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RESEARCH ARTICLE

REVISED PVDF membranes for membrane distillation prepared by VIPS – A combined study of artificial water channel effectiveness and membrane performance prediction

[version 2; peer review: 4 approved with reservations, 2 not approved]

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Abstract

Background

Self-supporting flat-sheet polyvinylidene fluoride (PVDF) membranes comprising amphiphilic I-quartet artificial water channels (AWC) were manufactured by a combining a VIPS pretreatment with a NIPS stage. The AWCs are formed in situ by the self-assembly of Hexylureido-ethyl-imidazole (HC6) molecules present in the dope solution, upon contact with the nonsolvent water during the phase separation process. The microporous membranes were employed for membrane distillation (MD).

Methods

A design of experiment (DoE) was used to investigate the influence of various experimental parameters and their interactions on membrane performance, namely polymer and AWC concentrations in the dope solution, relative humidity and duration of the VIPS treatment. Pure water permeability (PWP), liquid entry pressure (LEP) and MD flux were used to characterize membrane performance. A response surface methodology (RSM) was used to evaluate the DoE results and a second order model was fitted. Based on the model predictions several multiple response-optimized (MRO) membranes were

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Results

The performance improvement of the MRO membranes was 7.0 times for PWP (M-T4) and 3.3 times for MD flux (M-T3) over the average performance of the DoE membranes, while maintaining LEP of 1.9 bar and NaCl rejection of 99.9%. In addition, PVDF/HC6 hybrid MRO membranes improved PWP by 3.2 times and MD flux by 1.6 times over pure PVDF MRO membranes.

Conclusions

DoE in conjunction with RSM enabled the prediction of membrane PWP, LEP and MD flux performance by varying the levels of the experimental parameters within predefined limits. The HC6 additive improves PWP and MD flux without loss of LEP or selectivity.

Keywords
PVDF, Artificial Water Channels, VIPS-NIPS, Direct Contact Membrane Distillation, Design Of Experiment, Response Surface Methodology, ANOVA

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REVISED **Amendments from Version 1**

- The captions of figures and tables have been edited to include additional information to clarify the content.
- The authors have revised the entire introduction to provide a more focused overview of the paper's objective. The current publication builds on our previous work (Nursiah *et al.*, 2023) and continues our investigation of the potential of HC6-based AWCs in PVDF membranes for membrane distillation.
- We have expanded the section "Experimental design" in order to clarify how a DoE approach maintains statistical rigor through repeated measurements of only the center point.
- The authors have edited the first part of the section "Results of CCCD and RSM modelling" by including the original Table 5 and Table 6 into the original Table 4. In the first paragraph we discuss the mean results of the center point replications and their implications for the reproducibility of the entire DoE in the first paragraph.
- We revised the entire section "Morphological analysis" with the objective of preventing any misconceptions about the observed effects of HC6 addition to the polymer solution on membrane appearance and membrane performance.
- We also revised the conclusion to provide greater clarity regarding our key contribution.

Any further responses from the reviewers can be found at the end of the article

Introduction

Membrane distillation (MD) represents a promising technology for addressing the challenges that humanity is facing with regard to the provision of potable water (Rodell *et al.*, 2018; Vörösmarty *et al.*, 2010). Membrane distillation (MD) presents opportunities for the production of freshwater and the reduction of wastewater discharge in a variety of industrial-scale operations, including seawater/brackish water desalination, ultra-pure water production, process water treatment, and active substance concentration (Drioli *et al.*, 2011; Drioli *et al.*, 2012; Drioli *et al.*, 2015). Efficient MD requires bespoke membranes with well-defined properties that suit the task set out to perform. The advancement of membrane performance can be achieved through the development of novel membranes or through the modification of existing membranes (Peng *et al.*, 2023; Shang *et al.*, 2020).

The MD process is driven by a vapor pressure difference between the feed and permeate streams, which is induced by a temperature gradient across the membrane (Johnson & Nguyen, 2017). The majority of MD membranes are polymeric. Commonly used polymers include polypropylene (PP), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF). In the context of MD, a number of quantifiable factors, either affecting wetting resistance or mass and heat flux, are found to be correlated with membrane performance. Wetting resistance is defined by the Liquid Entry Pressure (LEP), as per the Laplace (Cantor) equation:

$$LEP = -\frac{2B\gamma_l \cos\theta}{r_{max}}$$

where B denotes a geometric factor (B=1 for cylindrical pores), γ_l represents the liquid surface tension, θ signifies the contact angle and r_{max} is the maximum pore radius. The contact angle (CA) is a measure of the surface energy of the membrane material. The aforementioned hydrophobic polymers provide wetting resistance towards water by exhibiting a low surface energy. The pore diameters of commercially available membranes suitable for MD applications typically range between 0.01 – 1 µm. The mass flux correlates with the pore diameter. Nevertheless, pore diameters > 0.3 µm only moderately enhance mass flux, while increasing the likelihood of wetting by reducing the LEP. The pore size distribution was found to have a negligible effect on flux. Mass flux and heat flux correlate inversely with membrane thickness, indicating the necessity of identifying an optimal thickness. The porosity of MD membranes should be as high as possible, while maintaining the required mechanical strength, given that mass flux correlates with porosity, whereas heat flux correlates inversely with porosity. Porosity is typically regarded as the most significant factor in MD (Eykens *et al.*, 2016; Eykens *et al.*, 2017).

The objective is to optimize membrane performance factors to enhance wetting resistance and flux. This can be achieved by carefully balancing the experimental factors involved in the membrane fabrication process. Each phase separation process, including NIPS, VIPS, EIPS, and TIPS, or a combination thereof, is associated with a distinct set of experimental factors. The type of polymer, the polymer content of the dope solution, the type of solvent, and process conditions, such as temperature and duration of the phase separation process, are common factors that must be considered. When considering NIPS and VIPS, the type of nonsolvent and the duration of the VIPS treatment must also be taken into account as additional experimental factors (Mulder, 1996). The development of new membranes is typically achieved by selecting a set of experimental factors and gradually varying each factor within a specified range while maintaining consistent levels for the remaining factors. The wetting resistance and flux of each specimen are then evaluated according to a defined set of performance factors to identify the most promising specimens. This approach, known as one-factor-at-a-time (OFAT), is not only laborious but also fails to identify interactions between experimental factors that affect performance (Montgomery, 2013). In order to circumvent the shortcomings of OFAT, the design of experiment (DoE) approach may be employed. The design of experiment (DoE) is a systematic approach that efficiently explores multiple factors and their interactions, thereby optimizing processes with minimal trials. The DoE approach saves time and resources, enhances result reliability through statistical rigor, and aids in targeted development by identifying key variables and generating predictive models (Siebertz *et al.*, 2010). Khayet *et al.*, used the DoE method to improve the performance of flat-sheet poly(vinylidene fluoride-co-hexafluoropropylene) membranes, prepared by a combined EIPS/NIPS method, for use in a DCMD application. A fractional factorial design yielded linear models of MD flux and NaCl rejection as functions of the experimental

factors, namely the polymer concentration, the PEG additive concentration, the solvent evaporation time, and the coagulant temperature (Khayet *et al.*, 2010). Dehban *et al.*, prepared PPSU/PES/Nano silica composite ultrafiltration membranes by a combined VIPS/NIPS method, to obtain high flux ultrafiltration membranes. RSM models of PWP and bovine serum albumin retention were derived from the experimental factors, namely the blending ratio of PPSU:PES, the polymer concentration, the SiO2 nanoparticle concentration, and the VIPS duration (Dehban *et al.*, 2020).

An additional strategy for improving membrane functionality is the incorporation of additives during the manufacturing process and/or the modification of existing membranes (Gontarek-Castro *et al.*, 2022; Sadrzadeh & Bhattacharjee, 2013). In 2011, a novel type of artificial water channel (AWC) was developed. The design of AWCs is inspired by the structure of biological aquaporins. Aquaporins are integral cell membrane proteins that serve as channels for the transport of water molecules across cell membranes. The AWCs are constructed from hexylureido-ethyl-imidazole (HC6) monomers, among other materials. HC6 undergoes self-assembly to form scaffolds comprising oligomeric, planar imidazole-quartets (I-quartets). The resulting solid supramolecular tubular architecture is observed to surround one-dimensional water wires. The AWC display water-channel conductance states in bilayer membranes, exhibiting trans-membrane water channel behavior that is analogous to that observed in aquaporins (Le Duc *et al.*, 2011; Licsandru *et al.*, 2016). In 2021, the AWC were successfully incorporated into composite polyamide membranes for the purpose of water desalination. Colloidal AWC aggregates were obtained by sonication of an ethanolic aqueous solution of HC6. The AWC aggregates were dispersed on the active surface of a commercial polysulfone support. Subsequently, a thin-film composite polyamide membrane was synthesized on the support by conventional interfacial polymerization. It was demonstrated that the AWCs were successfully incorporated into and remained within the PA matrix. The modified membranes demonstrated a 75% improvement in flux relative to the SOTA commercial membranes under reverse osmosis desalination conditions (Di Vincenzo *et al.*, 2021). Recently, we investigated the impact of HC6 incorporation into PVDF/DMAc dope on the fabrication of UF membranes via NIPS. The incorporation of CH6 into the membrane matrix was confirmed by FTIR-ATR, TGA, and DSC. The orientation of the amphiphilic HC6 molecule, with its hydrophobic tail oriented towards the PVDF matrix and its hydrophilic head oriented towards the pore space, was confirmed by scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (STEM-EDX). Furthermore, STEM-EDX revealed that clusters of water molecules tend to agglomerate within the void space between adjacent PVDF/HC6 crystallites, thereby indicating a hydrophilization of the membrane pores. The presence of AWC clusters within the membrane matrix was confirmed by XRD analysis. It was proposed that the initial mass flux of water into the cast dope solution and the initial mass flux of DMAc into the precipitation bath is high during NIPS. Consequently, near-instantaneous liquid-liquid demixing occurs at the interface between the precipitation bath and the dope solution. The polymer-rich phase solidifies rapidly, forming a dense outer layer. This leaves the HC6 molecules with insufficient time to form AWC aggregates. During the formation of the skin, the hydrophobic tails of the amphiphilic HC6 molecule tend to become embedded in the emerging PVDF matrix, while the hydrophilic heads are oriented towards the polymer-lean phase. Once formed, the skin impedes the influx of additional water and the outflux of DMAc across the interface. This results in a delay to the phase separation of the layers beneath the skin, thereby enabling the in-situ formation of AWC clusters from HC6. The AWC clusters are incorporated into the emerging PVDF/HC6 matrix, while also associating with imidazole heads protruding from the PVDF/HC6 matrix. This hydrophilization of the polymer-rich phase during membrane formation has been demonstrated to increase membrane porosity. The PVDF/HC6 hybrid membranes are true mixed matrix membranes, comprising networks of PVDF cores covered with PVDF/HC6 hybrid material on the surface. Additionally, AWC nanoparticles are present on the inner pore surfaces and are associated with it, creating a hydrophilic pore space and consequently enhancing water permeability (Nursiah *et al.*, 2023). The performance factors of the PVDF/HC6 hybrid membranes compared to pure PVDF membranes are shown in Table 1.

This study expands upon our previous publication, which detailed the effects of incorporating HC6-based AWC nanoparticles into PVDF UF membranes for MD prepared by NIPS. In particular, the impact of a VIPS pretreatment has been evaluated with the objective of enhancing the membrane performance in terms of LEP and NaCl rejection, while maintaining the PWP and MD flux. To that end, four experimental factors were controlled and varied according to a DoE methodology. The factors investigated were the polymer concentration and HC6 concentration in the dope solution, the relative humidity (RH) of the VIPS stage, and the duration of the VIPS treatment. Four regression models based on RSM have been proposed with the objective of establishing a link between the experimental factors and the four membrane performance characteristics. The statistical analysis demonstrated that the performance of the membranes in terms of PWP and LEP was reasonably predictable. Qualitative predictive capacity

Table 1. A summary of the membrane performance factors of the best performing membranes prepared by NIPS.

Membrane preparation	NIPS (Nursiah *et al.*, 2023)	
Membrane material	PVDF	PVDF/HC6
PWP	30.6	75.3
LEP	0.7	0.2
MD flux	48.9	54.1
NaCl rejection	98.4	99.8

was observed for the MD flux, whereas no predictive capacity was evident for the NaCl rejection. These findings corroborate the previously demonstrated efficacy of HC6 incorporation with respect to the enhancement of PWP and MD flux. Furthermore, the VIPS pretreatment significantly increased the LEP for both the pure PVDF and the PVDF/HC6 hybrid membranes, while maintaining NaCl rejection at 99.9%. It has been demonstrated that the DoE methodology and RSM modeling have the potential to reduce the necessary experimental effort while simultaneously establishing quantifiable correlations between experimental variables and observed outcomes.

Methods

Materials

PVDF pellets (CAS No.: 24937-79-9; MW = 530 000 g/mol) and N,N-Dimethylacetamide (CAS No.: 127-19-5) were provided by Sigma-Aldrich Germany. Laboratory produced distilled water (18 MΩ.cm^{-1}) was used as coagulation bath for membrane preparation and in the DCMD experiments. The HC6 AWC were synthesized according to a procedure described elsewhere (Le Duc *et al.*, 2011). All experimental designs, their analyses and modelling were performed using Minitab v. 20.3.

