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Natural organic matter fouling in pressure retarded osmosis

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ABSTRACT

Fouling is one of the major challenges to be solved in order to commercialise osmotic power generation by pressure retarded osmosis (PRO). This paper deals with natural organic matter (NOM) fouling. The impact of *i.a.* NOM concentration and ionic strength in the freshwater feed have been investigated for five different types of PRO membranes by performing fouling experiments in PRO mode at isobaric conditions.

An important finding was that fouling propensity in terms of relative flux decline as a function of accumulated NOM load was independent of the NOM concentration at otherwise identical conditions. Further, it was confirmed that increased ionic strength in the support structure, due to internal concentration polarisation and reverse salt diffusion, aggravates membrane fouling in PRO.

The observed variation in fouling propensity between different types of PRO membranes was significant. The CA membrane was less susceptible to NOM fouling than the four TFC types of PRO membranes. It is anticipated that the variation in fouling propensity that were observed for different membranes was related to both material and structural properties of the membranes. The results show the importance of applying fouling propensity as an additional main criterion to membrane performance during future research and development of PRO membranes.

1. Introduction

The exploitation of energy from salt gradients by pressure-retarded osmosis (PRO) has the potential of making an important contribution to the power market in the future. Skilhagen et al. [1] and Aaberg [2] report an unexploited osmotic power potential worldwide in the range of 1650 to 2000 TWh. In comparison, the global utilisation of conventional hydropower is in the range of 2500 TWh [1].

One main challenge that must be solved before PRO can become a commercially viable energy source is the development of membranes with improved transport properties in PRO. The best membranes available today show salt and water permeabilities in reverse osmosis operation that in general will be acceptable to PRO. However, these characteristics are not yet fully realized in PRO operation [3]. A significant part of the overall transport resistance in PRO is due to concentration polarisation inside the support membrane. The optimisation of the support structure in terms of reducing the resistance against transport of water and salt in this region will therefore be crucial [3,4]. Material selection and the wetting properties of the different membrane layers are also important in optimising membranes for PRO [5].

Further, spacer design will be important in order to minimise compaction when the membrane is pressed against the feed spacer at elevated pressures in PRO operation. Membrane compaction will reduce the open membrane area on the support side and may also reduce porosity and increase the tortuosity in parts of the membrane. The net effect will be an increased structure parameter and thus reduced PRO performance. The compaction effect has been referred to as the “shadow effect” by Kim and Elimelech [6].

Another crucial challenge will be to develop economically feasible procedures and measures for fouling control and mitigation that ensure stable long term performance of the PRO membrane. It is well established that fouling is a major challenge in operation of pressure driven membrane processes, and that effective fouling control is imperative for successful operation. Various fouling phenomena have been investigated for pressure driven processes in a significant number of publications, and the mechanisms of membrane fouling e.g. in seawater reverse osmosis is to some extent explained and understood [7–13].

However, several aspects related to fouling will be different in PRO compared to pressure driven processes. The significantly different operating conditions in reverse osmosis (RO) and PRO is one aspect that may impact the development and nature of membrane fouling. Mi and Elimelech [14] report that the cleaning efforts in forward osmosis (FO) might be reduced compared to RO as fouling deposits formed in FO will be less compacted and more

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easily removed. The same authors report similar flux decline for gypsum scaling in FO and RO, however, the flux recovery after a water rinse was shown to be 10% higher in FO [15].

Further, in order to maximise the specific power output in PRO, the membrane skin must be oriented towards the seawater [4]. As a consequence, the freshwater will flow through the porous support before the water permeates the skin. This membrane orientation is different from pressure driven filtration processes where the membrane skin will face the feed solution, and this will worsen the fouling situation in PRO. How the transport of freshwater into a porous membrane structure will impact the development of fouling have to be investigated in detail, and fundamental studies of fouling in PRO will be required.

Only a few papers concerning fouling in PRO have been published so far. Mi and Elimelech [16] have investigated several aspects regarding NOM fouling in forward osmosis (FO), such as intermolecular adhesion forces between membrane-foulant and foulant–foulant, calcium binding, the impact on initial permeate flux, as well as the significance of different skin orientation, i.e. RO mode (skin facing the high saline solution) and forward osmosis (FO) mode (skin facing the low saline solution).

The present paper addresses NOM fouling in PRO, and some important factors for flux decline have been investigated. PRO experiments with natural NOM water have been performed under controlled conditions in the laboratory, and the fouling propensity of a selection of different PRO/FO membranes has been investigated. Further, the obtained results are discussed in relation to practical aspects of PRO operation.

The work presented in this paper is part of a more comprehensive study, also addressing fouling mechanisms, fouling mitigation, characterisation of fouling deposits and scaling. The authors have previously investigated characterisation of PRO membranes, and modelling of mass transport in PRO, both at membrane and module level [3,17,18].

