective oven at a defined temperature. The concentration of PVA solution is reduced by more than 50% compared to the coating solution used for the fabrication of standard commercial membrane PERVAP™ 4100. Thus, the PVA concentration decrease resulted in thinner and defect-free membranes with a separation layer of <1000nm (Fig. 3a and 3b). A comparison of membrane thickness between the thin membrane and the standard PERVAP™ 4100 can be seen in the supplementary material (Fig. S1).

The degree of cross-linking in the PVA layer was reduced by decreasing the drying and cross-linking temperature, as well as the residence time (compared to the fabrication of PERVAP™ 4100). Once the reproducibility of the thin PVA membrane fabrication was confirmed at the pilot scale, the casting of the silicone layer on the PVA layer was optimized. The control of polymer solution concentration of both PVA and silicone, the temperature, and the time of drying and cross-linking, allowed us to obtain an outstanding defect-free multilayer membrane (Fig. 3c and 3d). As shown in the SEM pictures, each layer can be clearly distinguished, and they have thicknesses of less than 1000nm.

Table 1 summarizes the water contact angle on commercial PERVAP™ 4100, new thin PVA composite membrane (Fig. 3a), thick silicone film, and multilayer membrane (Fig. 3c) before and after the pervaporation test. A photo of the water drop shape on the membrane surface is also presented in the supplementary material (Fig. S2) to visually differentiate the hydrophilicity of the membranes.

Table 1

Water contact angle values on the commercial membrane and the newly developed membrane

Sample	Contact angle before PV test	Contact angle after PV test
PERVAP™ 4100	47° ± 3°	58° ± 2°
Thin PVA membrane	56° ± 1°	57° ± 1°
Thick silicone film	110° ± 4°	-
PAN/PVA/silicone multilayer	117° ± 3°	119° ± 2°

The water contact angle on the PAN/PVA/silicone multilayer membrane measured after long-term stability tests demonstrates that the silicon layer is intact. In addition to the water contact angle measurements, ATR-FTIR analyses also confirmed the presence of a silicon layer on the PVA layer (Fig. S3, supplementary material).