Membrane preparation

VIPS-NIPS assisted membrane preparation was performed according to the following protocol. Dope solutions, with compositions summarized in Table 4, were prepared by dissolving the PVDF pellets in N,N-dimethylacetamide (DMAc) for 6 h at a dissolution temperature T_d of 55°C, followed by a degassing period of 18 h at room temperature (22°C). The stainless-steel support used for dope casting was previously fixed in a temperature-controlled vapor box maintained at 25 °C. Figure 1 shows a process flow diagram of the VIPS pretreatment. The humidity in the vapor box was controlled by a compressed air piping system consisting of two wet lines and one dry line. The wet lines each consisted of a 1 L double-jacketed glass frit impinger. Thus, the desired relative humidity (RH) in the vapor box was set by adjusting the air flow rates in the wet and dry lines. The temperature and air flow rate in the box were held constant at 22°C and 7.7 L/min, respectively, and the humidity and exposure time were varied according to the values specified by the DoE. The flow rate of the conditioned air stream, its relative humidity, and the pressure and temperature of the air stream were constantly monitored. The degassed dope solution was cast onto the support using a casting knife (Micrometer Adjust Applicator 400 mm) with a gap size of 250 µm. After casting, the vapor box was closed and the nascent membrane was exposed to humid air for the desired time. The support was then removed from the vapor box into a dry atmosphere (relative humidity <18%). The steel plate was immersed in a coagulation bath (distilled water at 25 °C) for 24 h. The resulting membranes were dried in a stack. Each membrane was laid flat on a stainless-steel plate and held in place by four rectangular blocks of PTFE placed on each of the four edges. The plates with wet membrane sheets and blocks were then stacked. The PTFE blocks have horizontal holes so that a constant flow of dry air was blown horizontally through the stack by a fan to ensure a gentle and uniform drying process.

Membrane characterization

Morphological analysis by Scanning Electron Microscopy (SEM). The top surface and cross-section of the membranes were examined by means of scanning electron microscopy

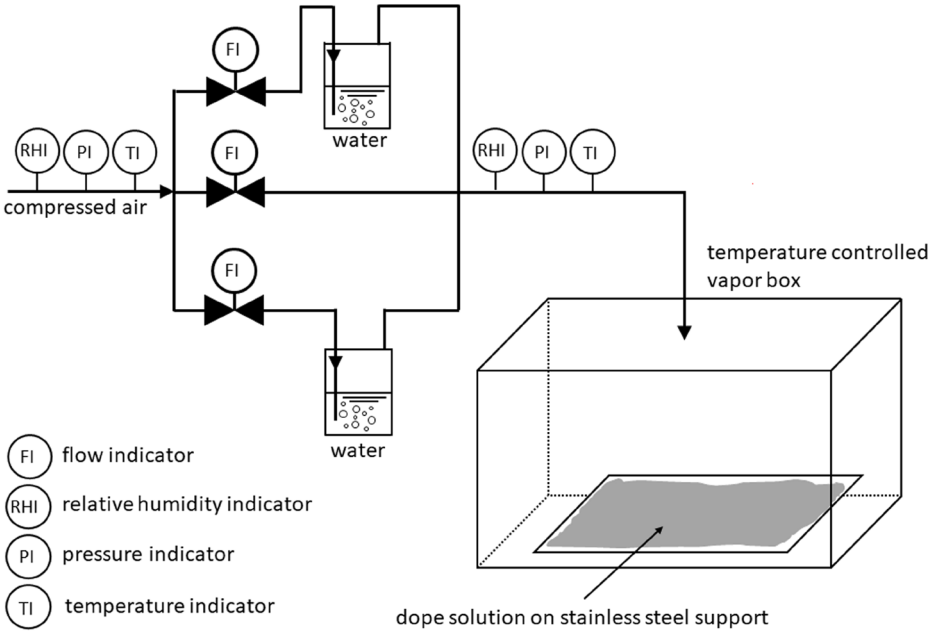

Figure 1. Process flow diagram of VIPS pretreatment.

(SEM). The images were taken with a MEB Hitachi S4800, with a resolution of 1 nm at 15 kV and capable of an acceleration voltage range of 0.1 kV to 30 kV.

Pure Water Permeability (PWP) and Liquid Entry Pressure (LEP). The PWP permeability measurements were carried out according to the following protocol, which is also described in detail in our previous work (Nursiah *et al.*, 2023).

The LEP was determined together with the pure water permeability to characterize the wetting resistance of the membranes. For this purpose, a water-filled dead-end filtration setup was used. The membrane was placed inside the cell and the pressure applied on the feed side was increased stepwise in 0.1 bar increments after two minutes of stabilization time after each step. After reaching the LEP, the membrane was compressed at 4.0 bar for 45 min. After compression, the pressure was decreased in 0.5 bar increments and the water flux was recorded and plotted as a function of transmembrane pressure. The PWP of the membrane was determined by considering the gradient of the slope of the obtained linear relationship.

Direct Contact Membrane Distillation (DCMD). The DCMD performance was investigated according to the following protocol, as described in our previous work (Nursiah *et al.*, 2023).

A pilot-scale MD setup was used for the DCMD experiments. The self-supporting flat sheet membranes were tightly clamped between two Teflon plates, leaving an effective operating area of 28.6 cm2. An aqueous sodium chloride solution (35 g/L) constituted the feed side, and the permeate was directly recovered in the circulating cooling system (18 MΩ.cm water). The feed inlet temperature T_f was fixed at 70°C (± 2°C) and the distillate inlet temperature T_p was maintained at 10°C (± 1°C). Two independent peristaltic pumps were used to circulate the feed and permeate sides. The pump for the former helped maintain a flow rate of 55 L/h. The main operating conditions used in the DCMD experiments are listed in Table 2.

Throughout the DCMD process, the distilled permeate was diluted in the cold circulating water. The diluted solution was collected and weighed after an average period of 3 h 30 min. The NaCl concentration *Cp* collected in the distilled permeate was monitored by conductivity σ (S.m^{-1}) (Conductometer VWR ® Phenomenal ® MU 6100H) and calculated according to a calibration curve (*Cp*=σ/5.5758). Finally, the water permeate flux was calculated according to Equation 1,

$$J_w = \Delta m / A \cdot t \quad (1)$$

where J_w represents the water permeate flux (kg/m^2·h), Δm is the permeate weight (kg), A is the effective membrane surface area (m^2) and t is the experiment duration (h).

The NaCl rejection R was determined according to Equation 2,

$$R\,[\%] = (1 - (C_p \div C_f)) \cdot 100 \quad (2)$$

where C_p and C_f represent the NaCl concentration in the permeate and the feed, respectively.

Table 2. Operating conditions used in DCMD setup.

Parameter	Range
Membrane module	Flat
Support	No
Feed temperature [°C]	70 ± 2
Feed flow rate [L/h]	55
Permeate temperature [°C]	10 ± 1
Permeate flow rate[L/h]	55

Model building and statistical analysis

A statistical approach such as RSM uses regression analysis to derive a model equation from the data that expresses the relationship between a response of interest, y (called the response variable), and a set of experimental parameters (called factors), denoted x_1, x_2, … , x_k. Each experimental factor has several values, called levels. Each response is considered as a function of the factors according to Equation 3, where ε represents the random experimental error observed in the response *yi*.

$$y_i = f(x_1, x_2, x_3, x_4) + \varepsilon \quad (3)$$

A second-order response surface model describes the functional relationship between a response variable and the experimental factors by recognizing main effect coefficient β_i, a quadratic effect coefficient β_{ii}, and a binary interaction coefficient β_{ij}, according to Equation 4. An effect quantifies the average change in a response variable with a change in factor level.

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum\sum_{i<j} \beta_{ij} x_i x_j + \varepsilon \quad (4)$$

Each experimental run yields a model equation that describes the effect of a particular combination of factor levels on a particular response variable. A regression model of a particular response is the solution to the system of equations resulting from the sum of the experimental runs. An analysis of variance (ANOVA) of the total sum of squares evaluates the statistical significance and accuracy of the individual effect coefficients of a model. Each regression model includes only effects with a p-value less than the significance level $\alpha < 0.1$. Those are color-coded blue, in the corresponding Pareto charts. Various residual plots were used to assess the validity and reliability of the regression models to ensure that the model assumptions of normality of residuals, constant variance of residuals and independence of errors were met. The adjusted coefficient of determination *Adj* R^2 compared the model fits. The utility of appropriate regression models for membrane performance optimization was tested by producing multiple response-optimized (MRO) membranes. In MRO, a desirability function simultaneously optimizes the factor levels of multiple regression models to yield a composite desirability.

First, each response y_i is converted into a desirability function d_i that varies over the range of

$$0 \leq d_i \leq 1$$

where if the response y is at its target, then $d = 1$, and if y is outside an acceptable range, then $d = 0$. Then the factor levels are chosen to maximize the overall desirability

$$D = (d_1 \cdot d_2 \cdot \cdots \cdot d_m)^{1/m} \quad (5)$$

for m responses (Montgomery, 2008).

Experimental design

A major goal of model building is to optimize the response variables by identifying desirable combinations of factor levels. A full factorial Central Composite Circumscribed Design (CCCD) is a form of DoE that examines the factor space uniformly and measures each factor at five levels, allowing the fitting of the second-order RSM described above. This approach has several advantages over the common OFAT method. It significantly reduces the experimental workload; it reveals quadratic effects and binary factor interactions; it does not miss optimal factor combinations because all factors are compared to each other on all levels (Hubadillah *et al.*, 2018).

In this case study, the investigated factor space consists of four experimental factors, also called predictors, on five levels each. The factors are the mass fraction of polymer in the dope solution w_P, the mass fraction of HC6 additive in the dope solution w_{HC6}, the duration of the VIPS pretreatment t_{VIPS}, and the relative humidity during the VIPS pretreatment RH. Table 3 summarizes the factors and their respective values. The range of factor levels was determined in accordance with the literature, specifically.

A full factorial CCCD with four factors on five levels each results in 30 experimental runs (prepared membranes). The CCCD consist of 16 cube points with 4 center points in the cube and 8 axial points with 2 center points in the axial. At the center point, each factor level represents the mean of its range. The 6 center points are thus repeated measurements. Center points in DoE are essential for detecting non-linearity and estimating the experimental error, providing a basis for discussing model adequacy and statistical validity. By comparing the results of the center points with those of the cube points and the axial points, they help identify model curvature, confirm model appropriateness, and ensure the reliability of the experiment's conclusions. A randomized running order, pooled in three blocks, ensures independent experiments and minimizes systematic errors. Each block contains two center point replications. Table 4 lists the 24 individual factor combinations of the cube points and the axial points, as well as the 6 center point replication measurements comprising the CCCD.

Results and discussion

In the following sections, a detailed ANOVA of the models derived from RSM evaluates their accuracy and statistical significance. Subsequently, the predictive power the models is investigated by MRO. The performance improvement of the MRO membranes was 7.0 times for PWP and 3.3 times for MD flux over the average performance of the DoE membranes, while maintaining LEP of 1.9 bar and NaCl rejection of 99.9%. In addition, PVDF/HC6 hybrid MRO membranes improved PWP by 3.2 times and MD flux by 1.6 times over pure PVDF MRO membranes. Lastly, the performance differences of the optimized membranes are discussed on the basis of SEM images of the surfaces and cross-sections.

Results of CCCD and RSM modelling

To effectively optimize membrane performance and to investigate the potential of the HC6 additive to further enhance performance, RSM was applied to the results of the CCCD. Table 5 lists the measured performance parameters of each membrane produced by the DoE, namely LEP, PWP, MD flux, and NaCl rejection. The range and mean values of each performance parameter are provided below the individual results. The upper end of each range was used as a benchmark for the ensuing MRO. The mean and the measurement uncertainty (n = 6, 95% confidence) of the center points are also provided in Table 5. The measurement uncertainty of the center point means indicates the reproducibility of the entire experiment. The data indicate a good reproducibility of the NaCl rejection and the MD flux, a moderate reproducibility of the LEP and a rather poor reproducibility of the PWP. A quadratic regression model, was fitted to the results of each of the four response parameters. Equation 6, Equation 7, Equation 8 and Equation 9 show the RSM models for PWP, LEP, MD flux,

Table 3. Each of the four experimental factors of the DoE is varied on 5 levels.

Polymer mass fraction w_P / wt.-%	Additive mass fraction w_{HC6} / wt.%	VIPS duration t_{VIPS} / s	Relative humidity RH / %
14	0	180	70
16	0.025	360	75
18	0.05	540	80
20	0.075	720	85
22	0.1	900	90

Table 4. The CCCD comprises of 30 experimental runs, yielding 30 membranes. Of these, 24 membranes were produced using unique factor level combinations, while the remaining 6 membranes were generated from identical center point replication.

Membrane code	Block	Experimental factors and their respective levels			
		Polymer mass fraction w_P / wt.-%	Additive mass fraction w_{HC6} / wt.%	VIPS duration t_{VIPS} / s	Relative humidity RH / %
M-1a	1	16	0.025	360	85
M-1b	1	16	0.025	720	75
M-1c	1	16	0.075	360	75
M-1d	1	16	0.075	720	85
M-1e*	1	18	0.05	540	80
M-1f*	1	18	0.05	540	80
M-1g	1	20	0.025	360	75
M-1h	1	20	0.025	720	85
M-1i	1	20	0.075	360	85
M-1j	1	20	0.075	720	75
M-2a	2	16	0.025	360	75
M-2b	2	16	0.025	720	85
M-2c	2	16	0.075	360	85
M-2d	2	16	0.075	720	75
M-2e*	2	18	0.05	540	80
M-2f*	2	18	0.05	540	80
M-2g	2	20	0.025	360	85
M-2h	2	20	0.025	720	75
M-2i	2	20	0.075	360	75
M-2j	2	20	0.075	720	85
M-3a	3	14	0.05	540	80
M-3b	3	18	0	540	80
M-3c	3	18	0.05	180	80
M-3d	3	18	0.05	540	70
M-3e*	3	18	0.05	540	80
M-3f*	3	18	0.05	540	80
M-3g	3	18	0.05	540	90
M-3h	3	18	0.05	900	80
M-3i	3	18	0.1	540	80
M-3j	3	22	0.05	540	80

* center points

Table 5. Each of the 30 membranes produced by the CCCD and their respective performance as characterized by LEP, PWP, MD flux, and NaCl rejection. The range and mean values for each performance parameter are presented in the two lower rows.