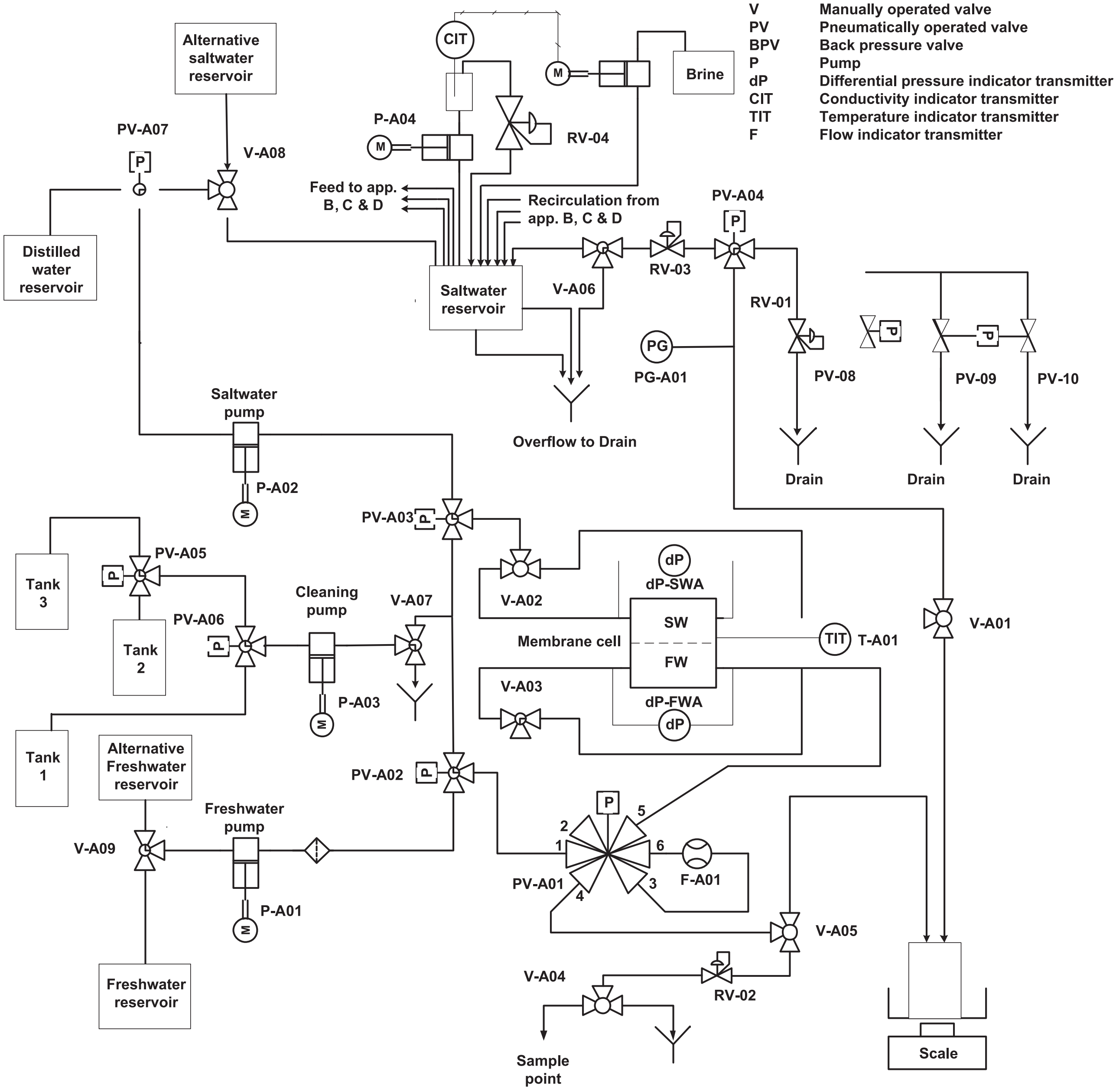

Fig. 1. Flow diagram for one of the four identical test rigs.

2. Materials and methods

2.1. PRO test units

Four identical cross flow units were designed for testing small samples of flat sheet membranes. The effective membrane area of each test cell was 29.4 cm^2. A standard permeate spacer from Di Censo of 0.5 mm thickness was applied in the freshwater channel, and a standard diamond spacer of 0.7 mm thickness was applied in the salt water channel. A flow diagram for one of the four test units is shown in Fig. 1.

The supply of fresh water to the membrane cell was provided by a Pharmacia P-500 piston pump (P-A01). The salt water was supplied to the membrane cell with the same type of pump (P-A02). The brackish water discharge from the membrane cell was recycled back to the salt water feed tank. An automated dosing system maintained stable salt concentration in the salt water feed tank by controlling the addition of concentrated brine against a conductivity set point.

The water flux through the membrane, J_w, was obtained by sequential measurements of the flow rate of freshwater before and after the membrane cell. The flow rate was measured by a Bronkhorst Hi-tech liquid flow meter (F-A01) with a measuring range of 0–200 ml/h. The alternating measuring mode was facilitated by switching a 6-port valve (PV-A01) at intervals of 30 min.

The differential pressures across the two respective membrane channels were monitored by two Fuji FCX-C pressure transmitters (dP-A01 and dP-A02). The temperature in each membrane cell was monitored by a PT-100 temperature sensor (T-A01). All instruments were logged to a computer with a logging interval of 60 s.

An automated utility system for membrane cleaning and backwash was integrated on each test rig. Cleaning sequences were programmed by applying a Crouzet Millennium II PLC platform. The PLC controls the valves PV-A01–PV-A10, and the pumps P-A01–P-A03. The automatic valves were operated by pneumatic actuators.

2.2. Test solutions

Synthetic salt water was made by dissolving sodium chloride and calcium chloride in pure water. Calcium chloride was added to the synthetic salt water in the same amount as in real seawater, *i.e.* 420 mg/l Ca^{2+} [19]. The concentration of sodium chloride was adjusted for each type of membrane in order to achieve desired water flux.

The concentrated brine that was applied for maintaining constant salinity in the feed tank was produced by dissolving 300 g/l sodium chloride in pure water. Calcium chloride was added to an amount such that the concentration of Ca^{2+} in the salt water tank was maintained at 420 mg/l. Thus, the concentration of Ca^{2+} in the brine varied according to the concentration of NaCl in the salt water feed.

The raw water that was used for preparation of the freshwater feed was collected downstream the intake screen (50 μm) at Mostadmark water work in Malvik, Norway. The water was collected batch wise and stored at 4 °C until used in the fouling experiments. Each of the collected raw water batches were subjected to standard water analyses, such as pH, alkalinity, turbidity, etc. before production of feed water for the fouling experiments. Metals were determined by ICP-MS. In addition biodegradable organic carbon (BDOC) was measured, and NOM fractionation according to hydrophobicity, as well as liquid chromatography-organic carbon detection (LC-OCD) was performed. The NOM fractionation was performed according to methodology given by Chow et. al [20]. In general the raw water can be categorised as a pedogenic source dominated by humic acids with an average molecular weight in the range of 850–900 g/mol. Typical raw water characteristics are given in Table 1.

Table 1
Typical raw water characteristics.

Turbidity [NTU]	pH	Alkalinity [mmol/l]	Colour [mgPt/l]	Conductivity [μS/cm]	DOC [mg/l]	Ca^{2+} [mg/l]
0.5–1.5	6.5–6.8	0.15–0.25	50–80	30–50	5–9	4–5

Table 2
Relative values of characteristic membrane parameters and polymer of support membrane.

Membrane	A	B	S	Support polymer
CA[a]	1.00	1.00	1.00	Cellulose tri-acetate
TFC Type 1	3.05	0.21	5.08	Not known
TFC Type 2	0.96	0.35	9.29	Polyether-imide
TFC Type 3	1.39	0.24	6.04	Polysulfone
TFC Type 4	13.39	4.81	2.13	Not known

[a] The value of *A*, *B* and *S* for the CA membrane are all set equal unity. The *A*, *B* and *S* for the remaining four membranes are given relative to the CA membrane.

Before use, the raw water was filtered batch wise through a 0.5 μm cartridge filter, and the water was diluted to the desired NOM concentration. Further, the NOM water was conditioned in order to obtain identical pH, ionic strength and Ca^{2+} concentration in all test solutions, irrespective of NOM concentration. The chemicals applied for conditioning of pH, ionic strength and Ca^{2+}, were 1.0 M HCl, 4.3 M NaCl and 1.4 M CaCl$_2$, respectively. After chemical addition the NOM waters were aerated by bubbling air through the solutions for 5–10 h in order to equilibrate the NOM water with CO$_2$ in the atmosphere, and avoid drift in pH during the NOM fouling experiments.

After conditioning, the pH and Ca^{2+} concentration were measured in all feed waters in order to verify that the value of these parameters were according to design. In addition the pH was re-measured after the NOM experiment in order to reveal any unexpected drift in pH during the experiments. The Ca^{2+} concentration was determined by potentiometric titration according to a standard Methrom application bulletin (No. 125/2e) by applying an ion selective calcium electrode.

2.3. Membranes

Five different types of membranes, either PRO membranes under development or commercially available FO membranes, were tested for NOM fouling propensity. One of the tested membranes was an asymmetric cellulose tri-acetate (CA) membrane, whereas the four remaining membranes were all of the thin film composite (TFC) type. The membranes are referred to in this paper either as CA or TFC membranes, and the manufacturer of each of the tested membranes will remain undisclosed. The chemistry of the support structure of TFC Type 1 and TFC Type 4 are unknown, whereas the chemistry of the support of TFC Type 2 and TFC Type 3 are given in Table 2. The skin of the TFC membranes were all aromatic polyamide based.

