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Graphical Abstract

Impact of membrane biofouling in the sequential development of performance indicators: feed channel pressure drop, permeability, and salt rejection

Nadine Siebdrath^{1*}, Nadia Farhat^{2*}, Wei Ding¹, Joop Kruithof³, Johannes S. Vrouwenvelder^{2,4}

¹ Technische Universität Dresden, Chair of Water Supply Engineering, 01062 Dresden, Germany.

² King Abdullah University of Science and Technology (KAUST), Water Desalination and Reuse Center (WDRC), Division of Biological and Environmental Science and Engineering (BESE), Thuwal 23955-6900, Saudi Arabia.

³ Wetsus, European Centre of Excellence for Sustainable Water Technology, Oostergoweg 9, 8911 MA Leeuwarden, The Netherlands.

⁴ Delft University of Technology, Faculty of Applied Sciences, Department of Biotechnology, Van der Maasweg 9, 2629 HZ Delft, The Netherlands.

*corresponding authors. E-mail address:

Nadine Siebdrath (nadine.siebdrath@tu-dresden.de)

Nadia Farhat (nadia.farhat@kaust.edu.sa)

Abstract

Biofouling development is affected by a variety of factors that change over the length of reverse osmosis (RO) membrane modules in pressure vessels. Spatially resolved biofouling formation was studied under conditions representative to practice using four one-meter Long Channel Membrane Test Cells (LCMTCs) in series, simulating an industrial pressure vessel.

Biofouling was induced by dosing an easily assimilable substrate to the feed water. The impact of biofouling on the sequential decline of RO membrane performance indicators (feed channel pressure drop, permeability and salt rejection) was investigated. Also, the temporal organic carbon (DOC) consumption was assessed spatially over the four test cells.

Results showed that all membrane performance indicators were impacted by biofouling formation. The feed channel pressure (FCP) drop increase was impacted earliest and strongest followed by permeability and salt rejection decline, underlining that FCP drop is a sensitive and early biofouling monitoring indicator. Spatially resolved biofouling investigations revealed that most biofouling was formed in the lead sections of membrane installation with a decreasing gradient over length, linked to DOC availability in the system. In this study, FCP drop played a crucial role: the FCP drop increase at the lead test cell of the membrane installation caused performance losses for the downstream test cells.

Minimizing the effect of biofouling on membrane performance should be pursued by a combination of strategies involving (i) early detection and preventive cleaning, (ii) substrate limitation for delaying biofouling built-up and (iii) optimized (early) cleaning procedures for more effective biofilm removal.

Keywords

Biofouling, Reverse Osmosis, Feed channel pressure drop, Permeability, Salt rejection, Long channel membrane test cell.

1. Introduction

Treatment plants applying reverse osmosis (RO) or nanofiltration (NF) produce high-quality water from different sources for irrigation or potable use. RO and NF membranes enable the extensive removal of salts, heavy metals, pathogens, micro-pollutants and other organic compounds. Fouling – the unwanted accumulation of deposits on the membrane – is a major drawback in RO processes as it results in lower product quality, decrease of the produced water quantity, membrane damage, and more frequent membrane cleaning increasing the process costs. Hydrodynamics, water quality, operational conditions, and design of spacer and membrane influence the development of fouling in spacer-filled membrane channels [1-4]. Biofouling, one of the most critical fouling types in membrane systems can be restricted, but not completely prevented [5, 6]. Biofouling increases the feed channel pressure (FCP) drop while permeate quantity and salt rejection decrease leading to overall membrane performance decline [7-9]. Hence, advanced anti-biofouling strategies are required. Extensive pre-treatment for biofouling reduction has been applied to reduce the concentration of bacteria and assimilable organic compounds in the feed water [10-12]. However, even very few bacterial cells and a limited amount of substrate can still cause biofouling. Some recent approaches to minimize biofouling occurrence include surface modifications and coatings for spacers and membranes by natural or chemical antifouling compounds, surface-bound biocides, surface smoothing, or antimicrobial peptides [5, 13]. Most of these approaches were ineffective in controlling biofouling as these strategies were successful only in delaying biofilm formation [14]. To limit biofouling formation, a detailed knowledge of its formation is crucial. Key factors that affect biofouling development such as membrane characteristics, feed spacers, operating conditions, etc., are widely researched [7, 15-19]. However, not all studies lead to the same conclusions (e.g. [18-21]), because they vary in operating conditions such as hydrodynamics, permeate flux, substrate supply and microbial composition, leading to