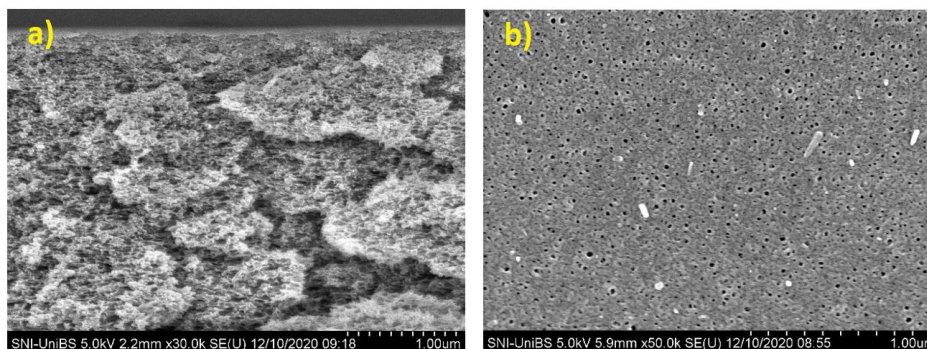


Fig. 2. SEM pictures of PAN membrane: a) top cross-section and b) surface

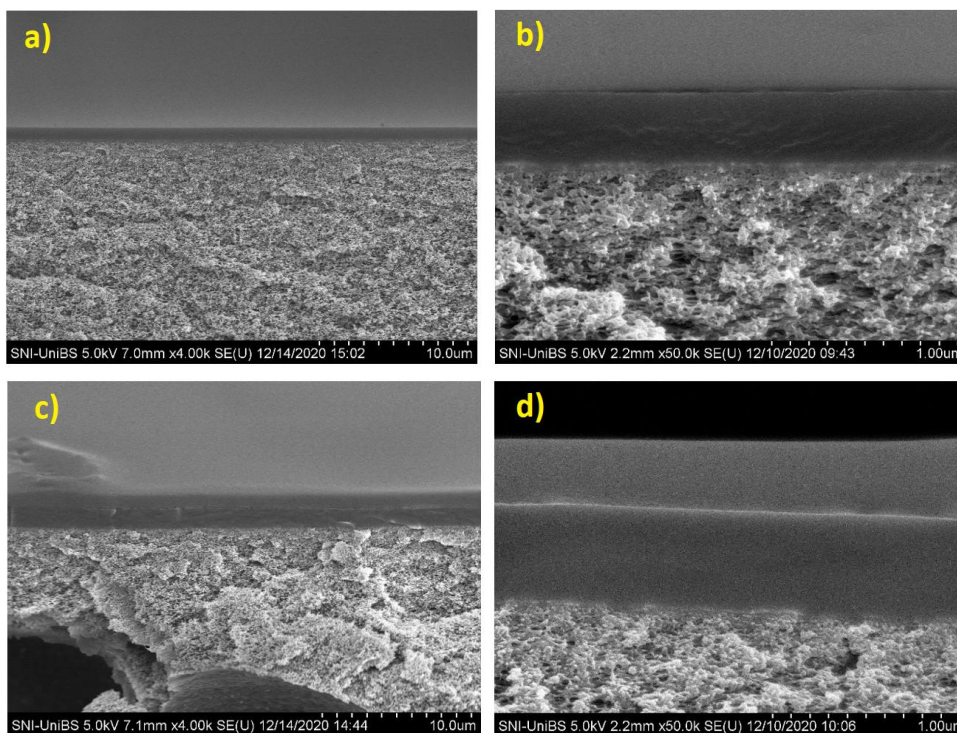


Fig. 3. SEM pictures of membrane cross-section: a) and b) single thin PVA layer, and c) and d) PVA/silicone multilayer membrane.

3.2. Membrane separation performance

3.2.1. Dehydration of solvents

The separation performance of the multilayer membrane is being investigated for dehydration of different solvents by pervaporation at DeltaMem. In this work, we report only the dehydration of ethanol and glycol ether.

Fig. 4 shows typical separation performance curves for ethanol dehydration i.e., permeate concentration and water permeate flux as a function of feed water concentration. The circular points represent the separation performance of PERVAP™ 4100, the triangular points correspond to the thin PVA composite membrane without a silicone layer, while the diamond points are for the PVA/silicone multilayer membrane (filled points correspond to water flux, and unfilled points to water concentration in permeate). All tests were performed under identical operating conditions.

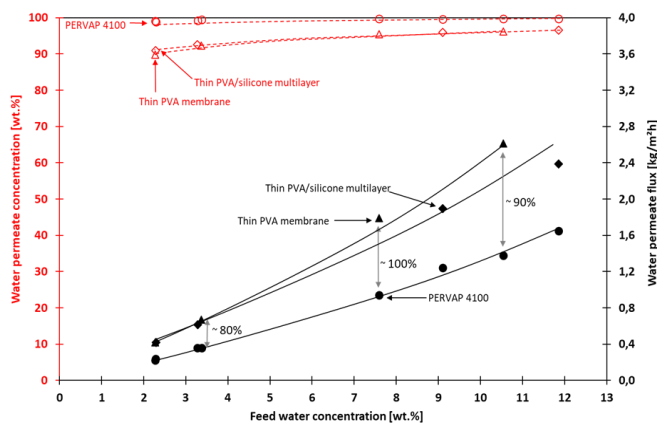


Fig. 4. Water permeate concentration and water permeate flux as a function of feed water concentration for PERVAP™ 4100, thin PVA composite membrane, and PVA/silicone multilayer membrane. Pervaporation tests at 95°C and 10mbar at the permeate side.

The water permeate flux through the thin PVA composite membrane is almost 100% higher than PERVAP™ 4100. However, the water concentrations in the permeate are a bit low. As expected, the thinner membrane with less degree of cross-linking than PERVAP™ 4100 exhibited higher permeate fluxes.

After casting the silicone layer on the thin PVA membrane, the separation performance of the PVA layer remained almost unchanged, especially at low feed water concentrations (compare the triangular and diamond-filled points). The fact that the water flux has not dramatically changed makes this membrane very promising since the water flux in hydrophilic membranes coated with perfluoro-polymers dropped threefold [30, 32, 42]. Our results indicate that the mass-transfer resistance of the silicone layer to the water vapor permeation is negligible in the multilayer membrane. Partly, this membrane behavior is explained by the unique and high vapor permeability of silicone rubber (~40000 Barrer) compared to the permeability of PVA (~19 Barrer) [35]. Our hypothesis on negligible mass-transfer resistance for water transport is supported by the studies recently reported by Bian et al [34]. They rediscovered the anomalous water permeability of silicones and suggested a mechanism very similar to or the same as those proposed for carbon nanotubes and aquaporins.

In supplementary material, we present additional results on water flux and the poor ethanol/water selectivity of a silicone rubber membrane (Fig. S4 and S5). Those results confirm that the silicone rubber as a protective layer is not ethanol selective. The presence of ethanol within the silicone layer may even enhance the water transport due to the coupling effect [43]. Therefore, this evidence supports our results concerning the high water permeation through the silicone layer and through the new multilayer membrane.

To confirm the pervaporation results with ethanol mixtures containing low water concentration in the feed (<0.5 wt.%), as well as the reproducibility of membrane fabrication, additional pervaporation tests were performed with new prototypes. Fig. 5 presents the permeance and selectivity values (mathematical equations for permeance and selectivity are presented in supplementary material) for feed water concentration from 0.5 wt.% to 11 wt.%. The behavior of the PVA/silicone multilayer membrane is confirmed, i.e., the permeance values (~2000 GPU) are higher than PERVAP™ 4100 (~1000 GPU) and are nearly constant in this range of concentration (Fig. 5a). Although the water/ethanol selectivity value (1000) is lower than the commercial membrane (Fig. 5b), it is still acceptable for industrial applications.