The water permeability (*A*), the salt permeability (*B*) and the structure parameter (*S*) for the five membranes that were tested are given in Table 2 as relative values.

2.4. Test protocol

Four samples of the same type of membrane were tested simultaneously in the four identical test units. If prescribed by the manufacturer, the membranes were immersed in 50% methanol for 60 s and subsequently immersed in pure water for minimum 60 min prior to assembly in the membrane cells. The membranes that were not treated with methanol were solely conditioned in pure water prior to assembly in the membrane cells.

After assembly, the membranes were operated in RO mode with pure water for at least one hour. The applied pressures were varied in the range of 10–20 bar for the different membrane types, and was selected according to each membranes tolerance against pressure. The RO operation with pure water was accomplished both in order to stabilise the membrane performance, and to estimate the water permeability of the membrane.

Further, the isobaric osmotic water flux with pure water was measured in PRO mode, *i.e.* skin against saltwater, at three different salt concentrations for each type of membrane. The obtained data from measurement of the osmotic water flux were later used for determining the salt concentration that were required in order to achieve the desired start flux for the NOM experiments. Subsequently, the concentration in the salt water feed tank was adjusted, and after 10–20 hours of stable operation at desired start flux, the membranes were exposed to NOM water. The membranes were exposed to NOM water for approximately two weeks before the experiments were terminated.

2.5. Process conditions and data processing

The fouling experiments were performed with linear flow rates based on open channel of 0.60 cm/s and 0.42 cm/s for the salt water channel and the freshwater channel, respectively. Further, all experiments were performed with zero trans-membrane pressure.

No temperature control was provided during the fouling experiments. Consequently, the membrane cells experienced daily fluctuations according to variations in the ambient temperature in the laboratory that was typically in the range of 1–3 °C. The average temperature was close to 22 °C. However, the fluctuations in temperature in the lab were somewhat larger in warm periods during the summer. In order to account for the impact of temperature fluctuations, the measured water flux was normalised according to variations in temperature. The temperature correction was based on empirical correlations obtained for each type of membrane by measurement of the osmotic water flux with pure water at different temperatures and salt concentrations.

The water flux was obtained by subtracting the water flow measured at the outlet of the membrane cell from the water flow measured at the inlet. Calibration curves were obtained for each flow meter by applying a high precision scale, and the measured water flows were corrected according to the calibration data in a spread sheet.

3. Results and discussion

3.1. Baseline experiments

All membranes were conditioned and tested according to the procedures described in Section 2.4. Fig. 2 shows the osmotic flux of pure water as a function of time for a series of four experiments that was performed with the TFC Type 1 membrane.

The variation in measured conductivity reflects that the pure water flux was obtained by using four different concentrations of NaCl in the saltwater feed. The NaCl concentration corresponding to the desired start flux around 15 l/(m^2 h) was determined on the basis of the measured flux obtained at the first three salt concentrations. Similar baseline experiments were performed for all of the five types of membranes that were tested for NOM fouling propensity.

3.2. NOM fouling experiments

3.2.1. NOM concentration

Five series of fouling experiments dedicated for investigation of the effect of NOM concentration in the freshwater feed have been performed. Each of the five series was performed with different membrane types. Typically, three or four parallel experiments with varying NOM concentration in the range of 1–5 ppm were

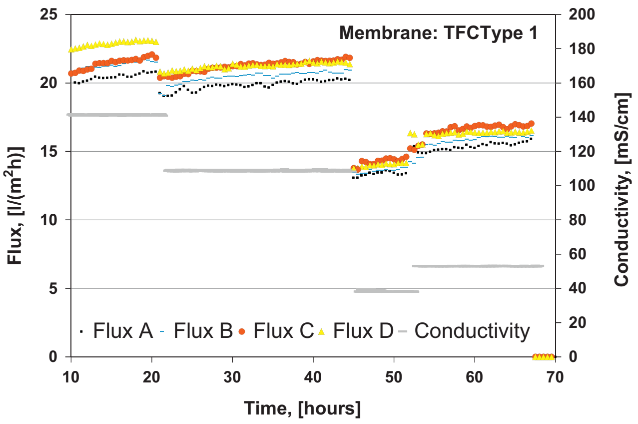

Fig. 2. Osmotic water flux of pure water as a function of time for TFC Type 1.

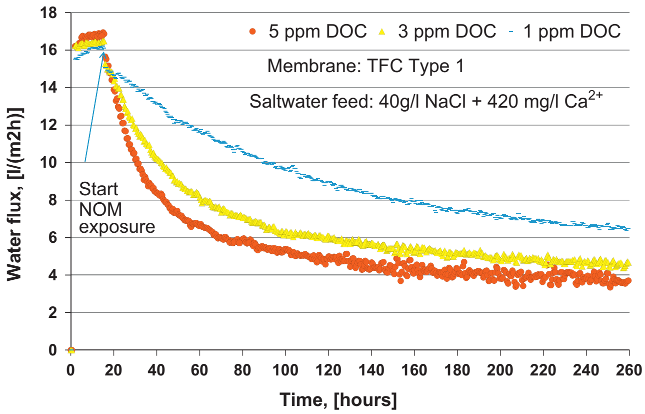

Fig. 3. Osmotic water flux of pure water as a function of time for TFC Type 1. After 15 h of operation with pure water the membranes were exposed to NOM water.

Table 3
Design conditions for NOM fouling experiments with TFC Type 1.

Membrane	u_{SW} [cm/s]	u_{FW} [cm/s]	J_w^0 [l/(m^2 h)]	DOC [mg/l]	$C_{Ca^{2+}}$ [mg/l]	pH	Ionic strength [mmol/l]	Filter pore size, [μm]
TFC Type 1	0.6	0.4	~15	1	3.45	6.7	2.0	0.5
TFC Type 1	0.6	0.4	~15	3	3.45	6.7	2.0	0.5
TFC Type 1	0.6	0.4	~15	5	3.45	6.7	2.0	0.5

performed for each type of membrane. The design conditions for the series of NOM experiments performed with the TFC Type 1 membrane is listed in Table 3. The fouling experiments with the other four membrane types were performed under similar conditions.

Fig. 3 shows the osmotic water flux plotted as a function of time for three samples of the TFC Type 1 membrane. Initially the osmotic water flux was obtained with pure water. After approximately 15 h of operation the membranes were exposed to NOM water with concentrations of 1, 3 and 5 ppm TOC, respectively.

As expected the flux decline as a function of time was observed to be more severe for higher concentrations of NOM in the freshwater feed. Similar trends were observed for all five membrane types that were tested.

