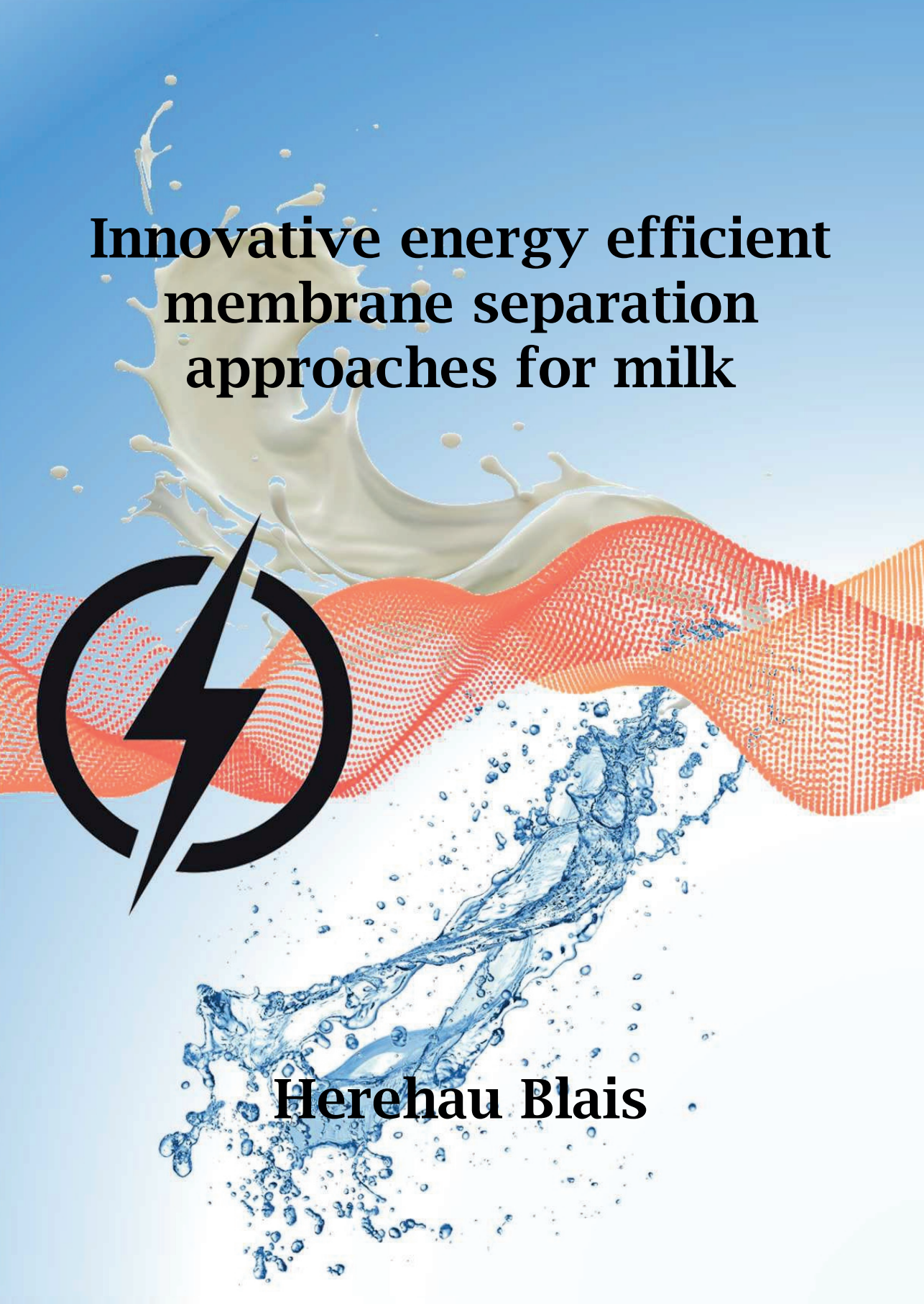
Innovative energy efficient membrane separation approaches for milk



Herehau Blais

Propositions

1. Its versatility makes membrane filtration the ideal candidate for fractionation processes that fit within a circular economy.
   (this thesis)
2. A concentrated waste stream as draw solution greatly reduces the footprint of forward osmosis processes.
   (this thesis)
3. A scientist's recognition should be based as much on the quality of her/his work as on human qualities.
4. Just like erroneous/obsolete scientific theories are corrected/updated, so should political ones.
5. Taking health, justice and education for granted is the best way to lose them.
6. Sending people who initiate wars on the front line would bring more peace to the world.

Propositions belonging to the thesis, entitled

Innovative energy efficient membrane separation approaches for milk

Herehau Blais

Wageningen, 9 December 2022

Innovative energy efficient membrane separation approaches for milk

Herehau Blais

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Innovative energy efficient membrane separation approaches for milk

Herehau Blais

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Content

Chapter 1

Introduction and thesis outline

1.1 General introduction

Bovine milk contains roughly 87% water, 4.9% carbohydrates, 3.9% protein, 3.5% fat and 0.7% ash (Lu and Wang 2017), of which exact concentration varies according to the cattle species, as well as the environment and conditions in which the cows live (e.g., outdoors/indoors, feeding regime, interval between milking, season). These components provide a range of nutritional, biological and technological benefits making their isolation of high interest for dairy industries, and also more generally for food industries as dairy ingredients are omnipresent in food products.

Whey proteins are for instance employed in products related to muscle building, exercise recovery, weight management and healthy aging, whereas immunoglobulins have proven to efficiently protect against complex diseases (Chandan 1997). Furthermore, whey proteins combined with micellar caseins allow preparation of protein gels with flexible stiffness, elasticity and structure (Kharlamova, Nicolai et al. 2019), depending on the size of the micelles (Glantz, Devold et al. 2010).

Apart from proteins, lactose is used by pharmaceutical industries as a filling agent, or by food industries in the preparation of babyfood, pastries, chocolate, sugar confectionery, soups and sauces, or in its hydrolysed form for ice cream, non-alcoholic beverages, yogurt, salad dressing, etc. Finally, some minor lipids, namely glycolipids and glycoproteins, have interesting emulsifying and foaming properties properties, and benefits related to health such as antiviral, bactericidal, anticancer and anti-oxydant properties (Jiménez-Flores and Brisson 2008).

Numerous techniques (e.g., centrifugal and gravitational separation (Rolland and Riel 1966), coagulation, chromatography, electrophoresis (Maubois 1984)) are currently employed to fractionate these components but there is not a one-size-fits all solution. There are two main challenges and these relate to i) the diverse physicochemical nature of components present, including their size, which requires that a number of processes needs to be applied (consecutively, or in parallel), leading to ii) various purities of components that ideally are tuned to the application in which they are going to be used. As an overall consideration, it also should be kept in mind that a production line would need to be able to process rather large amounts of feed material, and not all separation techniques are able to do so. For instance, chromatography will lead to high purity, but the throughput is low, relative to equipment scale, compared to other separation techniques.

In its whole form or following the isolation of its components, milk can be concentrated to reduce its transportation and storage costs and extend its shelf life, allowing it to be stored at ambient temperature for extended periods of time (ca. 1 year) without substantial loss of quality (Sharma, Jana et al. 2012). This is conventionally done using thermal processes such as evaporation leading to concentrations of up to ca. 50% dry matter content (Sharma, Jana et al. 2012), followed by spray-drying to produce milk powder (Ramírez, Patel et al. 2006). These two steps are energy-intensive operations (Schuck, Jeantet et al. 2015) and although progress has been made to improve their performance (e.g., through design of dryers (Fox, Akkerman et al. 2010)), pre-concentration of the feed solution through means other than thermal treatments holds promise to improve overall process performance.

The production of skim milk powder in the European Union is projected to increase by 11% by 2026 compared to 2021, and that of whole milk powder by

12% (Nations 2017), highlighting the need for more sustainable production, with a lower carbon footprint and by proxy a reduction in operational costs. More specifically, when taking into account varying energy sources, technological changes and implementation of environmental regulations, the specific energy consumption for whole milk powder production worldwide ranges from 4.6 $MJ \cdot kg^{-1}$ to 221.4 $MJ \cdot kg^{-1}$ for milk powder (Xu and Flapper 2011). This large gap across countries emphasizes that considerable energy savings are possible.

1.2 Membrane filtration for fractionation or concentration

In order to make the best use of the diverse nutritional, biological and technological properties of milk components, their fractionation or concentration can be carried out using membrane filtration technology. The operating parameters of this non-thermal technology are adjusted based on target molecules through e.g., pore size ranges from sub-nanometer to tens of micrometers, which implies that the full range of milk components can be covered (Figure 1-1). Yet, component size is not the only criterium to consider for an efficient fractionation.

The use of dense membranes, e.g., reverse osmosis or nanofiltration for water removal, reduces the thermal load of milk concentrates, thus preserving functional and biological properties of milk proteins better than a combination of evaporation and drying. Indeed, milk exposure to e.g., 72 °C for 20 s during pasteurization has been shown to trigger the denaturation and aggregation of some heat-labile milk proteins such as lactoferrin and lactadherin resulting in a loss of their biological functionality (Brick, Ege et al. 2017).

With cut-offs in the micrometer range, down to ca. 0.1 µm, microfiltration (MF) membranes retain most bacteria and spores as well as somatic cells present in dairy solutions and as such provide an alternative to traditional heat treatments

for heat-sensitive products (Zydney 1998). MF is also successfully employed for specific retention of fat globules (small <2 µm versus large globules >2 µm). These two fractions can be exploited for their different functional properties unlike droplets obtained through centrifugation that are separated as a whole. For instance, small globules were found to yield products with finer textural characteristics compared to large or untreated fat globules (Daufin, Escudier et al. 2001).

MF can also be used to produce micellar casein concentrates (or isolates) to increase the yield of cheese or yoghurt production while allowing whey proteins and other dissolved compounds (lactose, non-protein nitrogen compounds, minerals and organic acids) to permeate (Carvalho and Maubois 2009, Xia, Tobin et al. 2021). This altered ratio of caseins to serum proteins can be beneficial for the preparation of structured dairy products for athletes or medical purposes (Stark, Lukaszuk et al. 2012).

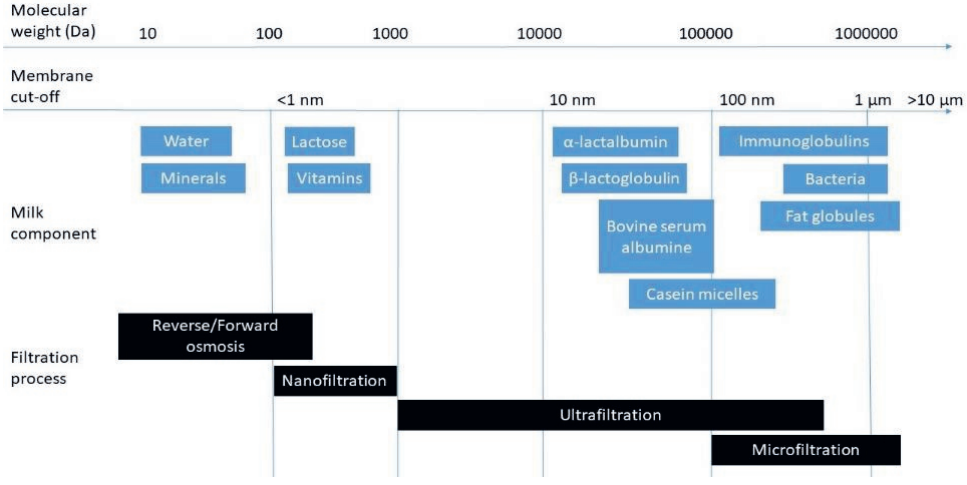

Fig. 1-1. Milk components and associated membrane filtration processes.

Ultrafiltration (UF) membranes have a molecular weight cut-off (MWCO) in the nanometer range (2-100 nm) and are used for the production of whey protein concentrates or isolates (Gésan-Guiziou 2007). Compared to coagulation and precipitation that lead to denaturation when using heat, acid, urea or alkali, UF preserves the native properties of whey proteins (e.g., solubility, ability to gel, whip and emulsify) (Hill, Irvine et al. 1982). Furthermore, UF does not require chemical precipitants (polyphosphates or carboxy-methylcellulose), and yields protein fractions without contaminants thus preventing disposal of large quantities of effluent. When implemented commercially, UF is more economical than ion-exchange or affinity chromatography, albeit that the products are less pure. Finally, this process can be used for the decalcification of permeates (following a thermocalcic aggregation) or for lactose reduction in milk (Vyas and Tong 2003).

Nanofiltration (NF) membranes have a MWCO of 1 nm and below, allowing predominantly monovalent ions and water to permeate while most of the multivalent ions, as well as larger components, are retained. They are commonly employed for partial demineralization of whey (removal of monovalent and divalent ions by up to 90 and 20% respectively (Daufin, Escudier et al. 2001)), or for volume reduction of whey (Mistry and Maubois 2017). Demineralization can be performed in the range of 50-95% using electrodialysis or ion exchange; however, NF can be performed at lower capital and operational costs, does not yield any polluting effluent and has a higher selectivity than electrodialysis (Daufin, Escudier et al. 2001).

Finally, reverse osmosis (RO) and forward osmosis (FO) membranes are dense membranes that theoretically only allow water to permeate. Consequently, they are used for concentration of milk or whey, milk solids recovery or water

reclamation. The main difference between these two processes lies in the driving force and the pressure range they employ, resulting indifferent energy needs; in general, FO tends to consume less energy than RO, and applies a concentration gradient as driving force while for RO a pressure gradient is used.

Depending on the target component(s), membranes can be applied as a single operation, or in a cascade configuration. Since separation processes nowadays revolves more and more around prevention of waste, or making good use of what used to be waste streams, combined uses of membranes have been suggested for a more sustainable approach. In dairy factories, membranes are generally operated as multi-stage systems, and ideally these processes can be tuned to be flexible in their products. In chapter 2, an overview of different cascaded membrane systems for dairy applications is presented.

In this thesis, we investigate two systems: multistage filtration (e.g., microfiltration and reverse osmosis as described in chapter 3) and forward osmosis (chapter 5). Both systems have specific advantages that are described in more detail at the end of the next section.

1.3 Principles of membrane filtration processes

During continuous filtration, fluid passes the filter while the retained solids accumulate upstream of the membrane element (Singh 2005); the rate of this accumulation is co-determined by the cross-flow velocity applied during the process. This leads to an additional resistance resulting in a decrease in permeate flux and altered solute selectivity (Saxena, Tripathi et al. 2009). In concentration processes where membrane pores are negligible (e.g., RO or FO), the retention of virtually all solutes considerably enhances feed viscosity and osmotic pressure, thus limiting the pre-concentration of milk/whey to ~27% dry matter (Daufin,

Escudier et al. 2001). The main advantage of cross-flow operation is that by limiting fouling accumulation, a high flux can be maintained over time thus prolonging the intervals between chemical cleaning steps (Van der Bruggen 2018). In this thesis, the membrane processes investigated are all operated in a cross-flow configuration.

The driving force in MF, UF, NF and RO processes is a hydraulic pressure difference between the feed and permeate, so-called transmembrane pressure (TMP), of which the magnitude depends on the process used (Kumar, Sharma et al. 2013) (Figure 1-2). The highest transmembrane pressure is used in RO processes, ranging from 3.5 to 10 MPa, to compensate for the increasing osmotic pressure of the feed (Cui, Jiang et al. 2010). As this pressure requirement is associated with high energy costs, reducing the processing time of RO per unit mass of permeate obtained would result in lower overall energy costs. This is investigated in chapter 3 where skim milk was subjected to a combination of MF and RO.

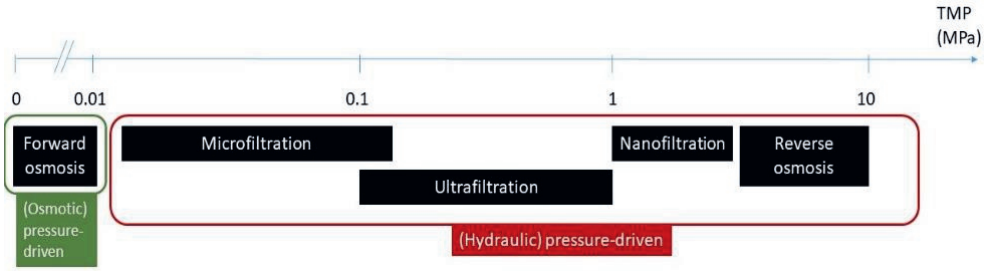

Fig. 1-2. Range of transmembrane pressures of membrane filtration processes.

Conversely, FO uses a difference in osmotic pressure between a dilute feed and a concentrated draw solution to draw water from the former to the latter. Two major challenges for application of FO is the risk of cross-contamination from draw to feed as well as the need to reconcentrate the draw solution (e.g., by thermal evaporation if reused, which leads to additional costs. It is therefore

interesting to use a concentrated waste stream as draw solution, since its large availability would negate the need for reconcentration. This is investigated in chapter 5 where delactosed permeate, a dairy-waste effluent, was employed to concentrate skim milk from 9 to 18% dry matter.

