Author/s:
Artemi, A;Chen, GQ;Kentish, SE;Lee, J

Title:
The relevance of critical flux concept in the concentration of skim milk using forward osmosis and reverse osmosis

Date:
2020-10-01

Citation:
Artemi, A., Chen, G. Q., Kentish, S. E. & Lee, J. (2020). The relevance of critical flux concept in the concentration of skim milk using forward osmosis and reverse osmosis. Journal of Membrane Science, 611, https://doi.org/10.1016/j.memsci.2020.118357.

# The relevance of critical flux concept in the concentration of skim milk using forward osmosis and reverse osmosis

Anna Artemi[1], George Q. Chen[2], Sandra E. Kentish[2], Judy Lee[1]

[1]Department of Chemical and Process Engineering, University of Surrey, Guildford GU2 7XH, United Kingdom

[2] The ARC Dairy Innovation Hub, Department of Chemical Engineering, The University of Melbourne, Parkville, Victoria 3010, Australia

Key words: dairy concentration, protein fouling, pressure-assisted forward osmosis, hydraulic pressure, osmotic pressure.

# Abstract

Skim milk was concentrated at 10 °C using forward osmosis (FO), reverse osmosis (RO) and pressure-assisted forward osmosis (PAFO). A pressure of 40 bar, in the form of draw solution osmotic pressure (FO and PAFO modes) or transmembrane hydraulic pressure (RO mode) was applied; an additional hydraulic pressure of 2 bar was applied in the PAFO mode. More severe protein fouling was observed in RO, followed by PAFO and then FO. This was credited to the differences in the initial permeate flux, induced by the different effective driving pressures, with RO having a greater deviation of the initial flux from the critical flux value. The critical flux was determined for the FO and RO modes using a step-wise increase of draw solution osmotic pressure or hydraulic pressure, at a constant milk solids content. The critical flux was between 5.4 $L/m^2h$ ($1.5\times10^{-6}$ $m^3/m^2s$) and 7.2 $L/m^2h$ ($2\times10^{-6}$ $m^3/m^2s$) for both the FO and RO modes at a cross flow velocity of 0.2 m/s. The similarities in the critical flux for FO and RO suggests that the critical flux does not depend on the nature of pressure applied on the system (hydraulic or osmotic). Therefore, when operated at the same flux and crossflow velocity, FO would not fundamentally provide a lower fouling environment compared to RO. An increase of the solids content from 8.7 % to 17.3 % caused a reduction in the critical flux from 5.4 $L/m^2h$ to 3.1 $L/m^2h$ ($8.5\times10^{-7}$ $m^3/m^2s$).

# 1 Introduction

The concentration of dairy streams is an important unit operation in the production of dairy powders. Hydraulic pressure-driven membrane filtration processes, including nanofiltration and reverse osmosis (RO) are employed for concentrating lactose solutions, milk, whey or whey protein concentrates prior to crystallisation or evaporation and drying [1]. However, reverse osmosis usually operates under high pressure and when coupled with suspended components such as fat globules and casein micelles, or soluble components such as whey proteins, severe membrane fouling is often reported [1–4]. Forward osmosis (FO) has been investigated as an alternative to reverse osmosis for the concentration of milk [5], and whey [5–7] among other food streams [8], owing to its reported lower fouling propensity.

Previous comparative investigations suggested that the higher fouling tendency of reverse osmosis lies in the use of a hydraulic pressure as opposed to an osmotic pressure driving force, which results in a highly compacted fouling layer and a reduced fouling reversibility [9–11]. Such conclusions were based on systems containing silicone dioxide nanoparticles [12] and solutions of organic model foulants such as sodium alginate [9,11,13], humic acid [11], bovine serum albumin [11] and reconstituted whey protein [14]. However, it was not clear whether the effect of hydraulic pressure is direct, via applying a direct force on the cake, or indirect, via inducing a higher permeate flux. These investigations have also not related fouling reversibility to flux, irrespective of the type of driving force employed or other conditions that may affect it (including concentration polarisation) under either forward osmosis or reverse osmosis conditions. To further support this, a different investigation suggested that the low fouling propensity of forward osmosis is a result of the low flux, as opposed to the higher flux generally observed in reverse osmosis [12]. In a recent study, the ‘compaction’ of a sodium alginate fouling layer was performed using hydraulic pressure, for a completely restricted permeate flux. The hydraulic resistance of the foulant layer had not increased after the compaction stage, proving that the hydraulic drag force was responsible for fouling, and not the hydraulic pressure [15].

Understanding of the fouling behaviour of dairy systems comes mainly from microfiltration and ultrafiltration studies. Cake formation during the microfiltration of protein solutions has been shown to depend on the kinetics of protein aggregation and aggregate deposition. These kinetics are influenced by electrostatic and hydrophobic effects in the solution which can be controlled by operating the system below its critical flux [16–18]. The critical flux was first defined for microfiltration as the flux below which flux decline does not occur, whilst above it fouling occurs [16]. In addition, microfiltration of bovine serum albumin has shown that sub-critical flux operation can result in negligible fouling only when a solution merely containing protein is used. On the other hand, the presence of sodium chloride at low concentrations in the feed was proven sufficient for protein aggregation, which was initiated after a certain lag time during filtration [17].

Methodologies proposed for determining the critical flux of dairy solutions for hydraulic pressure-driven membrane filtration involve pressure-controlled [19] or flux controlled experiments [17]. The first method can be applied for reverse osmosis and involves recording flux using a step-wise increase in transmembrane pressure. The point at which flux is no longer linearly proportional to transmembrane pressure indicates the value of critical flux. Nonetheless, the concept of critical flux in forward osmosis fouling has been given limited attention. A study reported on the direct microscopic observation of a cake layer in forward osmosis, which was proposed to be the point of exceeding the critical flux [20]. Recent studies determined the onset of fouling in forward osmosis by comparing the flux obtained for a baseline feed solution containing or not containing foulants, as a function of the draw solution osmotic pressure [20,21].

The present work aims to provide understanding on the relevance of critical flux in the fouling of skim milk concentrated using forward osmosis. The intent is to_clarify whether forward osmosis actually provides a lower fouling environment for filtration compared to reverse osmosis, as has been previously claimed in some literature. To verify the dependence of fouling on flux, flux data obtained under either constant or increasing milk concentration are compared to the reverse osmosis filtration mode. Skim milk contains negligible fat, inferring that fouling is predominantly induced by proteins. The effect of hydraulic pressure on fouling under pressure-assisted forward osmosis (PAFO) filtration mode is also discussed. Critical flux is located using a graphical approach for experiments in both forward osmosis and reverse osmosis filtration modes. Furthermore, the effect of the total solids content on the location of critical flux in forward osmosis mode is presented.

# 2 Experimental

## 2.1 Materials

### 2.1.1 Feed and draw solution

Non-fat (skim) milk (Great Ocean Road, Coles Australia) was utilised. The composition of this milk is shown in Table 1, as analysed in a previous study [22]. Analytical grade sodium chloride (NaCl) (Merck, Germany) was utilised for preparation of the draw solution, including a concentrated stock solution of 6 mol NaCl/kg water for dosing.