differences in biofouling formation. Therefore, representative, reproducible and systematic investigations are needed.

Spiral wound modules (SWM) with dense thin-film composite RO membranes in 4- or 8-inch diameter are standard elements used for water desalination. Feed spacers, placed between two membrane sheets, promote mixing and influence the hydrodynamics in the flow channel [22]. The SWMs of one-meter length are usually installed in series, with 4-8 modules in one pressure vessel. Along the length of the pressure vessel, an increase in the concentration of dissolved solutes and a decrease in the feed flow occur, leading to a change in the filtration conditions (substrate load, crossflow velocity, concentration polarization, and osmotic pressure); thus, impacting biofouling formation and membrane performance [23]. For a better understanding of fouling development in full-scale RO systems, a Long Channel Membrane Test Cell (LCMTC) of one-meter length was developed and validated under hydrodynamic conditions representative of SWMs [24].

Aiming to understand the impact of biofouling formation under representative practice conditions on the development of performance indicators (FCP drop, membrane permeability and salt rejection), this study investigated biofouling development over the length of one RO-LCMTC simulating a 1 m long membrane element and over the length of 4 membrane elements in series (4 m) representing a pressure vessel. Novel are the sequence of membrane performance indicator decline over four elements in series, as well as, spatially resolved biofouling development and temporal DOC consumption in the LCMTC and its impact on performance indicators.

2. Material & Methods

2.1. Experimental set-up

2.1.1. Long Channel Membrane Test Cell (LCMTC)

Biofouling development was investigated with LCMTCs of 1 m length each, made of Polymethylmethacrylate. The test cells were constructed to simulate spiral wound RO modules enabling permeability and salt rejection measurements over five segments along the one meter long test cell. The test cells had been validated with respect to the hydraulic behavior of spiral wound modules. A detailed description of the test cells and the validation is given in [24]. Briefly, the length and width of the feed channel were 0.91 m $\times$ 0.04 m. A 31 mil (0.787mm) thick diamond shape feed spacer was placed in the feed channel. The permeate channel of 0.3 mm height was divided into five separated segments of 18 cm, each of them equipped with a permeate spacer (0.3 mm thick). Pictures of the LCMTC are shown in figure S1 in the supplementary material. Both, feed and permeate spacers were supplied by Hydranautics. An outlet for permeate release in each of the five segments was used for flux and salt rejection measurements. A low-pressure polyamide RO membrane (ESPA2, Hydranautics) was used. The membrane characteristics, based on literature and manufacturer data are summarized in Table 1.

TABLE 1

2.1.2. Pilot plant

The experiments were conducted with one test cell and with four test cells in series. Figure 1 presents a scheme of the experimental set up. The high-pressure membrane-metering pump (Hydra-Cell P200, Wanner engineering, UK) generated the feed pressure. Pressure transmitters (IMP 331, ICS Schneider Messtechnik, GmbH Germany and Type 8314, Bürkert Fluid Control Systems, Germany) were installed before each test cell as well as at the end of the system for sensitive transmembrane pressure and FCP drop measurements. A mechanical

pressure relief valve from Swagelok, Germany, was installed for constant pressure operation. A turbine impeller wheel flow meter (PEL, Kobold Messring GmbH, Germany) measured the feed flow. Temperature measurements of feed and concentrate were performed with a resistance thermometer (PT100, TMH GmbH, Germany). Temperature inside the feed reservoir was controlled with a heating element connected to a thermostat (Rommelsbacher, Germany). Stainless steel valves (Swagelok, Germany) between the cells allowed sampling of feed and concentrate of each cell. Valves and tubes (em technik GmbH, Germany) were used for permeate collection. For process control and data acquisition TopMessage (Delphin Technology AG, Germany) was used.