3.2.2. *Accumulated NOM load*

In order to explore the importance of NOM concentration in more detail, the flux data presented in Fig. 3 were normalised and plotted as a function of accumulated NOM load in Fig. 4. The accumulated NOM load can be calculated from the specific NOM load, which can be defined as the product of concentration of NOM in the freshwater feed, C_{NOM}, and the water flux, J_w, at time t.

$$\text{Specific NOM load }(t) = C_{NOM}J_w(t), \quad [\text{mg}/(\text{m}^2\text{h})] \qquad (1)$$

The accumulated NOM load will correspond to the time integral of the specific NOM load

$$\int_{t0}^{t1} C_{NOM}J_w(t)dt \qquad (2)$$

which can be approximated to

$$\sum(C_{NOM}J_w^{Av}\Delta t), \quad [\text{mg}/\text{m}^2] \qquad (3)$$

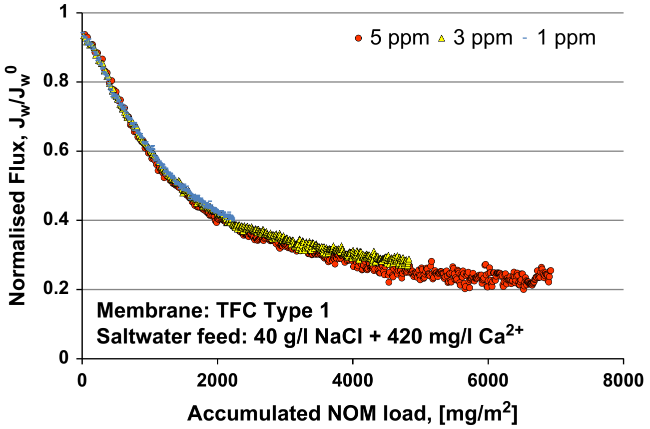

Fig. 4. Normalised water flux plotted as a function of accumulated NOM load for TFC Type 1.

An interesting observation from Fig. 4 is that the flux decline for experiments performed with different NOM concentration was identical when plotting the normalised water flux as a function of accumulated NOM load. Fig. 5 shows the normalised water flux as a function of accumulated NOM load for the other four types of PRO membranes that were tested. Note that all experiments were performed with similar start fluxes in the range of 15 l/(m^2 h), and that the concentration of NaCl in the saltwater feed was adjusted for each type of membrane in order to achieve the desired start flux.

It can be observed from Fig. 5 that for each type of membrane the flux decline for experiments performed with different NOM concentration was identical when plotting the normalised water flux as a function of accumulated NOM load. These observations indicate that the observed flux decline at a given accumulated NOM load will be independent of the concentration of NOM in the feed water. However, the higher concentration of NOM in the freshwater feed, the faster a given accumulated NOM load will be reached, and as a consequence the flux will decline faster at higher NOM concentrations.

As it has been confirmed that the fouling propensity in terms of flux decline as a function of accumulated NOM load will be independent of NOM concentration in the freshwater feed, it is

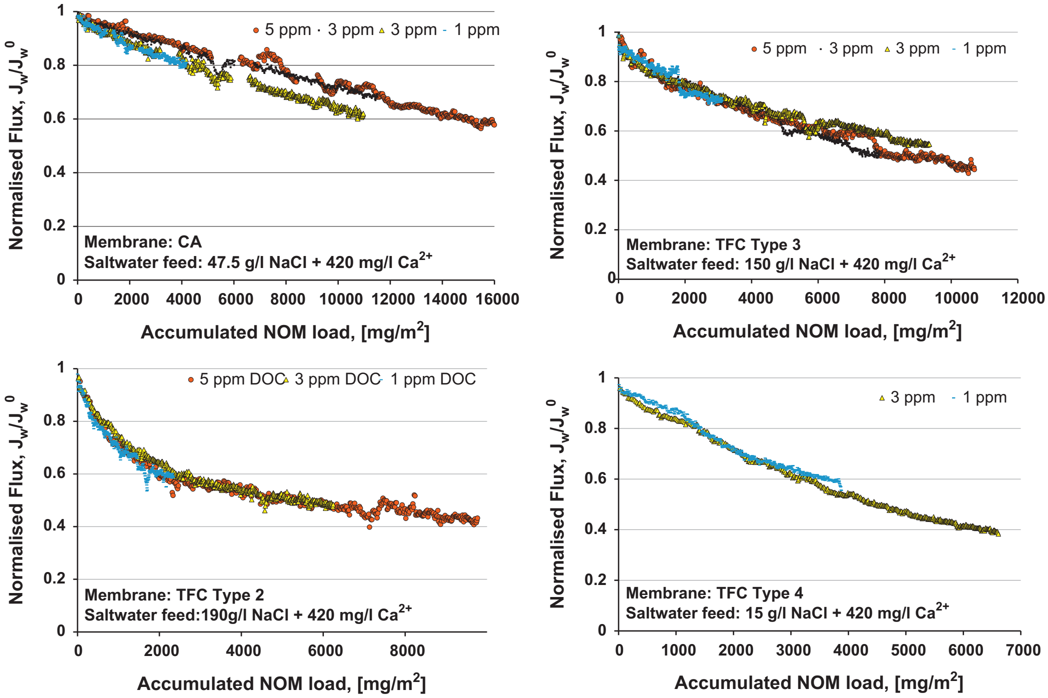

Fig. 5. Normalised water flux plotted as a function of accumulated NOM load for four different types of PRO membranes. Note that the scale of the 1st axis varies between the different figures.

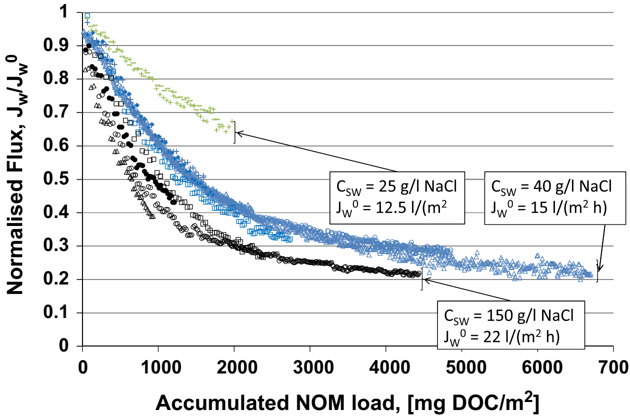

Fig. 6. Normalised water flux as a function of accumulated NOM load obtained with three different concentrations of NaCl in the saltwater feed. The number of experiments that were performed at the different saltwater concentrations were 2, 6 and 4 for 25, 40 and 150 g/l of NaCl, respectively. The NOM concentration in the freshwater feed for the different experiments was ranging from 1 to 9 mg/l DOC.

relevant to raise the question whether the fouling propensity also will be independent of the water flux, J_w. Fig. 6 shows several experiments performed with TFC Type 1 and identical NOM water characteristics, except from variation in the concentration of NOM. The different start fluxes were achieved by adjusting the concentration of NaCl in the saltwater feed.

The curves corresponding to experiments performed with similar start fluxes appear as clusters in Fig. 6. Further, it is apparent that the observed fouling propensity at a given accumulated NOM load was higher for experiments performed at higher water fluxes. However, as the variation in water flux was achieved by adjustment of the osmotic gradient across the membrane, the experiments were designed with a co-variation between water flux and salt concentration.

The importance of ionic strength in relation to NOM fouling has been studied by e.g. Hong and Elimelech [10]. They found that increased ionic strength promote NOM fouling due to double layer compression and charge screening at high ionic strength in the support structure. Thus, the experimental constrains, which the experiments referred to in Fig. 6 are encumbered with, makes it impossible to differentiate if the more severe flux decline observed at higher start fluxes were ascribed to the flux level itself, or ionic strength effects.