***Table 1: Properties and composition of skim milk concentrated via forward osmosis and reverse osmosis.***

| Property | Value |
|---|---|
| Total solids content (%) | 8.7 ± 0.3 |
| Protein (%, total N×6.38) | 3.9 ± 0.5 |
| Lactose (g/L) | 50.8 ± 0.3 |
| K (mg/L) | 1000 ± 40 |
| Ca (mg/L) | 1020 ± 40 |
| P (mg/L) | 860 ± 40 |
| Na (mg/L) | 360 ± 10 |
| Mg (mg/L) | 108 ± 4 |

### 2.1.2 Membranes

Cellulose triacetate (CTA) and polyamide membranes were selected to represent the membrane materials most widely used in forward osmosis and reverse osmosis, respectively. Cellulose triacetate (CTA) membranes (Fluid Technology Systems) were used in the FO and PAFO experiments. All the CTA membrane membranes were conditioned by measuring the water permeability in the RO mode at a hydraulic transmembrane pressure of 2 bar, where a constant water flux was obtained. The intrinsic water permeability coefficient of these CTA membranes was found to be equal to 0.68 ± 0.07 L/m$^2$h bar (or1.9 ± 0.2×10$^{-7}$ m$^3$/m$^2$s bar). This conditioning was carried out to ensure a consistent treatment of all the membranes prior to the use of the membranes in the skim milk experiments.

The CTA membranes demonstrated deformation when a hydraulic transmembrane pressure greater than 2.5 bar was applied on the feed side, which caused the water flux to deviate from linearity (Fig. A.1, Appendix A). Therefore, a maximum transmembrane pressure of 2 bar was used in the PAFO mode.

Sea water reverse osmosis membranes (Dow Chemicals SW30HR, Sterlitech Corporation, US) were used in the RO experiments. The water permeability coefficient of the SW30HR membranes was evaluated at a transmembrane pressure of 40 bar as 0.47 ± 0.04 L/m$^2$h (or 1.3 ± 0.1×10$^{-7}$ m$^3$/m$^2$s bar), which is within the typical range of water permeability of polyamide thin-film composite membranes for reverse osmosis desalination [23,24]. The intrinsic permeability of both membranes was obtained at a feed cross-flow velocity of 0.2 ± 0.05 m/s and a temperature of 10 ± 0.5 °C. Temperature was regulated using a water bath and temperature controller.

## 2.2 Methods

### 2.2.1 Estimation of osmotic pressure of feed and draw solution

The osmotic pressure of the milk, $\pi$, was determined via the method of water activity (Eq. 1), where $R$ is the ideal gas constant, $T$ is the absolute temperature, $V°$ is the molar volume of water solvent and $\alpha_w$ is the activity of water. The water activity was assumed to be approximately equal to its mole fraction, $x_w$, by considering a water activity coefficient, $\gamma_w$, equal to 1 (Eq. 2). The mole fraction of water was estimated considering the mass fractions, $w_i$, and molecular weights, $M_i$, of the main constituents of milk including protein, lactose and minerals sodium, potassium, calcium, magnesium and phosphate (Eq. 3).

$$\pi = -\frac{RT}{V^{\circ}}\ln(\alpha_w) \tag{1}$$

$$\alpha_w = \gamma_w x_w \tag{2}$$

$$x_w = \frac{w_w/M_w}{\sum z_i w_i/M_i} \tag{3}$$

The osmotic pressure of the draw solution was calculated from water activity data for water-NaCl solutions generated in Aspen Plus (Eq. 1). The Pitzer model was used over a range of NaCl concentrations from 5.8 to 350 g NaCl/kg water at 10 °C.

### 2.2.2 Experimental apparatus

A custom-made FO filtration cell described in a previous work [22] was utilised for the FO and PAFO experiments (FO and PAFO modes). This cell is based on the design of a SEPA cross flow cell (Sterlitech Corporation) with the only alteration to the permeate side design to allow for an input flow. The feed was pumped via a positive displacement pump (Hydra-Cell, Wanner Engineering) fitted with a variable speed drive for flow rate control. The draw solution was circulated via a gear pump (Micropump Inc.). The pressure of both the feed and draw solution was indicated by pressure gauges on the four ports of the filtration cell. In the PAFO mode, the pressure was adjusted via a back-pressure valve. A SEPA cross flow cell (Sterlitech Corporation) was used for the RO experiments (RO mode). Feed flow was delivered via a positive displacement pump (Hydra-cell, Wanner Engineering) and the transmembrane pressure was controlled via a back-pressure regulator. The two filtration cells have identical cross-flow channel dimensions and provide an effective membrane area of 0.014 $m^2$. For all filtration modes, medium foulant 47 mil diamond spacers (Sterlitech Corporation) were used in the feed channel to simulate conditions in a spiral-wound membrane module. The draw solution side for the FO and PAFO modes was fitted with 31 mil diamond low foulant spacers whereas the permeate side for the RO mode was fitted with 17 mil mesh spacers (Sterlitech Corporation). The mass change of the feed side was recorded on an analytical balance in the FO experiments (Ohaus). The mass of the permeate collected was measured in the RO experiments.

### 2.2.3 Experimental conditions

Temperature in all experiments was maintained to 10 ± 0.5 °C. Low temperature filtration is favoured in the dairy industry to prevent bacterial growth [1]. The feed cross-flow velocity for the FO and PAFO filtration modes was 0.2 ± 0.05 m/s, which lies in the typical range of cross-flow velocity used in previous forward osmosis studies [14,25]. In the RO mode, cross-flow velocities of 0.2 ± 0.05 and 0.5 ± 0.05 m/s were used. These cross-flow velocities were used for both the constant pressure and step pressure experiments. The cross-flow velocity was evaluated from the volumetric flow rate of the milk leaving the filtration cell. In the PAFO and RO modes, the flow was partly restricted by a back-pressure valve. Minor adjustments of the back-pressure valve setting were required during the experiments in order to maintain a constant hydraulic transmembrane pressure, and this resulted in small fluctuations of the flow rate. The reported ranges of cross-flow velocity reflect the fluctuations in the milk flow rate both due to back-pressure valve adjustments, as well as the changes in density and viscosity during milk concentration.

Milk concentration experiments were performed under the same bulk pressure driving force in the FO and RO modes. In the FO mode, a bulk draw solution osmotic pressure of 40 bar was maintained by dosing with the concentrated NaCl stock solution. The solute concentration in the draw solution was determined by a calibrated conductivity probe (Crison Instruments). In the RO mode, a hydraulic transmembrane pressure of 40 bar was used. In the PAFO mode, a hydraulic transmembrane pressure of 2 bar was applied in addition to the bulk draw solution osmotic pressure at 40 bar. This was done to investigate whether addition of hydraulic pressure to the already existing osmotic pressure driving force enhanced water flux, as suggested in previous PAFO studies [5,13].

Step-pressure increase experiments were performed in the FO and RO modes. In this case, the feed milk concentration was maintained constant by adding fresh water into the feed container to balance the amount of permeate removed. In the FO mode, a bulk draw solution osmotic pressure in the range of 5 bar to 50 bar was used. In the RO mode, transmembrane hydraulic pressures in the range of 10 to 40 bar were employed. For both the FO or RO modes, each pressure step was maintained for approximately 60 min, where a constant value of flux was achieved.