The higher permeance values and lower selectivity than PERVAP™ 4100 are due to the lower degree of PVA cross-linking and the thickness. The thinner membrane exhibits higher fluxes and by controlling the degree of cross-linking, the water flux has been increased, while keeping the water/ethanol selectivity to a level that is acceptable. As the less cross-linked PVA membrane tends to swell more than the PERVAP™ 4100, by applying the silicone layer as a protective layer, the PVA swelling is hindered (Fig. S6, supplementary material). In addition, the silicone protective layer makes the membrane more robust, since the overall thickness becomes thicker (see Fig. 3).

The next step of our work was to demonstrate that the thin and less cross-linked membrane with the protective layer performs well at higher temperatures with mixtures containing high water concentrations. In this case, the pervaporation tests were performed at 110°C with glycol ether containing 60 wt.% water.

The water permeance (~10000 GPU) at high feed water concentration is very high (Fig. 6a), and the water concentration in the permeate is >99.5 wt.%. This results in selectivity values between 1000 and 25000 (Fig. 6b). On the one hand, the relatively low selectivity for high feed water concentration is due to the PVA plasticization (due to water). On the other hand, the high selectivity compared to the ethanol/water system is due to the slower diffusion of glycol ether than ethanol through the membrane.

At low feed water concentration, the swelling and plasticization of the PVA layer due to the water is less, so the diffusion of the glycol ether is even slower, consequently its permeance is low (see Fig. 6a, triangular points at low feed water concentration). Therefore, the membrane selectivity (~25000) is very high (Fig. 6b) under this condition.

The exact mechanism of water molecule permeation through the multilayer membrane, the water-polymer-solvent interactions, and the structural changes of silicone and PVA in the multilayer system with pure water and water/solvent mixtures are being investigated and will be reported elsewhere.

3.2.2. Long term stability tests

The long-term stability and reproducibility of membranes are crucial for scaling up and commercialization. In this section, we present two procedures of stability tests at a laboratory scale: 1) by dehydrating a feed mixture to the final specification (batch system) and 2) by keeping constant the feed concentration. Although both methods are valid to confirm the membrane stability, we consider that the first one is more realistic because the membrane is exposed to the whole feed concentration.

Fig. 7 presents data from long-term stability tests obtained by both methods. On the one hand, the membrane is in contact with the ethanol/water mixture containing water from 0.5 to 7.0 wt.% (Fig. 7a). The data collected for each batch during the dehydration process (each color represents a different batch) are on the same curve of water flux and permeate concentration, i.e., the separation performance of the membrane does not change over time. These results demonstrate that the membrane is stable in the whole water concentration range (0.5-7.0 wt.%). On the other hand, if we want to keep constant the feed water concentration, the permeate (condensed) must be sent back (pumped) to the feed tank. Thus, the membrane performance is monitored at a single feedwater concentration (Fig. 7b).

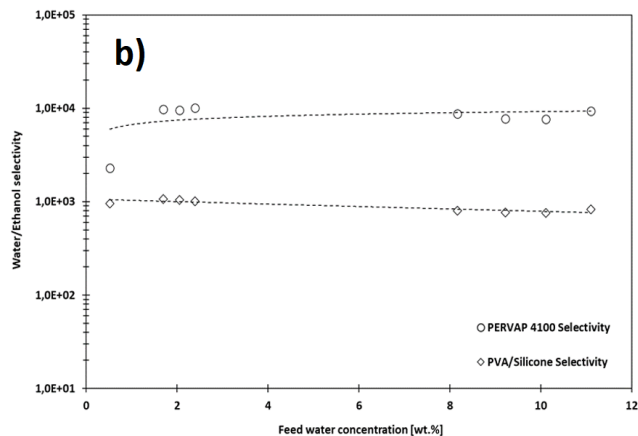
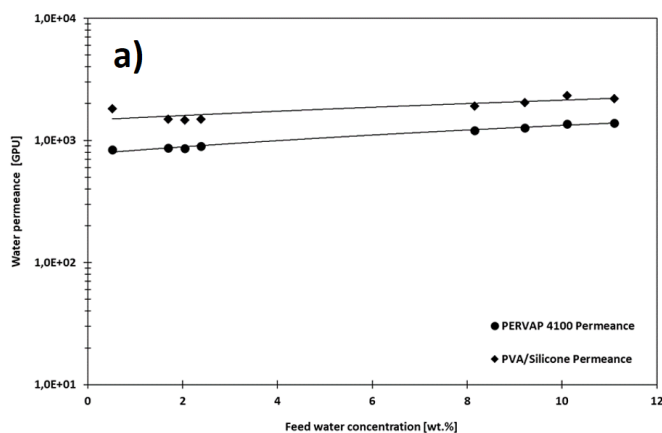


Fig. 5. Water permeance (a) and water/ethanol selectivity (b) as a function of feed water concentration for PERVAP™ 4100 and PVA/silicone multilayer membrane. Pervaporation tests at 95°C and 10mbar at the permeate side.