Membrane code	Results of the characterization of the DoE membranes			
	LEP / bar	PWP / $Lm^{-2}h^{-1}bar^{-1}$	MD flux / $Lm^{-2}h^{-1}$	NaCl rejection / %
M-1a	1.5	16.2	0.1	99.9
M-1b	1.9	1.5	2.8	99.9
M-1c	3.4	3.6	2.6	99.9
M-1d	0.8	58.6	4.9	99.9
M-1e*	1.0	22.5	4.7	99.9
M-1f*	2.7	9.2	5.1	99.9
M-1g	3.9	0.8	2.7	99.9
M-1h	2.3	3.0	3.1	99.9
M-1i	2.2	0.9	4.0	93.9
M-1j	2.4	4.2	4.7	99.9
M-2a	3.7	8.4	2.0	99.9
M-2b	1.4	70.8	1.2	99.9
M-2c	1.9	10.1	0.2	99.9
M-2d	0.8	21.4	0.2	<10.0
M-2e*	0.9	22.4	4.4	99.9
M-2f*	2.6	3.6	3.9	99.9
M-2g	3.3	1.5	2.5	99.9
M-2h	2.0	15.5	0.5	99.9
M-2i	2.4	4.5	2.0	98.5
M-2j	0.9	27.9	2.7	87.1
M-3a	0.4	68.3	2.2	<10.0
M-3b	2.3	13.6	0.5	72.2
M-3c	3.4	6.1	1.8	<10.0
M-3d	0.4	8.3	2.8	99.9
M-3e*	2.2	15.3	5.8	99.9
M-3f*	2.4	42.3	5.2	99.9
M-3g	2.0	6.2	2.8	99.9
M-3h	2.6	8.8	0.5	99.9
M-3i	2.0	8.6	0.2	99.9
M-3j	2.6	3.1	0.6	17.4
Range of all results	0.1 – 3.9	0.8 – 70.8	0.1 – 5.8	<10 – 99.9
Mean of all results	2.1	16.2	2.5	86.6
Mean of center points	2.0 ± 0.8	19.2 ± 13.0	4.8 ± 0.6	99.9 ± 0

* center points

and NaCl rejection, respectively, in uncoded units. The statistical significance of each model and of its constituents is determined by ANOVA.

The ANOVA of the PWP model reported in Table 6 indicates that 42.77% of the variance is accounted for by linear terms, primarily w_P (26.61%) and t_{VIPS} (10.14%), followed by 13.87% from two 2-way interactions and 6.75% from square w_P. These statistically significant predictors are highlighted in blue in Figure 2 (a). The residuals appear to be independent (Figure 2 (b)) and normally distributed (Figure 2 (c)), except that Figure 2 (d) shows four outliers representing comparatively large PWP values, possibly due to defects in the membrane. The model fit is 63.4%, but the error due to Lack-of-Fit is not statistically significant with a p value of 0.686. The PWP model performance as a function of factor levels is plotted in Figure 6 (a).

$$\mathrm{PWP} = -280 + 5.5\, w_P - 0.553\, \mathrm{t}_{VIPS} + 9.72\, \mathrm{RH} + 1.258\, w_P \cdot w_P - 0.703\, w_P \cdot \mathrm{RH} + 0.00738\, \mathrm{t}_{VIPS} \cdot \mathrm{RH} \quad (6)$$

The LEP model explains 31.78% of the variance with linear terms, namely t_{VIPS} (20.59%) and w_P (11.18%), and 10.16% with a square t_{VIPS} term. These sources represent the significant effects (Figure 3 (a)). The validity and reliability of the model are sufficient according to Figure 3 (b) – (d). The model fit is 42.4%, but the main error due to Lack-of-Fit is not statistically significant with a p-value of 0.829, as summarized in Table 7. Figure 6 (b) plots the LEP model as a function of factor levels.

$$\mathrm{LEP} = 2.90 + 0.1750\, w_P - 0.01301\, \mathrm{t}_{VIPS} + 0.000010\, \mathrm{t}_{VIPS} \cdot \mathrm{t}_{VIPS} \quad (7)$$

The MD flux model includes three quadratic terms, namely w_{HC6}*w_{HC6} (23.0%), t_{VIPS}*t_{VIPS} (16.84%), and w_P*w_P (7.63%). The quadratic terms all show significant effect sizes (Figure 4 (a)). This suggests an optimum of MD performance for intermediate factor levels, as shown in Figure 6 (c), to which all factors contribute significantly. Another source of statistically significant variance is a block term with a contribution of 14.45%. The residual analysis is unremarkable (Figure 4 (b) – (d)). The model fits the data to 61.9% and the Lack-of-Fit error is statistically significant with a p-value of 0.031, concluding that the model does not correctly specify the relationship between response and predictor (see Table 8).

$$MD\ flux = 4{,}416 - 0{,}669\, w_P \cdot w_P - 0{,}937\, \mathrm{w}_{HC6} \cdot \mathrm{w}_{HC6} - 0{,}729\, \mathrm{t}_{VIPS} \cdot \mathrm{t}_{VIPS} \quad (8)$$

Table 6. The ANOVA of the PWP model details how the various sources contribute to the model.

Source	DF	Seq SS	Contribution / %	Adj SS	Adj MS	F-Value	P-Value
Model	6	6844.8	63.40	6844.8	1140.8	6.64	0.000
Linear	3	4618.0	42.7	4618.0	1539.3	8.96	0.000
w_P	1	2872.8	26.61	2872.8	2872.8	16.72	0.000
t_{VIPS}	1	1095.1	10.14	1095.1	1095.1	6.37	0.019
RH	1	650.0	6.02	650.0	650.0	3.78	0.064
Square	1	729.0	6.75	729.0	729.0	4.24	0.051
w_P*w_P	1	729.0	6.75	729.0	729.0	4.24	0.051
2-Way Interaction	2	1497.8	13.87	1497.8	748.9	4.36	0.025
w_P*RH	1	791.9	7.33	791.9	791.9	4.61	0.043
t_{VIPS}*RH	1	706.0	6.54	706.0	706.0	4.11	0.054
Error	23	3951.6	36.60	3951.6	171.8		
Lack-of-Fit	20	3322.4	30.77	3322.4	166.1	0.79	0.686
Pure Error	3	629.1	5.83	629.1	209.7		
Total	29	10796.3	100.00				
Std. Dev	13.11						
PRESS	7290.1						
R^2	0.634						
Adj R^2	0.539						
Pred R^2	0.325						

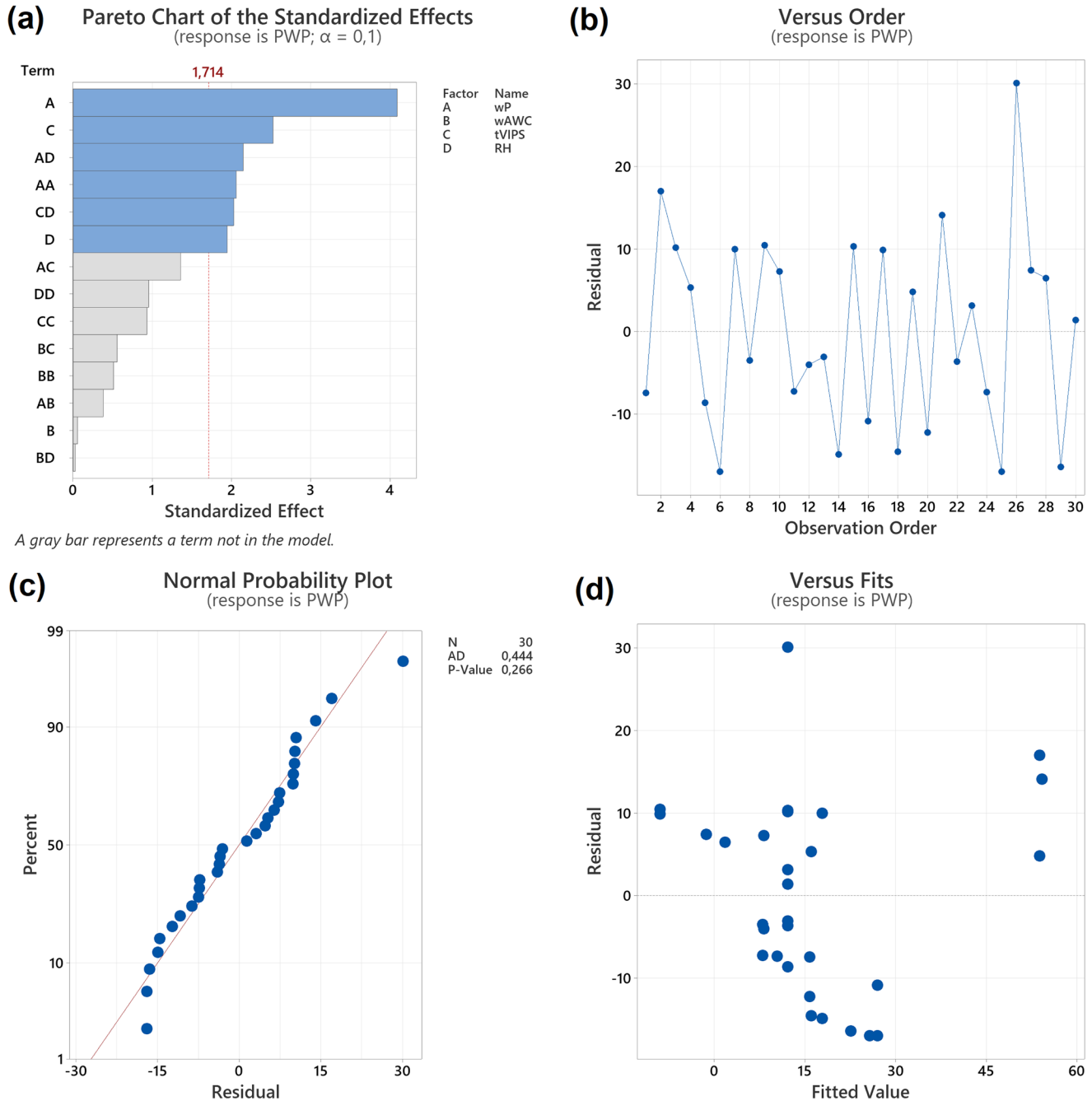

Figure 2. Effects and residual plots for PWP model. (**a**) The Pareto chart highlights the statistically significant predictors (α < 0.1) of the PWP performance, represented in blue. The residuals of the PWP model are shown in relation to the run order (**b**), a normal probability distribution (**c**), and the fitted values (**d**).

The ANOVA of the NaCl rejection model in Table 9 suggests only square w_p (29.93%) as a source of variation with a significant effect size (Figure 5 (a)), suggesting an optimal factor level within the factor space examined. Furthermore, a block contribution of 15.59% with a p value of 0.038 suggests a change in response due to different conditions between runs. The residuals vs. run plot in Figure 5 (b) shows several severe outliers, which are further confirmed by Figure 5 (c) & (d). The pattern suggests a violation of the model assumptions proposed in the section "Model building and statistical analysis". NaCl rejection was consistently 99.9%, except for a few runs where it was <10%. This suggests defective membranes as

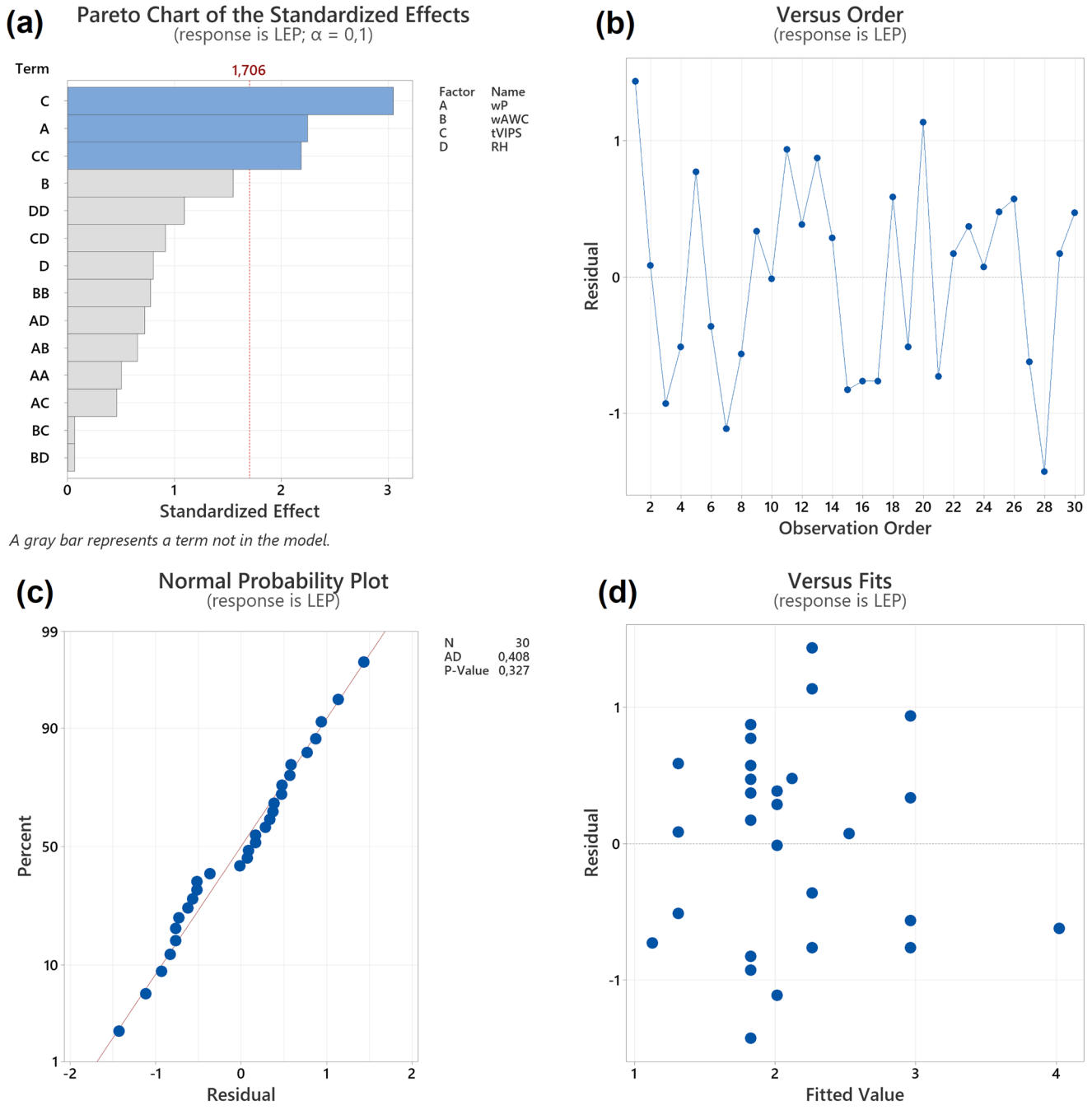

Figure 3. Effects and residual plots for LEP model. (**a**) The Pareto chart highlights the statistically significant predictors (α < 0.1) of the LEP performance, represented in blue. The residuals of the LEP model are shown in relation to the run order (**b**), a normal probability distribution (**c**), and the fitted values (**d**).

a source of poor rejection. The RSM is not suitable for modelling this type of behavior.

$$\text{NaCl } \textit{rejection} = -1281 + 151.6\, w_P - 4.16\, w_P \cdot w_P \qquad (9)$$

The four regression models and the comparison of their errors and their coefficients of correlation are summarized in Figure 6 and Table 10, respectively. Each model is plotted as a function of the four experimental factors. The predictors are on the x-axis and the responses are on the y-axis. A plot with a grey background indicates the absence of a statistically significant relationship between predictor and response. The PWP shown in Figure 6 (a) improves with decreasing w_P, which is expected as porosity increases. The lack of

Table 7. The ANOVA of the LEP model details how the various sources contribute to the model.