In this thesis, both hydraulic- and osmotic- pressure driven membrane processes are studied, operated either as individual systems, or as cascaded systems that are interesting from both a perspective of fractionation possibilities, as well as overall energy reduction.

1.4 Modelling of filtration performance

The performance of membrane filtration processes is generally evaluated in a top-down manner i.e. from a macro to microscale, whereby flux evolution is used as the main macro-indicator to infer solute permeation and accumulation of particles at the membrane surface, named fouling. Fouling being the limiting factor in dairy filtration (Brans, Schroën et al. 2004), a plethora of studies have focused on techniques to decrease or avoid it altogether by assessing the influence of individual operating parameter (e.g., recirculation flow rate, feed flow rate, temperature, module configuration) on its occurrence, via successive experimental trials (Lee and Merson 1976, Hiddink, De Boer et al. 1980, Maubois 1984, Luo, Ding et al. 2011, Valiño, San Román et al. 2014).

Although effective, this approach is tedious and costly and numerical simulations can considerably facilitate optimization by highlighting the most relevant parameters. Numerous studies provide insights in how to theoretically enhance the performance of MF (Le Berre and Daufin 1998), UF (Rajendran, Mason et al. 2021), NF (van der Horst, Timmer et al. 1995, Mucchetti, Zardi et al. 2000, Bowen and Welfoot 2002, Bargeman, Vollenbroek et al. 2005,

Bargeman 2016) or RO when applied to dairy streams or comparable solutions. It was shown that during MF of various dairy solutions selectivity depends on size (Le Berre and Daufin 1998), while solute rejection was correlated with pore radius and membrane charge (Bowen and Welfoot 2002), or with permeate flux (van der Horst, Timmer et al. 1995), during NF of a model salt solution.

Based on a semi-empirical approach and previously obtained experimental data, chapter 4 of this thesis proposes a model for the RO process employed for the concentration of MF-pretreated skim milk, and compares that process with conventional evaporative concentration. The influence of various operating parameters (number of membrane modules, configuration (in series or in parallel), temperature, recirculation and feed flow rate) on fouling accumulation and energy consumption is evaluated, which provides insights into optimization of RO performance and efficiency.

1.5 Thesis outline

The research described in this thesis aims at using membrane filtration technology (Figure 1-3) for dairy concentration and fractionation purposes. The performance of these processes, either as single effect or cascaded systems, is evaluated through flux measurements, and energy consumption, and compared to thermal processes.

Chapter 1 is a general introduction to this thesis.

Chapter 2 reviews the current application of cascade membrane filtration processes for the concentration or fractionation of dairy components (e.g., proteins, lactose, minerals or fat globules) for food, pharmaceutical or other industrial uses.

In **chapter 3**, a combination of microfiltration and reverse osmosis is proposed to reduce the energy consumption per unit mass of water removed compared to single-stage cold RO or evaporation.

Via numerical simulations, **chapter 4** investigates the influence of individual operating parameters on the performance of RO employed to concentrate MF-treated skim milk. The energy consumption of the proposed set-up is compared to that of conventional evaporative concentration.

Chapter 5 demonstrates the potential of delactosed permeate as an innovative draw solution in forward osmosis for the concentration of skim milk. The energy consumed by this process is compared to that of reverse osmosis.

In **chapter 6**, the main findings of chapters 2-5 are summarized and discussed in terms of their applicability in practice.

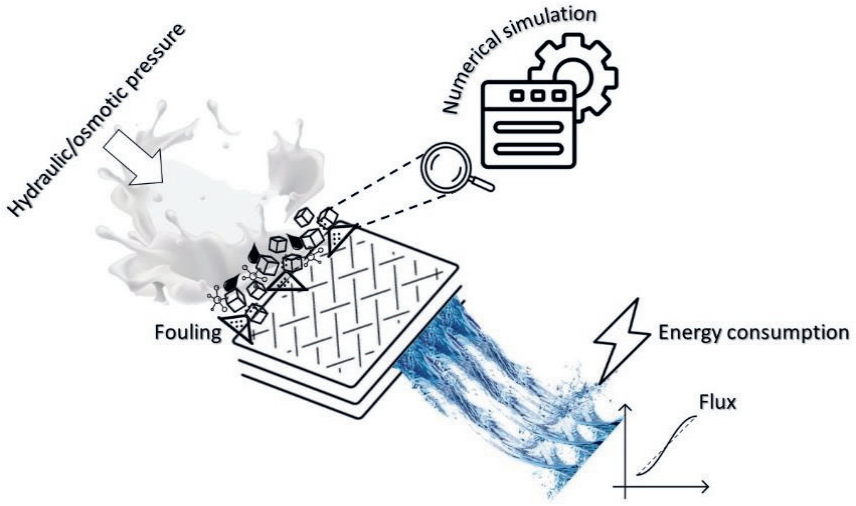

Fig. 1-3. Schematic representation of the thesis outline.

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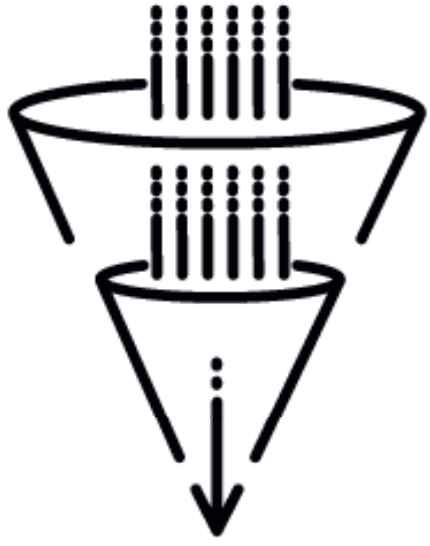
Chapter 2

A review of cascade membrane filtration systems used for enhanced concentration or fractionation of dairy streams



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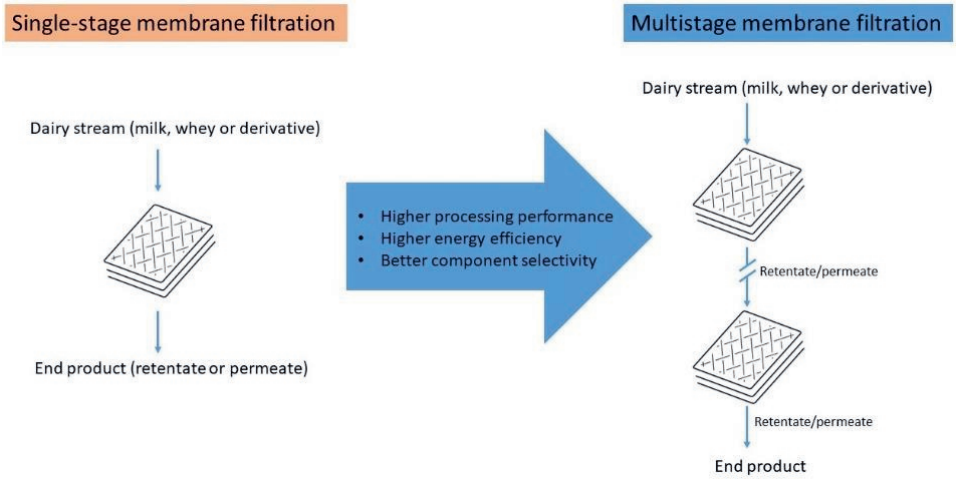
Abstract

This review considers the impact of combining discrete membrane filtration configurations in a multistage or sequential configuration to improve processing performance, energy efficiency and component selectivity in dairy processes. The review focuses on the impact of multistage membrane filtration on i) concentration processes, through the examination of fouling accumulation and its impact on flux and energy efficiency and ii) fractionation processes, whereby the yield/purity of dairy components is assessed. Observations from single-stage and batch microfiltration, ultrafiltration, nanofiltration and reverse osmosis processes reported in the literature are compared to the continuous multistage filtration processes common in commercial dairy installations.

Graphical abstract



Performance gains provided by single-stage *versus* multistage membrane filtration processes.

2.1 Introduction: improved processing efficiency at industrial scale

While for practical reasons the literature mostly addresses the application of single-stage filtration processes to dairy streams, milk processors employ nearly exclusively multistage filtration processes to improve flux performance, reduce fouling and enhance membrane selectivity (Saxena, Tripathi et al. 2009, Meyer, Petermeier et al. 2017). In a multistage membrane filtration process, the retentate or the permeate of one step totally or partially feeds the next one in series or in parallel, thereby taking advantage of complementary membrane characteristics (cut-off, material, module configuration etc.) and operating parameters (temperature, TMP, cross-flow velocity etc.).

For instance, a combination of ultrafiltration (UF) → microfiltration (MF) → UF is typically applied to whey to produce whey protein concentrates or isolates whereby the first UF step concentrates the whey by a factor of 4-5 on a volume basis, thus reducing the feed volume delivered to the subsequent MF step. The MF (~0.1 μm) step retains residual casein, protein aggregates, fat globules and microorganisms, thus reducing fouling during subsequent UF of the MF permeate (Akpinar-Bayizit, Ozcan et al. 2009).

Depending on the pore size of the MF membrane used, the retention of denatured/aggregated whey proteins may also provide the final protein concentrates with enhanced functional properties such as improved solution clarity in beverage applications. This concept as applied to whey is described by Carvalho and Maubois (2009) who reported a two-fold increase in flux performance for a multistage MF-UF process compared to a single-stage UF as a result of upstream retention of fat globules. Per unit of plant footprint and membrane area, a UF plant represents a lower capital and operational cost than

an equivalent MF plant, whereby the feed volume reduction from the initial UF step reduces the capital costs associated with the MF plant, and thus the process as a whole, in particular when utilizing ceramic MF.

In some whey protein isolates manufacturing processes, a final NF or RO step may be applied to the UF retentate for concentration prior to spray-drying, thereby removing the need for energy intensive evaporation, thus preserving the native properties of whey proteins in the absence of a thermal treatment. Notwithstanding the lower rejection of NF relative to low molecular weight milk components compared to RO, the former may be employed as a less energy-intensive process (due to lower TMP requirements) downstream of a concentrating RO plant in order to increase the final dry matter of the concentrate prior to spray drying.

Blais, Ho et al. (2021) examined the potential of a cascade of MF and RO for concentration of skim milk to improve process performance compared to RO alone. These authors did not observe improved RO performance associated with altered fouling accumulation when the system was operated at low temperature (15 °C). However, at higher temperatures (50 °C), RO flux performance was improved by a factor of 2, associated more with a lower retentate viscosity and higher crossflow velocity rather than the upstream retention of foulants by the MF step.

It was hypothesized that the multistage process, whereby microorganisms were retained by MF, would prevent microbial growth during subsequent RO concentration at this higher temperature. More precisely, the 1.4 µm MF pre-treatment of skim milk was expected to retain mesophilic and thermoduric bacteria such as Bacillus cereus, Salmonella typhimerium, Brucella abortus, Mycobacterium tuberculosis and Listeria monocytogenes as well as non-

pathogenic flora (Daufin, Escudier et al. 2001, Carvalho and Maubois 2009, Mistry and Maubois 2017).

Two-stage membrane filtration processes have also proven to be an effective method for the recovery of dairy effluents, isolating valuable components in these streams. As such, a nanofiltration pre-treatment of dairy wastewater can be employed to retain residual proteins and lactose while yielding a low-osmotic pressure permeate, from which water is recovered by a sequential RO process (Vourch, Balannec et al. 2005). To enhance permeate purification multiple NF membranes (Mavrov, Chmiel et al. 2001) or RO membranes (Koyuncu, Turan et al. 2000) can be used in series, with the permeate of one feeding the next membrane, successively retaining the organic matter from the initial feed. White water recovery strategies such as this can be used to lower the volume and chemical/biological load of effluents discharged to water treatment and also feed into a sustainable water reuse strategy for a manufacturing site.

This review considers the impact of combining discrete membrane filtration configurations in a multistage approach to improve processing performance, energy efficiency and component selectivity in dairy processes. The challenge is to compare and contrast the observations from single-stage and batch filtration processes reported in the literature to the continuous multistage filtration processes common in commercial dairy installations. For instance, when translating lab-scale findings obtained in batch mode to industrial scale trials run continuously, attention must be paid to ensure that the typically longer residence time distribution does not compromise product quality and food safety considerations. The review will address filtration processes employed to concentrate dairy streams whereby the role of MF, UF and NF on flux evolution and concentration dynamics are evaluated. In parallel, consideration will be given

to the impact of these discrete membrane processes on selectivity in terms of purity and yield of valuable milk components. While other concentration or fractionation filtration processes have been described using emerging technologies such as charged membranes (Brisson, Britten et al. 2007, Arunkumar and Etzel 2013, Arunkumar and Etzel 2014, Valiño, San Román et al. 2014, Arunkumar, Molitor et al. 2016), the authors have restricted the scope of this review to neutrally-charged membranes.

2.2 Membrane filtration processes employed by the dairy industry

Pressure-driven membrane filtration processes commonly used by the dairy industry can be broadly classified into four categories, according to pore size and rejection characteristics:

Microfiltration (MF) employs membranes with a cut-off of 0.1-10 μm in order to remove fat globules, somatic cells, vegetative bacteria or spores, and large protein aggregates from dairy streams, or for the fractionation of large macromolecules (e.g., enrichment of casein micelles and depletion of serum proteins prior to cheese-making) (Carvalho and Maubois 2009). Typical TMP varies from 0.03 to 0.2 MPa (Bhattacharyya, Williams et al. 1992).

Ultrafiltration (UF) typically uses membranes with a cut-off of 1-800 kDa operated within a TMP range of 0.1-1 MPa (Cui, Jiang et al. 2010). It is primarily used for the production of protein concentrates or isolates from milk/whey (e.g., whey protein concentrates) from which salts, lactose, water-soluble vitamins, non-protein nitrogen and other soluble solutes are removed (Gésan-Guiziou 2007). Furthermore, it can be employed to standardize the total protein and fat content of cheese/drinking milk (Carvalho and Maubois 2009). The milk/whey

permeates generated during UF are typically used for standardization purposes or for subsequent lactose production (Atra, Vatai et al. 2005).

Nanofiltration (NF) uses membranes with a typical cut-off of 150-700 Da that are applied for the concentration and partial demineralisation of whey or milk streams; whereby, dissolved mineral salts are removed inversely proportional to their valence (Mistry and Maubois 2017). The demineralization capacity is counterbalanced by the partial permeation of low molecular weight components such as lactose, dependent upon their concentration in the retentate. Nanofiltration can concentrate skim milk or whey to 20-22% dry matter in tandem with 25-50% partition of monovalent ions, which can be increased to 90% through diafiltration of the retentate. Partial demineralisation of milk/whey permeates by NF increases lactose crystallization efficiency and can reduce the hygroscopicity of resulting powders (Daufin, Escudier et al. 2001). The operating pressures of this process are typically 1-3 MPa (Cui, Jiang et al. 2010).

Reverse osmosis (RO) uses membranes operated at pressures of 3.5-10 MPa (Cui, Jiang et al. 2010) that only allow water to permeate (Carvalho and Maubois 2009). This process is used to concentrate milk/whey up to ~27% dry matter (Gésan-Guiziou 2007) before evaporation in order to reduce the overall energy consumed during milk powder production. RO performance is limited by the osmotic pressure and viscosity of the retentate at higher dry matter contents, which reduces cross-flow velocity and leads to fouling build-up overtime.

2.3 Concentration processes

2.3.1 Performance gains by MF pre-treatment

Prior to milk powder production by spray-drying, in general, milk is concentrated by evaporation. An RO installation can be added at the front end of

the process, improving energy efficiency during milk concentration (Fox, Akkerman et al. 2010). As reported by Blais *et al.* (2021), the energy efficiency of the concentration of skim milk can be further improved by the addition of an MF (1.4 µm) treatment prior to RO (Table 2-1). The authors hypothesized that the upstream retention of microorganisms (and spores) from skim milk by MF (see Table 2-4), as reported by Elwell and Barbano (2006), allows the subsequent RO step to be carried out at 50 °C as opposed to normal operational temperatures of < 10 °C without compromising microbiological safety. This increased RO flux due to lower retentate viscosity, leading to ~57% reduction in energy usage per unit water removed compared to a single-stage RO process operated at 15 °C.