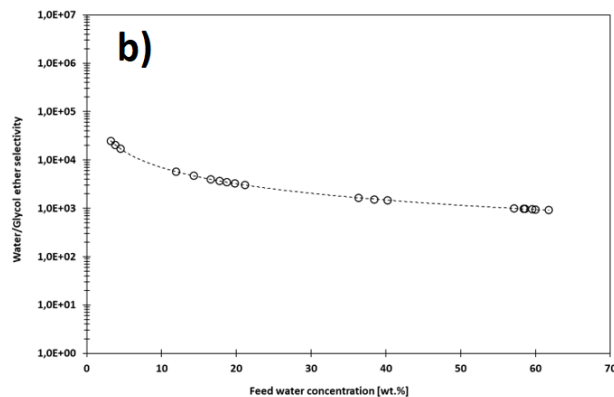
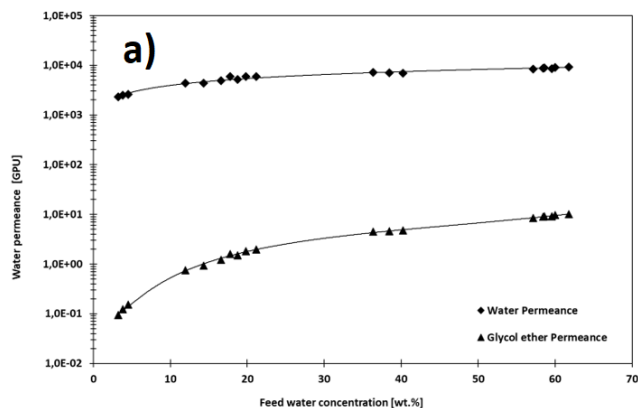


Fig. 6. Water permeance (a) and water/glycol ether selectivity (b) as a function feed water concentration for PVA/silicone multilayer membrane. Pervaporation tests at 110°C and 20mbar at the permeate side.

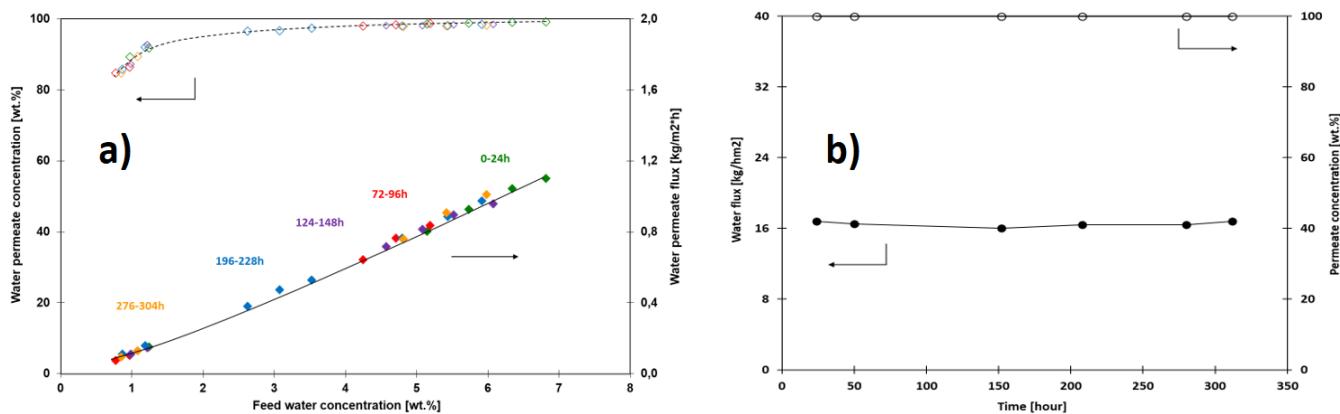


Fig. 7. Long-term stability test results: a) ethanol/water mixture, pervaporation tests at 95°C and 10mbar at permeate side, and b) glycol ether/water mixture, 60 wt.% of feed water concentration, pervaporation tests at 110°C and 20mbar at permeate side.

In the tests with a glycol ether stream, the water flux (~16 kg/m²h) and permeate concentration (99.7 - 99.9 wt.%) are quite constant too. This confirms that the membrane is stable.

Therefore, both test procedures demonstrated that the new PVA/silicone multilayer membrane is very stable under different operating conditions.

3.2.3. Desalination tests

The new multilayer membrane has been also tested for desalination by pervaporation. Although desalination of salty water (seawater) is dominated by reverse osmosis (RO), pervaporation is being investigated as an alternative to RO due to some advantages such as the production of high-quality water, better performance in streams with high salt concentrations, the required energy does not depend on salt concentration, less fouling, etc. [44-51].