Two additional experiments were performed in order to investigate the mutual impact of start flux and ionic strength on NOM fouling propensity in PRO. The experiments were again performed with the same type of membrane (TFC Type 1) and identical NOM water characteristics. The membranes were backwashed with pure water every 24 hours for 45 minutes at 10 bar. Further, the concentration of NaCl in the saltwater feed was successively increased after each backwash. The normalised water flux as a function of time is given in Fig. 7a. The initial slopes (given as absolute values) of the flux decline after each backwash, calculated on the basis of 2nd order regression of the water flux *vs.* time curves, are given in Fig. 7b. Fig. 7b also indicates the start flux for each period of NOM exposure.

As shown in Fig. 7 the slope of the flux decline increases with increasing salt concentration in the saltwater feed. Further, the increasing slope at increasing salt concentration was observed at successively lower start fluxes after each backwash. This is an observation that supports the hypothesis that the higher fouling propensity observed at higher fluxes, was at least partly related to the indirect effect of higher ionic strength. However, it cannot be excluded on the basis of the performed experiments that also the flux level does impact fouling propensity.

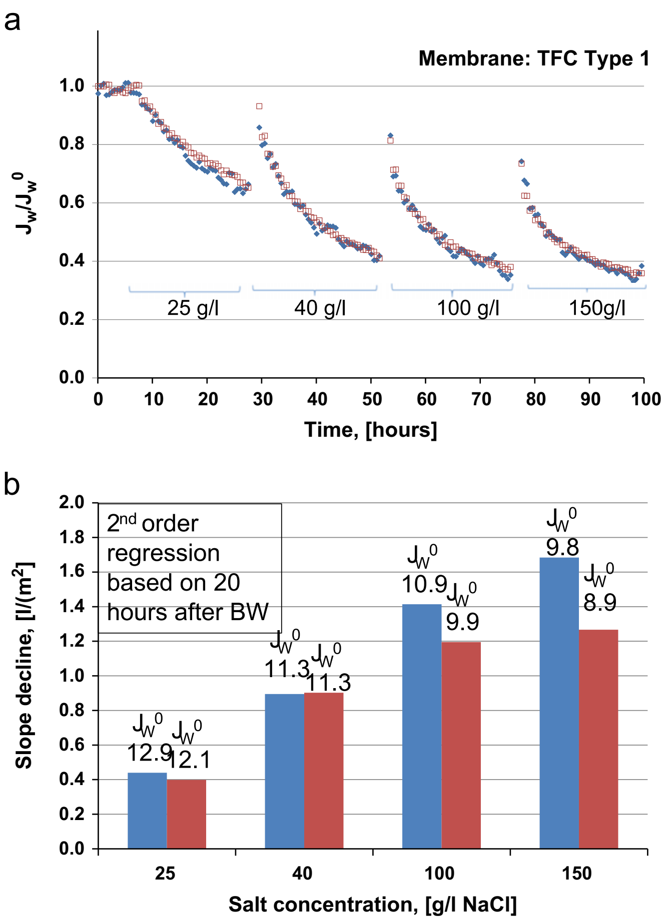

Fig. 7. Two identical NOM fouling experiments with periodic backwash and successive increase in osmotic gradient in relation to each backwash. (a) Normalised flux as a function of time. (b) Initial water flux, J_w^0, in l/(m^2 h), and slope (absolute values) of the flux decline for each period with NOM exposure.

3.2.3. Impact of raw water origin

As mentioned in Section 2.2 the NOM water was collected batch wise at the raw water intake of Mostadmark water works. Due to practical reasons the amount of water collected each time was limited, and typically one raw water batch was sufficient for performing two series of four fouling experiments. As a consequence, three different batches collected at different times have been used as NOM water source for testing the five membranes reported in Section 3.2.2. The CA membrane was tested with NOM water originating from raw water Batch 1, TFC Type 2 and 3 were tested with raw water Batch 2, and TFC 1 and 4 were tested with raw water Batch 3. In order to reveal differences in fouling potential between the different raw water batches, two identical experiments, except from the different raw water origin, was performed when a new batch of raw water was taken into use. Thus, the series of fouling experiments performed with TFC Type 2 and feed water originating from raw water Batch 2 was also including one replication performed with NOM water prepared with raw water Batch 1. The results are shown in Fig. 8a. Similarly, the series of experiments performed with TFC 1 and raw water Batch 3 did also include one replication with NOM water prepared from the previous raw water batch. The results are shown in Fig. 8b.

It can be seen from Fig. 8 that for both series the flux decline for the experiment performed with a different raw water batch was significantly different from the flux decline of the other three experiments that were performed with feed water from the same raw water batch. The conditions for all experiments were identical

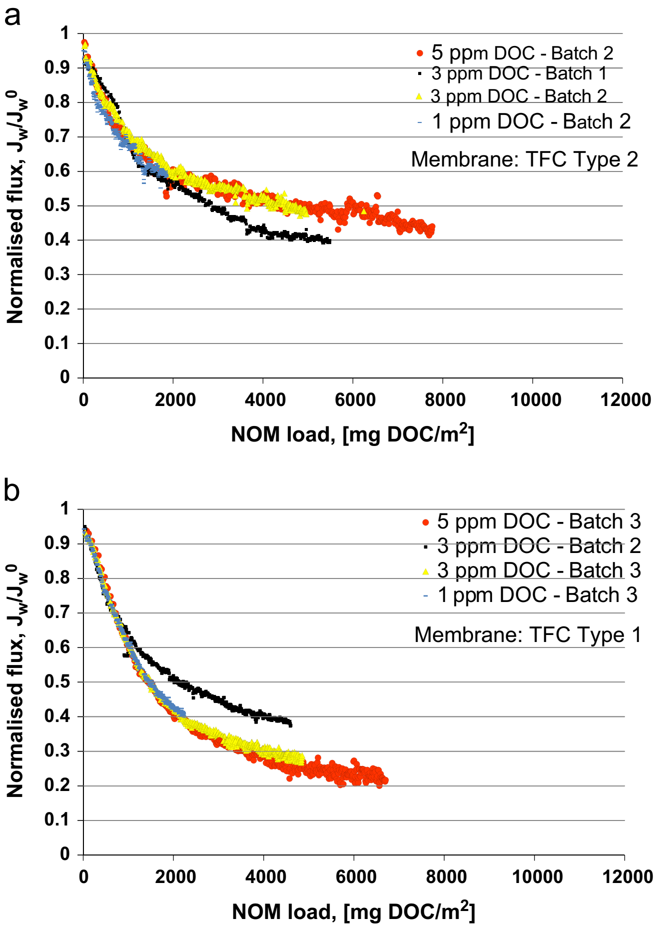

Fig. 8. NOM fouling experiments performed with NOM water prepared from different raw water batches. (a) Raw water Batch 1 and 2 were utilised for preparation of the NOM water feed. (b) Raw water Batch 2 and 3 were utilised for preparation of the NOM water feed.