Similarly, retention of microorganisms during MF (0.2 µm) pre-treatment of mozzarella whey allowed Rektor and Vatai (2004) to subject the resulting permeate to NF (400 Da) at temperatures ranging from 30 to 50 °C (Figure 2-1). Compared to subjecting whey directly to NF at 40 °C, the retention of ~67% of proteins from whey by the initial 0.2 µm MF step (see Table 2-4) increased the subsequent NF flux by a factor ~3 for volume concentration factors (VCF) up to 4.5, most likely due to a lower retentate viscosity due to the lower protein content, and possibly due to altered fouling accumulation. The retention of 19.5% lactose from whey in the initial 0.2 µm MF indicates that the VCF was in the range of 4-5 although it was not reported. The authors also evaluated the performance of the MF permeate during subsequent RO at 30 °C and observed a flux increase of 20% (from ~10 to 12 $L \cdot m^{-2} \cdot h^{-1}$) at a VCF of 2 compared to subjecting the whey directly to RO. These results are in line with observations of Blais et al (2021) who noted a marginal flux improvement when a combination of MF and RO was applied to skim milk at low temperatures, where osmotic pressure has a more significant effect on RO performance than viscosity at lower concentration factors.

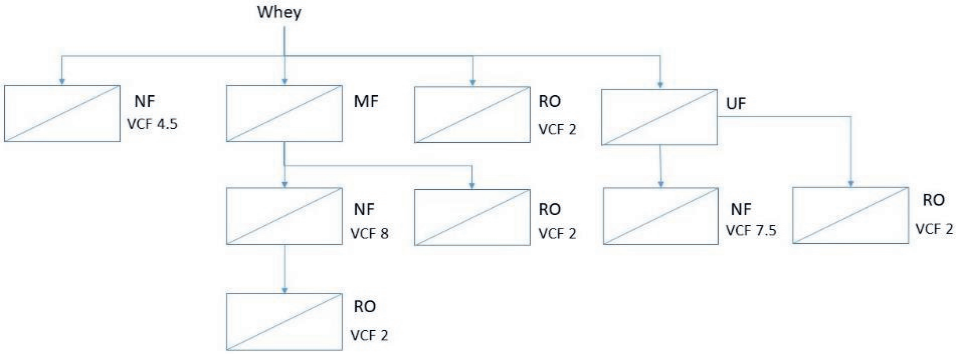


Fig. 2-1. Cascade filtration process for mozzarella whey reported by Rektor and Vatai (2004).

2.3.2 Performance gains by UF pre-treatment

In order to assess the efficacy of a UF (10 kDa) pre-treatment to reduce feed osmotic pressure, which is seen as the main limitation to RO performance, Meyer and Kulozik (2016) compared the RO flux obtained in batch-mode using three different feed solutions: skim milk, sweet whey and UF permeate (originating from clarified sweet whey). Due to the upstream protein retention of the UF treatment (see Table 2-4), the osmotic pressure and viscosity of the resulting protein-free serum was lower than that of the other feed solutions, allowing a VCF of 5.8 to be reached during subsequent RO of the ultrafiltrate compared to 3.8 or 5 during RO of skim milk or sweet whey, respectively. Furthermore, the RO flux for UF permeate increased by a factor of 1.3 and 3.4 at a VCF of 3 compared to sweet whey and skim milk, respectively. It should be noted that the UF process was performed in batch-mode and did not account for the progressive introduction of foulants, nor their accumulation during continuous filtration.

Meyer and Kulozik (2016) stated that mixing of both UF and RO retentates prior to evaporation/drying improved the efficiency of production of a recombined skim milk, or sweet whey concentrate. When directly comparing these observations to conventionally used concentration factors prior to evaporation, the benefits of the sequential UF – RO process are limited in terms of overall VCF and flux, considering the relatively low concentration factors applied during commercial RO of milk/whey. In corollary the complexity of running two discrete membrane processes in series, coupled with the additional capital and operational costs are challenged considering that the same concentration outcome can be achieved by RO alone.

Similarly, to reduce the osmotic pressure of mozzarella whey, Rektor and Vatai (2004) subjected this stream to a UF (100 kDa) treatment before either NF (400 Da) or RO of the resulting UF permeate (Table 2-1). As expected, the UF treatment retained all the fat present in the original whey, as well as 75% of the proteins and 41% of the lactose (Table 2-4), with the latter retention due to the relatively low concentration factors applied. The protein retention <100% can be explained by the permeation of individual whey proteins smaller than 100 kDa (e.g., α-lactalbumin and β-lactoglobulin), as well as to the presence of non-protein nitrogen compounds in the permeate, affecting the measured protein concentration. Due to the upstream solute retention and lower feed osmotic pressure and viscosity, a VCF of 7.5 was reached during NF of the UF permeate, compared to 4.5 for the original whey, with a concomitant ~5 fold increase in flux.

The flux improvement was significantly lower during concentration of the UF permeate by RO, increasing by a factor of 1.6 compared to direct RO of the whey at a VCF of 2. This may be associated with the higher rejection efficiency

of RO membranes, whereas the larger pore size NF membrane has a lower rejection coefficient for monovalent ions and other low molecular weight milk components, making the membrane less susceptible to osmotic pressure differentials. As the NF was operated at a 10 °C higher temperature compared to the RO process this alone may account for a significant proportion of the flux improvement observed.

Flux evolution is dependent upon feed composition, membrane cut-off, plant configuration, temperature and batch or continuous operation with many configurations reported among the studies reviewed. Patil, Janssen et al. (2014) observed that reducing the ionic strength of a whey protein isolate suspension (5 vs 50 mM NaCl at pH 7.2) resulted in a higher flux (45 vs 35 $L \cdot m^{-2} \cdot h^{-1}$). The authors suggested that the resulting change in charge affected protein-membrane interactions.

When subjecting whey to a batch UF (6-8 kDa) process, Atra et al. (2005) observed that increasing transmembrane pressure from 0.1 to 0.5 MPa resulted in an average flux increase of 40% within a VCF range of 1-5.5, although it is difficult to extrapolate this to a continuous process, due to the relatively low feed mass involved (25 kg). Nevertheless, improved flux performance relative to increasing TMP is often short lived above a so-called critical flux value, regardless of VCF, as performance gains are soon counteracted by increased concentration polarization (fouling) at the membrane surface.

In parallel, these authors observed a decrease of total protein rejection of 4.3% at the highest transmembrane pressure up to a VCF of 5, after which fouling accumulation and increased solution viscosity increased protein rejection. This can be further influenced by processing temperature whereby increasing the operating temperature from 30 to 50 °C resulted in a ~50% flux increase, linked

to a reduced viscosity and higher diffusivity of soluble components. Similarly, increasing the recirculation flow rate, and thus cross-flow velocity, from 100 to 400 $L \cdot h^{-1}$ resulted in a 100% increase in flux linked to altered fouling resistance at the membrane surface (Atra, Vatai et al. 2005).

A cascade UF/NF process has also been investigated to improve the efficiency of white water recovery during treatment of wastewater from dairy processes (Luo, Ding et al. 2011). Using a model dairy wastewater (skim milk diluted by a factor ten) and UF membranes with cut-offs ranging from 5-30 kDa, these authors achieved retention of 99.46-100% of the proteins from the dairy wastewater, while permeating most of the lactose and salts (Table 2-4). The protein retention of 99.46% was obtained with the membrane cut-off of 30 kDa thereby allowing the permeation of small whey proteins; the permeate obtained from the 10 kDa membrane was selected to feed subsequent NF. The NF treatment retained most soluble components at slightly varying selectivity dependent on TMP and VCF. Under conditions of constant flux, the TMP of this NF process was compared to that of a single-stage NF directly concentrating model wastewater. While TMP for the NF step in the cascade process remained constant (~0.8 MPa) over 120 min of filtration, it increased to 3.57 MPa in 12 min for the single-stage NF due to foulant accumulation and increases in viscosity in the filtration plant.

2.3.3 Performance gains by NF pre-treatment

To reduce the biological/chemical oxygen demand of process effluents discharged to water treatment, Yorgun, Balcioglu et al. (2008) subjected cheese whey to either single-stage UF (20 kDa, VCF 8), NF (<200 Da VCF 4), RO (VCF 1.7) or a cascade of NF/RO (VCF 6.5/1.6) processes (Table 2-1). They observed that 96% of total protein was retained by the overall cascade NF/RO process

compared to 78, 90 or 94% for single-stage UF, NF or RO, respectively (Table 2-4). Atra *et al.* (2005) retained 93-98% of total proteins from whey subjected to a UF (6-8 kDa) process, using similar transmembrane pressures (0.3-0.5 MPa) to those used by Yorgun *et al.* (0.3 MPa). The considerably higher retention from Atra *et al.* (2005) may partially be attributed to these authors not differentiating between crude (including non-protein nitrogen (NPN)) and true protein (Mariotti, Tomé et al. 2008), thus overestimating protein content as highlighted by Yorgun, Balcioglu et al. (2008).

Rektor *et al.* (2004) subjected an MF permeate (originating from mozzarella whey) to a cascade NF/RO process, whereby the NF permeate was used as feed for the subsequent RO step (Table 2-1). These authors reported a flux increase by a factor 1.6 or 1.8 for the cascaded RO step at a VCF of 1.5 or 2, respectively, compared to direct concentration by RO. The higher flux was expected as the NF process retained most solutes with the exception of a proportion of the monovalent ions and non-protein-nitrogen, resulting in a very low osmotic pressure during RO. Considering the high energy consumption of the RO process when concentrating feed at high osmotic pressures, the addition of an NF pre-treatment may be beneficial as part of a concentration and water recovery process in commercial installations.

2.4 Fractionation processes

Membrane filtration presents several advantages over conventional thermal and mechanical concentration processes (e.g., evaporation, decantation and centrifugation) such as separation of components in their native form, without deleterious effects associated with shear/temperature (Daufin, Escudier et al. 2001). Membrane filtration technology allows for a clean label approach to

fractionation of dairy components since it does not require the addition of any chemical (e.g., an enzyme or processing aide).

One of the widest applications of membranes is in the manufacture of whey fractions including concentrates and isolates, for use in infant formulae and sports nutrition products, where nutritional and functional properties can be tailored to end user requirements. Whey ingredients allow reformulation of bovine milk to closer reflect the whey/casein ratio found in human milk (fluctuating between 80/20 and 50/50 in early and late lactation, respectively (Martin, Ling et al. 2016)) rather than the 20/80 ratio of these proteins in bovine milk (Lara-Villoslada, Olivares et al. 2005). More recently attempts have been made to selectively separate individual bovine milk components such as α-lactalbumin, immunoglobulin G (IGG), and phospholipids to further humanize infant nutrition products.

2.4.1 Caseins and whey proteins

Caseins and whey proteins are valuable functional and nutritional ingredients within the food industry which can be successfully isolated by membrane filtration (Carvalho and Maubois 2009). Microfiltration in both ceramic and polymeric formats has emerged as the technology of choice for casein/whey separation with ongoing research focused on purity, and overall filtration efficiency. The following sections will assess the performance gains when using a cascade of MF, UF or NF, correlating membrane characteristics and operating parameters (where possible) to fractionation outcomes; with the filtration operational parameters of the studies reviewed reported in Table 2-2.

2.4.2 Improved selectivity by MF

Prior to cheese-making, Nelson and Barbano (2005) subjected skim milk to a 3-stage cascade filtration process to concentrate caseins and remove whey proteins while maintaining the concentration of lactose, salts and non-protein nitrogen in the retentate similar to that of milk. Initially, skim milk was subjected to MF (0.1 μm) at 50 °C to preferentially isolate whey proteins, lactose and salts from casein micelles. The MF permeate was then subjected to UF (10 kDa) at 50 °C and the UF permeate was used as a diafiltrant during subsequent MF processing. The cascade filtration process successfully partitioned 95% of the serum proteins from the original skim milk (see Table 2-4) while the casein content of the MF retentate was concentrated 3.1 times compared to that of the starting material.

When subjecting skim milk to MF (0.1 μm), Hartinger et al. (2019) obtained a higher transmission of both α-lactalbumin and β-lactoglobulin at 10 compared to 50 °C when a steady flux was reached (53 and 45% at 10 °C *versus* 50 and 38% at 50 °C, respectively) (Table 2-4). These authors also observed that β-lactoglobulin transmission decreased by a factor >11 with increasing transmembrane pressure (from 0.05 to 0.3 MPa), attributable to deformation, accumulation and compaction of casein micelles at the membrane surface.

By subjecting raw skim milk to a slightly larger membrane cut-off (0.14 μm) at 50 °C, Heidebrecht et al. (2018) retained more than 99% of intact caseins from milk, and observed increasing rejection coefficients for β-lactoglobulin and immunoglobulin G, at 35% and 50% for 0.1 and 0.2 MPa TMP respectively (Table 2-4). At higher TMP, the transmission of whey proteins progressively decreased due to either an increased accumulation at the membrane, or a pore plugging effect. It is clear that there is a critical relationship between the

application of sufficient TMP to allow protein convection towards and through the membrane, and accumulation of a fouling layer which acts as a secondary filtration layer of lower permeability. The manipulation of VCF, TMP and diafiltrant, such as use of UF permeates to maintain ionic equilibrium, are all strategies to maximise whey protein partition during MF (Nelson and Barbano (2005).

To compare protein functionality in whey obtained from either MF of milk, or from UF of cheese whey, Britten and Pouliot (1996) subjected raw milk to sequential MF treatments (1.4 μm and 0.1 μm) followed by concentration of the resulting MF permeate by UF (10 kDa) (see Table 2-2). In parallel, cheese whey was directly concentrated by UF (10 kDa). The authors observed an overall higher quality in the whey proteins produced by MF of milk compared to those produced by UF of cheese whey due to: i) the absence of degradation products from the starter culture and the upstream retention of fat by MF, which increased whey protein purity, ii) microorganism retention by MF allowed a milder heat treatment to be performed after the UF process thereby preserving native protein structures, and iii) better gelling and foaming properties as well as a higher solubility.

Table 2-1. Process parameters used in studies focusing on the concentration of dairy streams.

Ref.	Feed type	Filtration process(es)	VCF	TMP (MPa)	Temperature (°C)
Blais, Ho et al. (2021)	Skim milk	MF (1.4 μm) using tubular ceramic modules, in series with RO using spiral-wound composite polyamide modules	2-11	0.210 (MF), 2.92 (RO)	50 (MF), 15 or 50 (RO)
Rektor and	Mozzarell a whey	MF (0.2 μm) hollow-fiber or ceramic multi-tube modules,	2-7.5	0.2 (MF),	30-50 (NF), 30 (RO)

Vatai (2004)		UF (100 kDa) spiral-wound modules, NF (400 Da), RO using plate-and-frame modules		2.5-3 (NF), 4 (RO)	
Meyer and Kulozik (2016)	Sweet whey, skim milk, UF permeate (RO)	UF (10 kDa) using spiral-wound modules in series with RO using spiral-wound polyamide modules	3.8-5.8	0.3 (UF), 4 (RO)	10 (UF and RO)
Patil, Janssen et al. (2014)	Whey protein isolate solution	UF (60 kDa) using flat-sheet modules	-	0.066-0.1	25
Atra, Vatai et al. (2005)	Whey	UF (6-8 kDa) using polyvinil-difluoride or polyethersulfone modules	~5.5	0.1-0.5	30/50
Luo, Ding et al. (2011)	Diluted skim milk	UF (5-30 kDa) using polyethersulfone or regenerated cellulose modules, in series with NF (90-400 Da) using polyamide modules	5	0.1-0.4 (UF), 0.8-3.7 (NF)	25
Yorgun, Balcioglu et al. (2008)	Curd and white cheese whey	UF (20 kDa) using polyethersulfone modules, NF (<200 Da) using polyethersulfone, polyamide or polysulfone modules, RO using polyamide-urea modules	1.7-8	(UF), 0.5-0.8 (NF), 1.2 (RO)	-

*VCF: volume concentration factor; TMP: transmembrane pressure; MF: microfiltration; UF: ultrafiltration; NF: nanofiltration; RO: reverse osmosis.

When subjecting raw or heat-treated skimmed milk to MF (0.1 μm) at 50 °C, Le Berre and Daufin (1998) retained 99 and 84% of the lactoferrin (77 kDa) and lactoperoxidase (77.5 kDa) present in milk, respectively (Table 2-4). With increasing ionic strength of the feed (from 0.08 to 0.97 M) by addition of 0.92 M NaCl, lactoferrin and lactoperoxidase retention decreased to 49 and 73%, respectively highlighting the influence of ionic conditions on protein partitioning. When using MF pore sizes of 0.14 or 0.20 μm for the partition of skimmed colostrum, Gosch, Apprich et al. (2013) retained >98% of caseins, while lactoferrin retention was 73-78% and 69% for 0.14 and 0.20 μm MF membranes, respectively. The authors reported that lactoferrin purity was higher in the 0.20 μm than in the 0.14 μm MF permeate, with the retention of 89% of immunoglobulin G in the former case compared to 75-84% in the latter.

Further optimization of this process may include additional downstream cascaded filtration steps to isolate whey protein fractions of interest. A MF (0.1 μm) pre-treatment at high ionic strength, that removes caseins and immunoglobulin G, while permeating lactoferrin and lactoperoxidase, could be coupled with a sequential MF step at lower ionic strength to selectively retain lactoferrin and lactoperoxidase while allowing other whey proteins to permeate.