FIGURE 1

2.2. Experimental procedure and sampling

2.2.1. Biofouling investigations with one and four test cells in series

Tap water with an unadjusted pH of 7.6 ± 0.2 , was used as feed and easily biodegradable substrate (acetate) was dosed to accelerate bacterial growth [25]. A 10 μm pore size cartridge filter and an activated carbon filter (both Weinert Prozesstechnik GmbH, Germany) were used to remove particles and residual chlorine from the feed water prior to substrate dosage. The test cell feed water total bacterial cell count was 10^4 cells/mL, assessed using flow cytometry. Substrates, dissolved in ultra-pure water provided as stock solution, were kept in a small reservoir with a pH of 11.5 to avoid microbial growth in the reservoir. Sodium acetate, sodium nitrate and sodium dihydrogen phosphate (all Merck KGaA, Germany) were dissolved in DI water with a C:N:P ratio of 100:20:10 [19]. The substrate stock solution was dosed continuously to the feed prior to the test cells using Stepdos dosage pump (KNF, Switzerland) at a flow rate of 28 mL/hour resulting in a concentration increase of 0.5 mg L^{-1} carbon. The dosing of easily biodegradable substrate (acetate) to the feed water was sufficient to induce bacterial growth for the experiment, enabling rapid biofouling in the LCMTCs

within 6 days. The system was run continuously with single pass flow and permeate, and feed water were discharged to the drain (figure 1).

Prior to the study, the membrane, feed spacer and product spacer were flushed and compacted with DI water for 12 hours at the chosen operation pressure and finally stabilized for 12 hours with DI water. During the biofouling studies, the transparent cells and substrate reservoirs were covered to avoid growth of phototrophic bacteria. For all experiments, flow conditions as typical for full scale water production were justified. Thus, the inlet side of the first test cell linear flow velocity was 0.16 m.s^{-1} and the initial flux was set to $24 \text{ L.m}^{-2}.\text{h}^{-1}$. Feed pressure was adjusted accordingly and kept constant during operation. The temperature was kept constant at $25 \pm 0.5 \text{ }^{\circ}\text{C}$. The permeate flux was measured manually via permeate collection every 12 hours, the measurement was done 5 times and each measurement was taken over 20 minutes. Experiments were stopped when an overall reduction in membrane permeability of $>10 \%$ was reached over all the test cells.

The feed channel pressure (FCP) drop was calculated as

$$\Delta p = p_{in} - p_{out} \quad (1)$$

The permeability P_{seg} was calculated separately for the five segments according to the following calculation:

$$P_{seg} = \frac{J_{seg}}{TMP_{seg}} \quad (2)$$

J_{seg} is the flux of each segment and TMP_{seg} is the corresponding average pressure in the segment. The pressure was recorded every 12 hours; the measurements were done in duplicates and the average and standard deviation were calculated. The pressure drop over the length of the membrane module was assumed to be linear. For each segment the average pressure TMP_{seg} was calculated.

For each segment salt rejection, R_{seg} was calculated by the following equation:

$$R_{seg} = \left(1 - \frac{C_{P,seg}}{C_{F,seg}}\right) \cdot 100\% \quad (3)$$

Here, $C_{P,seg}$ is the permeate conductivity of each segment and $C_{F,seg}$ is the average feed conductivity for each segment. The conductivity was recorded every 12 hours; the measurements were done five times and the average and standard deviation were calculated.