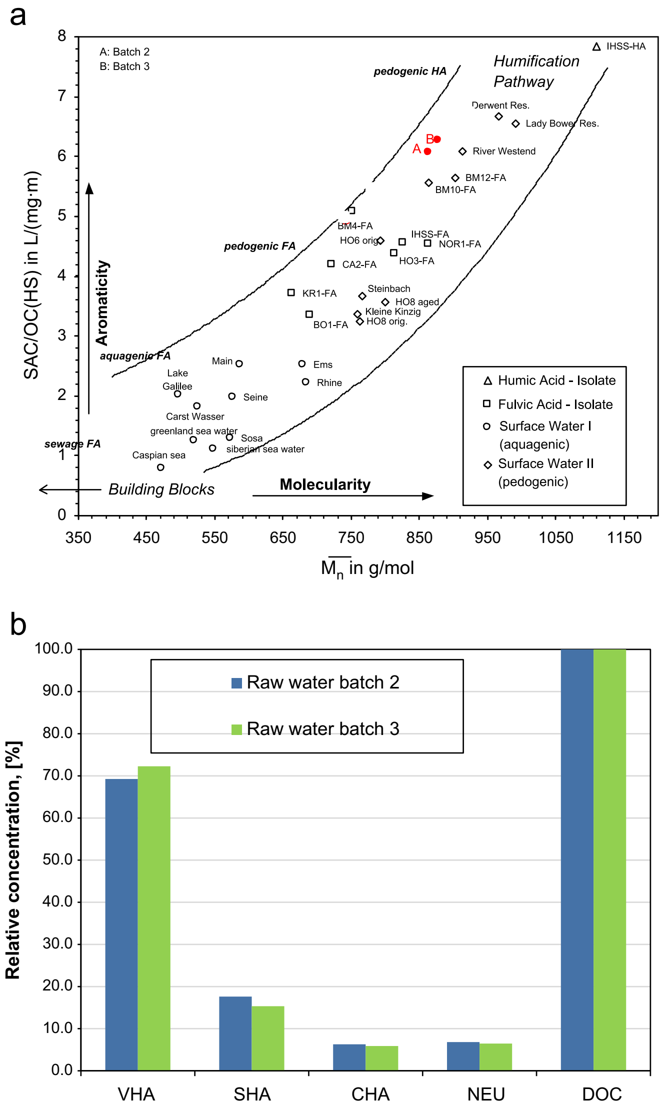

Fig. 9. (a) LC-OCD analysis of raw water Batch 2 and 3. The two red data points indicated as A and B correspond to Batch 2 and Batch 3, respectively.[21], (b) NOM fractionation of raw water Batch 2 and 3.VHA is very hydrophobic acids, SHA is slightly hydrophobic acids, CHA is hydrophilic charged and NEU is hydrophilic neutrals. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

except from the indicated difference in origin of the raw water. Thus, it seems apparent that the fouling potential varied between the different raw water batches.

Since pH, ionic strength, and the concentration of Ca^{2+} and DOC were adjusted to the same level for experiments performed with feed water from different batches, the observed impact of batch variation cannot be related to the mentioned parameters. As can be observed in Fig. 9a and b the results from LC-OCD and NOM fractionation indicated only minor variation in the nature of NOM between the different raw water batches. Note that Batch 1 was not subjected LC-OCD analysis and NOM fractionation. However, we have no indication that Batch 1 was significantly different from Batch 2 and Batch 3.Thus, most likely the observed batch variations were not ascribed to NOM characteristics.

3.3. *Fouling propensity of different membrane types*

In Section 3.2.2 it was shown that the observed flux decline did correlate against accumulated NOM load and was independent of the concentration of NOM in the freshwater feed. Further, the rate of flux decline as a function of accumulated NOM load was also shown to depend on the type of membrane that was applied for the experiments. However, in Section 3.2.3 it was found that identical feed characteristics in terms of pH, ionic strength and the concentration of NOM and Ca^{2+} will not be sufficient for accurate prediction of flux decline of a given membrane type if the origin of the NOM source is changed.

Another factor that prevents accurate comparison of fouling propensity between different types on membranes on the basis of the results presented in Section 3.2.2 is the large variation in salt water concentration used for the different membranes. The ionic strength inside the support membranes will be influenced by the salt leakage from the salt water side, and apparently the ionic strength in the support membrane did vary between experiments performed with different membranes. Thus, in order to make a more fair comparison of fouling propensity between different membrane types, it is considered important to apply NOM water of identical origin, and at the same time facilitate a more similar osmotic gradient across the membrane, irrespective of membrane type. Therefore the five different membrane types were re-tested with identical feed water originating from the same raw water batch and with identical saltwater feed. The raw water used for the retests was confirmed to have similar characteristics as Batch 2 and Batch 3 that were used for the original tests. The common saltwater feed contained 40.0 g/l NaCl and 420 mg/l Ca^{2+}. The results from the repeated tests with identical raw water origin and

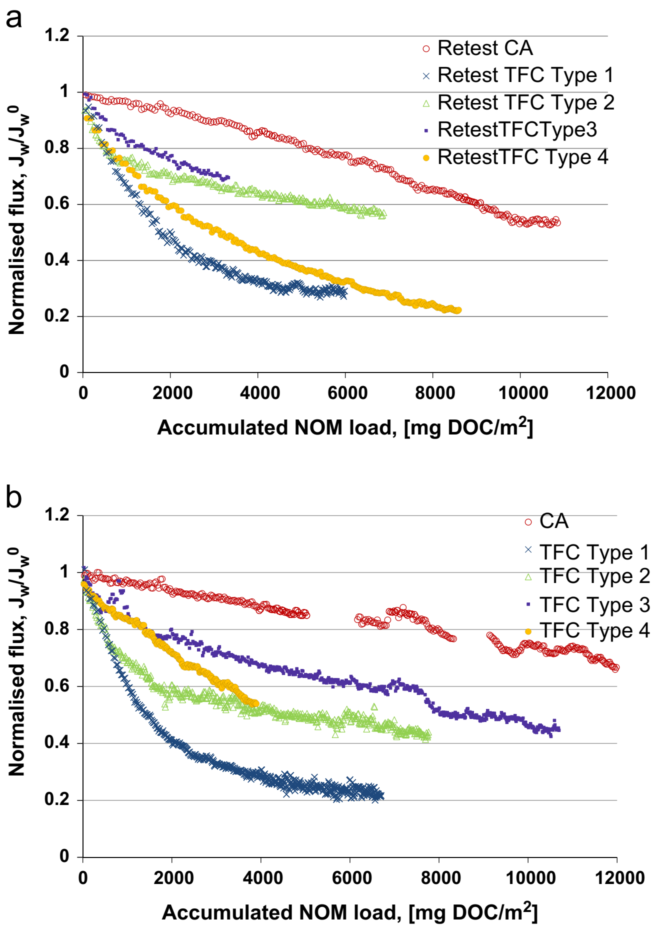

Fig. 10. Normalised water flux as a function of accumulated NOM load for five different types of PRO membranes. (a) Experiments performed with identical concentration of NaCl in saltwater feed, and with NOM water feed of identical quality and origin. (b) Original experiments performed with identical start flux.

salt water feed are shown in Fig. 10a, and the results from the original tests that were performed with feed water prepared from different raw water batches are plotted in Fig. 10b for comparison.

Fig. 10 shows that the fouling propensity for CA, TFC 1 and TFC 3 was similar during the original test and the retest. However, comparison of the original test and the retest revealed some deviation in fouling propensity for TFC 2 and TFC 4. Nevertheless, the results from the retests were relatively similar to the data that were originally obtained, and confirm that membrane type has large impact on NOM fouling propensity.