Table 2-2. Process parameters used in studies focusing on milk protein fractionation.

Reference	Feed	Filtration process	VCF	TMP (MPa)	Temperature (°C)
Nelson and Barbano (2005)	Pasteurized skim	MF (0.1 μm) ceramic modules, in series with UF (10 kDa) plate-and-frame polysulfone modules	3-20	0.023-0.028 (MF)	50

Le Berre and Daufin (1998)	Raw milk	MF (0.1 µm) using ceramic modules	2	0.3	50
Hartinger et al. (2019)	Skim milk	MF (0.1 µm) using spiral-wound polyvinylidene fluoride modules	-	0.05-0.3	10 / 50
Heidebrecht et al. (2018)	Raw skim milk	MF (0.14 µm) using ceramic modules	-	0.1-0.2	50
Britten and Pouliot (1996)	Raw milk Cheddar cheese whey	MF (1.4 µm), in series with MF (0.1 µm), in series with UF (10 kDa) using hollow-fiber polysulfone modules	16	0.12	50
Cheang and Zydney (2004)	Whey protein isolate enriched with 0.1% bovine serum albumin	UF (30 or 100 kDa) using composite regenerated cellulose modules	-	-	-
Almécija, Ibáñez et al. (2007)	Clarified acid whey	UF (300 kDa) with ceramic modules	5	0.1	30
Patil, Janssen et al. (2014)	Whey protein isolate solution	UF (60 kDa) using flat-sheet modules	-	0.066-0.1	25
Atra, Vatai et al. (2005)	Whey, batch-mode	UF (6-8 kDa) using flat-sheet modules	~5.5	0.1-0.5	30/50

*VCF: volume concentration factor; TMP: transmembrane pressure; MF: microfiltration; UF: ultrafiltration

2.4.3 Improved selectivity by UF

Cheang and Zydney (2004) compared the yield and purity of α-lactalbumin and β-lactoglobulin obtained when subjecting a solution of whey protein isolate (enriched with bovine serum albumin) to a two-stage UF with diafiltration, operated in batch-mode, using either a 100 kDa followed by a 30 kDa membrane, or in the reversed order (Figure 2-2). These authors observed retention of 0% α-lactalbumin and 22% β-lactoglobulin from the initial feed solution using a 100 kDa UF step (Process 1). When the permeate was further processed using a 30 kDa UF, ~30% of the overall β-lactoglobulin and 5% of the α-lactalbumin was retained by the membrane (Table 2-4).

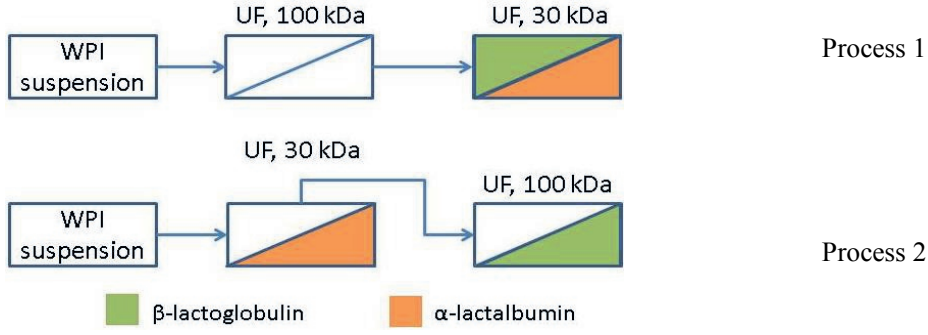


Fig. 2-2. Isolation of α-lactalbumin and β-lactoglobulin from whey protein isolate suspension using a two-stage batch UF process (Cheang and Zydney 2004).

In the second process, nearly all of the β-lactoglobulin was retained by the 30 kDa UF module and 10% of the α-lactalbumin, yielding a permeate with an α-lactalbumin purity 10-fold higher than that of the feed. Subsequently, the 100 kDa UF module retained 30% of the β-lactoglobulin, yielding a permeate with a 4-fold higher purity compared to the initial feed. The authors retained >90% of bovine serum albumin in the 100 kDa UF step of process 1; however the purity was

relatively low due to a concomitant retention of β-lactoglobulin. It should be noted that the levels of transmission of whey proteins reported by these authors are not typical for UF.

Patil, Janssen et al. (2014) proposed a cascaded UF (60 kDa) process using three identical membrane modules operated within a TMP range of 0.066-0.1 MPa in order to isolate α-lactalbumin from a whey protein isolate solution (Figure 2-3). The final product stream is the cumulative permeate obtained from the three UF processes connected in series, making use of the sequential rejection characteristics of the membrane to optimise recovery of the component of interest. While the TMP of modules 1 and 2 operated at 0.1 MPa, module 3 could only achieve a maximum TMP of 0.066 MPa due to volume constraints associated with the lab-scale process design. Despite the challenges encountered by the authors the cascade filtration process yielded an α-lactalbumin recovery of ~80% with a ratio of product to waste of 16:1. The partitioned α-lactalbumin fraction had a purity of ~70% on a protein basis. To maximize product recovery (although potentially at lower purity), the authors suggested reducing the membrane surface area of module 3 coupled with operation at a higher TMP.

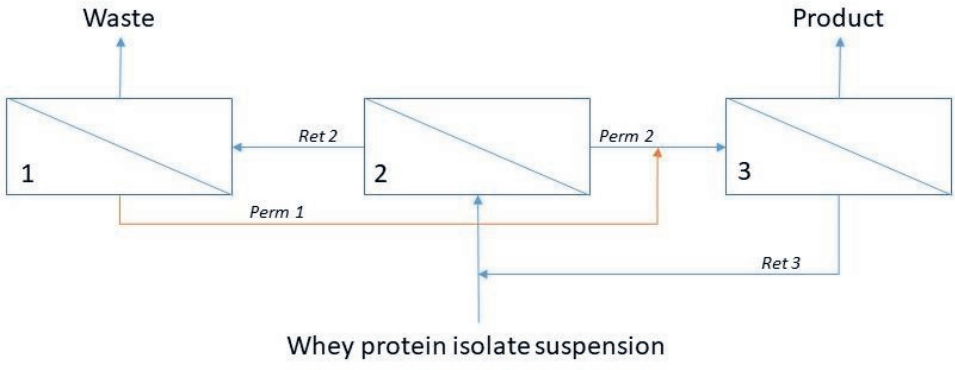


Fig. 2-3. Cascade UF process described by Patil, Janssen et al. (2014).

The observations from Patil, Janssen et al. (2014) were similar to those from Cheang and Zydney (2004), regarding the relatively low retention of α-lactalbumin by UF membranes; however, they do not align with other studies (Le Berre and Daufin 1998, Almécija, Ibáñez et al. 2007). When subjecting milk to a single-stage MF (0.1 μm, i.e. a much larger pore size), Le Berre and Daufin (1998) retained ~36% of α-lactalbumin and β-lactoglobulin, and ~87% of bovine serum albumin (Table 2-4). Similarly, Almécija et al. (2007), reported a 67 and 81% retention of α-lactalbumin and β-lactoglobulin, respectively, when clarified whey was subjected to UF (300 kDa) with diafiltration, while retaining bovine serum albumin and immunoglobulin G at ~95%. Even after additional diafiltration, 46 and 70% of α-lactalbumin and β-lactoglobulin, respectively, were retained.

The wide range of partition behaviours reported for whey proteins in the literature, particularly within the MF/UF category, makes interpretation of likely rejection coefficients a complex task. Membrane properties such as pore size (and distribution), module configuration and cascade arrangements, together with feed characteristics (including the ionic environment), and process conditions such as transmembrane pressure and fouling accumulation all affect separation performance, and should be carefully considered during process design.

2.4.4 Fractionation of milk phospholipids

The isolation of milk phospholipids by membrane filtration is the focus of a number of studies seeking to exploit their nutraceutical and techno-functional properties (Huang, Zheng et al. 2020). A summary of the operating parameters employed in these single-stage processes is presented in Table 2.3, and although many differences can be noted, the common trend is to seek process conditions conducive to counteract retention of casein micelles (50-600 nm diameter) (Fox

and Brodkorb 2008) and protein aggregates that are similar in size to milk fat globule membranes fragments (300-1000 nm) (Holzmüller and Kulozik 2016).

When subjecting buttermilk whey, generated from renneting of rehydrated buttermilk powder, to MF (0.22 μm), Miocinovic et al. (2014) obtained a retentate with a phospholipid concentration of 20.97 g·100 g^{-1} of dry matter compared to 2.49 g·100 g^{-1} of dry matter in the starting material (Table 2-4). In comparison, when using buttermilk or butter serum, phospholipid concentration went from 3.18 and 9.32 g·100 g^{-1} of dry matter in the initial feed solutions to 8.05 and 23.31 g·100 g^{-1} of dry matter, respectively, in the corresponding retentate. This was associated with simultaneous casein retention, despite the higher concentration of milk fat globule membrane in the butter serum compared to buttermilk whey.

These results are very similar to those obtained by Le, van Camp et al. (2011) and Phan, Asaduzzaman et al. (2013) who subjected reconstituted buttermilk to the same membrane cut-off (0.22 μm). The former authors obtained a phospholipid concentration of 8.4 g·100 g^{-1} of dry matter in the retentate compared to 3.36 g·100 g^{-1} in the starting material; the latter authors reported a phospholipid concentration of 9.30 g·100 g^{-1} of dry matter in the retentate compared to 3.27 g·100 g^{-1} of dry matter in the starting material. The slightly higher concentration factor obtained in these two studies compared to Miocinovic, Le Trung et al. (2014) is likely due to the concomitant addition of 1% trisodium citrate to the feed prior to MF in order to disrupt casein micelles and favour their permeation.

More generally, the removal of casein is a crucial element in separation/concentration of MFGM components from a variety of dairy streams especially when considering commercial membrane processes which may be

more susceptible to fouling during processing cycles, compared to flat-sheet membranes (Miocinovic et al (2014)).

When subjecting buttermilk whey to 0.45 μm MF to retain larger fragments, Morin et al. (2006) reported a much lower enrichment factor for phospholipids, increasing from 1.31 g·100 g^{-1} of dry matter in the feed to 1.72 g·100 g^{-1} of dry matter in the retentate, likely due to the simultaneous permeation of small fragments of MFGM (Table 2-4). Using UF (30 kDa) to minimize fat permeation, Rombaut et al. (2007) increased the concentration of phospholipids in acid buttermilk whey from 1.77 to 4.65 g·100 g^{-1} of dry matter in the retentate whereby co-retention of whey proteins was observed. This enrichment was much lower than that obtained by Barry et al. (2017) when subjecting hydrolysed buttermilk whey to UF (50 kDa) whereby the lipid content was enriched to 60.07 g·100 g^{-1} dry matter in the retentate compared to 6.84 g·100 g^{-1} of dry matter in the initial feed. Extensive hydrolysis of the whey proteins prior to UF allowed permeation of low molecular weight peptides, which when coupled with diafiltration, increased lipid purity in the retentate.

The use of higher filtration temperatures can also improve separation efficiency as reported by Konrad, Kleinschmidt et al. (2013) for hydrolysed buttermilk whey. These authors observed a 2-fold increase in phospholipid purity when increasing the filtration temperature from 10 to 40 °C. These authors also observed increased phospholipid purity with increasing molecular weight cut-off from 6 to 8.5 g·100 g^{-1} of dry matter in the retentate when using 30 or 300 kDa membranes respectively. Rombaut et al. (2007) observed a lower MFGM retention using MF (0.10 or 0.15 μm) with phospholipid concentrations in the respective retentates of 1.90 and 2.23 g·100 g^{-1} of dry matter respectively; while

for larger pore size (0.2-0.45 μm) no enrichment occurred, due to permeation of MFGM fragments (Table 2-4).

Conversely, when subjecting raw whole milk to MF (1.4 μm) thus through an even larger membrane cut-off, Hansen, Hogan et al. (2020) obtained a retentate with a total polar lipid concentration of 7.1-7.2 g·100 g^{-1} of dry matter compared to 2.5 g·100 g^{-1} of dry matter in the initial milk. Despite a larger membrane cut-off than in the previous study, this concentration factor is likely due to the less processed feed compared to acid buttermilk whey, containing therefore more preserved large MFGM fragments.

Considering the polydisperse nature of MFGM, a multistage MF process (0.1 to 10 μm) could be advantageous for separation of discrete fractions. However, the removal of casein and denatured whey proteins using an enzymatic or acidification step, or any other pre-treatment to partition colloidal or aggregated proteins is critical for selective concentration of MFGM components.

Table 2-3. Membrane processing conditions applied to milk phospholipid fractionation.

Reference	Feed	Filtration process	VCF	TMP (MPa)	Temperature (°C)
Miocinovic, Le Trung et al. (2014)	Butter serum Buttermilk Buttermilk whey	MF (0.22 μm) using hydrophilized polyvinylnilfluoride multi-flat-sheet membrane	2.5 2.5 1.25	-	45
Morin, Pouliot et al. (2006)	Buttermilk Buttermilk whey	MF (0.45 μm) using ceramic modules	2 -	0.08-0.095	8-10 -
Holzmüller and Kulozik (2016)	Buttermilk whey	MF (80 nm) using ceramic modules	-	0.1	50

Rombaut, Dejonckheere et al. (2007)	Acid buttermilk cheese whey	MF (0.1-0.45 μm) using cellulose acetate or polyethersulfone modules, UF (30 kDa) with polyethersulfone modules	4-5	0.1	40
Barry, Dinan et al. (2017)	Buttermilk whey	UF (50 kDa) using spiral-wound polyethersulfone modules	11	-	50
Konrad, Kleinschmidt et al. (2013)	Buttermilk whey	UF (30, 50, 100, 300 kDa) using flat-sheet polyethersulfone modules	20	0.15-0.2	10-55
Hansen, Hogan et al. (2020)	Raw whole milk	MF (1.4 μm) using tubular ceramic modules	-	0.05	50
Phan, Asaduzzaman et al. (2013)	Buttermilk	MF (0.22 μm) using PVDF modules	2.25	0.035-0.055	45
Le, van Camp et al. (2011)	Buttermilk	MF (0.22 μm) using PVDF modules	2.5	0.035-0.055	45

*VCF: volume concentration factor; TMP: transmembrane pressure; MF: microfiltration; UF: ultrafiltration

Table 2.4. Retention of feed components in studies focusing on the concentration or fractionation of dairy streams.