# 3 Results and discussion

## 3.1 Milk concentration in FO and PAFO modes

Skim milk was concentrated under the FO and PAFO modes, at a constant bulk draw solution osmotic pressure, $\pi_{D,b}$, of 40 bar (Fig. 1). The initial bulk osmotic pressure of the milk, $\pi_{F,b}$, was estimated to be equal to 5.8 ± 0.2 bar (Eq. 1). In the FO mode, flux decreased almost linearly from 5.6 L/m$^2$h (1.55×10$^{-6}$ m$^3$/m$^2$s) to 4 L/m$^2$h (1.1×10$^{-6}$ m$^3$/m$^2$s), corresponding to a flux reduction of 27%. The bulk osmotic pressure driving force reduced from 34.2 bar to approximately 30 bar, by concentrating milk to a concentration factor of 1.6. The slow flux reduction suggested the gradual loss of the bulk osmotic pressure of the milk as it became concentrated and potentially a gradual formation of a fouling cake layer as filtration progressed. In the PAFO mode, flux was shown to decline more steeply and approach a plateau beyond a concentration factor of 1.2. Given that the bulk draw solution osmotic pressure was maintained at 40 bar for both FO and PAFO, the sharp flux decline in PAFO demonstrates the formation of a fouling layer during the initial stages of of the filtration process. Specifically, over the first 20 min of filtration, the flux in the PAFO mode reduced to approximately 4.5 L/m$^2$h (1.25×10$^{-6}$ m$^3$/m$^2$s) while the flux in the FO mode was still above 5 L/m$^2$h (1. 5×10$^{-6}$ m$^3$/m$^2$s). This result is in line with previous work suggesting an increased rate in the development of a cake resistance for the PAFO mode when compared to FO [13]. Visual observation of the membranes at the end of the concentration experiments confirmed the presence of a gel layer on the membrane utilised in the PAFO mode, while this was absent from the membrane used in the FO mode (see Fig. B.1, Appendix B). The total duration of the concentration experiments to attain a concentration factor of milk of approximately 1.3 was 210 min for the FO mode and 290 min for the PAFO mode.

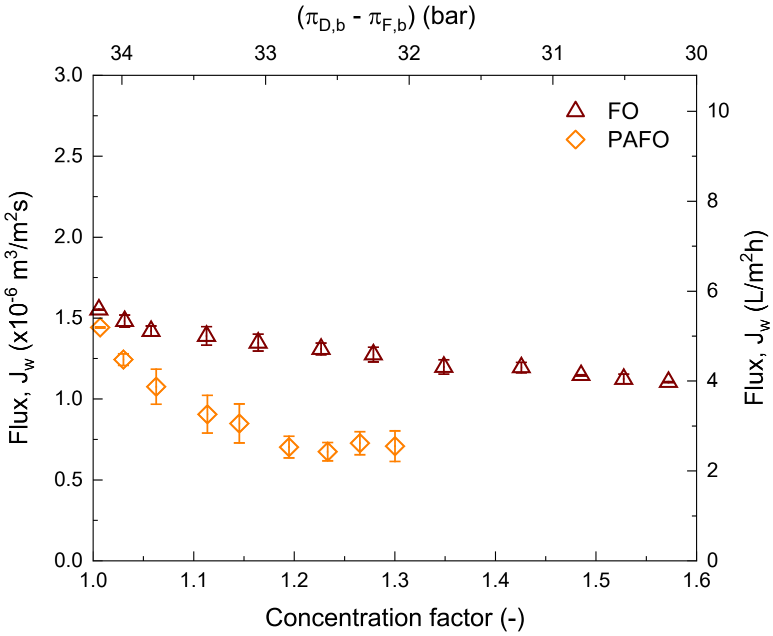


*Fig. 1. Flux as a function of concentration factor of milk in forward osmosis (FO) and pressure-assisted forward osmosis (PAFO) modes; a constant bulk draw solution osmotic pressure, $\boldsymbol{\pi_{D,b}}$, of 40 bar and milk cross-flow velocity of 0.2 ± 0.05 m/s were used for all experiments. Error bars represent standard deviations from two independent experiments.*

## 3.2 Effect of step pressure increase in PAFO mode

The applied hydraulic pressure was then increased in steps from 0.5 to 2 bar in the PAFO mode, while maintaining the concentration factor of milk constant (equal to 1). The flux over this step pressure increase was compared to the flux obtained under PAFO mode with a sudden pressure increase to 2 bar. This step increase in pressure was shown to cause a decrease in the rate of flux decline as compared to the sudden PAFO at 2 bar (Fig. 2). Interestingly, the initial flux obtained for both the PAFO at 2 bar and the step-pressure PAFO was nearly the same as the initial flux obtained in the FO mode (the dashed line represents the FO experimental data shown in Fig. 1). At the lower pressures of the step-pressure PAFO mode, 0.5 and 1 bar, the flux reduction rate is similar to that of the FO mode. However, flux reduction becomes more pronounced in the step-pressure PAFO mode as pressure is increased further to 1.5 and 2 bar. These results suggest that the magnitude of the additional applied hydraulic pressure has some effect on the development of a fouling layer. This effect is indirect, where the hydraulic pressure theoretically imposes a flux higher than the critical value. However, in practice no flux enhancement is evident, as the fouling layer starts to form. In addition, under the selected experimental conditions in the PAFO mode, the initial flux is predominantly affected by the effective osmotic pressure, which is much higher than the transmembrane hydraulic pressure. It was therefore hypothesised that the apparent reduction in flux for the FO and PAFO modes is due to operation above the critical flux value. The value of critical flux depends primarily on the nature of the feed, but also the hydrodynamic conditions within the feed channel.

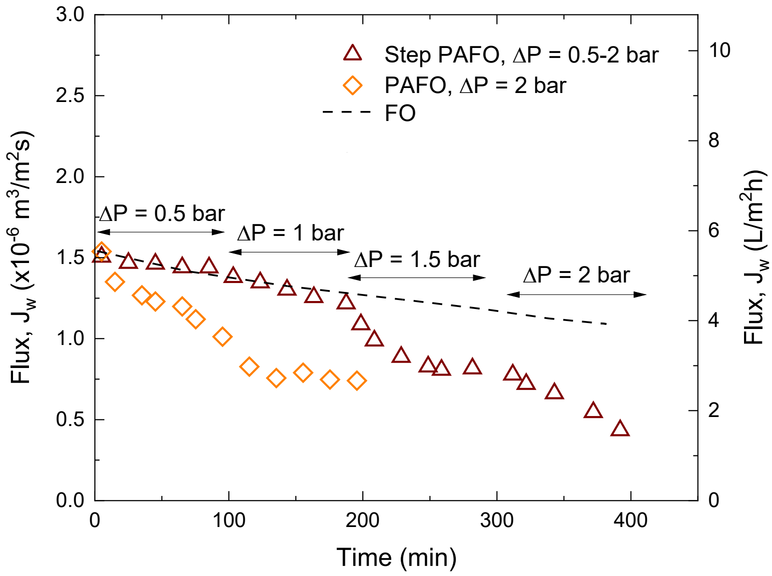


*Fig. 2. Flux as a function of time under a constant milk concentration factor of 1 for step pressure increase ($\Delta \boldsymbol{P}$ = 0.5 – 2 bar) and constant pressure (2 bar) pressure-assisted forward osmosis (PAFO) modes; constant bulk draw solution osmotic pressure, $\boldsymbol{\pi_{D,b}}$, of 40 bar and milk cross-flow velocity of 0.2 ± 0.05 m/s. The dashed line represents the flux obtained for milk concentration in the forward osmosis (FO) mode, at constant bulk draw solution osmotic pressure, $\boldsymbol{\pi_{D,b}}$, of 40 bar and milk cross-flow velocity of 0.2 ± 0.05 m/s (experimental data presented in Fig. 1).*