The desalination pervaporation tests using the PVA/silicone multilayer membrane had two objectives: 1) to confirm the robustness of the multilayer membrane in pure and salty water (high salt concentration) and 2) to compare the separation performance with the commercial PERVAP™ 4100 membrane, which is industrially applied for solvent dehydration.

The salt rejection (>99.9%) of the PVA/silicone multilayer membrane is very high (Fig. 8) for two different feed salt concentrations (3.5 and 10.0 wt.% NaCl). The water flux for the feed with 10.0 wt.% of NaCl is slightly lower compared to pure water and to the solution with 3.5 wt.% of NaCl, which exhibits similar fluxes. The trend of water flux decrease with high salt concentration was already reported for polymeric pervaporation membranes [46, 52]. Therefore, its discussion is out of the scope of this work.

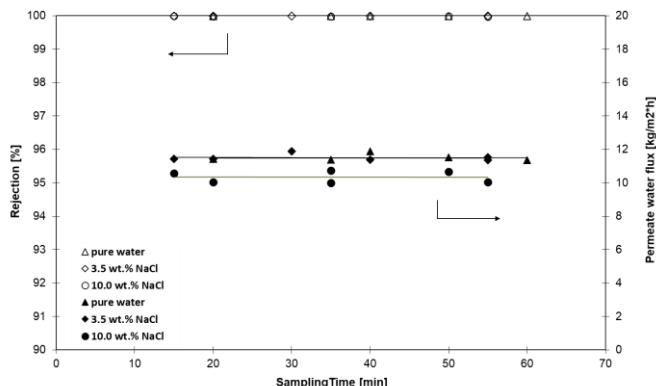


Fig. 8. Water flux and salt rejection as a function of sampling time and salt concentration of the PVA/silicone multilayer membrane. Pervaporation test at 65°C and 10mbar at permeate side.

The experimental results confirm that besides the high quality of water (salt rejection >99.9%), the water flux of the PVA/silicone multilayer membrane is comparable to other membranes developed for desalination by pervaporation (Table 1S, supplementary material).

A comparison between the new PVA/silicone multilayer membrane and the PERVAP™ 4100 is shown in Fig. 9. Because the PERVAP™ 4100 has a thickness of 2-3 μm and a higher degree of cross-linking than the multilayer membrane, the water flux is much lower (PERVAP™ is for solvent dehydration and not for desalination). Compared to RO commercial membranes (5-45 l/h m², depending on feed pressure), the new multilayer membrane seems to be attractive.

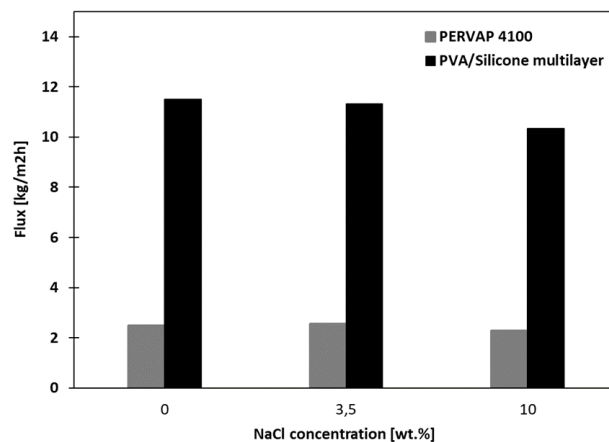


Fig. 9. Water flux comparison between commercial PERVAP™ 4100 and the new PVA/silicone multilayer membrane. Pervaporation test at 65°C and 10mbar at permeate side.

In summary, the silicone layer which is in contact with the liquid water (feed) makes the thin and less cross-linked PVA layer more robust (hindering the swelling and dissolution of the PVA layer), allowing only the permeation of water vapor, which is very high.

4. Conclusions

A new pervaporation membrane with enhanced separation performance was developed by combining PVA and silicone rubber. Thanks to the unique property of silicone material (repellent of liquid water but high vapor permeability), the silicone layer, which is used as a protective layer, did not alter the separation performance of the thin and less cross-linked PVA layer.

The improvement of the PVA membrane was achieved by decreasing the membrane thickness and the cross-linking degree. Although these changes

could compromise the stability and lifetime of the PVA membrane, the silicone rubber protective layer makes it robust, since, in this PVA/silicone multilayer formulation, the hot solvent mixture (liquid) containing high water concentration (or pure water) is not in contact with the PVA layer.

The pervaporation tests for both solvent dehydration and desalination demonstrated that this new membrane is robust, showing higher flux than the PERVAP™ membranes and high salt rejection. However, the water/ethanol selectivity was relatively low, but acceptable for industrial applications. In addition, the stability tests confirmed that the multilayer membrane is stable under different operating conditions.