2.2.2. Sampling and analysis of the fouling layer

Feed and concentrate were sampled daily (Table S1) and analyzed for pH, conductivity and dissolved organic carbon (DOC). pH and conductivity were measured with pH/oxi 340i and multi 340i, respectively (both WTW, Germany).

Immediately after an experiment was finished, sheets of membrane and spacer were taken from the different segments of the different test cells in series to analyze the developed biofilm for adenosine triphosphate (ATP) and dissolved organic carbon (DOC). The membrane and corresponding spacer sheets were placed in 50 mL of DI water for DOC analysis and 50 mL of sterile tap water for ATP analysis. To transfer the biofilm properly to the water, the membrane and the spacer coupons in the tubes were subjected to ultrasound (output 45 kHz, 130 W, VWR Ultrasonic cleaner, Germany) for 6×2 minutes and in between mixing with a vortex shaker (VV3, VWR, Germany) for 15 seconds. Biofilm DOC concentrations were determined from duplicate samples (two 25mL samples from the original 50mL sample) using a thermal catalytic method (liquiTOC trace, Elementar Analysensysteme, Germany). The samples were filtered with a 0.45 μ m pore size cellulose acetate filter (MF-Millipore™) prior to the size exclusion column. Average and standard deviation of the duplicate measurements is presented in the results. ATP samples were prepared according to the technical bulletin of the BacTiterGlo™ reagent [26] and measured using the multi-functional reader INFINITE 200 Pro (Tecan, Germany) at 570 nm wavelength

190 in duplicates. The measurements and sample preparation were carried out at 25°C. Calibration
191 was done using an ATP stock solution (Sigma Aldrich, Germany), measured in triplicates.

3. Results

3.1. Spatial impact of biofouling on performance indicators

Two independent biofouling studies with one test cell and four test cells in series were conducted using tap water supplemented with $0.5 \text{ mg}\cdot\text{L}^{-1}$ acetate carbon. The recorded FCP drop and the measured membrane permeability and salt rejection with time are shown in figure 2. In the study of four test cells in series, the FCP drop increased over all test cells with time (figure 2 A). The FCP drop increased most severely at the feed side of the four test cells in series (test cell 1, figure 2 A). After five days an FCP drop increase of 2.0 bar was recorded for the first test cell only, significantly higher than the FCP drop increase for the second (0.35 bar), third (0.10 bar) and fourth test LCMTC (0.07 bar), respectively (figure 2 A). The initial and final FCP drop for each test cell are shown in figure S2A in supplementary material.

Similarly, the membrane permeability declined with time in all test cells in the study of four test cells in series (figure 2 C) with the highest decline in membrane permeability (18 %) for the lead test cell. The permeability normalization method and the initial and final permeability values for each test cell are shown in figure S2B in supplementary material. Contrary to the permeability decline, the flux decline was most severe in the tail part of the membrane installation (figure 3, S3) in supplementary material. In the study of one test cell, the membrane permeability decline along the length of the test cell was strongest at the first segment (20 %), with a lower decline in the following segments (14 %, 14 %, 11 % and 5 % for segments 2 to 5 respectively, figure 2 D).

The membrane salt rejection declined in all the test cells in the study of four test cells in series (figure 2 E) similar to the permeability decline. Initially a limited decrease of salt rejection was observed in the first test cell. However, at the end of the five day experiment, a maximum salt rejection decline of 2.2% was detected at test cell four, and the least salt rejection decline for the first test cell (0.8 %). Comparing the salt rejection decline with time

in the different segments of the test cell for the one test cell experiment showed a higher decrease in salt rejection (1.3 %) for the first segment compared to the other segments (0.7 %). The results for segments 1, 3 and 5 are shown in figure 2 F to facilitate visibility due to overlapping curves. Overall, compared to changes in FCP drop and membrane permeability, a limited decrease in salt rejection occurred as a result of biofouling.