## 3.3 Milk concentration in RO mode

Concentration of milk under RO mode was performed at a constant hydraulic transmembrane pressure, $\Delta P$, of 40 bar, for two cross-flow velocities, 0.2 ± 0.05 and 0.5 ± 0.05 m/s (Fig. 3). At the cross-flow of 0.2 ± 0.05 m/s, the RO mode produced an initial flux higher compared to the FO mode, for the same bulk pressure driving force (approximately 34 bar once the osmotic pressure of the feed milk is included). This higher initial flux obtained for the RO mode can be related to a higher effective pressure driving force. That is, in the RO mode the system is subject to external concentration polarisation, which is dependent on the mass transfer coefficient in the feed channel. On the other hand, in the FO mode, in addition to the external concentration polarisation, internal concentration polarisation also occurs within the internal structure of the membrane, thereby reducing the effective osmotic pressure of the draw solution.

An increase in cross-flow velocity from 0.2 to 0.5 m/s was shown to cause an increase in the initial flux, but this higher flux induced a steeper rate of flux decline (Fig. 3). For both cross-flow velocities, the flux approached that obtained under the FO mode (dashed line in Fig. 3) after a concentration factor of 1.4. Altering the hydrodynamic conditions in the feed channel enhanced flux at the initial stages of the concentration process, however, the fouling layer developed at a faster rate and eventually controlled the concentration process. It has been previously demonstrated for an alginate-based system that under the same initial flux of approximately 16.5 L/m$^2$h (thin-film composite membrane, feed cross-flow velocity of 0.07 m/s), all the FO, PAFO and RO modes produce a similar rate of flux decline [9]. The initial flux in this case is hypothesised to be higher than the critical flux of sodium alginate, as fouling was detected via microscopic observation for all the three filtration modes. To further justify this, a recent study located the critical flux of sodium alginate to be between 12.5 and 16 L/m$^2$h (cellulose-triacetate membrane, cross-flow velocity of 0.085 m/s) [21]. The results obtained under the RO mode in the present study further support the argument that operation at an initial flux which is higher than the critical flux value is the predominant factor for the formation of a fouling layer. It can be further suggested as the deviation of the initial flux from the critical flux increases, the higher is the severity of fouling.

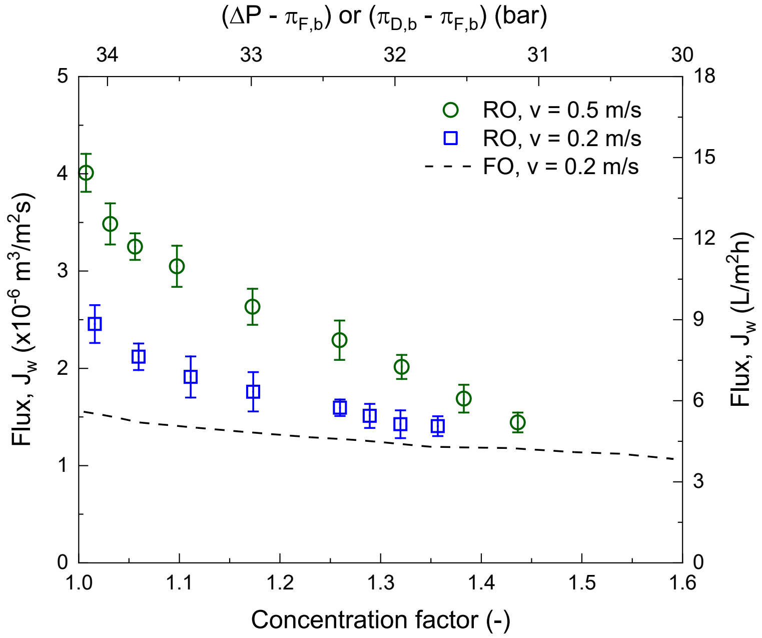


*Fig. 3. Flux as a function of concentration factor of milk in reverse osmosis (RO) mode; constant transmembrane hydraulic pressure, $\Delta \boldsymbol{P}$, of 40 bar and milk cross-flow velocities of 0.2 ± 0.05 and 0.5 ± 0.05 m/s. Error bars represent standard deviations from two independent experiments. The dashed line represents the flux obtained for milk concentration under forward osmosis (FO) mode, at constant bulk draw solution osmotic pressure, $\boldsymbol{\pi_{D,b}}$, of 40 bar and milk cross-flow velocity of 0.2 ± 0.05 m/s (experimental data presented in Fig. 1). Top axis represents the bulk pressure driving force; $(\Delta \boldsymbol{P} - \boldsymbol{\pi_{F,b}})$ for the RO mode and $(\boldsymbol{\pi_{D,b}} - \boldsymbol{\pi_{F,b}})$ for the FO mode.*

## 3.4 Critical flux of milk in RO mode

Step-pressure experiments were performed in RO mode, for a constant milk concentration factor of 1. In the RO mode, the transmembrane hydraulic pressure is the variable predominantly controlling flux. The flux obtained at the different pressures in the RO mode was plotted as a function of the bulk pressure driving force, $(\Delta P - \pi_{F,b})$ (Fig. 4). At the lower values of transmembrane hydraulic pressure, flux increased linearly with an increase in the bulk pressure driving force for both cross-flow velocities. This linear increase indicates that the apparent flux is below the critical value and, as expected, it is slightly lower than the intrinsic water flux of the clean membrane, due to a higher viscosity. Onset of fouling occurs at the point where the relationship between pressure and flux is no longer linear, implying that the value of critical flux has been exceeded. The critical flux values were estimated as 7.2 ± 0.7 L/m$^2$h (2.0 ± 0.2×10$^{-6}$ m$^3$/m$^2$s) and 14.4 ± 1 L/m$^2$h (4.0 ± 0.3×10$^{-6}$ m$^3$/m$^2$s) for the cross-flow velocities of 0.2 and 0.5 m/s, respectively. Use of a higher cross-flow velocity was proven to effectively increase the value of critical flux. A higher shear rate is induced at a higher cross-flow velocity, thereby reducing the ratio of the convective flow across the membrane over erosion due to cross-flow in the feed channel. This ratio has been previously defined as the critical flux to shear ratio [26]. In a previous study, a deviation from linearity was demonstrated to occur at a flux of 35 L/m$^2$h for a tubular RO membrane operated at a cross-flow velocity greater than 3 m/s [3].