Feed	Filtration process	% of feed components retained
Raw milk	MF (0.1 μm) (Le Berre and Daufin 1998)	23-42% of α-lactalbumin, 31-45% of β-lactoglobulin, 59-87% of bovine serum albumin, 70-72% of IgG, 49-99% of lactoferrin, 73-84% of lactoperoxidase
	MF (1.4 μm) (Hansen, Hogan et al. 2020)	97.3-97.4% of fat globules, 3% of true proteins including 3% of caseins, 1-4% serum proteins, 20-24% total solids
Skim milk	MF (1.4 μm) (Blais, Ho et al. 2021)	100% of somatic cells, residual fat globules
	UF (6-8 kDa) (Atra, Vatai et al. 2005)	87% of proteins
	3-stage MF (0.1 μm) (Nelson and Barbano 2005)	>99% of fat globules, ~100% of caseins, 95% of serum proteins
	MF (0.1 μm) (Hartinger, Heidebrecht et al. 2019)	35% of α-lactalbumin, 30-95% of β-lactoglobulin, 70-95% of caseins
	MF (0.14 μm) (Heidebrecht, Toro-Sierra et al. 2018)	35-55% of IgG, >99% of caseins
Whey	MF (0.2 μm) (Rektor and Vatai 2004)	99% of fat globules, 67% of proteins, 19% of lactose
	UF (100 kDa) (Rektor and Vatai 2004)	100% of fat globules; 75% of proteins, 40% of lactose
	UF (10 kDa) (Meyer and Kulozik 2016)	11% of dry matter, 100% of proteins, 9% of calcium; 3% of sodium
	UF (60 kDa) (Patil, Janssen et al. 2014)	varying levels of α-lactalbumin and β-lactoglobulin depending on pH and cascade configuration
	UF (6-8 kDa) (Atra, Vatai et al. 2005)	83% of proteins
	UF (20 kDa) (Yorgun, Balcioglu et al. 2008)	43% of chemical oxygen demand

	NF (<200 Da) (Yorgun, Balcioglu et al. 2008)	58-97% of chemical oxygen demand
	NF/RO (<200 Da) (Yorgun, Balcioglu et al. 2008)	94% of chemical oxygen demand
	RO (Yorgun, Balcioglu et al. 2008)	90-92% of chemical oxygen demand
	UF (100 kDa) (Cheang and Zydney 2004)	0% of α-lactalbumin, 22% of β-lactoglobulin, >90% of bovine serum albumin
	UF (30 kDa) (Cheang and Zydney 2004)	10% of α-lactalbumin, ~100% of β-lactoglobulin
	UF (300 kDa) (Almécija, Ibáñez et al. 2007)	43-100% of α-lactalbumin, 67-100% of β-lactoglobulin, 94-100% of bovine serum albumin, 53-100% of IgG, 26-100% of lactoferrin
MF permeate (from skim milk or cheese whey)	RO (Blais, Ho et al. 2021)	All feed components from MF permeate
	UF (10 kDa) (Britten and Pouliot 1996)	83-95% of nitrogen compounds, 16-18% of calcium
UF permeate (from skim milk or cheese whey)	NF (400 Da) (Atra, Vatai et al. 2005)	100% of proteins, 96% of lactose
	UF (30 kDa) (Cheang and Zydney 2004)	5% of α-lactalbumin, 30% of β-lactoglobulin
	UF (100 kDa) (Cheang and Zydney 2004)	30% of β-lactoglobulin
Dairy wastewater	UF (5-30 kDa) (Luo, Ding et al. 2011)	99-100% of proteins, 100% of lipids, 0-34% of lactose
UF permeate (from dairy wastewater)	NF (90-400 Da) (Luo, Ding et al. 2011)	68-99% of lactose; 62-95% of salts

Buttermilk	MF (0.22 µm) (Miocinovic, Le Trung et al. 2014)	24% of total proteins, 31% of total lipids, 4% of ash, 2% of lactose, 31% of polar lipids
	MF (0.45 µm) (Morin, Pouliot et al. 2006)	>90% of lipids, 60-80% of proteins, 0^{-1}0% of ash
	MF (0.22 µm) (Phan, Asaduzzaman et al. 2013)	90.3% of total proteins, 100% of total lipids, 20% of ash, 3% of lactose,
	MF (0.22 µm) (Le, van Camp et al. 2011)	78% of total proteins, 97% of total lipids, 100% of phospholipids, 12% of ash, 6% of lactose
Buttermilk whey	MF (0.22 µm) (Miocinovic, Le Trung et al. 2014)	100% of total proteins, 100% of total lipids, 100% of ash, 5% of lactose, 100% of polar lipids
	MF (0.45 µm) (Morin, Pouliot et al. 2006)	>90% of lipids, 72-80% of proteins, 22-40% of ash
	MF (80 nm) (Holzmüller and Kulozik 2016)	35% of xanthine oxidase/dehydrogenase, 20% of BTN, butyrophilin, 70% of periodic acid Schiff protein
	MF (0.1-0.45 µm) (Rombaut, Dejonckheere et al. 2007)	7.4-45.8% of dry matter, 0.3-61% of ash, 29.3-75.9% of total proteins, 0.3-9.6% of reducing sugars, 54.2-96.4% lipids, 12.2-98.4% of polar lipids
	UF (30 kDa) (Rombaut, Dejonckheere et al. 2007)	37.9% of dry matter, 5.6% of ash, 29.3-82.5% of total proteins, 7.2% of reducing sugars, 99.9% lipids, 98.8% of polar lipids
	UF (50 kDa) (Barry, Dinan et al. 2017)	80% of total lipids, 59% of phospholipids
	UF (30, 50, 100, 300 kDa) (Konrad, Kleinschmidt et al. 2013)	95-99% of phospholipids
Butter serum	MF (0.22 µm) (Miocinovic, Le Trung et al. 2014)	27% of total proteins, 31% of total lipids, 8% of ash, 0% of lactose, 34% of polar lipids

*MF: microfiltration; UF: ultrafiltration; NF: nanofiltration; RO: reverse osmosis

2.5 Conclusions

By taking advantage of the characteristics of each filtration step, the use of multistage membrane filtration processes enhances the efficiency of both concentration and fractionation processes for milk and derivatives thereof, compared to single-stage approaches. MF and UF processes can be used for the selective retention of fat, microorganisms and/or proteins from dairy streams and thereby improve the purity and yield of these fractions for use in tailored nutritional products. The resulting permeates can be concentrated by NF/RO processes with improved efficiency, relative to direct concentration of the feed material, due to their ability to achieve higher concentration factors due to lower osmotic pressure and viscosity.

The permeates from NF/RO concentration processes can finally either be discharged to effluent treatment with a lower chemical oxygen demand than conventional dairy effluents or reused within commercial plants as boiler feed, cleaning-in-place or cooling waters. In general, outside of the research laboratory, membrane systems are sequentially linked in terms of scale and complementary separation characteristics and it would be beneficial to see more multistage membrane approaches for concentration and isolation of dairy components described in the literature.

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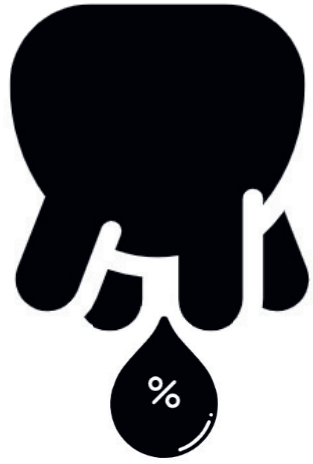
Chapter 3

Combination of microfiltration, reverse osmosis and evaporation to improve processing efficiency and reduce energy consumption during skim milk concentration



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Abstract

To improve the efficiency of water removal from skim milk, a cascade membrane process of microfiltration and reverse osmosis (RO) was developed whereby skim milk was concentrated to 18% dry matter (DM) by RO at either 15 or 50 °C. The average flux of the RO process at 50 °C was 82% higher than that observed at 15 °C, linked to altered membrane surface fouling behaviour due to lower viscosity, higher cross-flow velocity and increased diffusivity of the solvent phase. In corollary, a ~57% energy reduction per unit volume of water removed was observed when the RO process was operated at 50 °C. Evaluation of the physicochemical properties of control (9% DM content skim milk) and RO retentates post-heating (at 80, 90 and 120 °C) and post-evaporation (to 42% DM) demonstrated a clear relationship between heating at elevated DM contents and solution viscosity, an effect that was compounded at higher heating temperatures.

3.1 Introduction

3.1.1 Milk powder production: an energy-consuming process

With a global production estimated at 4–4.5 million tonnes in 2014 (Schuck, 2014), skim milk powder is one of the most widely produced dairy commodities, used as an ingredient in various food products such as yogurt, dairy desserts, baby food or animal feed. To produce skim milk powder, whole milk is pasteurized at 71–74 °C for 15 s, and skimmed using a centrifugal separator. Before evaporation, the skim milk is normally exposed to an additional heat treatment ranging from 75 to 125 °C for 5–15 s depending on product requirements relative to either microbiological safety or heat classification i.e., low, medium or high-heat (ADPI, volume IV, issue 5).

Commercially skim milk is typically concentrated using falling-film evaporators that operate under vacuum removing ~90% of the intrinsic water by indirect heat transfer. However, evaporation is an energy-intensive process, limited by product characteristics including viscosity and stability of heat labile components (Hasanoglu and Gül, 2016). To reduce energy consumption, skim milk can be pre-concentrated using reverse osmosis (RO), followed by evaporation to reach dry matter (DM) contents suitable for efficient stabilization through spray-drying (Cheryan et al., 1990; Ramirez et al., 2006).

3.1.2 A two-stage filtration approach to concentrate milk

RO membranes have a pore-equivalent diameter <0.1 nm and therefore retain all ions and larger components while allowing water to permeate. As the process is driven by pressure as opposed to heat transfer, RO preserves the native physicochemical properties of the resulting concentrates, while lowering their residence time during subsequent evaporative concentration steps (Cheryan et al.,

1990; Kulozik and Kessler, 1990; Syrios et al., 2011). However, RO has its limitations for pre-concentration due to osmotic pressure and viscosity increase of the retentate/concentrate stream. To overcome osmotic resistance, it is necessary to apply high transmembrane pressures (TMP) which negatively impact permeate fluxes which has been related to compaction of fouling materials on the membrane surface (Meyer and Kulozik, 2016). These authors found that subjecting skim milk to an ultrafiltration (UF) step before RO enhanced the processing efficiency of the latter. Indeed, owing to a larger membrane pore size facilitating the permeation of small components (e.g., lactose and minerals), the UF step yielded a protein-free serum, negating the effects of both protein-induced fouling and viscosity development during subsequent RO concentration.

These authors achieved a final VCF of 5.8 during concentration of a UF permeate by RO, which appeared advantageous compared to the maximum VCF of 3.8 observed during concentration of skim milk by RO only. Meyer and Kulozik (2016) considered the RO of UF permeate to be economically favourable when directly compared to the RO of skim milk, relative to both maximum achievable VCF and flux performance. However, the study did not elaborate on the total mass and energy balances of the cascade UF/RO process compared to a conventional RO process, which are key determinants of the industrial feasibility.

In this study, RO alone or a cascade of microfiltration (MF) and RO were assessed for pre-concentration of skim milk to a VCF of 2 before evaporation. MF was chosen to i) retain vegetative microorganisms and spores (Elwell and Barbano, 2006), which would allow the subsequent RO process to be performed at higher temperatures, resulting in an increased flux and a reduced energy consumption per unit permeate and ii) retain residual fat globules and somatic cells (Saboya and Maubois, 2000) to alter the fouling behaviour, and by proxy

flux, in the subsequent RO process. The impact of heat treatment (low, medium or high) of pre-concentrated skim milk (18% w/w DM) on the physicochemical properties of the resultant evaporated concentrate (42% w/w DM) was assessed to reflect the implications of pre-concentration relative to product viscosity and whey protein nitrogen index post-evaporation.

3.2 Materials and methods

3.2.1 Materials

Pasteurized skim milk (73.8 °C × 15 s) was obtained from a local dairy processor and was stored at 5 °C for 2 days maximum before use. Its composition was 0.5 $g \cdot kg^{-1}$ fat, 36.7 $g \cdot kg^{-1}$ total protein and 46.9 $g \cdot kg^{-1}$ lactose as measured using a MilkoScan™ FT2 (Foss Electric, Denmark), and 92.1 $g \cdot kg^{-1}$ DM as measured according to the ISO 5537-IDF26 method. Somatic cell content was measured using a Fossomatic 300 (Foss Alle, Denmark).

3.2.2 Preparation of skim milk concentrate

Concentration of pasteurized skim milk was performed according to four process scenarios (performed in duplicate) as described in Figure 3-1. In the first scenario (control), skim milk was subjected to a heat treatment, followed by evaporation to 42% (w/w) DM content. In the second scenario, skim milk was pre-concentrated to 18% (w/w) DM content by RO operated at 15 °C, followed by heat treatment and evaporation to 42% (w/w) DM content. The third ('MF/RO') and fourth ('MF/RO hot') scenarios comprised an MF step at 50 °C followed by RO concentration to 18% (w/w) DM content at 15 or 50 °C, followed by heat treatment and evaporation to 42% (w/w) DM content.

3.2.2.1 Membrane filtration

Both MF and RO processes were performed using a pilot-scale membrane plant (GEA Process Engineering A/S, Denmark) operated in continuous mode, with the retentate and permeate collected in separate tanks (Figure 3-1. B). The processing parameters are reported in Table 3-2. The feed and recirculation (retentate pressure in and retentate pressure out) pressures were constant throughout the filtration run, yielding a constant TMP. No permeate back pressure was applied during MF or RO. The plant and membranes were cleaned according to the standard clean-in-place procedure (see supporting information).

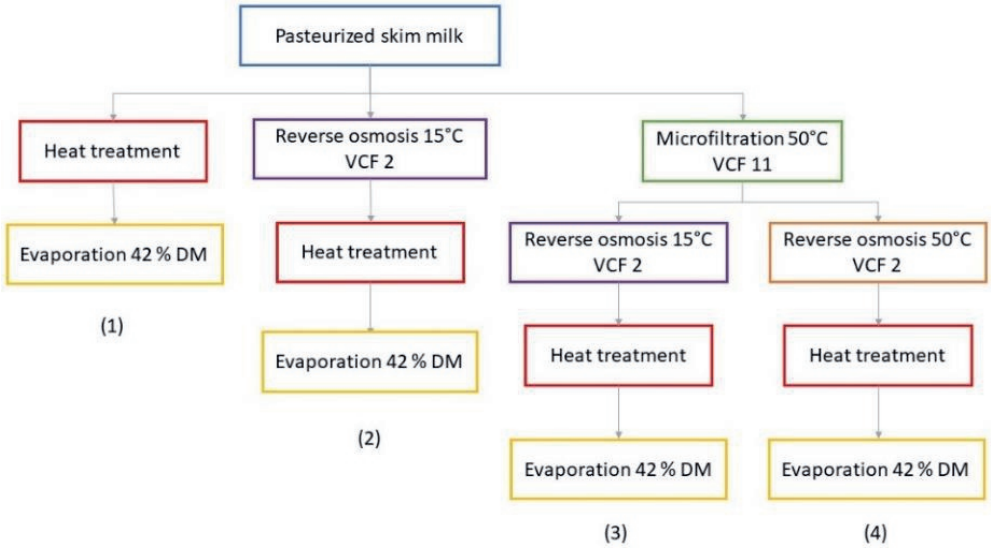

Fig. 3-1. (A) Process scenarios investigated in this study. Scenario 1 refers to the conventional concentration process while scenarios 2, 3 and 4 describe the combination of RO, MF/RO and MF/RO hot with evaporation.

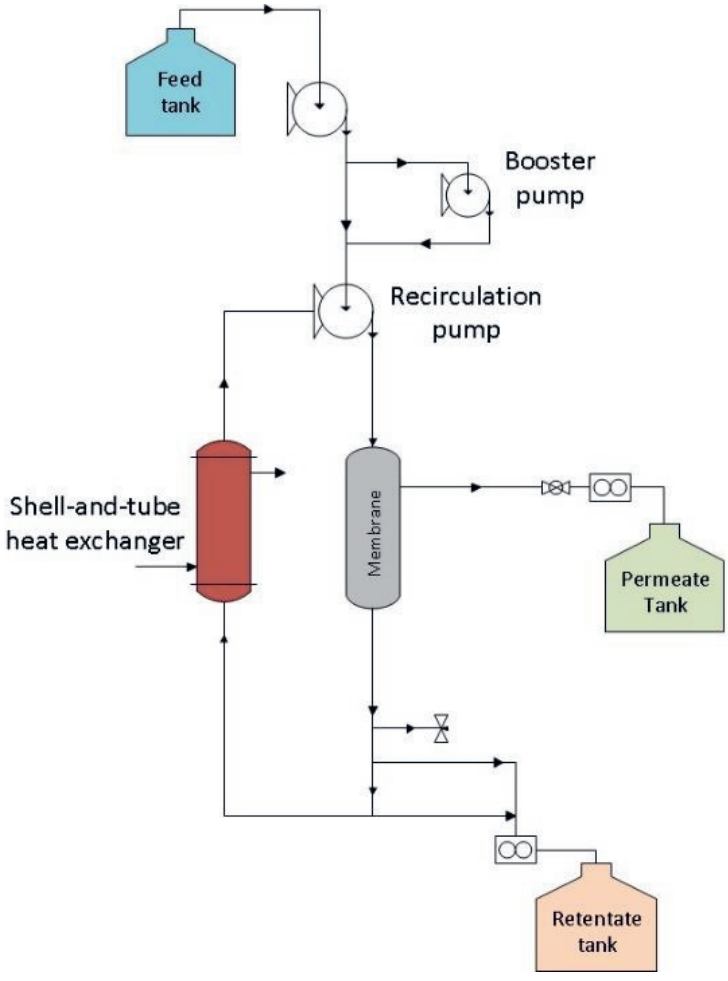

Fig. 3-1. (B) Schematic of the filtration plant.

Three tubular ceramic MF membranes with a nominal size cut-off of 1.4 µm (Isoflux™, Tami Industries, France) were used in parallel, with a total surface area of 1.05 m^2. The MF step was operated continuously for ~10 h, processing ~4800 kg of skim milk to ensure sufficient permeate was generated to feed the subsequent RO processes. RO processing was performed using two spiral-wound composite polyamide RO membranes (Dairy AF3838C30, General Electric)

connected in series, with a total surface area of 14.0 m^2. The RO processes were operated continuously for between 6-8 h at a VCF of 2; ~1300 kg of skim milk or MF permeate was fed to the RO or MF/RO processes, respectively, and ~2100 kg of MF permeate was fed to the MF/RO hot process.

The RO and MF/RO processes were performed at 15 °C, using a shell-and-tube heat exchanger within the recirculation loop to maintain the temperature throughout processing. In the hot RO process, a plate-and-frame heat exchanger was employed upstream of the feed inlet in order to heat the feed entering the membrane plant to ~42 °C. The heat generated from the high pressure pump brought the overall operational temperature of the filtration plant to 50 °C, which was maintained throughout processing.