FIGURE 2

FIGURE 3

3.2. Feed and concentrate DOC concentration

The concentration of DOC in the feed and the concentrate of each test cell was measured to investigate the relationship between the accumulated biofilm and the available substrate. The DOC concentration of the feed water before substrate dosage was $\sim 200\text{-}250 \mu\text{g-C}\cdot\text{L}^{-1}$ (figure 4). Acetate carbon $500 \mu\text{g}\cdot\text{L}^{-1}$ was dosed continuously in the feed water increasing the carbon concentration to a total of $\sim 750 \mu\text{g-C}\cdot\text{L}^{-1}$. Only on day 0, a DOC concentration of $\sim 750 \mu\text{g-C}\cdot\text{L}^{-1}$ similar to the feed DOC plus substrate dosing concentration, was measured in the concentrates of the four test cells in series and of the single test cell (figure 4 A, B). A constant concentrate DOC concentration of $\sim 200\text{-}250 \mu\text{g-C}\cdot\text{L}^{-1}$ was measured for all the test cells after day 0 as the biofilm started to develop in both experiments; indicating that after 1.8 days (four test cell experiment) and 1.4 days (one test cell experiment) the developing biofilm consumed all acetate dosed to the feed of the first test cell, strongly removing substrate from the water feeding the subsequent test cells. The almost complete use of substrate in the lead membrane module suggests major biofilm development in the lead module, followed by a clearly restricted biofilm development in cell 2, 3 and 4.

3.3. Spatial biomass deposition

Higher DOC and higher ATP concentrations were measured in the foulant deposits for (i) the first test cell compared to the following test cells in the experiment of four test cells in

series (figure 5 A) and (ii) in segment 1 compared to the following segments for the experiment of one test cell (figure 5 B). A declining amount of accumulated biofilm (DOC and ATP) was found with increasing distance from the feed side. These findings were most clearly observed in the experiment with four test cells in series (figure 5 A, C). The accumulated biofilm DOC and ATP concentrations were in agreement with the observed FCP drop increase and the permeability and salt rejection decline (figure 2). Moreover, the highest amount of accumulated biofilm in the first test cell is in agreement with the feed water DOC concentration trend in figure 4. However, the observed spatial flux decline trend (figure 3, S3) is not related to the deposited biomass amount (figure 5) but is attributed to the increase in the loss of system pressure with length (figure S5).

FIGURE 5

3.4. Sequential biofouling impact on performance

In this study, the effect of biofouling development on three performance indicators was monitored with time. In practice, membrane cleaning is applied when a decline in membrane performance occurs mainly defined as 10 -15 % increase of the FCP drop at constant flux and/or the permeability decreases by 10 % and/or the salt rejection decreases by 5 - 10% [27]. Within the duration of the study all performance indicators were impacted by the development of biofouling; however, the FCP drop was the indicator first and most severely affected by biofouling development (figure 6). The FCP drop increased by 430%, the permeability declined by 14%, and the salt rejection decreased by 1.4 % over the four test cells in series (figure 7 A) after the 5 day experimental period. The FCP drop increase over the lead test cell was twice the decline over the four test cells in series (figure 7 B) enabling earlier performance decline detection. The time needed to observe a 10 % decline in performance indicators is shown in table S2 in the supplementary material, with the shortest

time for the FCP drop measurement. Compared to the other indicators, FCP drop is the most sensitive performance indicator and can be used as an accurate indicator for biofouling.

FIGURE 6

FIGURE 7

4. Discussion

4.1. Impact of biofouling on membrane module performance indicators

Biofouling developed in one-meter-long membrane test cells (four in series simulating a pressure vessel) during dosing of an easily assimilable substrate (acetate) to the feed water. All performance indicators (FCP drop, permeability and salt rejection, figure 2) were impacted by biofouling development. Most biofilm accumulated in the module at the feed side of the membrane installation (figure 5) but the performance indicators were affected over the total length of the four test cells.