Source	DF	Seq SS	Contribution / %	Adj SS	Adj MS	F-Value	P-Value
Model	3	11.143	42.38	11.143	3.7142	6.37	0.002
Linear	2	8.355	31.78	8.355	4.1775	7.17	0.003
w_P	1	2.940	11.18	2.940	2.9400	5.05	0.033
t_{VIPS}	1	5.415	20.59	5.415	5.4150	9.29	0.005
Square	1	2.788	10.60	2.788	2.7876	4.78	0.038
t_{VIPS}*t_{VIPS}	1	2.788	10.60	2.788	2.7876	4.78	0.038
Error	26	15.151	57.62	15.151	0.5827		
Lack-of-Fit	23	12.241	46.56	12.241	0.5322	0.55	0.829
Pure Error	3	2.910	11.07	2.910	0.9700		
Total	29	26.294	100.00				
Std. Dev	0.76						
PRESS	21.1						
R^2	0.424						
Adj R^2	0.357						
Pred R^2	0.199						

relationship between PWP performance and HC6 content is puzzling, but a potential effect may be buried in the noise of the data. This is investigated in the section "Results of Multiple Response-Optimization". In addition, PWP increases linearly with increasing t_{VIPS} and *RH*. The hypothesis that longer t_{VIPS} at higher *RH* promotes delayed demixing leading to skin defects will be tested in the section "Morphological analysis". The plots in Figure 6 (b) show an increasing LEP with increasing w_P and decreasing t_{VIPS}. This behavior is reasonable as both actions promote skin densification. HC6 has no statistically significant effect on LEP. At first glance, no effect would be expected as LEP is mainly dependent on the porosity and pore size of the skin. However, the possible effects of HC6 on membrane morphology are discussed in the section "Morphological analysis". The dependence of LEP on RH cannot be modelled due to the step response between 70% and 75% *RH*. The MD flux regression model in Figure 6 (c) shows optimal flux for intermediate factor levels of $w_{P,}$ w_{AWC} and t_{VIPS}. This suggests good specified factor level ranges. RH appears to have an inconsistent effect on MD flux. In the case of NaCl rejection, no statistically significant relationships are expected due to the inadequacy of the RSM to fit the data, see Figure 6 (d).

According to Table 10, the models for MD flux and NaCl rejection have statistically significant Lack-of-Fit errors, meaning that these models do not correctly specify the relationship between response and predictors. A likely cause could be that the experiment contained an uncontrolled predictor variable. This proposition is supported by the fact that the ANOVA of both models shows statistically significant contributions of blocks as a source of variance. The Lack-of-Fit is not statistically significant for the remaining models, namely PWP and LEP. Overall, the adjusted coefficient of determination is below our expectations. Due to the inadequacy of the RSM model to fit the NaCl rejection data it is excluded from further investigation and verification.

Results of Multiple Response-Optimization

To test the predictive capabilities of the remaining three models and to elucidate the effect of HC6 on membrane performance, two multiple response-optimized (MRO) membranes were prepared. Each was part of a set of four additional membranes prepared at the MRO predicted factor levels, but with varying HC6 weight fractions. Finally, both sets consisted of one pure PVDF membrane and four PVDF/HC6 hybrid membranes with 0.025, 0.05, 0.075, and 0.1 wt. % HC6, respectively. The performance of the membranes was evaluated as described in the section "Membrane characterization".

The first MRO was fitted using the PWP and LEP model. The objective was to maximize PWP while LEP was set at a target of 2.0 bar, which is suitable for MD application. The MRO recommends factor levels to achieve the selected response targets. Table 11 summarizes the experimental parameters of the first MRO membrane set.

The predicted targets of the first MRO, along with the Standard Error (SE Fit), 95% Confidence Interval (95% CI), and 95% Prediction Interval (95% PI) of the fitted target values are

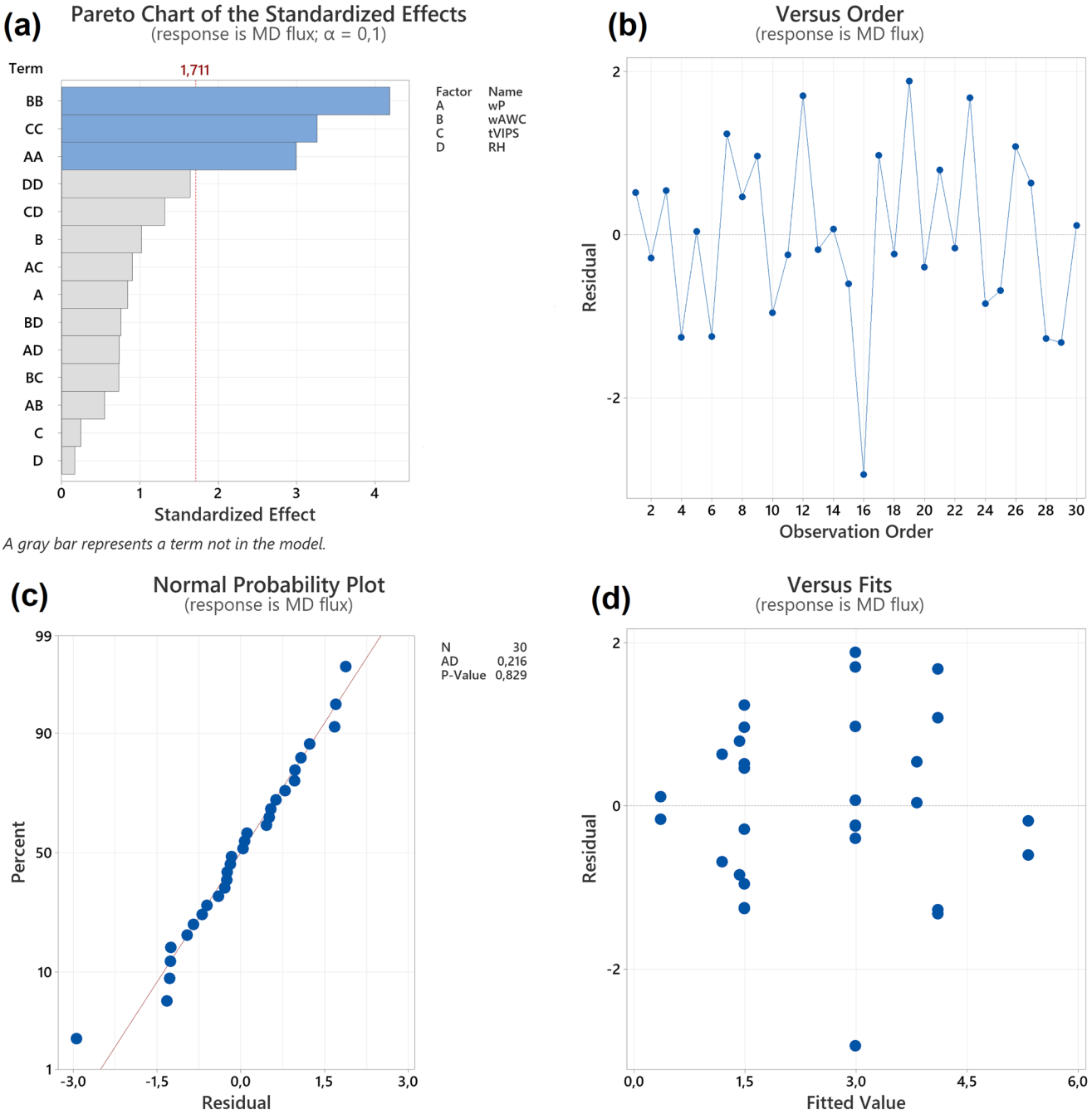

Figure 4. Effects and residual plots for MD flux model. (**a**) The Pareto chart highlights the statistically significant predictors (α < 0.1) of the MD flux performance, represented in blue. The residuals of the MD flux model are shown in relation to the run order (**b**), a normal probability distribution (**c**), and the fitted values (**d**).

shown in Table 12. The Standard Error of the Fit (SE Fit) estimates the variation in the estimated mean response for the specified factor levels. The Confidence Interval (CI) provides a range of likely values for the mean response given the specified factor levels. The Prediction Interval (PI) is a range that is likely to contain a single response for the specified factor levels.

Table 13 summarizes the membrane performance of the first MRO set. Green underlay indicates values within the 95% CI,

Table 8. The ANOVA of the MD flux model details how the various sources contribute to the model.

Source	DF	Seq SS	Contribution / %	Adj SS	Adj MS	F-Value	P-Value
Model	5	54.7262	61.93	54.7262	10.9452	7.81	0.000
Blocks	2	12.7708	14.45	12.7708	6.3854	4.55	0.021
Square	3	41.9553	47.48	41.9553	13.9851	9.98	0.000
w_P*w_P	1	6.7454	7.63	12.5324	12.5324	8.94	0.006
w_{HC6}*w_{HC6}	1	20.3288	23.00	24.5578	24.5578	17.52	0.000
t_{VIPS}*t_{VIPS}	1	14.8811	16.84	14.8811	14.8811	10.61	0.003
Error	24	33.6460	38.07	33.6460	1.4019		
Lack-of-Fit	21	33.2528	37.63	33.2528	1.5835	12.08	0.031
Pure Error	3	0.3932	0.44	0.3932	0.1311		
Total	29	88.3721	100.00				
Std. Dev	1.18						
PRESS	49.4						
R^2	0.619						
Adj R^2	0.540						
Pred R^2	0.441						

Table 9. The ANOVA of the NaCl rejection model details how the various sources contribute to the model.

Source	DF	Seq SS	Contribution / %	Adj SS	Adj MS	F-Value	P-Value
Model	3	12149.1	45.53	12149.1	4049.68	7.24	0.001
Blocks	2	4161.0	15.59	4161.0	2080.52	3.72	0.038
Square	1	7988.0	29.93	7988.0	7988.00	14.29	0.001
w_P*w_P	1	7988.0	29.93	7988.0	7988.00	14.29	0.001
Error	26	14536.6	54.47	14536.6	559.10		
Lack-of-Fit	23	14536.6	54.47	14536.6	632.02	*	*
Pure Error	3	0.0	0.00	0.0	0.00		
Total	29	26685.6	100.00				
Std. Dev	23.65						
PRESS	18569.9						
R^2	0.455						
Adj R^2	0.392						
Pred R^2	0.304						

orange within the 95% PI. This indicates that the predictive capabilities of the PWP and LEP models are within useful limits, although the MRO overpredicted membrane performance in both cases. An increase in PWP and MD flux performance was reported for all PVDF/HC6 hybrid membranes compared to the pure PVDF membrane, while LEP was also improved. In addition, NaCl rejection remained consistently high at 99%. These results confirm the efficacy of HC6