Parameters of membrane filtration such as recirculation, retentate and permeate flow rates, as well as temperature, pressure and energy consumption of the pumps (i.e., feed, booster and recirculation pumps) and the heat exchanger were recorded using a data logger (Endress + Hauser AG, Switzerland). The average energy consumed per unit volume of permeate produced (or water removed for RO processes) was calculated for all filtration processes. All equations used in calculations, and later used as a basis for modelling of filtration performance in chapter 4 are outlined in the supporting information.

3.2.2.2 Heat treatment

Heat treatment was performed using a MicroThermics tubular heat exchanger (MicroThermics, UHT/HTSTLab-25HVHE, USA), operated at a flow rate of 2 $L \cdot min^{-1}$. Briefly, 20 kg of skim milk (9% (w/w) DM) and 10 kg of skim concentrate (18% (w/w) DM, obtained from RO processing) were heated at 80, 90 or 120 °C for 30 s. Samples were cooled to 45 °C before evaporation.

3.2.2.3 Evaporation

Evaporation was performed using a pilot-scale single-effect falling-film evaporator (Anhydro F1 Lab, Denmark), operated at 66 °C (under vacuum) in recirculation mode, at a flow rate of 50 $L \cdot h^{-1}$, until a DM content of 42% (w/w) was achieved. The approximate evaporation time was 5 min. The DM content was chosen as the highest level achievable whereby the properties of the evaporated samples would remain stable before analysis.

3.2.3 Physicochemical properties of the concentrates

3.2.3.1 Viscosity

Viscosity measurements of the retentates and evaporated samples were performed at 50 °C, using a controlled stress rheometer (AR 2000ex Rheometer, TA Instruments, UK), equipped with a concentric cylinder geometry and controlled peltier heating system. A shear rate ramp from 0 to 300 s^{-1}, followed by a holding step at a shear rate of 300 s^{-1} for 5 min, was applied to each sample.

3.2.3.2 Particle size

Particle size was measured by static light scattering using a laser-light diffraction unit (Hydro MV, Mastersizer 3000, Malvern Instruments Ltd, UK). The maximum diameter under which 90% of particles reside, D90, is reported. Measurements were performed in triplicate, at 20 °C, using a dispersant refractive index of 1.330, a particle refractive index of 1.380, a particle absorption index of 0.001 and an obscuration range of 3.5–12%. Size distributions were recorded using polydisperse analysis.

3.2.3.2 Whey protein nitrogen index (WPNI)

WPNI was measured according to the GEA Niro method (A21, 2009). Results are presented as mg native protein per g DM ($mg \cdot g^{-1}$). A WPNI ($mg \cdot g^{-1}$)

value higher than 6 corresponds to a low heat treatment, 1.5–6 corresponds to a medium heat treatment and below 1.5 corresponds to a high heat treatment.

3.2.3.3 DM content, density, osmolality and osmotic pressure

DM content was measured according to the "ISO5537-IDF26" method (ISO, 2004). Density of skim control and RO concentrates was measured with a portable densitometer (DMA35, Anton Paar GmbH, Austria) at 25 °C. Osmolality of skim control and RO concentrate was measured with a cryoscopic osmometer (Osmomat auto, GONOTEC, Germany) at 25 °C. Samples (50 µL) were placed in an Eppendorf tube and freezing point depression of samples was measured and compared to that of pure water. The osmolality, indicating the concentration of all osmotically active dissolved parts in the solvent was calculated by the instrument according to equation (1) (Gonotec 2009):

$$C_{osl}=\frac{\Delta T}{K} \quad (1)$$

with C_{osl} the osmolality (osmol·kg^{-1}), ΔT the temperature difference between sample temperature and the freezing point depression (K) and K the freezing point constant (1.858 °C kg·osmol^{-1}·K^{-1}). Osmolality values were used to calculate the osmotic pressure π (Pa) according to equation (2) (Janacek and Sigler, 2000):

$$\pi = C_{osm} \cdot \rho \cdot R \cdot T \quad (2)$$

with C_{osm} the osmolarity (osmol·m^{-3}), R the universal gas constant (8.314 N m·mol^{-1}·K^{-1}), T the solution temperature (K) and ρ the density (kg·m^{-3}).

3.2.4 Statistical analysis

Physicochemical properties including viscosity, WPNI values, and particle size were analysed using one-way analysis of variance (ANOVA), with post-hoc Tukey method using the SPSS statistics software (SPSS V.18, IBM, US).

3.3 Results and discussion

3.3.1 MF performance

The permeate flux was recorded once the system stabilised at a VCF of 11 and the DM content of the retentate had reached 9% (w/w) to ensure minimal inclusion of water during transition to product. To maintain the TMP at 210 kPa, both feed and recirculation pressures were kept constant at 310 and 110 kPa, respectively, throughout processing. The initial flux of ~400 L m^{-2}·h^{-1} gradually decreased to ~200 L·m^{-2}·h^{-1} yielding an average of 320 L·m^{-2}·h^{-1} (Figure 3-2).

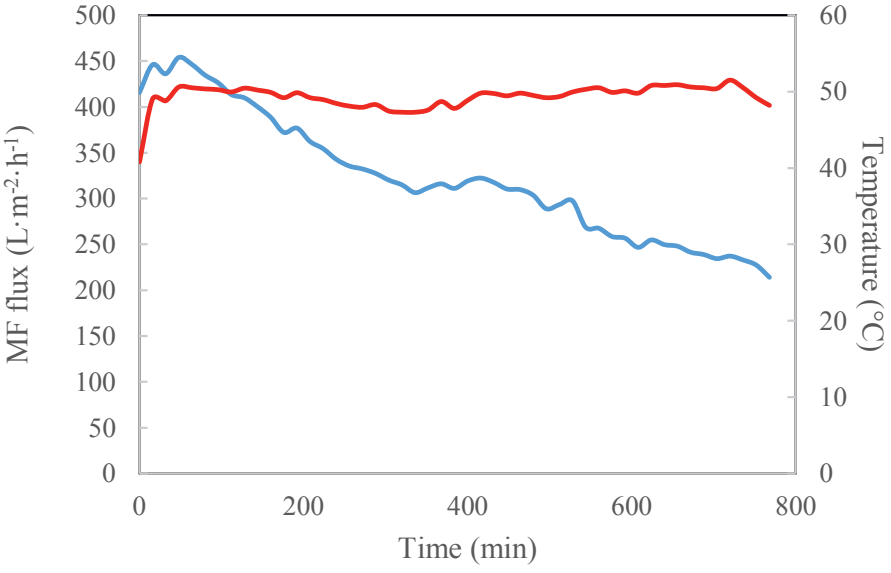

Fig. 3-2. MF permeate flux (blue) and temperature (red) as a function of time.

After initial stabilization effects, the overarching process behaviour was a progressive decrease in flux, as expected since various components (e.g., somatic cells, residual fat globules, protein aggregates) were retained, leading to a higher fouling resistance, limiting flow through the membrane. Compositional analysis (Table 3-1) showed that most of the residual fat globules and somatic cells from

the skim milk were retained, which potentially could reduce fouling and improve the efficiency of a subsequent RO step. These results align well with Elwell and Barbano (2006) who found somatic cell content reduced from 129.10^3 cells·mL^{-1} in raw skim milk to less than 3.10^3 cells·mL^{-1} in the permeate obtained from a 1.4 μm MF process. As expected at this pore size, smaller components such as minerals and lactose were found in relatively similar proportions as in skim milk.

Although no microbial analysis was performed, it can be inferred that more than 99.9% of bacteria in raw skim milk are retained by the 1.4 μm MF treatment. It was thus assumed that a subsequent RO concentration of the MF permeate could be performed at 50 °C without compromising the microbiological quality of the subsequent concentrated product. It should be noted that the utilization of the MF retentate was not described in this study as the main focus was on assessing potential efficiency gains during RO at 50 compared to 15 °C, the MF process being employed simply as pre-preparation step.

The very conservative VCF of 11 applied during MF was based on the limitations of the pilot filtration plant and the challenges surrounding accurate control of the retentate flow rate during continuous operation. Similar observations relative to the filtration performance of skim milk using large pore size MF membranes have been reported in the literature. Tan, Wang et al. (2014) observed a similar flux evolution to the current study when investigating a cold 1.4 μm MF treatment of skim milk under continuous operational conditions. These authors hypothesized a physicochemical effect whereby whey proteins tend to adsorb onto the ceramic membrane surface, while casein micelles contribute to the fouling layer proportionally to the pressure applied.

Table 3-1. Composition of the fractions obtained by membrane filtration.

Composition	Skim milk	MF permeate	MF retentate	RO retentate	MF/RO retentate	MF/RO hot retentate
Total solids (%)	9.21±0.07^{a}	9.05±0.30^{a}	9.28±0.16^{a}	17.71±0.35^{b}	17.26±0.30^{b}	17.48±0.22^{b}
Fat (%)	0.17±0.03	0.06±0.06	0.19±0.07	0.09±0.03	0.05±0.05	0.06±0.05
Total protein (%)	3.79±0.12^{a}	3.68±0.34^{a}	3.79±0.01^{a}	6.87±0.22^{b}	6.70±0.11^{b}	6.77±0.13^{b}
Lactose (%)	4.69±0.13^{a}	4.54±0.18^{a}	4.73±0.03^{a}	9.55±0.34^{b}	9.35±0.15^{b}	9.47±0.19^{b}
Casein (%)	2.82±0.11^{a}	2.73±0.37^{a}	2.82±0.01^{a}	5.36±0.15^{b}	5.17±0.05^{b}	5.25±0.07^{b}
Somatic cells (cell·mL^{-1})	105·10^{3a}	5·10^{3b}	789·10^{3c}	-	-	-
Particle size D_{90} (μm)	0.369±0.007^{a}	0.357±0.008^{a}	0.59±0.001^{b}	-	-	-

± standard deviation. Values within a row not sharing a common superscript differ significantly ($P < 0.05$)

Similar to the present study, Gosch et al. (2013) obtained an average permeate flux of ~200 $L \cdot m^{-2} \cdot h^{-1}$ when subjecting skim milk to 1.4 µm MF at 30 °C (VCF 2.4) in batch mode, with the lower averaged flux likely related to the lower processing temperature. When using a ceramic 1.4 µm MF module filled with glass beads to ensure a uniform TMP of 100 kPa, Pafylias, Cheryan et al. (1996) obtained a flux of 400 $L \cdot m^{-2} \cdot h^{-1}$ during filtration at 50 °C (VCF 10) in batch mode, most likely attributable to a higher cross-flow velocity and altered fouling behaviour compared to this study.

3.3.2 RO performance

3.3.2.1 Flux evolution in the three process scenarios

Flux evolution during RO, MF/RO and MF/RO hot processes is shown in Figure 3-3. The permeate flux was recorded as soon as the retentate DM content reached 17% (w/w) (approximately 15 min after introduction of skim milk or MF permeate into the plant). During the first hour of filtration, the flux rapidly declined in all three processes, followed by a gradual decrease throughout the remainder of the filtration processes. The strong initial decline can be associated with increasing viscosity and DM content in the retentate, causing concentration polarization during plant stabilization. Furthermore, the higher rate of flux decline for the MF/RO hot process can be explained by the higher convection of foulants towards the membrane surface per unit time as compared to the cold processes.

Once steady-state conditions relative to VCF and DM were achieved all processing parameters were kept constant thereafter, with the gradual flux decline likely attributable to the accumulation of additional fouling materials at the membrane surface leading to a concomitant increase in fouling resistance. Drawn by convective forces towards the membrane surface, solutes (protein, lactose and minerals) slowly accumulate to form a fouling layer (Skudder et al., 1977), which

increases in thickness and compaction relative to the duration of the filtration cycle (Hiddink et al., 1980). The averaged flux values of RO, MF/RO and MF/RO hot processes were 5.3±0.1, 5.7±1.0 and 10.0±2.0 $L \cdot m^{-2} \cdot h^{-1}$, respectively.

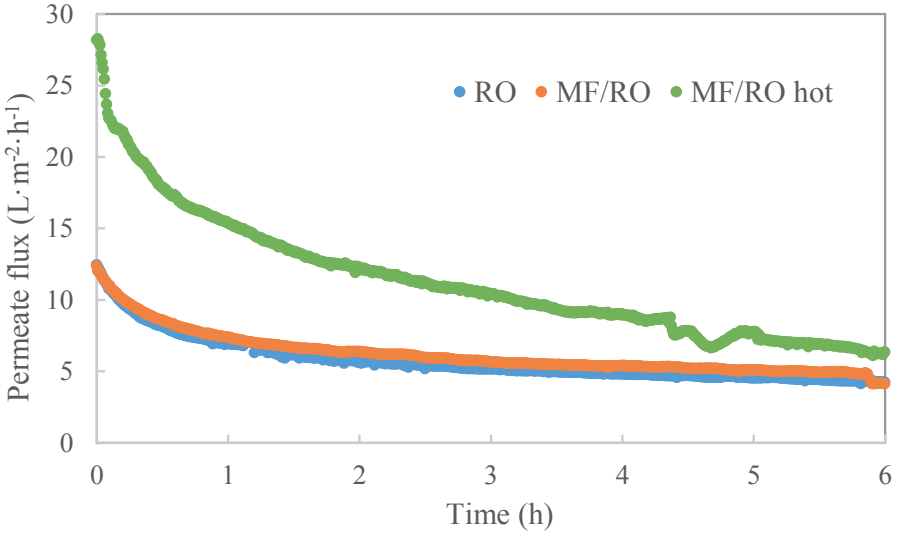

Fig. 3-3. Typical evolution of RO permeate fluxes as a function of time.

Although the difference in flux performance between the MF/RO and RO processes was small relative to the MF/RO hot process, it was significant (p-value=$3.48 \cdot 10^{-10}$), likely due to the removal of foulants (residual fat globules, somatic cells and microorganisms) by the MF pre-treatment. The MF/RO hot process had an average flux value ~82% higher compared to either cold processes. The difference in flux performance is mostly related to the lower permeate viscosity at 50 °C, coupled with a higher cross-flow velocity (Table 3-2), and possibly to a small extent the higher osmotic pressure in the MF/RO hot retentate (although the difference is very small, it may play a role near the membrane). This effect of permeate viscosity on flux is also consistent with its role in membrane resistance R_f, as described in equation (4) in the supporting information.

Table 3-2. Processing performance parameters.

	MF	RO	MF/RO	MF/RO hot
Recirculation flow rate ($kL \cdot h^{-1}$)	14.5	6.8	7.0	8.4
Crossflow velocity ($m \cdot s^{-1}$)	-	0.55	0.57	0.68
Feed pressure (kPa)	308		3005	
Recirculation pressure (kPa)	113		2830	
Permeate flux ($L \cdot m^{-2} \cdot h^{-1}$)	319.05	5.28	5.86	10.50
TMP (kPa)	210±10	2920±10	2920±10	2920±10
Viscosity of the permeate at trial temperature (mPa.s)	-	1.14±0.05	1.14±0.05	0.55±0.05
Viscosity of the retentate at trial temperature (mPa.s)	-	5.32±0.18	5.33±0.07	3.46±0.01
Osmotic pressure of the retentate (mPa)	-	1.59±0.04	1.60±0.06	1.78±0.05
VCF	11	2	2	2
Trial temperature (°C)	50±2	15±2	15±2	50±2

In corollary, as all RO retentates had similar composition and DM, the improved performance for the MF/RO hot process can also be linked to increased diffusivity of the solvent phase and altered fouling accumulation associated with a lower retentate viscosity. Thus, it appears that reduced permeate and retentate viscosity and higher cross-flow velocity are instrumental in circumventing limitations typically observed at high temperature such as calcium phosphate precipitation (Rice, Barber et al. 2009), while proliferation of thermophilic bacteria or biofilm formation, which occur at a significantly faster rate at 50 than 15 °C during UF of skim milk, are negated by the MF pretreatment (Chamberland, Messier et al. 2019).

These observations were consistent with those of Cheryan (2014) who reported a flux decrease for UF of cheese whey when increasing temperature from 10 to 30 °C followed by a flux increase at temperatures beyond 30 °C due to the outweighing benefits of lower viscosity and higher diffusivity. Likewise, Ibrahim and Mohammad (2001) noted the positive effect of temperature on RO performance, with an increase of 1 °C resulting in 3% higher flux.

3.3.2.2 Comparison of continuous to batch concentration processes

An accurate comparison with studies focusing on skim milk concentration by RO is difficult due to the prevalence of batch concentration processes in the literature compared to the continuous concentration process investigated in this study, with the latter being closer to commercial plant operation (Cheryan et al., 1990; Meyer and Kulozik, 2016). Indeed, while a fixed quantity of fouling materials is recirculating in batch mode, a continuous mode implies an increasing quantity of fouling materials being introduced to the plant, thus affecting fouling accumulation dynamics, whereby an increasing fouling resistance causes a more pronounced flux decline in continuous as opposed to batch mode.