Biofilm accumulated on the membrane and between the spacer filaments increased the hydraulic resistance in the feed channel due to changes in flow direction and stagnation zones resulting in a FCP drop increase [4, 28]. Consequently, the most severe FCP drop increase occurred in the lead section of the first test cell, where most of the biofilm was present (figures 2, 4). The FCP drop increase and the amount of biomass accumulated during the biofouling study were comparable with other studies in literature dosing a similar concentration of acetate carbon, e.g. [29, 30].

Biofilm development reduced membrane permeability and permeate flux in all the test cells. A decline in permeate flux as biofilm develops on the membrane is mainly due to two mechanisms: increased membrane hydraulic resistance and increased biofilm enhanced concentration polarization in the presence of salts [1, 7, 31, 32]. The two above mechanisms occur in a direction perpendicular to the membrane between the feed channel and the permeate channel [33]. However, the increase in FCP drop over the lead test cell resulted in a loss in system pressure strongly reducing the permeate production at the tail test cells [32], although in the tail test cells only a minor amount of biofilm was deposited (figure 3, S3). Flux reduction and recovery reduction (figure 3, S3-5) caused by reduced driving forces, as described by Gutman et al. [32], results in increased energy costs for water production [19].

Salt rejection is affected by the feed water salt concentration, salt concentration polarization (CP), permeation and fouling. At the end of the experiment a decline in salt rejection was observed in all test cells operated in series. The salt rejection decline in the lead test cell is due to biofouling accumulation. However, the strongest decline in salt rejection was observed in the tail test cell mainly as a result of a high flux decline (dilution effect [1]), as an indirect effect of the severe biofouling in the lead element reducing the system pressure. Interestingly, the influence of system pressure reduction on the permeate flux and salt rejection in the tail test cell was stronger than the impact of biofouling occurrence on salt rejection and flux in the lead test cell. In industrial applications, where permeate production must be achieved with a high productivity and quality, identifying the reasons behind permeate quality and quantity deterioration is highly important.

In this study, the impact of biofouling on all performance indicators was significant. Most severely impacted was FCP drop and least affected was salt rejection. Therefore, salt rejection is not feasible to be used as a control indicator in practice. The earliest and highest decline in FCP drop underlines the suitability of FCP drop as a biofouling monitoring indicator as proposed by [34].

4.2. Substrate availability predicting the extent of biofilm accumulation

In this study, most biofilm deposited at the inlet side of the lead membrane installation, with a significantly decreasing gradient towards the tail position (figure 5). Substrate availability is the key indicator for biofilm formation [35]. The DOC results revealed that the dosed acetate was consumed by the developing biofilm in the first test cell during the early stages of the experiment (<2 days, figure 4). The carbon concentration in the permeate was below the detection limit eliminating the possible occurrence of carbon penetration through the membrane. Initial bacterial adhesion followed by the production of extracellular polymeric substances (EPS) occurs very rapidly and induces biofilm formation within several

hours [15, 36]. Since each test cell had a membrane surface area of 0.0364 m² and spacer surface area of 0.0290 m² (calculated based on [37]) bacterial cells attached in the first test cells started to grow and consumed the carbon very quickly. After an experimental period of 1.4 - 1.8 days almost all carbon was consumed in the first positions of the membrane installation. Therefore, hardly any substrate was available for biofilm development in the subsequent three test cells. The biofilm that developed in test cells 2, 3 and 4 was formed when acetate was still available the first 1.4 - 1.8 days of the experiment and/or from reattached biofilm that detached from the preceding test cell. Therefore, the gradient in biofilm development over the length of the test cells was directly correlated to the availability of biodegradable organic substrate in the water (figure 4).