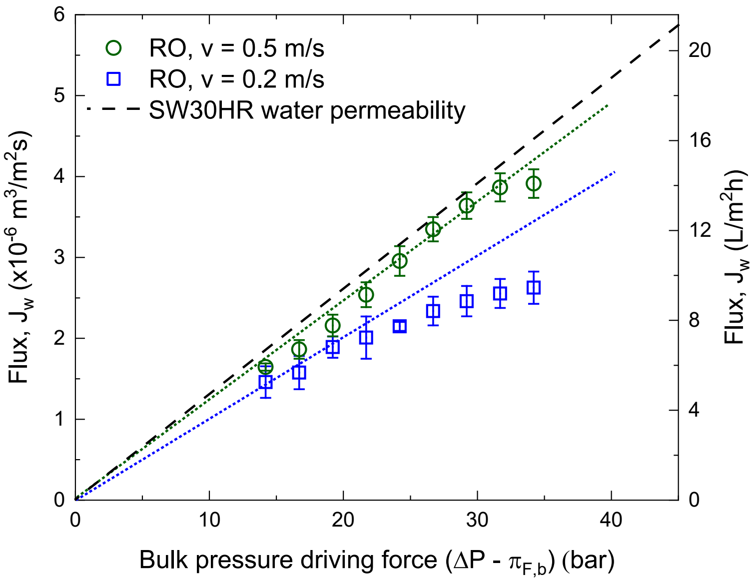


*Fig. 4. Flux as a function of bulk pressure driving force in step-pressure reverse osmosis (RO) mode, $(\Delta \boldsymbol{P} - \boldsymbol{\pi}_{F,b})$, under no milk concentration conditions; milk cross-flow velocities of 0.2 and 0.5 m/s. Error bars represent standard deviations from two independent experiments. Dashed line represents the intrinsic water permeability of the membrane. Dotted lines are to guide the eye and illustrate the deviation from linearity of flux and bulk pressure driving force upon exceeding the critical flux.*

## 3.5 Critical flux of milk in FO mode

In the FO mode, the bulk draw solution osmotic pressure, $\pi_{D,b}$, was varied step-wise to determine the critical flux in the same manner as previous researchers [21]. In this case, flux was not expected to increase linearly with the bulk osmotic pressure driving force, $(\pi_{D,b} - \pi_{F,b})$ due to internal concentration polarisation [27]. Therefore, in order to distinguish between the effects of concentration polarisation and fouling, a NaCl feed solution with the same bulk osmotic pressure as milk was used to give a baseline flux [14,20]. Flux was plotted as a function of $(\pi_{D,b} - \pi_{F,b})$ for both the NaCl model solution and milk (Fig. 5a). At low values of bulk osmotic pressure, the baseline flux with NaCl feed is slightly higher than the flux with milk feed for the two lower milk total solids (Fig 5a and Fig 5b) but at the highest milk total solids (Fig 5 c) there was some overlap. These differences can be attributed to the slight over estimation of the bulk osmotic pressure of the skim milk and also the difference in density and viscosities that could give rise to different concentration polarisation effects. Nevertheless, there exist a point where the milk flux curve deviates from that of the NaCl model solution. The point at which the deviation became significant was considered as the point of exceeding the critical flux.

The value of critical flux for fresh milk in the FO mode is approximately 5.4 L/m$^2$h (1.5 ± 0.15×10$^{-6}$ m$^3$/m$^2$s) (Fig. 5a). A similar flux deviation between the baseline and fouling solution flux was reported [20] in the FO filtration of a microalgae system. In this case, the critical flux in the step-pressure increase was located between approximately 9 and 15 L/m$^2$h while a direct microscopic observation of the microalgae deposition indicated a critical flux lower than 10 L/m$^2$h (CTA membrane, cross-flow velocity of 0.22 m/s) [20]. These critical flux values are higher yet comparable to the one observed for milk in the present study. It is anticipated that microalgal cells can be more easily moved away from the fouling layer compared to milk proteins due to their larger size [16,28]. A microfiltration study on milk proteins demonstrated that a higher shear stress causes the selective removal of larger particles (mainly casein micelles) away from the membrane surface, thereby promoting the formation of a fouling layer comprising of smaller particles (mainly whey proteins). The result is a thinner and less porous fouling layer which poses a greater resistance to flux [28].The effect of the total solids content of milk on critical flux was further investigated. Milk was concentrated in advance to total solids percentages of 12.6 and 17.3%, corresponding to bulk milk osmotic pressures, $\pi_{F,b}$, of 8.3 ± 0.2 and 12.2 ± 0.4 bar, respectively (Eq. 1). Flux was recorded under a step-pressure increase in FO mode (Fig. 5b and c). The critical flux was found to be approximately equal to 1×10$^{-6}$ m$^3$/m$^2$s and 0.85×10$^{-6}$ m$^3$/m$^2$s for total solids contents of 12.6% and 17.3%, respectively (Fig. 6). This reduction in critical flux with total solids content is anticipated, considering that a high concentration of protein in the feed favours the electrostatic forces and hydrophobic interactions responsible for protein aggregation [17]. Consequently, the higher the protein concentration at the membrane surface, the lower the flux required for aggregation and deposition to occur, implying a lower critical flux value. Similar results were obtained for bovine serum albumin solutions where the critical flux was found to decrease from 44 to 35 L/m$^2$h in the FO mode by an increase in concentration from 80 to 160 mg/L [29].