The most relevant study describing a cascade membrane approach to improve the efficiency of RO concentration of milk components is that of Meyer and Kulozik (2016) who assessed the efficiency of a cascade of UF and RO compared to that of RO alone for concentration of UF permeate and skim milk, respectively. Logically these authors observed improved performance in the absence of proteinaceous material during RO of UF permeate, compared to RO of skim milk, with volume reduction ratios (VRR) of 5.8 and 3.8 achieved respectively.

Evaluating the VRR applied by these authors using either UF/RO or RO and considering an arbitrary skim milk volume such as 1000 kg of skim milk as initial feed, the following observations can be made:

- If the conventional RO is carried out until a VRR of 3.8 then ~737 kg of RO permeate is produced.
- In the cascade UF/RO process, to produce ~737 kg of RO permeate from a UF permeate of 5.6% DM at a VRR of 5.8 necessitates a UF permeate feed of ~890 kg.
- To produce ~890 kg of UF permeate from 1000 kg of skim milk necessitates that the UF process be performed at a VCF of 9.1 i.e. with the remaining 110 kg being the UF retentate.
- To produce a UF retentate at a VCF of 9.1 means that the ~110 kg of UF retentate would contain 34% (w/w) protein (based on a skim milk protein content of 3.71% (w/w) and not accounting for NPN loss to the UF permeate). This concentration would not be possible in the absence of substantial diafiltrationvolumes, which would necessitate additional water removal by RO.
- The production of skim milk concentrate, through recombination of the proposed cascade UF/RO retentates, necessitates a UF plant designed to produce at minimum a composition reflecting MPC70 in the UF retentate stream.
- Several authors have described the maximum concentration factors achievable during UF of skim milk relative to VCF (1.7–7), retentate total protein concentration (17–21%) and the necessity for DF water (Gesan-Guiziou, 2013; Klarenbeek, 1994; Mistry and Maubois, 2017).

It is possible that the combination of UF and RO presented by the authors as more economically efficient for concentration of total milk solids than RO alone would in fact be limited by the efficiency of the UF step in terms of achievable VCF, the implications of high protein (casein) content and high viscosity limiting UF performance at higher VCF and the requirement for DF water addition which would have to be removed during subsequent RO. In contrast a cascade MF/RO hot process as presented in this study, has a number of advantages over either a UF/RO or RO alone approach for the following reasons:

- 1.4 μm MF step can easily achieve a VCF of >50, allowing most milk components to cross the membrane.
- The large pore size MF membrane used in this study achieved an average flux value of 319 $L \cdot m^{-2} \cdot h^{-1}$ essentially limiting the need for a very large MF plant, and by proxy, limiting capital and operational costs.
- Removal of >99.9% of microorganisms (Elwell and Barbano, 2006) allows the subsequent RO process to be performed at 50 °C without compromising the microbiological quality of either the RO plant or the subsequent skim concentrate.
- Operation of the RO plant at 50 °C increases the cumulative permeate volume for a given operational cycle and hence enhances flux performance compared to cold operation, providing a realistic approach to skim milk concentration whereby capital and operational costs are minimized.

3.3.3 Fouling resistance

Throughout RO processing, fouling was expected to occur under two forms: i) organic caused by proteins, lactose or organic acids and ii) inorganic mostly related to calcium phosphate precipitation, especially at higher protein

concentrations (Hiddink et al., 1980). The third common fouling form, namely biofouling associated with growth of biomass, was excluded as i) two out of the three RO processes were performed at low temperatures, ii) for the MF/RO hot process, most microorganisms originally present in the milk were expected to be retained during the MF pre-treatment. Furthermore, the RO was operated for a relatively short duration thereby limiting microbial growth over time.

At the start of the filtration i.e. when fouling was considered negligible, the membrane resistance R_m was measured using equation (2) from the supporting information. It was found to be higher for the cold RO processes ($2.60 \cdot 10^{13}$ m^{-1}) than for MF/RO hot ($2.04 \cdot 10^{13}$ m^{-1}) certainly due to differences in osmotic pressure difference and permeate viscosity. The calculated fouling resistance (R_f) (equation 3) was then correlated to time or cumulative permeate volume (F_c), for the three RO processes, as shown in Figure 3-4. During processing, the accumulation of foulants at the membrane surface limits flux performance and plays a determining role in both operational cycle duration and subsequent cleaning requirements. Often, changes in R_f as function of processing time (Figure 3-4 A) fail to take into account variations in plant operational conditions, such as temperature, which affect permeate flux and hence process efficiency. In contrast, the expression of R_f relative to F_c (Figure 3-4 B) more accurately represents the impact of any change in operational conditions on process efficiency/flux and is thus preferred for evaluation of RO performance and fouling behaviour.

Consistently with the higher flux presented in Figure 3-3 for the MF/RO compared to RO process carried out at 15 °C, the R_f of the MF/RO process was also significantly lower (p-value=$6.02 \cdot 10^{-20}$) compared to RO, when expressed relative to time or cumulative permeate volume F_c, likely linked to foulant retention by the MF pre-treatment.

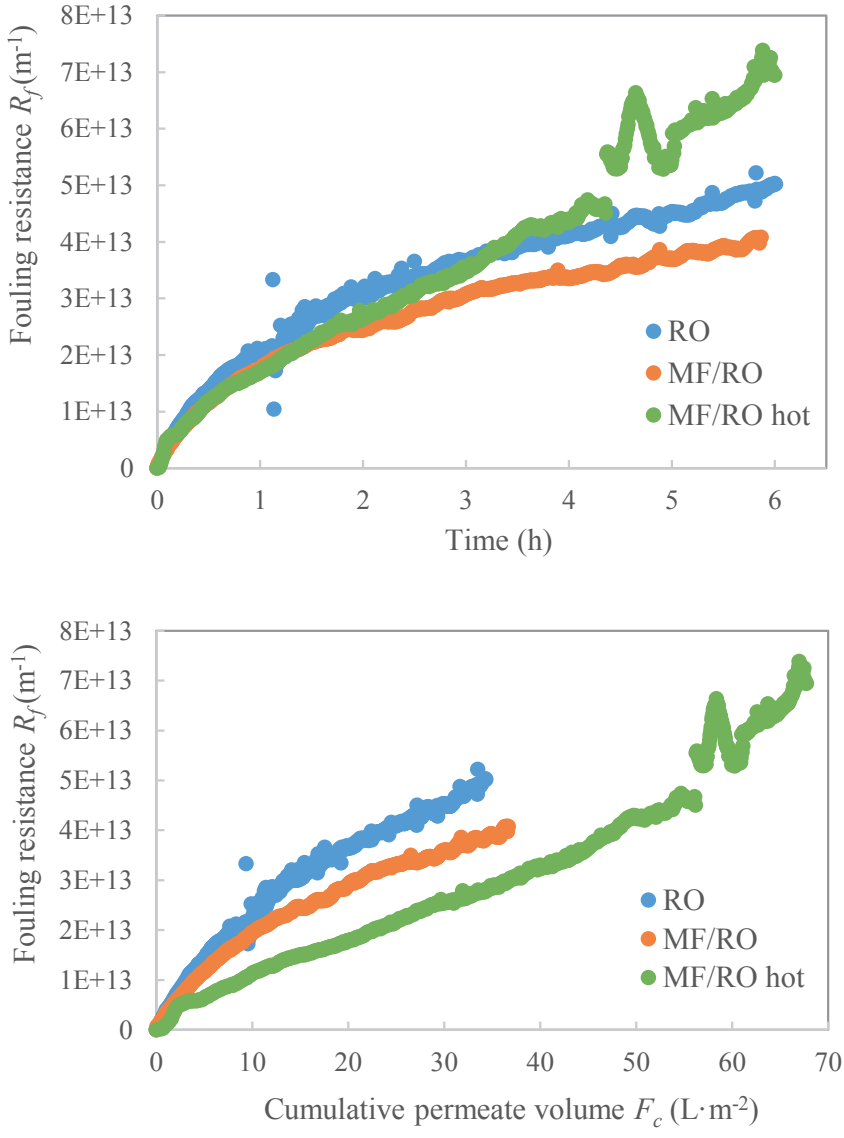

Fig. 3-4. Fouling resistances R_f of RO, MF/RO and MF/RO hot processes as a function of (A) processing time or (B) cumulative permeate volume.

The MF/RO hot process had a much higher R_f compared to the two cold processes when expressed as function of time, an observation that became particularly apparent for processing durations > 3 h (Figure 3-4 A). However, simply expressing R_f relative to time does not take into account the much higher flux at 50 compared to 15 °C which essentially means that approximately twice the volume of milk is processed per operational cycle with the potential for higher transportation rates of fouling materials towards the membrane per unit time. When expressing R_f relative to F_c, it is clear that for a given volume of permeate produced and hence skim milk processed, the R_f is actually lower at 50 than 15 °C (Figure 3-4 B). At a F_c of ~30 $L \cdot m^{-2}$, R_f values of $2.54 \cdot 10^{13}$, $3.57 \cdot 10^{13}$ or $4.51 \cdot 10^{13}$ m^{-1} were observed for the MF/RO hot, MF/RO and RO processes, respectively, clearly highlighting the potential benefits of higher operating temperatures.

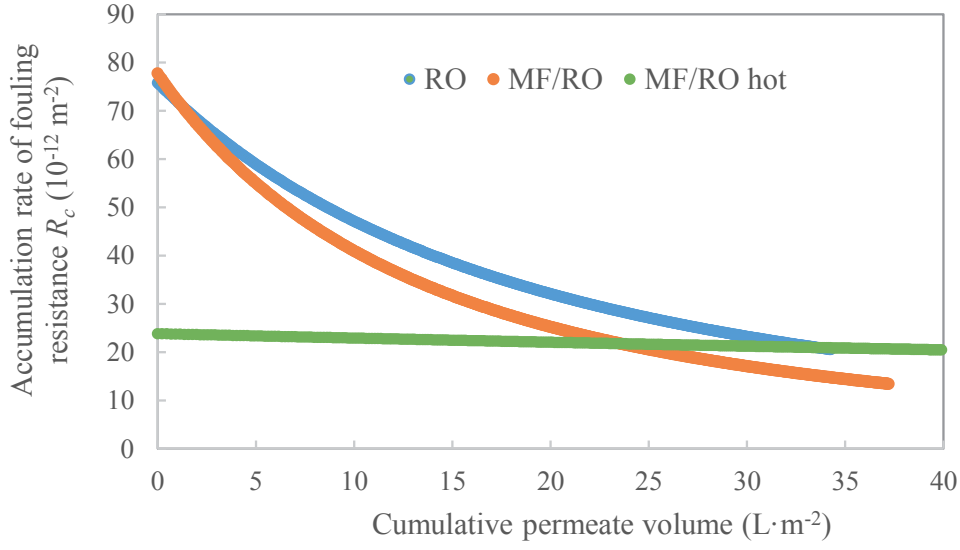

Fig. 3-5. Accumulation rate of fouling resistance R_c as a function of cumulative permeate volume.

The lower R_f relative to F_c for the MF/RO hot process could be related to lower viscosity in the MF/RO hot *retentate* (3.46 mPa·s) compared to that of RO (5.32 mPa·s) and MF/RO (5.33 mPa·s) retentates at 15°C, that allows more rapid back diffusion of components. The recirculation flow rate (Q_r) of ~8.4 $m^3 \cdot h^{-1}$ compared to 7 $m^3 \cdot h^{-1}$ for the hot and cold processes respectively, increases cross-flow velocity from 0.56 to 0.68 $m \cdot s^{-1}$, and the lower viscosity will lead to increased shear/turbulence at the membrane (Hiddink et al., 1980; Skudder et al., 1977).

When plotting the accumulation rate of fouling resistance, R_c, against the cumulative permeate volume F_c according to equation (9) from the supporting information, the coefficients shown in Table 3-3 (Figure 3-5) can be deduced. At the start of the filtration, the accumulation rate of fouling resistance R_c was found to be ~three times as high for the cold processes as compared to the MF/RO hot process, indicating a much more rapid fouling accumulation at 15 °C per unit volume of water removed.

Table 3-3. Parameters of fouling resistance R_f in function of cumulative permeate volume for RO, MF/RO and MF/RO hot processes.

	Coefficient c_1 (m^{-1})	Coefficient c_2 ($L \cdot m^{-2}$)
RO	$28.2 \cdot 10^{13}$	37.0
MF/RO	$20.6 \cdot 10^{13}$	26.3
MF/RO hot	$120 \cdot 10^{13}$	504.0

Consistently with Figures 3-3 & 3-4, this difference could be explained by the higher viscosity of the retentate and lower turbulence at the membrane surface at low temperature, enhancing concentration polarization. With increasing cumulative permeate volume F_c, the rate of fouling accumulation for both cold

processes (RO and MF/RO) decreased until it was approximately four times lower than its initial value when an F_c ~30 $L \cdot m^{-2} \cdot h^{-1}$ was reached. On average, R_c was significantly lower (p-value=$2.48 \cdot 10^{-20}$) for the MF/RO compared to RO processes at 15 °C. In contrast, R_c remained almost constant with increasing F_c during the MF/RO hot process, indicating a linear build-up of fouling resistance per unit volume of permeate produced, consistently with Figure 3-4. This suggests that lower retentate and permeate viscosity and higher cross-flow velocities at elevated temperatures are important factors for consideration during the development of R_f and subsequent evaluation of R_c.

3.3.4 Physicochemical properties of the concentrates

Skim milk control samples 9% (w/w) DM, and RO, MF/RO and MF/RO hot 18% (w/w) DM concentrates were heat-treated (80-120 °C) to ascertain the impact of pre-concentration on the physicochemical characteristics of the concentrated system post-heat treatment/evaporation using conditions commonly applied in commercial processes. The viscosity of the control and concentrates was measured directly after evaporation (42% w/w DM: Figure 3-6).

Heat treatment of RO, MF/RO and MF/RO hot concentrates (~18% (w/w) DM) at 80 and 120 °C did not significantly increase solution viscosity compared to control samples. In contrast, heat treatment at the intermediate temperature of 90 °C yielded significantly (P<0.05) higher post-evaporation viscosity for RO, MF/RO and MF/RO hot concentrates relative to the control sample, with the latter demonstrating a similar viscosity to that observed at 80 °C. WPNI values as presented in Figure 3-7, showed no significant (P>0.05) difference in heat classification between control and concentrated samples post-heat treatment at each individual treatment condition (80, 90 or 120 °C).

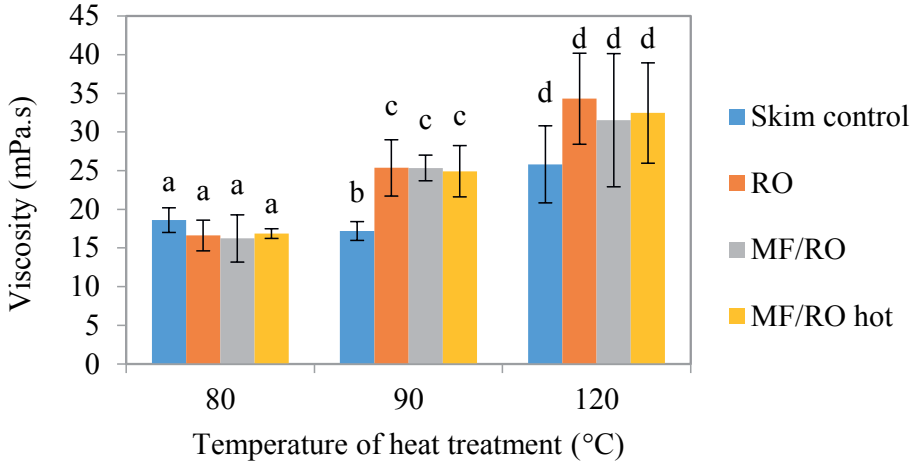

Fig. 3-6. Apparent viscosity (300 s^{-1}, 50 °C) of skim control and RO concentrates at 42% DM, subjected to heat treatments (80-120 °C). Samples not sharing a common superscript differ significantly ($P < 0.05$). Analysis of variance was performed within discrete treatment temperatures.

It is well-established that casein micelle structure is relatively heat stable (Vasbinder and de Kruif, 2003), with viscosity increases post-heat treatment likely related to whey protein denaturation/aggregation. Additionally, some of the unfolded whey proteins (primarily β-lactoglobulin) may interact with the hairy brush of casein micelles through covalent bonds between thiol groups and disulfide residues of κ- and α_{s2}-casein, increasing the volume fraction of the whey-casein micelle complexes and promoting their interactions, an effect likely exacerbated at higher DM contents (Vasbinder and de Kruif, 2003).