In contrast, full-scale studies using natural feed waters have diverging results regarding the locations in a plant that are dominated by biofouling. Khan et al. [38] found biofilms mainly in the lead section when using both tertiary wastewater and seawater as a feed source for the RO. However, different gradients of biofouling were observed for other feed water types primarily attributed to the amount of easily biodegradable substrate present in each water type. In severely fouled membranes, Vrouwenvelder et al. [30] observed that the lead membrane elements had the highest amount of biofilm in a full-scale plant compared to the downstream elements. However, when the membranes were moderately fouled, the biofilm was more evenly distributed among the elements in series. Xu et al. observed most biofouling in the tail section when non-nitrified micro-filtered secondary wastewater effluents were used as RO feed water while evenly distributed biofilm formation among the elements was observed when denitrified secondary wastewater effluent was used [39]. The discrepancy between the results found in the literature is attributed to the fact that natural RO feed waters such as seawater or wastewater contain different types of foulants. As a result, several fouling types occur simultaneously with foulant-foulant interactions that lead to changes in the

characteristics of the deposited material on the membrane. The type and amount of substrate present remain primarily influential to the spatial distribution and extent of biofouling development [40]. The ability of biofilm-associated bacteria to sense prevailing substrate conditions and modify their structural organization and species composition accordingly has been well documented [41-44]. Therefore, enriched substrate conditions lead to more biofouling in the lead elements while limited substrate conditions lead to biofouling in the tail elements [18]. What is highly important is the nature of the available substrate. The spatial distribution of biofouling as shown in this study and in literature is mainly the result of dosing easily biodegradable compounds while slowly biodegradable substrates will lead to biofouling that is more distributed over the membrane. Variation in spatial biofilm distribution results in a variation in performance declines [45]. More biofilm on the spacer will have more impact on the FCP drop while more biofilm on the membrane will have more impact on permeability and flux. Moreover, not only the amount of biofilm present but also the physical characteristics of the developed biofilm affect the performance decline.

Results from this study emphasize the importance of substrate availability for biofouling control as found by others [8, 46, 47]. Reducing the substrate concentration with proper pre-treatment prior to the RO can effectively delay biofouling onset allowing membrane operation without cleanings for longer periods [10, 12].

4.3. Further research

This study was performed under constant feed pressure conditions and thus the results are most relevant for treatment plants operated in the same mode. Loss of system pressure does not occur when operating under constant permeate flux mode, increasing the pressure continuously to maintain a constant permeate flux. Therefore, a study under constant permeate flux mode is suggested. Understanding how each performance indicator is affected by spatial biofilm development, and monitoring all performance indicators over time and

370 length of membrane installations, will help to gain more insights on biofouling development
371 and leading to more effective control strategies [30].

5. Conclusions

The effect of biofouling on RO membrane performance indicators with time was investigated by growing a biofilm using four 1 m Long Channel Membrane Test Cell (LCMTC) in series, simulating an industrial pressure vessel under constant feed pressure conditions. The following conclusions can be drawn:

- Biofouling impacted all performance indicators in a different sequence. Feed channel pressure (FCP) drop was the earliest and most sensitive indicator, underlining the suitability of FCP drop as a sensitive biofouling indicator. In contrast, salt rejection is not a suitable control indicator as it was least impacted by biofouling.
- Most biofilm deposited and formed in the lead positions of the membrane test cells. The gradient of biofouling over the length of test cells correlated well with the declining availability of easily assimilable substrate (measured as DOC) emphasizing the importance of substrate limitation to decrease the rate of biofilm build-up.
- High amounts of accumulated biomass in the inlet position of the lead membrane test cell resulted in spatially varying decline in performance indicators. In this study, the severe FCP drop increase at the inlet position caused the strongest permeate flux and salt rejection decline at the tail positions.

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396 **Abbreviation and Symbols**

ATP	Adenosine Triphosphate
CP	Concentration polarization
$C_{P,Seg} [\mu S\ cm^{-2}]$	Permeate conductivity for a segment
$C_{F,Seg} [\mu S\ cm^{-2}]$	Average feed conductivity over a segment
DI	De-ionized
DOC	Dissolved organic carbon
EPS	Extracellular polymeric substances
FCP	Feed channel pressure
$J_{,Seg} [L\ m^{-2}\ h^{-1}]$	Flux of a segment
LCMTC	Long Channel Membrane Test Cell
NF	Nanofiltration
OC	Organic carbon
$PSeg [L\ m^{-2}\ h^{-1}\ bar^{-1}]$	Permeability for a segment
$p_{Seg} [bar]$	Average pressure over a segment
RO	Reverse osmosis
$R_{Seg} [\%]$	Rejection of a segment
SWM	Spiral wound module

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Table 1 – Characteristics of the membrane, based on manufacturer's data and literature.