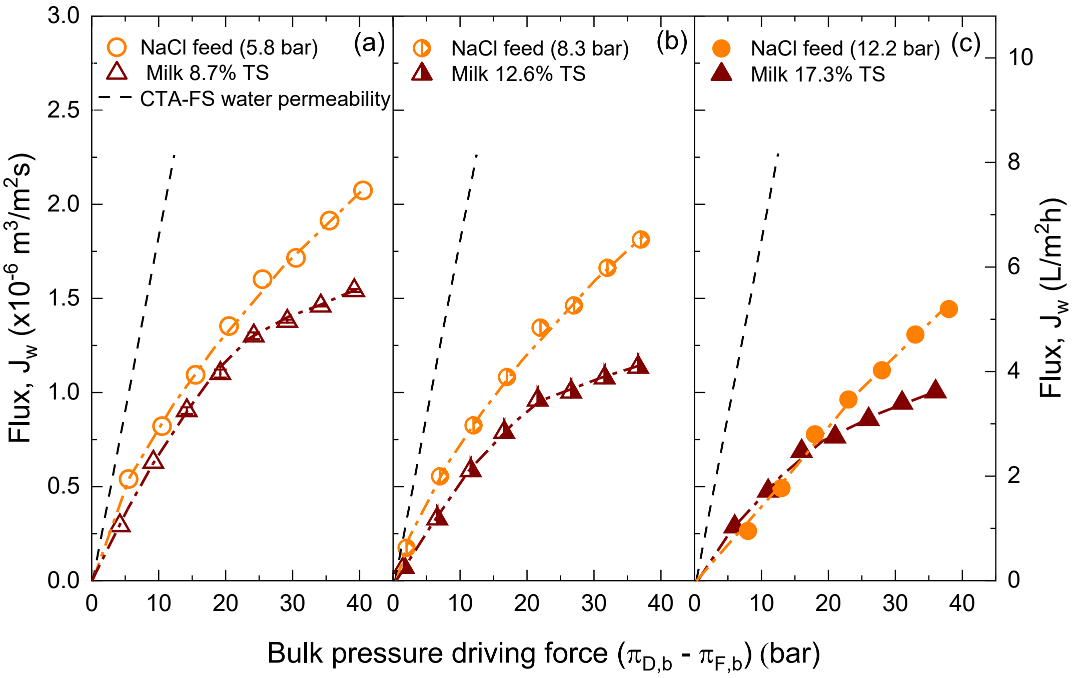


*Fig. 5. Flux as a function of bulk osmotic pressure driving force in step-pressure forward osmosis (FO) mode, $(\pi_{D,b} - \pi_{F,b})$, for (a) fresh milk with 8.7% total solids (b) milk with 12.6% total solids and (c) milk with 17.6% total solids; milk cross-flow velocity of 0.2 m/s. The flux of a sodium chloride model solution as feed with the same osmotic pressure as milk is compared to the flux of milk for each of the total solids contents. Error bars represent standard deviations from two independent experiments. Dashed line represents the intrinsic water permeability of the membrane.*

## 3.6 Critical flux: RO vs FO mode

A previous study has reported that in the FO mode the critical flux was slightly higher for polyamide thin-film composite (TFC) compared to cellulose triacetate membranes due to the TFC having a more hydrophilic and rougher surface [21]. Similar results are observed in the present case. That is, both forward osmosis (CTA) and reverse osmosis (TFC SW30HR) produced a comparable critical flux (Fig. 6) but that for the polyamide SW30HR reverse osmosis membrane at 7.2 L/m$^2$h, is slightly higher than that of the CTA membrane at 5.4 L/m$^2$h (Fig. 4 and Fig. 5). The small difference in the value of the critical flux for the FO and RO systems, which were deliberately operated at similar hydrodynamic conditions, is reasonable given that the two membranes are made of different materials with different surface properties. Nonetheless, both the RO and FO modes demonstrate that once the critical flux is attained for a given system, fouling occurs irrespective of the type of pressure driving force and membrane type. This would explain the previously reported similar flux decline observed for FO and RO when operated at the same initial flux [9,12].

The reliability of the step-pressure method is further supported by the fact that the initial fluxes obtained in either of the FO or RO modes (Fig. 1 and Fig. 3) are in line with the respective fluxes obtained in the step-pressure increase experiment. The bulk pressure driving force required for attaining the critical flux was approximately equal to 20 bar for the RO mode and 30 bar for the FO mode. This difference can be attributed to the different concentration polarisation phenomena associated with either the RO or FO filtration mode. Concentration polarisation is limited to external on the feed side in RO, whereas it also occurs internally in the support layer of the membrane in FO which would therefore lower the effective pressure driving force.

In our previous pilot-scale study on skim milk concentration under PAFO mode, flux was shown to increase from 4.3 to 5 L/m$^2$h when the average transmembrane hydraulic pressure was increased from 0.9 to 2.2 bar (the bulk osmotic pressure difference was approximately 30 bar) [5]. The small flux enhancement can be explained by the fact that the system was operated below and close to the critical flux of 5.4 L/m$^2$h obtained in the present study (Fig. 5a). Moreover, a previous bench-scale concentration of skim milk reported an initial flux of 7 L/m$^2$h for a bulk draw solution osmotic pressure of 150 bar (CTA membrane, cross-flow velocity of 0.2 m/s) [22]. This result further demonstrates that fouling limits the maximum flux observed, when an excessive pressure imposes a high flux.

It is important to note that for the FO mode, reverse salt diffusion may occur and could also influence the fouling behaviour and critical flux. At higher draw solution concentrations, there could be greater reverse salt flux and more salt accumulation on the feed side. However, sodium ions are generally much less likely to promote fouling in dairy systems, in comparison to other ions such as calcium [30]. Indeed it has been reported that NaCl at sufficiently high concentrations can increase the solubility of bovine serum albumin [17]. A microfiltration study reported that high concentrations of NaCl present in solutions of bovine serum albumin could accelerate the development of the fouling layer by influencing the protein-protein interactions, but it did not influence the location of the critical flux [17].

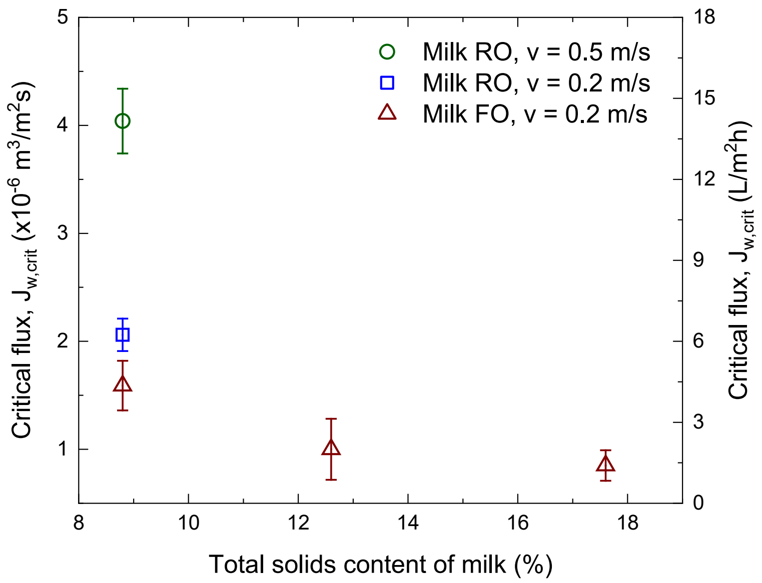


***Fig. 6: Critical flux of milk as a function of total solids content obtained from step-pressure increase in RO mode (cross-flow velocities of 0.2 and 0.5 m/s) and step-pressure increase in FO mode (cross-flow velocity of 0.2 m/s). Error bars represent the approximate error of the graphical determination of critical flux (Fig. 4 for RO mode and Fig. 5 for FO mode).***

# 4 Conclusions

The present study demonstrates that the fouling under forward osmosis and reverse osmosis concentration of skim milk predominantly depends on the initial flux induced by a certain hydraulic or osmotic pressure driving force. This result is in line with the concept of critical flux. That is, a higher pressure, irrespective of whether it is provided through hydraulic or osmotic means, is associated with more severe fouling because it causes a higher deviation of flux from the critical flux value. Consequently, the value of the initial flux is important to the subsequent development of the fouling layer.