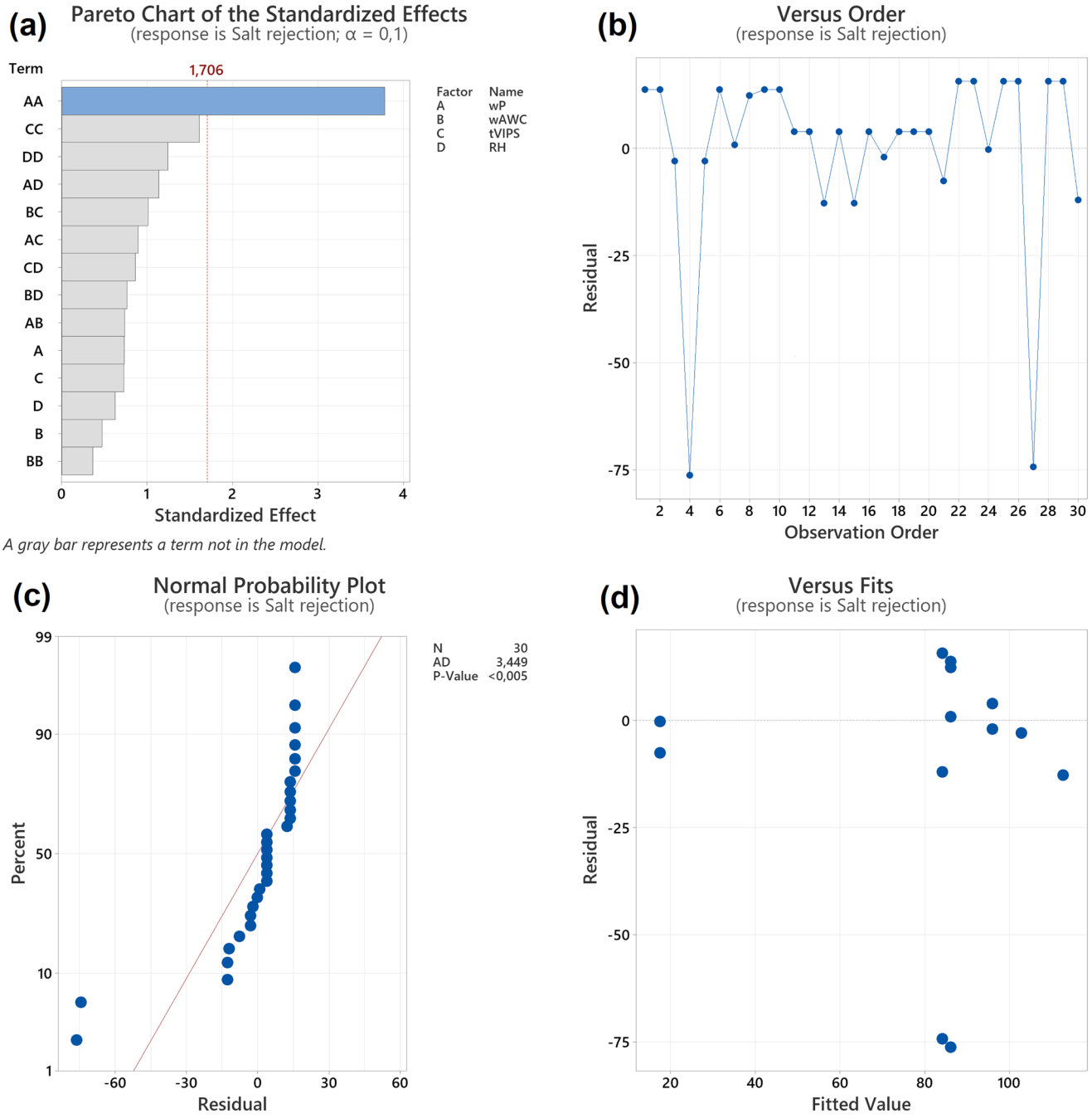

Figure 5. Effects and residual plots for NaCl rejection model. (**a**) The Pareto chart highlights the statistically significant predictor (α < 0.1) of the NaCl rejection performance, represented in blue. The residuals of the NaCl rejection model are shown in relation to the run order (**b**), a normal probability distribution (**c**), and the fitted values (**d**).

as an agent to improve membrane flux without compromising selectivity or membrane wetting resistance.

For the second MRO, both MD flux and PWP were maximized. The required factor levels and fitted response targets, including estimated errors and 95% intervals, are shown in Table 14.

Table 15 summarizes the experimental conditions of the second MRO membrane set.

The membrane performance of the second MRO set is summarized in Table 16. The PWP is within the 95% CI, further confirming the predictive ability of the model. The MD flux performance as a function of HC6 concentration qualitatively

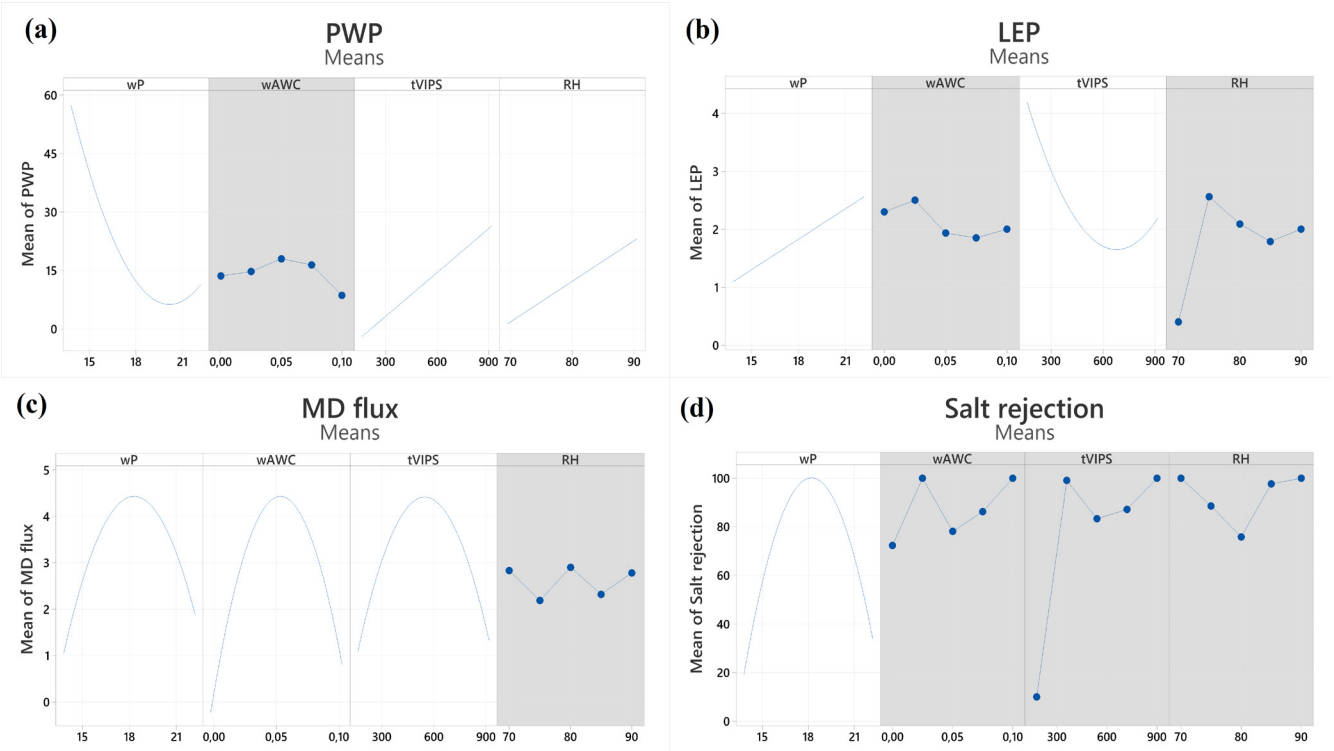

Figure 6. Each model is plotted as a function of the four predictor variables. The x-axis of each predictor shows its range. A grey background signifies no statistically significant dependence of the predictor on the respective model. (**a**) The PWP performance is determined by w_P, t_{VIPS}, and RH. (**b**) The LEP performance is determined by w_P, and t_{VIPS}. (**c**) The MD flux performance is determined by w_P, w_{HC6}, and t_{VIPS}. (**d**) The NaCl rejection model is determined only by w_P.

Table 10. The Lack-of-Fit error and the adjusted coefficient of correlation of the four regression models.

Model	PWP	LEP	MD flux	NaCl rejection
Lack-of-Fit	insignificant	insignificant	significant	significant
Adj R^2	0.539	0.357	0.540	0.3924

Table 11. The dope solution compositions and process conditions of the VIPS pretreatment of first set of MRO membranes.

Membrane code	Polymer mass fraction w_P/wt.-%	Additive mass fraction w_{HC6}/wt.%	VIPS duration t_{VIPS}	Relative humidity RH / %
M-T0*	17.3	0	900	90
M-T1	17.3	0.025	900	90
M-T2	17.3	0.050	900	90
M-T3	17.3	0.075	900	90
M-T4	17.3	0.100	900	90

* MRO-predicted reference membrane

Table 12. **The model prediction for the first set of MRO membranes.**

Response	Target	SE Fit	95% CI	95% PI
PWP / $Lm^{-2}h^{-1}bar^{-1}$	72.1	15.6	39.8 – 104.3	29.9 – 114.2
LEP / bar	2.0	0.6	0.8 – 3.2	0.1 – 4.0

Table 13. **The performance of the first set of MRO membranes.**

Membrane	LEP / bar	PWP / $Lm^{-2}h^{-1}bar^{-1}$	MD flux / $Lm^{-2}h^{-1}$	NaCl rejection / %
M-T0*	1.3	35.4	5.2	99.9
M-T1	1.7	39.7	5.6	99.9
M-T2	1.6	66.8	6.2	99.9
M-T3	1.8	47.4	8.3	99.9
M-T4	1.9	113.6	6.4	99.9

* MRO-predicted reference membrane

Table 14. **The model prediction for the second set of MRO membranes.**

Response	Target	SE Fit	95% CI	95% PI
MD flux / $Lm^{-2}h^{-1}$	3.2	0.3	2.6 – 4.0	0.7 – 5.8
PWP / $Lm^{-2}h^{-1}bar^{-1}$	70.5	11.1	47.6 – 93.4	35.0 – 106.0

Table 15. **The dope solution compositions and the process conditions of the VIPS pretreatment of second set of MRO membranes.**

Membrane code	Polymer mass fraction w_P/wt.-%	Additive mass fraction w_{HC6} / wt.%	VIPS duration t_{VIPS} / s	Relative humidity RH / %
M-T5	15.6	0	638	90
M-T6	15.6	0.025	638	90
M-T7*	15.6	0.051	638	90
M-T8	15.6	0.075	638	90
M-T9	15.6	0.100	638	90

* MRO-predicted reference membrane

Table 16. **The performance of the second set of MRO membranes.**

Membrane	LEP / bar	PWP / $Lm^{-2}h^{-1}bar^{-1}$	MD flux / $Lm^{-2}h^{-1}$	NaCl rejection / %
M-T5	1.5	62.5	5.2	99.9
M-T6	1.5	81.6	5.3	98.43
M-T7*	1.3	91.8	7.9	87.89
M-T8	1.3	67.8	6.0	98.12
M-T9	1.4	73.4	4.3	80.5

* MRO-predicted reference membrane

agrees exactly with the model prediction, although the model underpredicts the membrane performance to an extent outside the 95% PI. This suggests that the MD flux model is only qualitatively suitable for predicting membrane MD performance. Both PWP and MD flux are improved for the PVDF/HC6 hybrid membranes over the pure PVDF membrane, except for the MD flux of M-T9. LEP and NaCl rejection are lower compared to the first MRO, possibly due to reduced polymer content, which increases porosity.

The multiple response optimization was a twofold success. On the one hand, the combined DoE and MRO approach resulted in membranes with a performance improvement that clearly exceeded the benchmark of the best performing CCCD membranes. Compared to these membranes, the performance improvement was 7.0 times for PWP (M-T4) and 3.3 times for MD flux (M-T3). In addition, a comparison of pure PVDF and PVDF/HC6 hybrid membranes within each MRO set shows the improved performance of the hybrid membranes. The first MRO set maximized PWP and targeted an LEP of 2.0 bar. The pure PVDF membrane M-T0 showed a PWP of 35.4 $Lm^{-2}h^{-1}bar^{-1}$ and an LEP of 1.3 bar. The best performing hybrid membrane, M T4, measured 113.6 $Lm^{-2}h^{-1}bar^{-1}$ with an LEP of 1.9 bar. In addition, MD flux improved from 5.2 $Lm^{-2}h^{-1}$ to 8.3 $Lm^{-2}h^{-1}$ for M-T3 over M-T0. This represents a 3.2-fold increase in PWP and a 1.6-fold increase in MD flux. MD selectivity remained high for both hybrid membranes with a NaCl rejection of 99.99%. The second MRO was optimized to maximize MD flux and PWP. The pure PVDF membrane M-T5 showed an MD flux of 5.2 $Lm^{-2}h^{-1}$ and a PWP flux of 62.5 $Lm^{-2}h^{-1}bar^{-1}$. The best performing hybrid membrane, M-T7, showed an MD flux of 7.9 $Lm^{-2}h^{-1}$ and a PWP of 91.8 $Lm^{-2}h^{-1}bar^{-1}$, representing a 1.5-fold increase in MD and PWP performance. On the other hand, three out of four regression models, namely LEP, PWP and MD flux, were validated despite the mediocre *Adj* R^2. The incorporation of a VIPS pretreatment resulted in a notable enhancement in LEP, accompanied by an optimal NaCl rejection, at the cost of MD flux. Furthermore, the PWP exhibited enhanced performance in comparison to the pure NIPS approach. The details of the comparison are shown in Table 17.

Morphological analysis

The impact of HC6 on the morphology of MRO membranes was investigated through the analysis of scanning electron microscopy (SEM) micrographs of the top surfaces and cross-sections. For the first set of MRO membranes, the surface of the pure PVDF membrane (Figure 7(a)) displays a skin layer devoid of defects, while the surfaces of the PVDF/HC6 hybrid membranes exhibit a progressive increase in skin defects with rising HC6 content (Figure 7(b)–(e)). This observation can be attributed to the VIPS pretreatment. The sole application of NIPS, however, has been observed to yield the opposite effect, namely a decrease in surface porosity with increasing HC6 presence (Nursiah *et al.*, 2023). Furthermore, the incorporation of AWCs appears to result in an increased volume of voids and cavities throughout the membrane cross-sections. This is evidenced by the evolution of the finger-like voids observed in the reference membrane (Figure 7(f)) into deeper and larger voids in the hybrid membrane (Figure 7(g)–(j)). This shift in the cross-section morphology due to HC6 presence is comparable to that observed in our previous publication employing only NIPS (Nursiah *et al.*, 2023).