Although the silicone rubber has been investigated as a gutter and protective layer a long time ago for gas separation membranes, here, we demonstrate for the first time that it can be used for hydrophilic pervaporation membranes. These results suggest that the use of silicone material can be extended to other hydrophilic membranes with even thinner thicknesses.

Acknowledgments

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References

- [1] W. Yave, The improved pervaporation PERVAP™ membranes, *Filtration+ Separation* 54 (2017) 14-15. [https://doi.org/10.1016/S0015-1882\(17\)30126-X](https://doi.org/10.1016/S0015-1882(17)30126-X).
- [2] DeltaMem web: <https://www.deltamem.ch/>
- [3] DeltaMem industrial plant reference (contact the authors for full reference).
- [4] H. Rosemarie, Process of producing water-insoluble polymers of polyvinyl alcohol, US patent 3033842A, 1962
- [5] C. A. Finch, Polyvinyl alcohol, properties and applications, John Wiley & Sons, New York, 1973
- [6] H. Bruschke, Multi-layer membrane and the use thereof for the separation of liquid mixtures according to the pervaporation process, US Patent 4755299, 1988
- [7] W. Yave, Separation performance of improved PERVAP™ membrane and its dependence on operating conditions, *J. Membr. Sci. & Res.* 5 (2019) 216-221. <https://dx.doi.org/10.22079/jmsr.2018.88186.1198>.
- [8] N. A. Peppas and E. W. Merrill, Crosslinked poly(vinyl alcohol) hydrogels as swollen elastic networks, *J. Appl. Polym. Sci.* 21 (1977) 1763-1770. <https://doi.org/10.1002/app.1977.070210704>.
- [9] W. H. Philipp and L.-C. Hsu, Three methods for in situ cross-linking of polyvinyl alcohol films for application as ion-conducting membranes in potassium hydroxide electrolyte, NASA Technical Paper 1407, 1979
- [10] B. Bolto, T. Tran, M. Hoang, and Z. Xie, Crosslinked poly(vinyl alcohol) membranes, *Prog. Polym. Sci.* 34 (2009) 269-281. <https://doi.org/10.1016/j.progpolymsci.2009.05.003>.
- [11] J. M. L. Neel, Q. T. Nguyen and H. Bruschke, Composite membrane for separating water from fluids containing organic components by means of pervaporation, US Patent 5334314, 1994
- [12] S.K. Yong, W.L. Sang, Y.K. Un and S.S. Jyong, Pervaporation of water-ethanol mixtures through crosslinked and surface-modified poly(vinyl alcohol) membrane, *J. Membr. Sci.* 51 (1990) 215-226. [https://doi.org/10.1016/S0376-7388\(00\)80904-7](https://doi.org/10.1016/S0376-7388(00)80904-7).
- [13] O. Farid, F. Mansour, M. Habib J. Robinson, S. Tarleton, Investigating the sorption influence of poly(vinyl alcohol) (PVA) at different crosslinking content, *J. Environ. Chem. Eng.* 4 (2016) 293-298. <https://doi.org/10.1016/j.jece.2015.08.007>.
- [14] N. Mahdi, F. Salah, S. Ibrahima, L. Leva, W. Yave, Q. F. Alsalyha, The combination of a new PERVAP™ membrane and molecular sieves enhances the ethanol drying process, *Chem. Eng. Process: Process Intensif.* 174 (2022) 108863. <https://doi.org/10.1016/j.cep.2022.108863>.
- [15] Z. Tian, S. Wang, S. Dai, D. Jiang, Ultrathin membranes for gas separation, Chapter 6, *Materials for Carbon Capture*, edited by D. Jiang, S. M. Mahurin, S. Dai John Wiley & Sons Ltd., 2019. <https://doi.org/10.1002/9781119091219.ch6>.
- [16] W. Yave, H. Huth, A. Car and C. Schick, Peculiarity of a CO₂-philic block copolymer confined in thin films with constrained thickness: "a super membrane for CO₂-capture, *Energy Environ. Sci.* 4 (2011) 4656-4661. <https://doi.org/10.1039/C1EE02139G>.
- [17] K. Xie, Q. Fu, G. G. Qiao, P. A. Webley, Recent progress on fabrication methods of polymeric thin-film gas separation membranes for CO₂ capture, *J. Membr. Sci.* 572 (2019) 38-60. <https://doi.org/10.1016/j.memsci.2018.10.049>.
- [18] M. N. Hyder, R. Y. M. Huang, P. Chen, Effect of selective layer thickness on pervaporation of composite poly(vinyl alcohol)-poly(sulfone) membranes, *J. Membr. Sci.* 318 (2008) 387-396. <https://doi.org/10.1016/j.memsci.2008.03.002>.
- [19] U. Thiele, Structure Formation in Thin Liquid Films. In: Kalliadasis S., Thiele U. (eds) *Thin Films of Soft Matter*. CISM International Centre for Mechanical Sciences, vol 490. Springer, Vienna (2007) 25-93. https://doi.org/10.1007/978-3-211-69808-2_2.