The bulk osmotic pressure driving force in the FO mode was only sufficient to produce an initial flux of 5.6 $L/m^2h$ which was marginally close to the critical flux of 5.4 $L/m^2h$ obtained for the FO mode. As a result, the flux in the FO mode reduced at a relatively low rate. On the other hand, the bulk pressure driving force in the RO mode produced a flux of approximately 9 $L/m^2h$ that exceeded the critical flux value of 7.2 $L/m^2h$ obtained in the RO mode. Consequently, the flux decrease was faster, and eventually approached the flux obtained under the FO mode. It is further suggested that the additional hydraulic pressure in the PAFO mode accelerated the development of fouling, where the initial flux was almost identical to the critical flux value within experimental error. Results regarding the location of critical flux suggest that under the same hydrodynamic conditions, forward osmosis and reverse osmosis exhibit a similar critical flux, although the two membranes are of a different material and have a different intrinsic water hydrophilicity and roughness. The critical flux under FO was shown to reduce as the total solids content of milk increases, which is in line with previous studies suggesting a stronger interaction between proteins at higher concentrations. An increased shear stress in the RO mode was proven effective in increasing the value of critical flux. Nonetheless, excessive shear can promote the selective fouling of the membrane by smaller particles, which eventually results to a more compact fouling layer, as demonstrated in previous skim milk filtration studies [20]. Overall, the effective pressure driving force dictates the initial flux value, irrespective of whether a hydraulic or osmotic pressure driving force is used. Subsequently, the rate of flux reduction will depend on the extent of deviation from the critical flux.

## Acknowledgements

Anna Artemi would like to acknowledge the financial support by the Cyprus State Scholarship Foundation, through the PhD scholarship IKYK 99.

## References

[1] G.Q. Chen, T.S.H. Leong, S.E. Kentish, M. Ashokkumar, G.J.O. Martin, Membrane Separations in the Dairy Industry, in: Sep. Funct. Mol. Food by Membr. Technol., Elsevier, 2019: pp. 267–304.

[2] U. Kulozik, H.G. Kessler, The kinetics of the formation of a deposited layer during the reverse osmosis of skim milk, J. Memb. Sci. 54 (1990) 13–27.

[3] U. Kulozik, H.-G. Kessler, Permeation Rate During Reverse Osmosis of Milk Influenced by Osmotic Pressure and Deposit Formation, J. Food Sci. 53 (1988) 1377–1383.

[4] M. Cheryan, B. Veeranjaneyulu, L.R. Schlicher, Reverse osmosis of milk with thin-film composite membranes, J. Memb. Sci. 48 (1990) 103–114.

[5] G.Q. Chen, A. Artemi, J. Lee, S.L. Gras, S.E. Kentish, A pilot scale study on the concentration of milk and whey by forward osmosis, Sep. Purif. Technol. (2019).

[6] C. Aydiner, U. Sen, S. Topcu, D. Ekinci, A.D. Altinay, D.Y. Koseoglu-Imer, B. Keskinler, Techno-economic viability of innovative membrane systems in water and mass recovery from dairy wastewater, J. Memb. Sci. 458 (2014) 66–75.

[7] C. Aydiner, S. Topcu, C. Tortop, F. Kuvvet, D. Ekinci, N. Dizge, B. Keskinler, A novel implementation of water recovery from whey:“forward–reverse osmosis” integrated membrane system, Desalin. Water Treat. 51 (2013) 786–799.

[8] N.S. Terefe, F. Janakievski, O. Glagovskaia, K. De Silva, M. Horne, R. Stockmann, Forward osmosis: A novel membrane separation technology of relevance to food and related industries, Innov. Food Process. Technol. (2016) 177–205.

[9] M. Xie, J. Lee, L.D. Nghiem, M. Elimelech, Role of pressure in organic fouling in forward osmosis and reverse osmosis, J. Memb. Sci. 493 (2015) 748–754.

[10] B. Mi, M. Elimelech, Organic fouling of forward osmosis membranes: Fouling reversibility and cleaning without chemical reagents, J. Memb. Sci. 348 (2010) 337–345.

[11] S. Lee, C. Boo, M. Elimelech, S. Hong, Comparison of fouling behavior in forward osmosis (FO) and reverse osmosis (RO), J. Memb. Sci. 365 (2010) 34–39.

[12] W.C.L. Lay, T.H. Chong, C.Y. Tang, A.G. Fane, J. Zhang, Y. Liu, Fouling propensity of forward osmosis: investigation of the slower flux decline phenomenon, Water Sci. Technol. 61 (2010) 927–936.

[13] J. Lee, S. Kook, C. Lee, I.S. Kim, Effect of intermittent pressure-assisted forward osmosis (I-PAFO) on organic fouling, Desalination. 419 (2017) 60–69.

[14] Y.-N. Wang, R. Wang, W. Li, C.Y. Tang, Whey recovery using forward osmosis–Evaluating the factors limiting the flux performance, J. Memb. Sci. 533 (2017) 179–189.

[15] F.A. Siddiqui, Q. She, A.G. Fane, R.W. Field, Exploring the differences between forward osmosis and reverse osmosis fouling, J. Memb. Sci. 565 (2018) 241–253.

[16] R.W. Field, D. Wu, J.A. Howell, B.B. Gupta, Critical flux concept for microfiltration fouling, J. Memb. Sci. 100 (1995) 259–272.

[17] R. Chan, V. Chen, The effects of electrolyte concentration and pH on protein aggregation and deposition: critical flux and constant flux membrane filtration, J. Memb. Sci. 185 (2001) 177–192.

[18] W. Youravong, M.J. Lewis, A.S. Grandison, Critical Flux in Ultrafiltration of Skimmed Milk, Food Bioprod. Process. 81 (2003) 303–308.

[19] V. Chen, A.G. Fane, S. Madaeni, I.G. Wenten, Particle deposition during membrane filtration of colloids: Transition between concentration polarization and cake formation, J. Memb. Sci. 125 (1997) 109–122.

[20] S. Zou, Y.-N. Wang, F. Wicaksana, T. Aung, P.C.Y. Wong, A.G. Fane, C.Y. Tang, Direct microscopic observation of forward osmosis membrane fouling by microalgae: Critical flux and the role of operational conditions, J. Memb. Sci. 436 (2013) 174–185.

[21] T.T. Nguyen, S. Kook, C. Lee, R.W. Field, I.S. Kim, Critical flux-based membrane fouling control of forward osmosis: Behavior, sustainability, and reversibility, J. Memb. Sci. 570–571 (2019) 380–393.

[22] G.Q. Chen, S.L. Gras, S.E. Kentish, The application of forward osmosis to dairy processing, Sep. Purif. Technol. 246 (2020) 116900.

[23] Z. Yang, H. Guo, C.Y. Tang, The upper bound of thin-film composite (TFC) polyamide membranes for desalination, J. Memb. Sci. 590 (2019).

[24] C.Y. Tang, Y.N. Kwon, J.O. Leckie, Effect of membrane chemistry and coating layer on physiochemical properties of thin film composite polyamide RO and NF membranes. II. Membrane physiochemical properties and their dependence on polyamide and coating layers, Desalination. 242 (2009) 168–182.

[25] C. Boo, S. Lee, M. Elimelech, Z. Meng, S. Hong, Colloidal fouling in forward osmosis: Role of reverse salt diffusion, J. Memb. Sci. 390–391 (2012) 277–284.