A comparative analysis of the surface morphologies of the two sets of MRO membranes reveals a notable increase in surface porosity for the second set, as illustrated in Figure 8 (a)–(e). Even the pure PVDF reference membrane (Figure 8 (a)) exhibits evidence of skin defects. The top surfaces of the PVDF/HC6 hybrid membranes (Figure 8 (b)–(e)) also demonstrate a correlation between surface porosity and HC6 content, exhibiting an increase in surface porosity with an increase in HC6 content. The mean LEP and NaCl rejection values for the first MRO set are 1.7 ± 0.2 bar and 99.9 ± 0 %, respectively, while those for the second MRO set are 1.4 ± 0.1 bar and 93.0 ± 6.6 %. This can be attributed to the fact that the total porosity of the skins throughout the second MRO set is greater than that of the first set. This is a consequence of the lower w_p and the shorter t_{VIPS} employed in the second MRO. The cross-sections of the membranes of the second MRO (Figure 8 (f)–(j)) follow the same trend as those observed in the first MRO. The morphology of the cross-sections of the PVDF/HC6 hybrid membranes substantiates the suggested mechanism of incorporation of HC6 and AWCs into the PVDF

Table 17. A comparison of the membrane performance factors of the best-performing membranes prepared by NIPS and those prepared by VIPS/NIPS.

Membrane preparation	NIPS (Nursiah *et al.*, 2023)		VIPS/NIPS (this publication)	
Membrane material	**PVDF**	**PVDF/HC6**	**PVDF M(HC6)-T5**	**PVDF/HC6 M(HC6)-T4**
PWP	30.6	75.3	62.5	113.6
LEP	0.7	0.2	1.5	1.9
MD flux	48.9	54.1	5.2	6.4
NaCl rejection	98.4	99.8	99.9	99.9

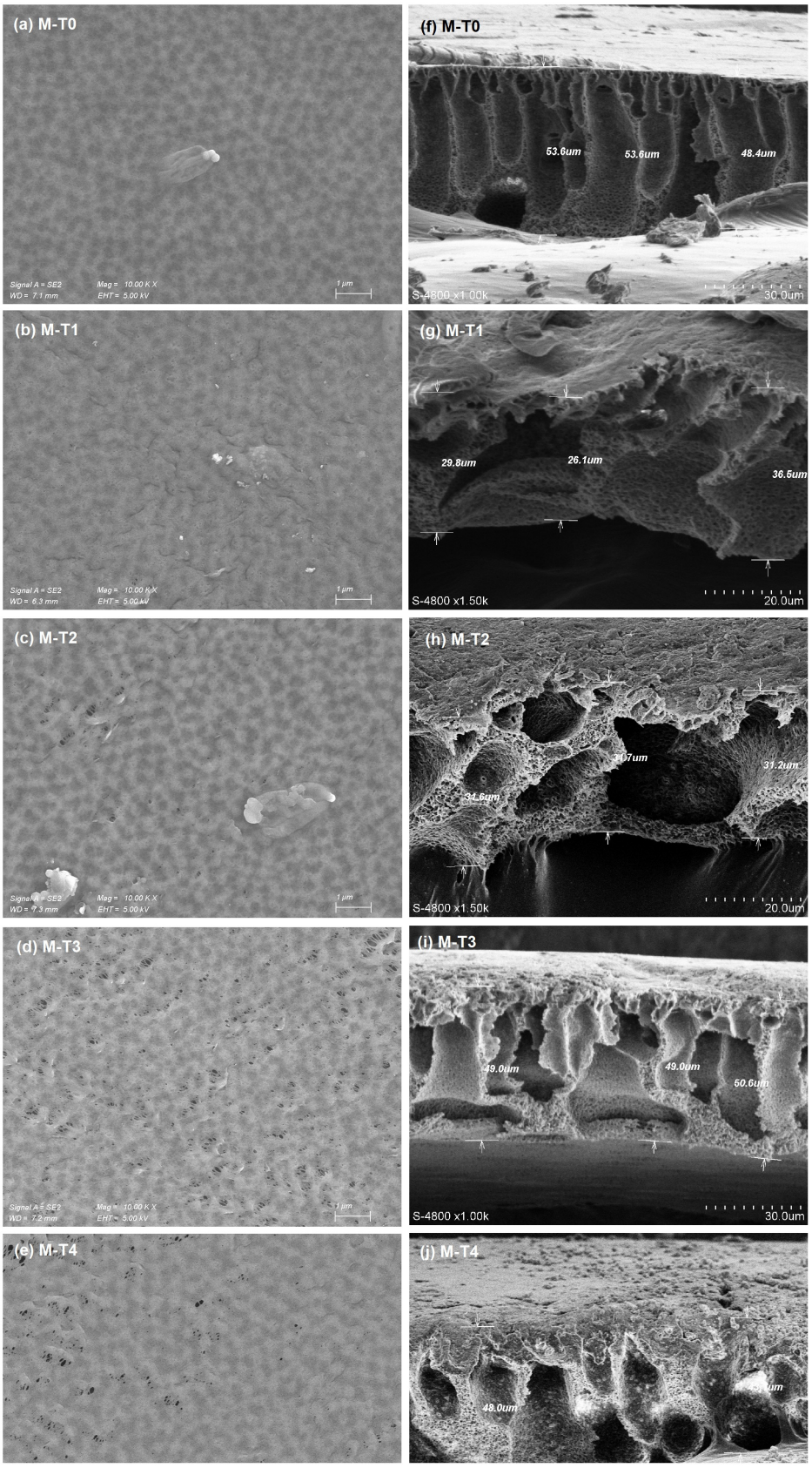

Figure 7. SEM micrographs of top surfaces and cross-sections of the second MRO membranes. (**a**)–(**e**): Top surfaces; (**f**)–(**j**): Cross-sections. The HC6 content increases from (**a**) to (**e**) in 0.025 incremental steps from 0 to 0.1 wt.-%.

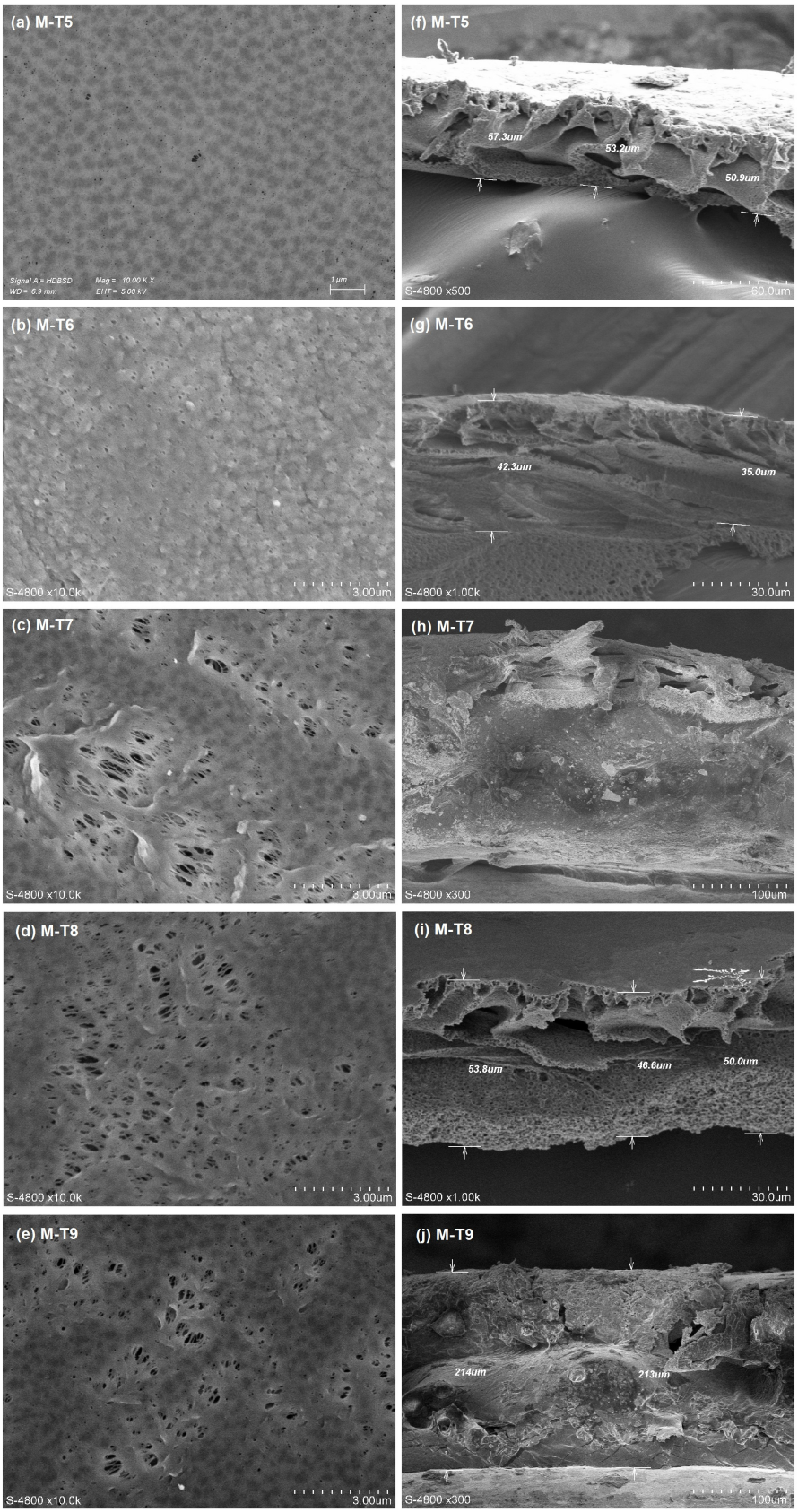

Figure 8. SEM micrographs of top surfaces and cross-sections of the second MRO membranes. (**a**)–(**e**): Top surfaces; (**f**)–(**j**): Cross-sections. The HC6 content increases from (**a**) to (**e**) in 0.025 incremental steps from 0 to 0.1 wt.-%.

matrix, as described in the introduction. The incorporation of HC6 results in an increase in the size of the voids that constitute the sublayer situated beneath the skin. In the case of a VIPS pretreatment, the voids exhibit a further extension towards the lower interface, which is in contact with the support. In contrast, in the case of solay NIPS, a sponge-like third sublayer, situated beneath the finger-like sublayer, forms the lower interface.

The morphological analysis of the two sets of MRO membranes allows for three assertions to be made.

1. The incorporation of a VIPS pretreatment, followed by a NIPS stage, results in the formation of membranes with asymmetric cross-sections, indicating that the VIPS pretreatment alone is insufficient to achieve complete phase separation. The asymmetric cross-sections suggest that the phase separation process is completed during the NIPS stage.

2. The VIPS pretreatment does not prevent skin formation. However, skin porosity correlates with HC6 content. It is proposed that the reduced water mass flux during VIPS facilitates the formation of AWC crystals within the dope prior to phase separation, thereby disrupting the skin formation during the NIPS stage.

3. The hydrophilicity of the HC6 imidazole head enhances the water mass flux during the NIPS stage, leading to the formation of larger macrovoids in the sublayer with increasing HC6 content. The porous skin, resulting from the VIPS pretreatment, further elevates the mass flux during the NIPS stage, thereby inhibiting the development of a third sponge-like sublayer.

Conclusion

The influence of a VIPS pretreatment on the NIPS of a PVDF/HC6/DMAc/water system has been investigated. The VIPS pretreatment was demonstrated to significantly improve PWP, LEP, and NaCl rejection. The hybrid membranes, comprising PVDF and HC6-based AWCs, demonstrated superior performance in terms of PWP, MD flux, and LEP in comparison to pure PVDF membranes. The presence of HC6 in the dope solution, as well as the incorporation of HC6 and AWCs into the PVDF matrix, have been identified as the primary factors responsible for the enhanced performance and alterations in skin porosity and cross-section morphology of the hybrid membranes. The employed DoE methodology and RSM modeling have demonstrated the potential to reduce the experimental effort while establishing quantifiable correlations between experimental variables and membrane performance.

Ethics and consent

Ethical approval and consent were not required.

Data availability

Open Science Framework: PVDF membranes for membrane distillation prepared by VIPS – A combined study of artificial water channel effectiveness and membrane performance prediction. https://doi.org/10.17605/OSF.IO/R5QBV (Bohr *et al.*, 2024).

The repository contains the following underlying data:

- PVDF_AWC_VIPS_Nursiah_Bohr_2024.ods (The dataset)
- Figure 7.tif (SEM images of first MRO)
- Figure 8.tif (SEM images of second MRO)

Data are available under the terms of the Creative Commons Attribution 4.0 International license (CC-BY 4.0).

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Open Peer Review

Current Peer Review Status: ✗ ? ? ? ? ✗

Version 2

Reviewer Report 28 March 2025

https://doi.org/10.21956/openreseurope.20007.r50599

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✗

Sama M Al-Jubouri
University of Baghdad, Baghdad, Iraq

I have read the sent manuscript and reviewer reports and the reply to their comments. In my perspective, I feel the manuscript misses the most important information which makes it suitable for getting approved for indexing, so far. Supporting the presented results with some important characterization will add significant value to the manuscript.

It would be better if the illustration of the membrane fabrication included both the VIPS procedures and the NIPS procedures. The SEM images did not reflect the development that occurred during the fabrication. The authors did not mention why the authors specified 55 L/h as a feed flow rate. Also, they did not specify the reason behind choosing the salt concentration in the feed as 35 g/L. Will the concentration of salt be kept constant over the experiment time?

Is the work clearly and accurately presented and does it cite the current literature?
Partly

Is the study design appropriate and does the work have academic merit?
Partly

Are sufficient details of methods and analysis provided to allow replication by others?
Partly

If applicable, is the statistical analysis and its interpretation appropriate?
Yes

Are all the source data underlying the results available to ensure full reproducibility?
Partly

Are the conclusions drawn adequately supported by the results?
Partly

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Wastewater treatment by filitration and porous materials technologies

I confirm that I have read this submission and believe that I have an appropriate level of expertise to state that I do not consider it to be of an acceptable scientific standard, for reasons outlined above.