- [20] J. M. S. Henis and M. K. Tripodi, Composite hollow fiber membranes for gas separation: the resistance model approach, *J. Membr. Sci.* 8 (1981) 233-246. [https://doi.org/10.1016/S0376-7388\(00\)82312-1](https://doi.org/10.1016/S0376-7388(00)82312-1).
- [21] J.G. Wijmans, P. Hao, Influence of the porous support on diffusion in composite membranes, *J. Membr. Sci.* 494 (2015) 78-85. <https://doi.org/10.1016/j.memsci.2015.07.047>.
- [22] P. Hao, J.G. Wijmans, Z. He and L.S. White, Effect of pore location and pore size of the support membrane on the permeance of composite membranes, *J. Membr. Sci.* 594 (2020) 117465. <https://doi.org/10.1016/j.memsci.2019.117465>.
- [23] J. M. S. Henis and M. K. Tripodi, A novel approach to gas separations using composite hollow fiber membranes, *Sep. Sci. Technol.* 15 (1980) 1059-1068. <https://doi.org/10.1080/01496398008076287>.
- [24] J. M. S. Henis and M. K. Tripodi, The developing technology of gas separating membranes, *Science* 220 (1983) 11-17. <https://doi.org/10.1126/science.220.4592.11>.
- [25] J. J. Chiou, Composite gas separation membrane having a gutter layer comprising a crosslinked polar phenyl containing organopolysiloxane, and method for making the same, US Patent 5286280, 1994
- [26] W. Yave, A. Car, J. Wind and K.V. Peinemann, Nanometric thin-film membranes manufactured on square meter scale: ultra-thin films for CO₂ capture, *Nanotechnology* 21 (2010) 395301. <https://doi.org/10.1088/0957-4484/21/39/395301>.
- [27] H. Yasuda, Plasma polymerization for protective coatings and composite membranes, *J. Membr. Sci.* 18 (1984) 273-284. [https://doi.org/10.1016/S0376-7388\(00\)85039-5](https://doi.org/10.1016/S0376-7388(00)85039-5).
- [28] W.J. Koros and I. Pinnau, Membrane formation for gas separation processes, In *Polymeric Gas Separation Membranes*; D. R. Paul, Y. P. Yampol'skii, Eds.; CRC Press: Boca Raton, FL, 1994
- [29] T. S. Chung, J.-J. Shieh, W. W. Y. Lau, M. P. Srinivasan and D. R. Paul, Fabrication of multi-layer composite hollow fiber membranes for gas separation, *J. Membr. Sci.* 152 (1999) 211-225. [https://doi.org/10.1016/S0376-7388\(98\)00225-7](https://doi.org/10.1016/S0376-7388(98)00225-7).
- [30] Y. Huang, R. W. Baker and J. G. Wijmans, Perfluoro-coated Hydrophilic Membranes with Improved Selectivity, *Ind. Eng. Chem. Res.* 52 (2013) 1141-1149. <https://doi.org/10.1021/ie3020654>.
- [31] S.-H. Choi, M. S. Qahtani and E. A. Qasem, Multilayer thin-film composite membranes for helium enrichment, *J. Membr. Sci.* 553 (2018) 180-188. <https://doi.org/10.1016/j.memsci.2018.02.057>.
- [32] Y. Huang, R. W. Baker, T. Aldajani, J. Ly, Dehydration processes using membranes with hydrophobic coatings, US Patent 8,496,831 B2, 2013
- [33] <https://www.wacker.com/h/de-de/medias/6415-EN.pdf>
- [34] P. Bian, Y. Wang, T. J. McCarthy, Rediscovering Silicones: The anomalous water permeability of "Hydrophobic" PDMS suggests nanostructure and applications in water purification and anti-icing, *Macromol. Rapid Commun.* 2021, 42, 2000682. <https://doi.org/10.1002/marc.202000682>.
- [35] S.J. Metz, W.J.C. van de Ven, J. Potreck, M.H.V. Mulder and M. Wessling, Transport of water vapor and inert gas mixtures through highly selective and highly permeable polymer membranes, *J. Membr. Sci.* 251 (2005) 29-41. <https://doi.org/10.1016/j.memsci.2004.08.036>.
- [36] W. L. Rob, Thin silicone membranes-their permeation properties and some applications, *Ann. N. Y. Acad. Sci.* 146 (1968) 119-137. <https://doi.org/10.1111/j.1749-6632.1968.tb20277.x>.
- [37] E. Favre, P. Schaetzl, Q.T. Nguyen, R. Clément, J. Néel, Sorption, diffusion and vapor permeation of various penetrants through dense poly(dimethylsiloxane) membranes: a transport analysis, *J. Membr. Sci.* 92 (1994) 169-184. [https://doi.org/10.1016/0376-7388\(94\)00060-3](https://doi.org/10.1016/0376-7388(94)00060-3).
- [38] J. M. Watson, M.G. Baron, The behavior of water in poly(dimethylsiloxane), *J. Membr. Sci.* 110 (1996) 47-57. [https://doi.org/10.1016/0376-7388\(95\)00229-4](https://doi.org/10.1016/0376-7388(95)00229-4).