3.3.1. *Ionic strength effects*

Since the retest of each membrane type was performed with different concentration of NaCl in the saltwater feed compared to the original tests, the observed deviation in fouling propensity for TFC 2 and TFC 4 is likely to be related to ionic strength effects. In order to explore this further the NaCl concentration at the membrane skin on the freshwater side of the membrane were estimated for both original tests and retests by applying the model described by Thorsen and Holt [3]. The concentration at the skin on the freshwater side of the membrane was also estimated relative to the concentration in the salt water feed, and is in the following called relative ICP. The modelled data, as well as the relative flux after 2000 mg/m^2 of NOM load are given Table 4 for all experiments.

It can be seen from Table 4 that fouling propensity, here illustrated as relative water flux after 2000 mg/m^2 NOM load, increases at higher concentration of salt inside the support membrane for TFC 2 and TFC 4. For CA and TFC 1 the saltwater concentration was relatively similar for the original tests and the retest, and consequently no significant change in fouling propensity should be expected. This assumption was more or less confirmed, however, a small variation in fouling propensity between original test and retest of TFC1 was observed. Regarding TFC 3 no significant variation in fouling propensity was observed in despite of the large difference in saltwater concentration between original test and retest. Batch variation of the raw water is likely to be responsible for at least part of the deviation form expected trend for TFC 3.

Table 4
Modelled salt concentration and fouling propensity at 2000 mg/m2 for original tests and retests which are reported in Fig. 10.

Membrane/ experiment	C_{NaCl}, [g/l]		Relative ICP,	Relative flux, [%]
	Saltwater feed	Skin (FW side)	[%]	(2000 mg/m^2)
CA—Original	47.5	5.6	11.7	93
CA—Re-test	40	4.5	11.3	94
TFC1—Original	40	20.1	50.1	41
TFC1—Re-test	40	20.1	50.1	46
TFC2—Original	190	140.7	74.1	57
TFC2—Re-test	40	23.4	58.4	70
TFC3—Original	150	92.6	61.7	78
TFC3—Re-test	40	18.2	45.6	76
TFC4—Original	15	8.4	55.7	71
TFC4—Re-test	40	22.3	55.7	59

Further, it can be seen from Table 4 that there is large difference between the membranes in terms of internal concentration polarisation (ICP). The CA membrane, which was observed to have the best fouling properties, has a significantly lower ICP than the TFC membranes. However, there is no clear correlation between either relative ICP, or absolute salt concentration, and fouling propensity for the four TFC membranes. Thus, even ionic strength is found to impact fouling propensity, ionic strength effects cannot explain the large differences in fouling propensity that have been observed among the different TFC membranes.

3.3.2. *Proposed fouling mechanisms*

Table 5 summarises both structural and material related characteristics of each of the five membranes, and also include the relative water flux after a NOM exposure of 2000 mg/m^2 as a measure of the fouling propensity for each of the membranes. The relative water flux after 2000 mg/m^2 are selected from the series of experiments that were performed with identical raw water and concentration in the salt water feed.

The properties for the membranes given in Table 5 can be ranked as follows:

Structure parameter: CA < TFC4 < TFC1 < TFC3 (PS) < TFC2 (PEI)
Contact angle: CA < TFC2 (PEI) < TFC3 (PS)
Zeta potential: CA < TFC2 (PEI) < TFC3 (PS) < TFC1
Fouling propensity: CA < TFC3 (PS) < TFC2 (PEI) < TFC4

Some general observations were made. (1) The CA membrane which is observed to have significantly better fouling properties than the TFC membranes is also found to have the most negative zeta potential (most negatively charged support surface), the lowest contact angle (most hydrophilic) and the lowest structure

Table 5
Structural and material characteristics of PRO membranes. The fouling propensity of each membrane is given as the water flux at a NOM load of 2000 mg/m^2, and the water flux is given relative to the start flux before NOM exposure.

Membrane	S[a]	Support polymer	Contact angle, [°][b]	Zeta potential (pH 6.7), [mV][c]	Relative flux at 2000 mg NOM/m[b]
CA	1.00	Cellulose tri-acetate	59	−11.9	0.94
TFC Type 1	5.08	Not known	Not measured	Not measured	0.46
TFC Type 2	9.29	Polyether-imide	79	−11.5	0.70
TFC Type 3	6.04	Polysulfone	82	−7.2	0.76
TFC Type 4	2.13	Not known	Not measured	Not measured	0.59

[a] Relative values

[b] Data collected from Cornelissen et al. [22]

[c] Zeta potential measurements performed at Lappeenranta University, Finland. Measurement performed on support side of the membrane [23].

parameter (best conditions for back diffusion). (2) The two TFC membranes of unknown composition (Type1 and Type4) were observed to have the lowest structure parameters among the TFC membranes, were also observed to have the highest fouling propensity. This indicates that other characteristics than the structure parameter is of more importance for the fouling characteristics of a PRO membrane. Considering the low possibility for back diffusion of NOM molecules inside a membrane pore, both due to low diffusion coefficients and relatively long diffusion path, such finding seem reasonable. (3) The zeta potential measured on the support side of three of the membranes show some correlation to fouling propensity. However, for some of the TFC membranes, which were casted on a non-woven fabric made of polyester, the zeta potential of the actual support membranes, are not known. Depending on the relative importance of the charge properties of the fabric compared to the surface charge of the support membrane, the relevance of measuring zeta potential of PRO membranes which are casted on a fabric of different material than the support membrane is made of, can be questioned. (4) Fouling propensity of the different membranes also show some correlation to contact angle indicating the importance of hydrophilic support material. As shown both by Mi and Elimelech [16], and Cornelissen et al. [22], it can be expected that free energy of adhesion, which are reflecting both the hydrophillic characteristics of the membrane and the affinity between the foulant and the membrane material, might be more suitable as indicator for fouling propensity.

An important observation from Fig. 10 is that the slope of the initial flux decline varies significantly between the different membranes. It should be noted that the flux for the CA membrane was observed to decline at a constant rate throughout the experiment. In contrast, all four TFC membranes were observed to be hampered with a rapid initial flux decline. The rate of flux decline tended to decrease as the fouling developed, and reached a stable region with apparently constant slope that seemed to be relatively independent of membrane type. However, the flux level in the stable region was observed to vary significantly between the different TFC membranes.

The observed correlation between zeta potential and contact angle, respectively, and fouling propensity, are likely to be related to tendency of NOM adsorption on the different membranes. Further, it seems reasonable that the observed difference in initial slope of the flux decline to some extent is related to the affinity between NOM and the membrane polymer. The flux decline in the region with relatively constant slope was assumed to be attributed to NOM accumulation within the porous support and cake formation at the surface of the support membrane.

To summarise, both contact angle and the zeta potential are assumed to impact the fouling propensity of a PRO membrane. The lack of correlation between fouling propensity and structure parameter that was found in this study indicates that this parameter is of minor importance with respect to fouling, even the parameter is very important in terms of PRO efficiency. Nevertheless, the structure parameter can be considered to impact fouling propensity indirectly through ionic strength effects related to internal concentration polarisation. It should be mentioned that other structural characteristics such as *e.g.* surface roughness, both on the support surface and inside pores, might be of importance in relation to the fouling characteristics of a PRO membrane. Further research should focus on establishing knowledge that correlates mentioned membrane properties to fouling propensity, and should also emphasise the attraction forces between foulant and membrane.