Reviewer Report 24 March 2025

https://doi.org/10.21956/openreseurope.20007.r50310

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?

Md All Amin Newton
School of Textiles and Fashion, Shanghai University of Engineering Science, Tsinghua University, Shanghai, China

As a reviewer for this revised manuscript, I appreciate the authors' efforts to address the concerns raised in the previous round of reviews. The revisions have improved the clarity and focus of the paper. However, there are still some areas that require further attention:

1. Methodology: While the authors have clarified their use of DoE and RSM, more details on the statistical rigor of their approach would be beneficial. Specifically, how the reproducibility of the entire DoE is ensured with only center point replications needs further explanation.

2. Membrane characterization: The lack of quantitative data on membrane properties such as pore size, porosity, and thickness is still a concern. While I understand the authors' rationale for focusing on performance parameters, some basic structural characterization would strengthen the paper's conclusions.

3. AWC incorporation: The authors have referenced their previous work to support claims about AWC incorporation. However, a brief summary of key evidence from that study would be helpful for readers of this paper.

4. Morphological analysis: The discussion of SEM results has been improved, but could be further strengthened by more clearly linking observed morphological changes to performance data.

5. The regression models for MD flux and NaCl rejection show statistically significant Lack-of-Fit errors, indicating that these models may not correctly specify the relationship between response and predictors.

6. Potential loss of AWC during membrane formation: The authors suggest that AWCs may be lost during membrane formation, but this is not experimentally verified in this study. This uncertainty

could affect the interpretation of results and the proposed mechanisms of membrane formation and performance

Overall, while the revisions have addressed many of the previous concerns, some additional clarifications and data would further improve this manuscript before indexing.

Is the work clearly and accurately presented and does it cite the current literature?
Yes

Is the study design appropriate and does the work have academic merit?
Yes

Are sufficient details of methods and analysis provided to allow replication by others?
Partly

If applicable, is the statistical analysis and its interpretation appropriate?
I cannot comment. A qualified statistician is required.

Are all the source data underlying the results available to ensure full reproducibility?
Partly

Are the conclusions drawn adequately supported by the results?
Yes

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: I am a researcher in materials science, focusing on the development and optimization of advanced membrane materials for energy and water treatment applications. My work involves the design of polymer-based membranes and their performance in various separation processes, aligning with the study's focus on membrane distillation and membrane optimization.

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Reviewer Report 17 February 2025

https://doi.org/10.21956/openreseurope.20007.r50237

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?

Yi-Chen Lin

The University of Sydney, Sydney, New South Wales, Australia

The centre point provided by the author had the same preparation conditions but a very broad water permeation flux (from 3.6 to 42.3 LMH/bar). How can the statistics meaningful to the results and discussion be justified?

Can the author change the dot point color of the centre point (M-1e, M-1f...) in each model simulation to determine if the fitting follows the centre point provided by the author?

The cross-section of PVDF membrane seems to have a breakage by external damage. Can the authors provide the process for the sample for SEM images preparation?

Can the authors make a conclusion with which parameter is the best condition for preparing the PVDF membrane for the DCMD process? And which condition can significant change the membrane performance (such as salt rejection or permeation flux)?

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: PVDF TIPS-NIPS preparation, UF membrane, Gas separation membrane and the protein purification

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Reviewer Report 10 February 2025

https://doi.org/10.21956/openreseurope.20007.r50303

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?

Shouhong Fan
[1] Membrane Application, Science, and Technology (MAST) Center, Paul M. Rady Mechanical Engineering, University of Colorado at Boulder, Boulder, USA
[2] material science and engineeting, University of Pennsylvania, Philadelphia, Pennsylvania, USA

1. In the introduction, the author listed the Laplace equation, commonly used to predict the maximum pore size and the liquid entry pressure. When it comes to the contact angle (q), it is recommended that the author specify how the angle is quantified. Specifically, is it measured on the porous membrane or the bulk polymer that is used to make the membrane?
2. The membrane performance factors listed in Table 1 need an appropriate unit assigned to each number.
3. In the introduction, proper citations are needed for statements like" the majority of MD

membranes are polymeric. Commonly used polymers include polypropylene (PP), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF)".

4. A schematic illustration of the whole membrane fabrication procedure, including both VIPS pretreatment and the following NIPS, is recommended to be included in the draft.
5. For the flow rate of the feed and the permeate, why did the author choose 55 L/h in particular for the MD? Was it picked for the optimized thermal efficiency or for the sake of minimizing the temperature and concentration polarization in the boundary layer?
6. The salt concentration of the feed was specified as 35 g/L. Was the salt concentration maintained constant over the 3 hr. 30min MD? This information is important as a higher salt concentration will likely induce salt scaling on the membrane surface over a long course of MD. It is also recommended to include the data on permeate conductivity, although 99.9% salt rejection looks promising.
7. What is the purpose of stacking the pristine PVDF membranes between the stainless-steel plate and the PTFE blocks? Is it for the flatness of the membrane, or in other words, to prevent the curving of membranes after drying? If so, could the surface tension generated by water evaporation lead to crack formation since the wet membranes are compressed to maintain their flatness?
8. What about the mass fraction of HC6 in the PVDF membrane? Table 4 summarizes the weight percentage in the dope solution, but could some of the HC6 be lost to the water bath during the NIPS, given the hydrophilicity of the HC6 and the rapid mass transfer between the polymer dope and the nonsolvent?

Is the work clearly and accurately presented and does it cite the current literature?
Partly

Is the study design appropriate and does the work have academic merit?
Yes

Are sufficient details of methods and analysis provided to allow replication by others?
Partly

If applicable, is the statistical analysis and its interpretation appropriate?
I cannot comment. A qualified statistician is required.

Are all the source data underlying the results available to ensure full reproducibility?
Partly

Are the conclusions drawn adequately supported by the results?
Yes

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Membrane engineering & technology; desalination & water purification

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Reviewer Report 06 February 2025

https://doi.org/10.21956/openreseurope.20007.r50239

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?

Annarosa Gugliuzza
Institute on Membrane Technology (ITM-CNR), Rende, Italy

The authors have provided a revision of this study, thus improving its usefulness. However, a question remains open.
Normally, a publication is the consequence of progress in research. But, the reader must be able to understand a work independently of the previously published ones, even if due citations provide chances for a better understanding and an in-depth study of the topic covered.
If this study uses membranes that have been previously fabricated and characterized, then basic morphological and chemical properties have to be resumed in tables at least. Even more so in the case of new or additional membranes proposed within the frame of the current study. Here, a new characterization is needed to understand the effects of HC6 on morphological aspects, which affect the parameters selected as relevant for the predictive models. So, it is rightful to report the values of pore size along with porosity and thickness for each membrane, at least. Especially since all discussion revolves around the concept of porosity and resistance to transport.
In the previous work (ref 1), the authors highlighted an important increase in both the pore size and porosity due to the addition of HC6 (see table 4). Why don't they do it here as well? The quantification of these morphological data could give support to the closing remarks in agreement with the predictive models. Please cite the paper (ref 1) where some speculations need to be supported.

References

1. Nursiah K, Musteata V, Cerneaux S, Barboiu M: Artificial water channels-embedded PVDF membranes for direct contact membrane distillation and ultrafiltration. *Frontiers in Membrane Science and Technology*. 2023; **2**. Publisher Full Text

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Membrane preparation and characterization; Membrane processes

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Version 1

Reviewer Report 22 July 2024

https://doi.org/10.21956/openreseurope.18871.r41581

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Annarosa Gugliuzza
[1] Institute on Membrane Technology (ITM-CNR), Rende, Italy
[2] Institute on Membrane Technology (ITM-CNR), Rende, Italy

A paper entitled 'PVDF membranes for membrane distillation prepared by VIPS – A combined study of artificial water channel effectiveness and membrane performance prediction' has been proposed to investigate benefits on MD desalination from combined VIPS and NIPS processes to form PVDF membranes filled with amphiphilic I-quartet Artificial Water Channels (AWC). In particular, effects of AWC filler and VIPS pretreatment have been assessed with a view to enhance the performance of the membranes in terms of permeability to water (PWP), resistance to liquid intrusion (LEP), MD flux and NaCl rejections. A regression model-based prediction has been proposed considering the response variables such as polymer concentration, mass fraction of HC6 additive, time of exposure to vapor before coagulation, RH. Four predictor factors have been selected, including PWP, LEP MD flux and NaCl rejection. The first two factors have been suggested as reasonably predictive for membrane performance; MD flux has been indicated as a qualitative predictive factor, whereas salt rejection fails.
To evaluate the effects of various experimental parameters on the membrane performance, a statistical approach based on regression analysis (RSM) has been used and combined with experimental data through an optimization of response variables combining various factor levels. As a result, membranes with different AWC improve PWP and MD flux without affecting LEP or selectivity.

Predictive models are desirable to reduce the trials necessary to find good structure-property relationships for materials and membrane processes. In this work there is an effort towards this direction. However, the manuscript cannot be considered in current form. Some comments hereafter

- The description of MD process is coarse and rough. It would be in a more closely reasoned form, considering the key role of structural and chemical features of the membrane in controlling wetting, resistance to liquid intrusion, contrast to heat dissipation and so on, without neglecting complexity and effects of real environments.
- The authors should explain the need to design new membranes since there are with characteristics of hydrophobicity and porosity on the market.
- The description of phase inversion is also somewhat rough and incomplete. The authors would well explain how various morphology-types can be really obtained by NIPS and VIPS, rather focusing on the formation of PVDF membranes and related issues for what concerns with MD processes.
- The authors stay that NIPS generally results in anisotropic porous membranes with a dense skin and finger-like macro voids, whereas VIPS results in an isotropic sponge-like morphology with a more open porous surface. All this is not completely accurate because affinity of materials, solubility parameters as well as working conditions affect liquid-liquid vs solid-liquid demixing so that several morphologies and structures can be generated from

the same polymer by changing one or more parameters according to the same phase inversion-type. These aspects need to be well described and clarified.

- In VIPS process the relative humidity is mostly used, but other solvents could be utilized in principle. The discussion is again rough.
- The authors stay ...'To the best of our knowledge, only a few studies have applied DoE and RSM as a method for membrane optimization designed for MD'...However, they cite only one paper. Please, cite the other ones and explain how your work differs.
- The numbering of the tables has to follow the order of citation through the text. Please check and adjust the order of tables according to the description of data entered in them.
- Can you add a picture of a dried PVDF membrane?
- The mean value reported in the first line of table 5 is not clear.
- The figure captions are too short. Please, add useful information to explain the data reported in the figures.
- The predictive models would include or take in account relationships between structural features of the membranes, i.e. pore size, porosity, thickness, etc., and response variables that cause them. MD performance is strongly affected by all these membrane morphological features. But, no indication about pore size, pore distribution, overall porosity and thickness are reported in this work.
- In the section dedicated to the statistical analysis, the outputs deriving from RSM modelling would be concerned with experimental results anticipating some concepts expressed in the section dedicated to morphological analysis. Really, this last section is suggested to be discussed after describing the membrane preparation so that a more complete information is provided where due.
- In the morphology section, the authors ascribe the increase in PWP and MD flux to the presence of AWC filler in the matrix. They speculate that SEM show the presence of AWC in the polymer matrix... This sentence is a little bit misleading, because SEM gives indication about morphology rather than functional groups distribution. They authors would investigate the effective presence of AWC through the surface by using other suitable techniques and then discern how it affects the surface properties and subsequently resistance to wetting and liquid intrusion. While LEP is investigated, no wetting estimation is proposed. This kind of measurement yields an indication about the degree of membrane hydrophobicity/surface free energy and hence an indirect suggestion about the presence or not of the filler throughout the membrane surface as well as surface roughness factor.
- The authors suggest the open skin as the result of AWC loss during membrane formation by citing the literature. This assumption must be justified experimentally also in this work. How did the authors discern if AWC was partially or completely lost? Also, a morphological analysis by SEM is not enough to evaluate and justify the role of the filler in the formation of macro voids, open skin, etc. What about the solution viscosity as AWC content is increased?
- The authors assumed that 'The high affinity of the amphiphilic imidazole head of the HC6 molecule for water increases the mass transfer rates ...' What about the solubility parameters and related effects on demixing -type?
- The authors conclude that 'A combined VIPS-NIPS process was used to better tailor the morphological and mechanical properties of the membranes for MD'. However, no evidence about the mechanical resistance is reported in this work.

Is the work clearly and accurately presented and does it cite the current literature?
Partly

Is the study design appropriate and does the work have academic merit?
Partly

Are sufficient details of methods and analysis provided to allow replication by others?
Partly

If applicable, is the statistical analysis and its interpretation appropriate?
I cannot comment. A qualified statistician is required.

Are all the source data underlying the results available to ensure full reproducibility?
Partly

Are the conclusions drawn adequately supported by the results?
No

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Membrane preparation and characterization; surface engineering; membrane distillation; membrane crystallization; water desalination and reuse; environmental remediation

I confirm that I have read this submission and believe that I have an appropriate level of expertise to state that I do not consider it to be of an acceptable scientific standard, for reasons outlined above.

Author Response 02 Sep 2024

Stéphan Barbe

Dear Reviewer, Thank you for your insightful comments and valuable comments. We appreciate your feedback on our work and are committed to incorporating your points to improve the quality and impact of this manuscript. A paper entitled 'PVDF membranes for membrane distillation prepared by VIPS – A combined study of artificial water channel effectiveness and membrane performance prediction' has been proposed to investigate benefits on MD desalination from combined VIPS and NIPS processes to form PVDF membranes filled with amphiphilic I-quartet Artificial Water Channels (AWC). In particular, effects of AWC filler and VIPS pretreatment have been assessed with a view to enhance the performance of the membranes in terms of permeability to water (PWP), resistance to liquid intrusion (LEP), MD flux and NaCl rejections. A regression model-based prediction has been proposed considering the response variables such as polymer concentration, mass fraction of HC6 additive, time of exposure to vapor before coagulation, RH. Four predictor factors have been selected, including PWP, LEP MD flux and NaCl rejection. The first two factors have been suggested as reasonably predictive for membrane performance; MD flux has been indicated as a qualitative predictive factor, whereas salt rejection fails.
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affecting LEP or selectivity.