- [39] C. Z. Liang, T.-S. Chung, Robust thin-film composite PDMS/PAN hollow fiber membranes for water vapor removal from humid air and gases, *Sep. Purif. Technol.* 202 (2018) 345-356. <https://doi.org/10.1016/j.seppur.2018.03.005>.
- [40] M. Frania, A. Huebner and E. Maus, Membrane having a pore-free separating layer and use and method of manufacturing a membrane, US Patent 9873091B2, 2018
- [41] A. Angelini, C. Fodor, L. Leva, A. Car, I. A. Dinu, W. Yave, W. Meier, Synthesis and characterization of tailor-made N-vinylpyrrolidone copolymers and their blend membranes with polyvinyl alcohol for bioethanol dehydration by pervaporation, *J. Appl. Polym. Sci.* 139 (2022) 51562. <https://doi.org/10.1002/app.51562>.
- [42] Y. Huang, J. Ly, D. Nguyen, R. W. Baker, Ethanol dehydration using hydrophobic and hydrophilic polymer membranes, *Ind. Eng. Chem. Res.* 49 (2010) 12067–12073. <https://doi.org/10.1021/ie100608s>.
- [43] P. Radovanovic, S. W. Thiel, S.-T. Hwang, Transport of ethanol-water dimers in pervaporation through a silicone rubber membrane, *J. Membr. Sci.* 48 (1990) 55-65. [https://doi.org/10.1016/S0376-7388\(00\)80795-4](https://doi.org/10.1016/S0376-7388(00)80795-4).
- [44] G. Yang, Z. Xie, M. Cran, D. Ng, S. Gray, Enhanced desalination performance of poly (vinyl alcohol)/carbon nanotube composite pervaporation membranes via interfacial engineering, *J. Membr. Sci.* 579 (2019) 40-51. <https://doi.org/10.1016/j.memsci.2019.02.034>.
- [45] E. Korin, I. Ladizhensky and E. Korngold, Hydrophilic hollow fiber membranes for water desalination by the pervaporation method, *Chem. Eng. Process.* 35 (1996) 451–457. [https://doi.org/10.1016/S0255-2701\(96\)04157-8](https://doi.org/10.1016/S0255-2701(96)04157-8).
- [46] Q. Wang, N. Li, B. Bolto, M. Hoang and Z. Xie, Desalination by pervaporation: A review, *Desalination* 387 (2016) 46-60. <https://doi.org/10.1016/j.desal.2016.02.036>.
- [47] S. G. Chaudhri, B. H. Rajai and P. S. Singh, Preparation of ultra-thin poly(vinyl alcohol) membranes supported on polysulfone hollow fiber and their application for production of pure water from seawater, *Desalination* 367 (2015) 272-284. <https://doi.org/10.1016/j.desal.2015.04.016>.
- [48] Z. Xie, M. Hoang, T. Duong, D. Ng, B. Dao and S. Gray, Sol-gel derived poly(vinyl alcohol)/maleic acid/silica hybrid membrane for desalination by pervaporation, *J. Membr. Sci.* 383 (2011) 96-103. <https://doi.org/10.1016/j.memsci.2011.08.036>.
- [49] L. Li, J. Hou, Y. Ye, J. Mansouri, and Vicki Chen, Composite PVA/PVDF pervaporation membrane for concentrated brine desalination: Salt rejection, membrane fouling and defect control, *Desalination* 422 (2017) 49-58. <https://doi.org/10.1016/j.desal.2017.08.011>.
- [50] J. Sun, X. Qian, Z. Wang, F. Zeng, H. Bai, and N. Li, Tailoring the microstructure of poly(vinyl alcohol)-intercalated graphene oxide membranes for enhanced desalination performance of high-salinity water by pervaporation, *J. Membr. Sci.* 599 (2020) 117838. <https://doi.org/10.1016/j.memsci.2020.117838>.
- [51] E. Halakoo and X. Feng, Layer-by-layer assembly of polyethyleneimine/graphene oxide membranes for desalination of high-salinity water via pervaporation, *Sep. Purif. Technol.* 234 (2020) 116077. <https://doi.org/10.1016/j.seppur.2019.116077>.
- [52] R. Zhang, X. Xu, B. Cao, P. Li, Fabrication of high-performance PVA/PAN composite pervaporation membranes crosslinked by PMDA for wastewater desalination, *Petroleum Science* 15 (2018) 146-156. <https://doi.org/10.1007/s12182-017-0204-z>.