3.4. NOM fouling and practical PRO operation

Several aspects should be discussed when considering the results obtained from the fouling experiments in relation to practical operation of a PRO plant. Firstly, the results obtained during the current study are strictly speaking valid only for the applied water source. The NOM characteristics of other natural waters might vary according to *i.a.* size distribution and distribution of fractions with different hydrophilic and/or chemical characteristics. Nevertheless, it is considered advantageous to base fouling studies on natural waters, as such waters contain the entire spectra of NOM that membranes in real applications will face. Thus, the level of fouling propensity that was observed for the different types of membranes is considered to be of significant relevance for practical PRO operation. Secondly, it is important to notice that the applied fouling experiments were accelerated by applying higher NOM concentrations than typically found in many rivers that might be potential candidates for PRO. Thus, the elapsed time to reach a certain accumulated NOM load will be prolonged significantly by applying *e.g.* a river with low NOM content as freshwater source instead of the feed waters with high NOM concentration that was applied in the current fouling experiments. Thirdly, as the authors believe the general fouling situation will be more severe on the freshwater side of the PRO membrane, the experiments in this study have addressed fouling on the freshwater side only. Several considerations support that the author's assumption is valid: (1) Due to the direction of the water flux and the preferred membrane orientation in PRO, all foulants in the freshwater feed will be transported into the porous support structure. Thus, foulants will tend to accumulate within the pores of the support membrane which is considered disadvantageous. (2) In contradiction, foulants that are introduced with the saltwater feed will tend to be washed away from the membrane skin due to the direction of the water flux in PRO, and as a consequence the concentration of foulants will decline towards the membrane skin. Thus, it is considered that deposition of colloidal and particulate matter to some extent will be prohibited on the saltwater side of the membrane. Nevertheless, fouling on the saltwater side should be carefully considered, and biofouling is assumed to be of particular importance in that respect.

However, even the NOM level in many rivers that are candidates for PRO are significantly lower that the NOM concentrations applied in the fouling experiments, it is apparent that the PRO performance will drop relatively fast. It was observed that the performance of TFC1, which was the membrane being most susceptible to fouling, was reduced to 50% after one week of operation even at a feed concentration of only 1 mg/l DOC.

Considering the positive extreme, the CA membrane maintained 80% of its initial performance after 2 weeks of operation under similar conditions. Consequently, it is apparent that fouling mitigation will be of large importance in order to maintain viable PRO performance over time.

Three main strategies for fouling mitigation can be identified; (1) reducing the fouling potential of the feed water by pre-treatment, (2) reducing the fouling propensity of the membrane by improving structural characteristics and reducing its affinity towards foulants in the feed water, and (3) oppose the development of fouling by operational measures such as *e.g.* backwashing and chemical cleaning.

As a basis for further discussion of the three main strategies for fouling mitigation, the nature of NOM fouling should be considered more carefully. In PRO the membrane is oppositely oriented compared to typical filtration applications where the membrane skin faces the feed side. The pore size at the surface of the support membrane, which in PRO is facing the feed side, is typically in the order of magnitude of 100 nm. The hydraulic diameters of NOM are typically 10 times smaller or more. Thus, it can be assumed that NOM to a large extent will follow the convective flow of water due to the water flux, and enter into the pores of the support membrane. Due to low rate of back diffusion attributed to the relatively large particle size of NOM, as well as long diffusion length inside the support membrane, it can be anticipated that practically all NOM entering the membrane pores will tend to accumulate in the interior of the support membrane.

Based on the above discussion it seems evident that in order to mitigate fouling in PRO, the progress of accumulating NOM inside the porous support must be reversed, *e.g.* by performing intermittent backwashing of the membrane in RO mode with freshwater. Initial attempts with backwashing show promising results, and also show that the efficiency of backwashing will need to be optimised with respect to both frequency duration and pressure. It is further anticipated that less frequent chemical cleaning will be a beneficial supplement to relatively frequent backwashing.

Equally important is probably that the selection of membrane must be based on its fouling characteristics, as an additional requirement to high PRO efficiency. As discussed in Section 3.3.2 the latter aspect might be attributed to both material and structural properties of the membrane, and will influence both the development of fouling as well as the effect of backwashing. Hydrophilic and negatively charged support materials are considered suitable for reducing the affinity between NOM and the support membrane and thus reduce membrane fouling. *E.g.* coating of the support membrane in order to increase hydrophilicity and/or modifying surface charge is anticipated to have potential in this respect. Further, a smooth support surface with low surface roughness will in combination with a hydrophilic polymer be considered advantageous to avoid cake formation on the support surface.

Pre-treatment of the feed water which is listed as the first main strategy for fouling mitigation is not addressed specifically in the current study. The experiments were all performed with feed water that was pre-treated by 0.5 μm cartridge filtration. In general such pre-treatment will hardly impact the NOM concentration in the feed water. Further, it is difficult to imagine economically feasible pre-treatment that will remove NOM and other foulants of similar molecular size to a larger extent than achieved by 0.5 μm cartridge filtration. Nevertheless, even successful fouling mitigation can be anticipated to depend mainly on careful membrane selection and suitable cleaning protocols, the removal of larger particles, *e.g.* above 0.5 μm, will still be important in order to avoid spacer fouling and channel blocking that both are potential obstacles towards stable PRO performance. Thus, selection of efficient pre-treatment will still be of importance. Both economic and technical feasibility must be criteria for such selection.

Common for further development and progress within the three main strategies for fouling mitigation which are listed above, are a more fundamental understanding of the fouling mechanisms in PRO. More specifically, fundamental understanding on how various types of foulant, categorised both according to size and chemistry, as well as material and structural characteristics of the PRO membrane, are related to fouling.

4. Conclusion

It has been established that the accumulated NOM load determines the flux decline in PRO. For a given membrane type and at otherwise constant conditions, the flux decline as a function of accumulated NOM load was observed to be independent of NOM concentration in the freshwater feed. Further, the flux decline in relation to accumulated NOM load was observed to increase with increasing start flux. Dedicated experiments, where the osmotic gradient was increased at declining flux levels, indicated that ionic strength effects in the support membrane contributed to the higher fouling propensity observed at increasing start fluxes.

It has also been verified that the fouling potential of different batches of natural water collected from the same source at different times might vary despite of adjustment of pH, ionic strength and the concentration of Ca^{2+} and DOC. The composition of NOM, which was analysed by fractionation and LC-OCD analysis, was observed to remain stable despite significant variation in NOM concentration between different batches.

Significant variation in fouling propensity have been demonstrated for different types of membranes by performing fouling experiments with a selection of five different PRO membranes with identical feed water and otherwise identical conditions. It was observed that the CA membrane exhibit superior fouling characteristics compared to the four TFC membranes that were tested. Further, the CA membrane was not observed to be hampered with the same rapid initial flux decline as were observed for all four types of TFC membranes.

Three main strategies for fouling mitigation are identified; (1) reducing the fouling potential of the feed water by pre-treatment, (2) reducing the fouling propensity of the membrane by improving structural properties and reducing its affinity towards foulants in the feed water, and (3) oppose the development of fouling by operational measures such as *e.g.* backwashing and chemical cleaning.

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