Predictive models are desirable to reduce the trials necessary to find good structure-property relationships for materials and membrane processes. In this work there is an effort towards this direction. However, the manuscript cannot be considered in current form. Some comments hereafter

1. Reviewer: The description of MD process is coarse and rough. It would be in a more closely reasoned form, considering the key role of structural and chemical features of the membrane in controlling wetting, resistance to liquid intrusion, contrast to heat dissipation and so on, without neglecting complexity and effects of real environments.
Author: We revised the entire introduction section in order to clarify the scope of the publication more concise.

2. Reviewer: The authors should explain the need to design new membranes since there are with characteristics of hydrophobicity and porosity on the market.
Author: The first paragraph of the introduction now explains the need for advancements in membrane technology.

3. Reviewer: The description of phase inversion is also somewhat rough and incomplete. The authors would well explain how various morphology-types can be really obtained by NIPS and VIPS, rather focusing on the formation of PVDF membranes and related issues for what concerns with MD processes.
Author: We revised the entire introduction section in order to clarify the scope of the publication in a concise way.

4. Reviewer: The authors stay that NIPS generally results in anisotropic porous membranes with a dense skin and finger-like macro voids, whereas VIPS results in an isotropic sponge-like morphology with a more open porous surface. All this is not completely accurate because affinity of materials, solubility parameters as well as working conditions affect liquid-liquid vs solid-liquid demixing so that several morphologies and structures can be generated from the same polymer by changing one or more parameters according to the same phase inversion-type. These aspects need to be well described and clarified.
Author: We revised the entire introduction section in order to clarify the scope of the publication in a concise way.

5. Reviewer: In VIPS process the relative humidity is mostly used, but other solvents could be utilized in principle. The discussion is again rough.
Author: We revised the entire introduction section in order to clarify the scope of the publication in a concise way.

6. Reviewer: The authors stay ...'To the best of our knowledge, only a few studies have applied DoE and RSM as a method for membrane optimization designed for MD'...However, they cite only one paper. Please, cite the other ones and explain how your work differs.
Author: We clarified this, by rephrasing the statement.

7. Reviewer: The numbering of the tables has to follow the order of citation through the

text. Please check and adjust the order of tables according to the description of data entered in them.
Author: The numbering of tables in a document should be according to the order of appearance in the text. This means that tables should be numbered sequentially as they first appear in the document, regardless of when they are cited or referenced.

8. Reviewer: Can you add a picture of a dried PVDF membrane?
Author: The membranes look like ordinary white polymer membranes. A picture would not add value to the publication.

9. Reviewer: The mean value reported in the first line of table 5 is not clear.
Author: We need to check with the editor. In our manuscript the mean value reads “2.1” as intended.

10. Reviewer: The figure captions are too short. Please, add useful information to explain the data reported in the figures.
Author: We added useful information to the captions of the figures.

11. Reviewer: The predictive models would include or take in account relationships between structural features of the membranes, i.e. pore size, porosity, thickness, etc., and response variables that cause them. MD performance is strongly affected by all these membrane morphological features. But, no indication about pore size, pore distribution, overall porosity and thickness are reported in this work.
Author: We are aware that membrane performance is strongly affected by pore size, porosity, thickness, etc., and mentioned this in the introduction. The scope of the publication is on the investigation of the efficacy of a VIPS pretreatment and the incorporation of AWCs in an MD context. The performance parameters chosen by us are by PWP, MD flux, LEP and NaCl rejection. Those four factors served as the basis for the regression models. We refrained from investigating additional membrane characteristics, in order to avoid overfitting of the models by employing too many model parameters.

12. Reviewer: In the section dedicated to the statistical analysis, the outputs deriving from RSM modelling would be concerned with experimental results anticipating some concepts expressed in the section dedicated to morphological analysis. Really, this last section is suggested to be discussed after describing the membrane preparation so that a more complete information is provided where due.
Author: We understand your point, but the morphological analysis only investigates the RSM optimized membranes. It should therefore be put after the statistical analysis of the MRO optimization.

13. Reviewer: In the morphology section, the authors ascribe the increase in PWP and MD flux to the presence of AWC filler in the matrix. They speculate that SEM show the presence of AWC in the polymer matrix... This sentence is a little bit misleading, because SEM gives indication about morphology rather than functional groups distribution. They authors would investigate the effective presence of AWC through the surface by using other suitable techniques and then discern how it affects the surface properties and subsequently resistance to wetting and liquid intrusion. While LEP is investigated, no wetting estimation is

proposed. This kind of measurement yields an indication about the degree of membrane hydrophobicity/surface free energy and hence an indirect suggestion about the presence or not of the filler throughout the membrane surface as well as surface roughness factor.
Author: We revised the first paragraph of the morphological analysis. As now mentioned in the introduction, this contribution should be regarded as a follow-up publication tour previous work (https://doi.org/10.3389/frmst.2023.1241526). We confirmed the incorporation of AWCs in the PVDF membrane matrix by FTIR-ATR, XRD, and STEM-EDX. We agree, that a more in-depth investigation of wetting phenomena would be of great value, but it would be out of the scope if this publication.

14. Reviewer: The authors suggest the open skin as the result of AWC loss during membrane formation by citing the literature. This assumption must be justified experimentally also in this work. How did the authors discern if AWC was partially or completely lost? Also, a morphological analysis by SEM is not enough to evaluate and justify the role of the filler in the formation of macro voids, open skin, etc. What about the solution viscosity as AWC content is increased?
Author: We cited our own past work, where three independent methods (FTIR-ATR, XRD, and STEM-EDX) confirmed our assumptions, regarding the incorporation of AWCs into the PVDF matrix. The system investigated here is identical to the former, only adding a VIPS pretreatment.
Since the only change was the addition of HC6 to the dope solution, it is reasonable to assume that the changes in morphology may be attributed to HC6. To your second point, no significant change in viscosity of the dope solution was measured.

15. Reviewer: The authors assumed that 'The high affinity of the amphiphilic imidazole head of the HC6 molecule for water increases the mass transfer rates …' What about the solubility parameters and related effects on demixing -type?
Author: We did not calculate solubility parameters. Because of its amphiphilic nature HC6 acts also as a surfactant, clearly improving water influx.

16. Reviewer: The authors conclude that 'A combined VIPS-NIPS process was used to better tailor the morphological and mechanical properties of the membranes for MD'. However, no evidence about the mechanical resistance is reported in this work.
Author: We rephrased our conclusion.

Competing Interests: No competing interests were disclosed.

Reviewer Report 04 July 2024

https://doi.org/10.21956/openreseurope.18871.r41588

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1. The database for the prediction methodology is insufficient, with only one data set for each membrane. This will make the result hard to reproduce.
2. The membrane code is hard to understand and seems inconsistent with the prediction process.
3. Lack of characteristics to agree the surface porosity and the hydrophilicity.
4. What is the mechanism of the HC6 doping amount that can improve the PWP without reducing the salt rejection? Did it grafted on the PVDF membranes? Or is it only to be the pore former? Why did M-T3 not follow the trends if it is a pore former?
5. The critical parameters for the VIPS membrane preparation condition are difficult to understand. Is that the PVDF membrane concentration? Or the vapour exploration time? Or the RH%? Also, this result only provides the raw data for each parameter but does not include a detailed discussion of each parameter.

Is the work clearly and accurately presented and does it cite the current literature?
Yes

Is the study design appropriate and does the work have academic merit?
Yes

Are sufficient details of methods and analysis provided to allow replication by others?
Partly

If applicable, is the statistical analysis and its interpretation appropriate?
I cannot comment. A qualified statistician is required.

Are all the source data underlying the results available to ensure full reproducibility?
Partly

Are the conclusions drawn adequately supported by the results?
Yes

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: PVDF TIPS-NIPS preparation, UF membrane, Gas separation membrane and the protein purification

I confirm that I have read this submission and believe that I have an appropriate level of expertise to state that I do not consider it to be of an acceptable scientific standard, for reasons outlined above.

Author Response 02 Sep 2024
Stéphan Barbe

Dear Reviewer. Thank you for your feedback. We thoroughly addressed your points as follows:

- **The database for the prediction methodology is insufficient, with only one data set for each membrane. This will make the result hard to reproduce.**
  - DoE circumvents the necessity of multiple data sets to draw substantiated conclusions, by applying statistics. This was discussed in great detail in the section “Model building and statistical analysis”

- **The membrane code is hard to understand and seems inconsistent with the prediction process.**
  - After revision, the membrane code is much more consistent and clearer.

- **Lack of characteristics to agree the surface porosity and the hydrophilicity.**
  - The change in surface porosity was observed by visual inspection of SEM images.
  - Membrane hydrophilicity was not claimed by us in any way.
  - We are aware that membrane performance is strongly affected by pore size, porosity, thickness, etc., and mentioned this in the introduction. The scope of the publication is on the investigation of the efficacy of a VIPS pretreatment and the incorporation of AWCs in an MD context. The performance parameters chosen by us are by PWP, MD flux, LEP and NaCl rejection. Those four factors served as the basis for the regression models. We refrained from investigating additional membrane characteristics, in order to avoid overfitting of the models by employing too many model parameters.

- **What is the mechanism of the HC6 doping amount that can improve the PWP without reducing the salt rejection? Did it grafted on the PVDF membranes? Or is it only to be the pore former? Why did M-T3 not follow the trends if it is a pore former?**

As now made clear in the introduction, this contribution should be regarded as a follow-up publication to our previous work (https://doi.org/10.3389/frmst.2023.1241526). We confirmed the incorporation of HC6-based AWCs in the PVDF membrane matrix by FTIR-ATR, XRD, and STEM-EDX. The effect of HC6 is twofold. Due to its amphiphilic nature, HC6 acts as pore former during membrane formation, and stays in the membrane matrix as AWC.

  - M-T3 is an artifact. We do not know why it does not follow the trend.

- **The critical parameters for the VIPS membrane preparation condition are difficult to understand. Is that the PVDF membrane concentration? Or the vapour exploration time? Or the RH%? Also, this result only provides the raw data for each parameter but does not include a detailed discussion of each parameter.**
  - We clarified the VIPS conditions.
  - The results in Table 5 are only shown for completeness. A detailed

discussion of the results is provided in the last two paragraphs of section "Results of CCCD and RSM modelling". Especially Figure 6 shows the relationship between experimental parameters and membrane performance parameters in detail.

Competing Interests: No competing interests were disclosed.

Reviewer Report 26 June 2024

https://doi.org/10.21956/openreseurope.18871.r41585

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Author
1. Please provide Contact angle for membrane. how author has confirmed the hydrophobic
2. amphiphilic I-quartet Artificial Water Channels supported membrane is not confirmed using any characterization method. Like FTIR, XPS, EDAX Mapping etc.
3. Give a schematic for surface modification.
4. Schematic of the process is missing
5. Author should produce sufficient data to support the surface roughness of the membrane
6. Porosity analysis is missing (no sufficient data to support)

Is the work clearly and accurately presented and does it cite the current literature?
Partly

Is the study design appropriate and does the work have academic merit?
Yes

Are sufficient details of methods and analysis provided to allow replication by others?
No

If applicable, is the statistical analysis and its interpretation appropriate?
I cannot comment. A qualified statistician is required.

Are all the source data underlying the results available to ensure full reproducibility?
No

Are the conclusions drawn adequately supported by the results?

No

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: PVDF based Flat sheet and hollow fiber membrane Fabrication and characterization for Forward osmosis application.

I confirm that I have read this submission and believe that I have an appropriate level of expertise to state that I do not consider it to be of an acceptable scientific standard, for reasons outlined above.

Author Response 02 Sep 2024

Stéphan Barbe

Dear Reviewer, Thank you very much for your feedback. We have carefully considered your suggestions, confident that these revisions will strengthen the manuscript.

Reviewer Comment:
1) Please provide Contact angle for membrane. how author has confirmed the hydrophobic
Author Response:
Hydrophobicity was only mentioned in the introduction. No claim of hydrophobicity of our membranes was made. Consequently, we do not see the need for data to support this point.

Reviewer Comment:
2) amphiphilic I-quartet Artificial Water Channels supported membrane is not confirmed using any characterization method. Like FTIR, XPS, EDAX Mapping etc.
Author Response:
As now made clear in the revised introduction, this contribution should be regarded as a follow-up publication to our previous work (https://doi.org/10.3389/frmst.2023.1241526). We confirmed the incorporation of AWCs in the PVDF membrane matrix by FTIR-ATR, XRD, and STEM-EDX.

Reviewer Comment:
3) Give a schematic for surface modification.
Author Response:
Surface modification did not take place. The HC6 additive was added to the dope solution. The AWC form upon water contact during membrane formation via VIPS/NIPS.

Reviewer Comment:
4) Schematic of the process is missing
Author Response:
Can the reviewer please elaborate on which process is meant here?

Reviewer Comment:
5) Author should produce sufficient data to support the surface roughness of the membrane
Author Response:

No claims of surface roughness of the produced membranes were made in the publication. Consequently, we do not see the need for data to support this point.

Reviewer Comment:
6) Porosity analysis is missing (no sufficient data to support)
Author Response:
We are aware that membrane performance is strongly affected by pore size, porosity, thickness, etc., and mentioned this in the introduction. The scope of the publication is on the investigation of the efficacy of a VIPS pretreatment and the incorporation of AWCs in an MD context. The performance parameters chosen by us are by PWP, MD flux, LEP and NaCl rejection. Those four factors served as the basis for the regression models. We refrained from investigating additional membrane characteristics, in order to avoid overfitting of the models by employing too many model parameters.

Competing Interests: No competing interests were disclosed.