	ESPA2 (Hydranautics)	Ref.
NaCl rejection	99.6 % (1.5 g/L feed)	(Hydranautics 2009)
Test pressure, bar	10.5	(Hydranautics 2009)
Zeta potential, mV (pH 7)	-26 ± 10 (10 mM KCl)	(Li et al. 2011, Fujioka et al. 2014, Tu et al. 2014)
Charge (pH 7)	negative	(Fujioka et al. 2014)
Roughness, nm (root mean square)	54 ± 20	(Alturki et al. 2010, Li et al. 2011, Varin et al. 2013)
Contact angle	44° ± 9°	(Li et al. 2011, Fujioka et al. 2014, Tu et al. 2014)

Figure 1 – Experimental set-up for the biofouling studies using four test cells operated in series.

Figure 2 – Spatially resolved development of (i) feed channel pressure drop (A,B), (ii) normalized permeability (C,D) and normalized salt rejection (E,F) with time induced by substrate dosage of $0.5 \text{ mg} \cdot \text{C} \cdot \text{L}^{-1}$ over the length of four membrane test cells in series (0 – 4 m) and one test cell (0-1 m). Segments 1, 2, 3, 4, and 5 are from 0-18 cm, 18-36 cm, 36-54 cm, 54-72 cm, and 72-90 cm respectively. Error bars indicate standard deviation of the five measurements ($n=5$, permeability and salt rejection). The permeability and salt rejection values were normalized by dividing them by the initial day 0 permeability and salt rejection.

Figure 3 – Spatially resolved development of normalized flux with time induced by substrate dosage of $0.5 \text{ mg-C}\cdot\text{L}^{-1}$ over the length of (A) four membrane test cells in series (0 – 4 m) and (B) one test cell (0-1 m). Segments 1, 2, 3, 4, and 5 are from 0-18 cm, 18-36 cm, 36-54 cm, 54-72 cm, and 72-90 cm respectively. The permeate flux values were normalized by dividing them by the initial day 0 permeate flux.

Figure 4 – DOC concentration in the feed water prior to substrate dosage and the concentrate after each test cell during substrate dosage of $0.5 \text{ mg-C}\cdot\text{L}^{-1}$ for (A) four test cells in series (0 – 4 m) and (B) one test cell length (0-1 m).

Figure 5 – Deposited foulants over the length of four membrane test cells in series (0 – 4 m) and one test cell (0-1 m) shown as organic carbon (A,B) and bacterial activity ATP (C,D). The test cells were operated for 5 and 6 days, respectively.

Figure 6 – Sequential impact of biofouling on performance indicators measured over the length of four membrane test cells in series (0 – 4 m): most severe and earliest impact was identified for FCP drop, which enables this indicator to be suitable for biofouling monitoring. Error bars indicate standard deviation of the five measurements (n=5, permeability and salt rejection).

Figure 7 – Performance decline of FCP drop, permeability and salt rejection for the average of (A) four membrane test cells in series (0 – 4 m) and (B) the first test cell (0 – 1 m) of four membrane test cells in series (0 – 4 m) after 5 days of operation.

Highlights

- Sequential impact of biofouling on membrane performance indicators.
- Spatial biofouling development in a pressure vessel.
- Feed channel pressure drop: Fastest and strongest impacted performance indicator.
- Lead membrane biofouling negatively affected downstream element performance.
- Most feed water DOC consumed rapidly by biofilm growth in lead membrane module.