[26] G. Gésan-Guiziou, E. Boyaval, G. Daufin, Critical stability conditions in crossflow microfiltration of skimmed milk: transition to irreversible deposition, J. Memb. Sci. 158 (1999) 211–222.

[27] G.T. Gray, J.R. McCutcheon, M. Elimelech, Internal concentration polarization in forward osmosis: role of membrane orientation, Desalination. 197 (2006) 1–8.

[28] O. Le Berre, G. Daufin, Skimmilk crossflow microfiltration performance versus permeation flux to wall shear stress ratio, J. Memb. Sci. 117 (1996) 261–270.

[29] T.-T. Nguyen, C. Lee, R.W. Field, I.S. Kim, Insight into organic fouling behavior in polyamide thin-film composite forward osmosis membrane: Critical flux and its impact on the economics of water reclamation, J. Memb. Sci. 606 (2020) 118118.

[30] L.L.A. Koh, M. Ashokkumar, S.E. Kentish, Membrane Fouling, Cleaning and Disinfection, in: Membr. Process., Blackwell Publishing Ltd., Oxford, UK, 2012: pp. 73–106.

# Appendix A. Water permeability of cellulose triacetate membranes

The pure water permeability of two samples of the cellulose triacete (CTA) membranes was measured over a range of hydraulic transmembrane pressure prior to the skim milk experiments. To determine whether the presence of spacers influences the intrinsic water permeability of these membrane, we measured the flux, $J_w$, of two membrane samples as a function of the hydraulic transmembrane pressure, $\Delta P$; $CTA_{S1}$ without feed spacers and $CTA_{S2}$ with spacers (Fig. A.1). It was shown that for a pressure up to 2 bar both membranes, and that the presence of spacers caused no, or at least not detectable, membrane deformation. The flux of the membrane sample $CTA_{S1}$ followed the anticipated linear relationship between flux and transmembrane pressure for a pressure up to 2 bar, while it started to deviate from linearity at pressures of 2.5 bar and 3 bar. This experiment provided a first indication of the pressure where membrane deformation becomes evident. To verify that a hydraulic pressure did not cause any membrane deformation in the presence of spacers, the membrane sample $CTA_{S2}$ was tested for pressures up to 2 bar. The intrinsic water permeability of the membrane sample $CTA_{S2}$ was similar to that of $CTA_{S1}$ and was not shown to be compromised by the presence of spacers, thus a pressure $\Delta P$ of 2 bar was considered 'safe' for operation in the PAFO mode. In order to ensure that all the membranes were treated in the same way before use, they were all first 'conditioned' by applying a hydraulic pressure of 2 bar, to measure the pure water flux. The flux in the conditioning experiment were in the range of to 1.9 ± 0.2×10-7 $m^3/m^2$s bar (or 0.68 ± 0.07 L/$m^2$h bar).

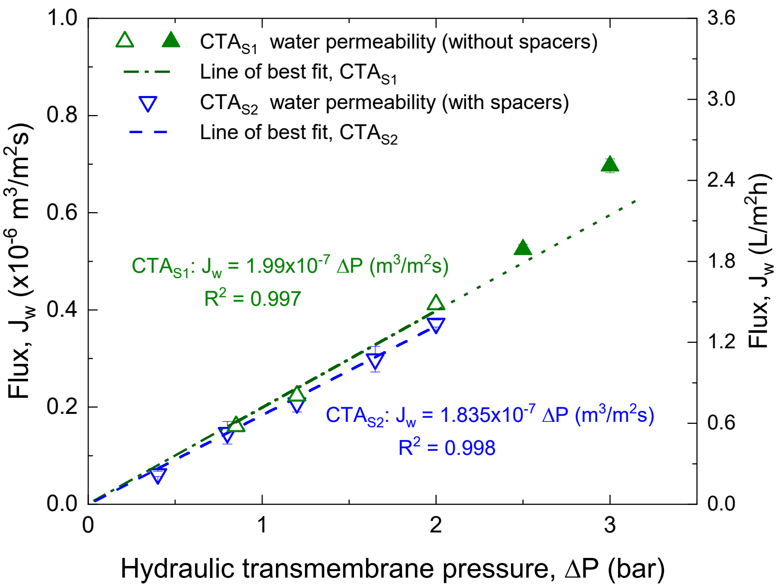


*Fig.A.1. Water flux of a sample as a function of the hydraulic transmembrane pressure, ΔP, for two membrane samples $CTA_{S1}$ tested with no spacers in feed channel and $CTA_{S2}$ with spacers; operating temperature of 10°C. The gradients of the lines of best fit were used to determine the intrinsic water permeability coefficients of the membranes.*

## Appendix B. Observation of fouling in the FO and PAFO modes

The membranes after the two typical skim milk concentration experiments performed in the FO and PAFO modes were visually observed. The presence of a deposited fouling layer on the surface of the membrane used in the PAFO experiment was clear (Fig. S2b) while a negligible material deposition had occurred for the membrane used in the FO mode (Fig. S2a). This observation was in line with the significant flux decline obtained for the milk concentration in the PAFO mode (Fig. 1).

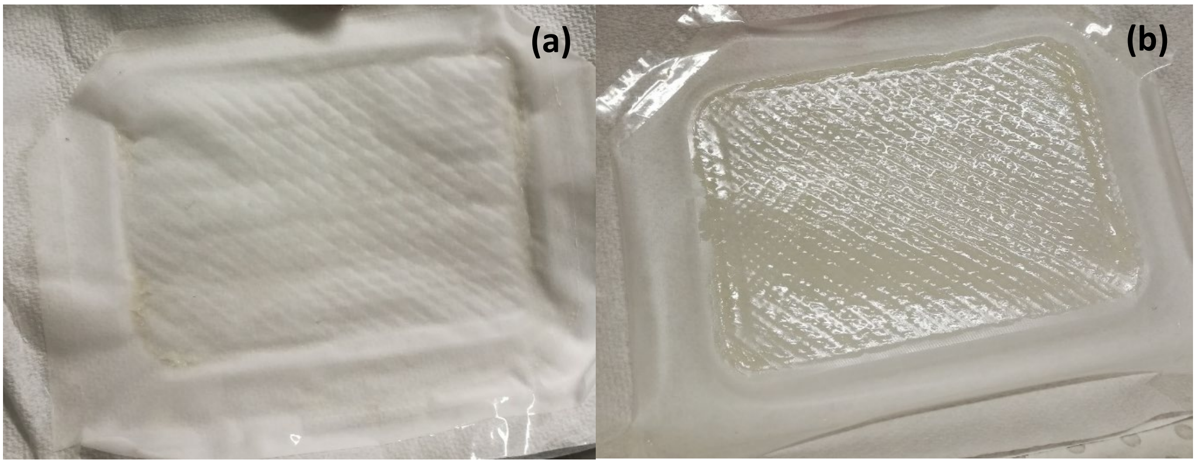


*Fig. B.1. Visual observation of the membranes used in the concentration of skim milk in (a) the forward osmosis (FO) mode and the pressure-assisted forward osmosis (PAFO) mode, at the end of the respective experiments. Fouling Is indicated in image (b) by the gel like deposit on the membrane surface. Negligible deposit is shown for image (a).*