While there was limited difference in sample properties within a given temperature treatment in this study, which may relate to slight compositional (protein/dry matter) differences between replicate samples post-evaporation, this may not be in line with true in-process behaviours. Heat treatment, before evaporation, remains necessary to inactivate pathogenic bacteria or prevent

spoilage, thus ensuring the production of microbiologically-safe concentrates; however, the impact on physicochemical properties may have far reaching consequences relative to process efficiency and heat classification at higher DM contents and by proxy high protein contents. Processing implications surrounding increased solution DM/viscosity may include reduced heat transfer coefficients, a higher propensity for fouling in heat exchangers/pipework, which may negatively impact equipment run times, CIP intervals and discharge of milk solids to effluent treatment (Wijayanti et al., 2014).

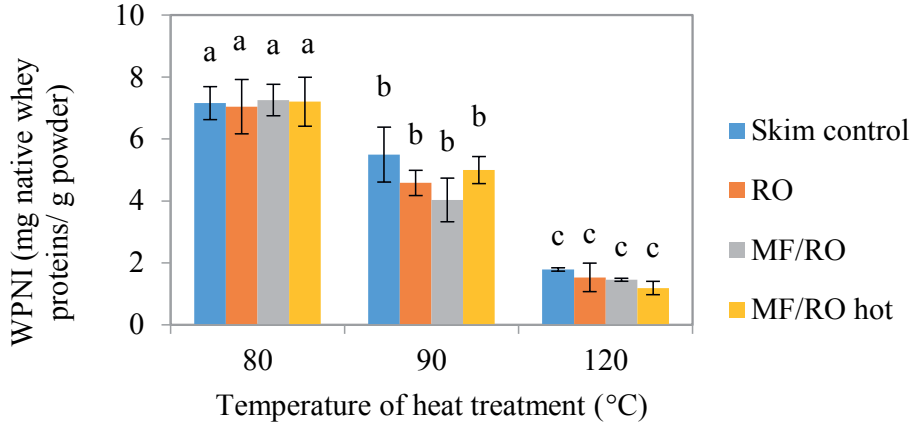

Fig. 3-7. WPNI values of skim control and RO concentrates subjected to heat treatments (80-120 °C). Analysis of variance was performed within discrete treatment temperatures.

If concentration of skim milk by RO before both heat treatment and evaporation was to be implemented at commercial scales, the addition of an MF step prior to RO could facilitate the use of lower heating temperatures before evaporation. This could limit any potential deleterious effect on both solution viscosity and WPNI values post-evaporation, while ensuring the microbiological stability and safety of the final product.

3.3.5 Energy consumption

The energy consumption of all filtration processes (MF, RO, MF/RO and MF/RO hot) was calculated based on the power consumption of the feed, recirculation and high pressure pumps, as well as that of the heat exchanger (employed to maintain RO plant at 15 °C). The total energy consumption of the RO and cascade MF/RO and MF/RO hot processes were 396.5±8.8, 421.2±21.2 and 178.5±25.4 $kJ \cdot L^{-1}$ of water removed, respectively (Table 3-4).

While the energy, utilities and chemical consumption of cleaning cycles were not considered in this manuscript, they would be relevant for operational cost at industrial scale. In order to compare the energy consumed per unit volume of water removed by the three RO processes (RO, MF/RO and MF/RO hot), the cascade MF/RO processes must also account for the energy consumed by the MF plant to produce a given volume of MF permeate to feed the subsequent RO process. In this study under a VCF of 2 for the RO process, 2 kg of MF permeate (RO feed) were required to produce 1 kg of RO permeate. Due to the relatively large pore size, low operational pressures and high temperatures employed during MF, this process consumed relatively little energy (20.6 $kJ \cdot L^{-1}$ of permeate).

On the other hand, the RO processes required a high hydrostatic pressure to overcome the osmotic resistance on the retentate side (Fell, 1995), primarily exerted by a multistage centrifugal high-pressure pump which consumed between 3.67 and 3.87 kW, with a large proportion of that energy converted directly into heat. Therefore, RO processes performed under cold conditions (RO and MF/RO) consumed more energy per unit of water removed than the MF/RO hot process, due to a combined effect of lower permeate flux and hence feed flow, coupled with the need to remove the heat generated by the high pressure pump to maintain the filtration process at 15 °C.

From the tubular heat exchanger within the membrane plant recirculation loop, that was equipped with a heat-meter it could be deduced that 2.84 - 2.94 kW was needed to maintain the plant at 15 °C. This provides a good insight into the actual energy being utilised for separation as opposed to direct conversion into heat. The cascade MF/RO process consumed ~6% more energy per unit volume of water removed compared to the RO process due to the additional filtration step in the former, as the flux characteristics for both RO and MF/RO were similar throughout processing.

Conversely, with an energy consumption of 178 $kJ \cdot L^{-1}$ of water removed, the MF/RO hot process consumed 58 and 55% less energy per unit volume of water removed compared to the MF/RO and RO processes, with ~ 421 and 396 $kJ \cdot L^{-1}$ respectively. This lower energy consumption is primarily related to the absence of cooling of the RO plant during processing at 50 °C. Essentially, the feed entering the plant at ~42 °C coupled with the heat generated by the high pressure pump yielded an overall process temperature of 50 °C.

In this study, the MF permeate feeding the MF/RO hot process was pre-heated from 5 to 42 °C using a plate heat exchanger; however, the energy consumed in this step has not been considered in the energy calculations as it was only included due to the logistics surrounding milk holding and quality implications thereof which were artefacts of the scheduling of the pilot-scale filtration trials. In the commercially envisaged process the cascade hot RO step would occur immediately after MF (50 °C), likely with some storage buffering, thus only requiring a heat exchanger to compensate for frictional heating but without a need for intermediate cooling or reheating prior to concentration.

A logical process configuration incorporating the MF/RO hot process would include pasteurisation (i.e., 73 °C × 15 s), regenerative cooling to 50 °C

before cream separation, with the skim milk thereof directly feeding the MF and subsequent RO steps, before either cooling and storage or further processing of the concentrated skim milk.

In commercial dairy plants, multiple-stage evaporators equipped with either thermal or mechanical vapour recompression (MVR/TVR) are typically employed to reduce the energy consumption associated with water removal (Ramírez, Patel, and Blok 2006). These authors reported that the typical energy demand for a 7-stage falling film evaporator equipped with TVR is ~300 $kJ \cdot L^{-1}$ of water removed. This energy demand is almost two-fold that for MF/RO hot process in this study, albeit that the concentration range was significantly lower under a VCF of 2.

Considering that a MVR evaporator consumes ~55 $kJ \cdot L^{-1}$ of water removed with a commercial RO plant consuming 20–40 $kJ \cdot L^{-1}$ (Fox et al., 2010), a number of conclusions can be drawn. Firstly, it is likely that the energy figures generated at pilot-scale greatly underestimate the efficiency of a multi-loop commercial installation. Secondly while there are clear advantages for RO pre-concentration relative to TVR evaporators the similarities in energy consumption between RO and MVR evaporators per unit water removed seem to rule out the latters combined use. However, the installation of a RO pre-concentration step to limit the size of the subsequent MVR evaporator could still be advantageous from a capital cost perspective. Finally careful consideration should be given to any retrofitting of an evaporator with a RO pre-concentration step as product flow rates, tube wetting and temperature conditions within the evaporator will all likely be affected with potentially unpredictable outcomes relative to product and process performance.

Table 3-4. Total energy consumption during performance of MF, RO, MF/RO and MF/RO hot processes.

	Feed pump (kW)	Recirculation pump (kW)	Booster pump (kW)	Heat exchanger (kW)	Total energy (kW)	Energy consumption ($kJ \cdot L^{-1}$ permeate)
RO	0.50±0.02	1.14±0.03	3.67±0.05	2.84±0.04	8.15±0.04	396±9
MF	0.17±0.11	1.85±0.05	-	-	2.03±0.03	21±2
MF/RO	0.52±0.01	1.23±0.15	3.87±0.00	2.94±0.31	8.56±0.15	380±69
Combined MF and MF/RO	-	-	-	-	-	421±21
MF	0.17±0.02	1.85±0.05	-	-	2.03±0.03	21±2
MF/RO hot	0.56±0.04	1.27±0.06	3.70±0.09	-	5.53±0.19	137±22
MF and MF/RO hot	-	-	-	-	-	178±25

± standard deviation

3.5 Conclusion

Reverse osmosis is an attractive low-cost solution for water removal from skim milk. The addition of an MF pre-treatment as part of a cascade filtration approach enhanced the subsequent RO performance at 15 °C by significantly increasing its flux and reducing its fouling resistance compared to RO alone. Furthermore, the introduction of an MF step, as a significant microbiological hurdle, allowed the subsequent RO step to be operated at 50 °C which considerably improved flux performance, limiting the accumulation of foulants at the membrane surface per unit volume of permeate produced due to a lower viscosity and higher diffusivity. Under the concentration factors applied (VCF2), >50% of the innate water in skim milk was removed, with >55% reduction in the energy usage for RO operated at 50 compared to 15 °C.

Assessment of the physicochemical characteristics of heat-treated and evaporated skim milk and RO concentrates determined no implications relative to WPNI values and by proxy heat classifications when heating RO concentrates compared to a skim milk control. However, heating RO concentrates at temperatures ⩾90 °C yielded a higher post-evaporation viscosity, which suggests that altered heating conditions pre-evaporation may be necessary to ensure subsequent drying performance is not compromised. Further work is required to determine the longevity of polymeric RO membranes subjected to operational use at 50 °C, in addition to careful monitoring of the microbiological quality of the MF permeate feeding the RO plant and the implications of high temperature processing on the growth of microorganisms within the RO plant itself during commercially representative production cycles.

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3.7 Supporting information

3.7.1 CIP procedure

Before each filtration, 2% aqueous solution of P3-Ultrasil-115 (caustic) was recirculated for 15 min at 45-50 °C and flushed with RO water. Post-filtration, three discrete cleaning steps were applied: i) a solution of 1% enzyme/caustic Ultrasil-69:67 in a 1:2 ratio (Eco lab, USA), ii) a 1% aqueous solution of Ultrasil-78 (nitric acid) (Eco lab, USA) and iii) a 2% aqueous solution of P3-Ultrasil-115. Each cleaning solution was recirculated for 15 minutes at 45-50 °C, followed by flushing with RO water for 15 minutes. Clean water flux was

measured gravimetrically before and after the filtration, as well as after CIP, using reverse osmosis water under operational conditions for both MF and RO processes.

3.7.2 Calculation of filtration performance

The transmembrane pressure $\Delta P_{TMP}(t)$ was calculated as follows:

$$\Delta P_{TMP}(t) = \frac{P_f(t)+P_r(t)}{2} - P_p(t) \quad (1)$$

with $P_f(t)$ the feed inlet pressure (Pa), $P_r(t)$ the outlet pressure of the retentate (Pa) and $P_p(t)$ the permeate pressure (Pa) at time t.

The initial RO membrane resistance at t_o, R_m, was calculated as follows:

$$R_m = \frac{A\left(\frac{P_f(t_0)+P_r(t_0)}{2} - P_p(t_0) - \Delta\pi(t_0)\right)}{Q_p(t_0).\eta(t_0)} \quad (2)$$

with A the membrane surface area (m^2), $Q_p(t_o)$ the permeate flow rate across the membrane ($m^{-3}\cdot s^{-1}$) at t_o and η the viscosity of the permeate (Pa·s).

For the fouling resistance R_f we followed (Persson and Nilsson 1991):

$$R_f(t) = \frac{A\left(\frac{P_f(t)+P_r(t)}{2} - P_p(t) - \Delta\pi(t)\right)}{Q_p(t).\eta(t)} - R_m \quad (3)$$

The total resistance $R_{tot}(t)$ is considered to be the sum of the initial membrane resistance at t_o, R_m, and the fouling resistance $R_f(t)$.

$$R_{tot}(t) = R_m + R_f(t) \quad (4)$$

Permeate flow rate Q_p ($m^3\cdot s^{-1}$) across the RO membrane is related to the hydraulic pressure (and osmotic pressure) across the membrane as follows (Shirazi, Lin et al. 2010):

$$Q_p(t) = A \cdot K_p(t)\frac{\Delta P_{TMP}(t)-\Delta\pi(t)}{\eta} = A\frac{\Delta P_{TMP}(t)-\Delta\pi(t)}{\eta \cdot R_{tot}(t)} \quad (5)$$

with $K_p(t)$ the membrane permeability (m).

The membrane permeability K_p was calculated from TMP and permeate flow Q_{po} recorded at the start of the experiment:

$$K_p = \frac{\eta \cdot L \cdot (Q_{recirc} - Q_{po})}{P_f - P_r} \quad (6)$$

with L (m) the length of the membrane module, P_f (Pa) the feed pressure at the module inlet and P_r (Pa) the recirculation pressure at the module outlet).

For RO, R_f was empirically expressed relative to cumulative permeate volume F_c in a non-linear relationship (Tong, Wu et al. 2020):

$$R_f = \frac{c_1 \cdot F_c}{c_2 + F_c} \quad (7)$$

with F_c the cumulative permeate volume across the membrane (L·m^{-2}), c_1 (m^{-1}) and c_2 (m) the coefficients of the model. Note that if $c_2 >> F_c$, the correlation between R_f and F_c would become linear as follows:

$$R_f = \frac{c_1 \cdot F_c}{c_2} \quad (8)$$

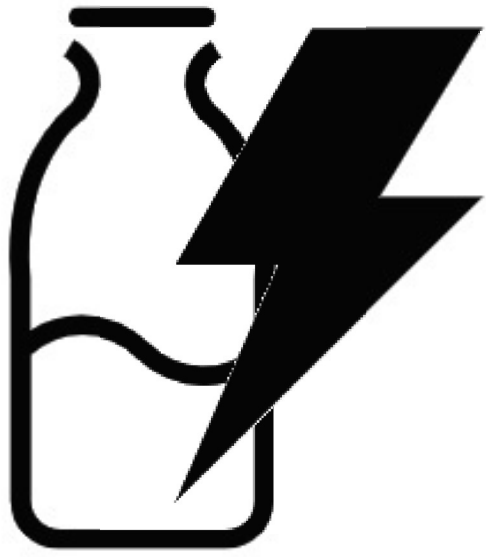
For each replicate trial, parameters c_1 and c_2 of this resistance model were estimated by minimising the sum square difference between the resistance values predicted by the model and the experimental ones using a non-linear estimation programme written in Matlab (The Mathworks, Inc., Natick, USA). The averaged coefficient values of both replicate trials were eventually used to model the fouling resistance R_f.

The rate of accumulation of fouling resistance R_c (m^{-2}) relative to cumulative permeate volume F_c was expressed as follows:

$$R_c = dR_f/dF_c = \frac{c_1 * c_2}{(c_2 + F_c)^2} \quad (9)$$

Chapter 4

Modelling reverse osmosis performance during skim milk concentration



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Abstract

Milk concentration by evaporation is the second most energy-intensive step in conventional milk powder production (next to the drying process itself). In an earlier study (chapter 3), it was shown experimentally that a combination of microfiltration and reverse osmosis (RO) reduces the specific energy consumption needed for concentration of skim milk. In the current study, the focus is on numerical simulations relative to the RO step. By modelling pressure drop and permeate flow across various module configurations, ranging from one to ten membrane elements in series or in parallel, at two temperatures (15 or 50 °C), the mean permeate flux and fouling resistance were captured. Using empirical correlations between pump energy consumption and feed or recirculation flow, the associated specific energy consumption of these processes was calculated. It was found that process efficiency was the highest when using two parallel series of five elements at 50 °C, resulting in an energy consumption of 82 $kJ \cdot L^{-1}$ of water removed. This corresponds to energy savings of 72% compared to a 7-stage falling-film evaporator equipped with thermal vapour recompression, or 54% compared to an MF-RO process operated with two elements in series, illustrating the importance of membrane configuration within the design of membrane filtration plants.

4.1 Introduction

Membrane filtration can be employed as a pre-concentration step to reduce the high-energy costs resulting from conventional skim milk concentration by evaporation (Liu, Dunstan et al. 2012, Meyer, Mayer et al. 2015, Arend, Castoldi et al. 2019). Through a combination of reverse osmosis (RO) and evaporation, for instance, skim milk was successfully concentrated to 35% dry matter, thereby reducing the cumulative energy demand associated with RO or evaporation alone, by 4 or 23%, respectively for the same dry matter content (Depping, Grunow et al. 2017).

Likewise, the combination of RO and evaporation to concentrate skim milk up to 45% dry matter reduced the energy consumed compared to six-stage evaporation, equipped with thermal vapour recompression, more than three-fold with otherwise equivalent capital and operating costs (Stabile 1983). In addition to forming part of the concentration process for a dried product, milk concentrate obtained from membrane filtration can be directly employed in a range of food products (e.g. yoghurt, ice cream, bakery products) with preserved native organoleptic and physicochemical properties due to the absence of substantial thermal treatment (Arend, Castoldi et al. 2019).

The performance of RO processes is limited by both osmotic pressure and viscosity of the concentrate, which influences the hydraulic pressure required to maintain the permeate flux at a desired level, to maximise process efficiency (Song and Tay 2011). An MF treatment preceding RO can be used to retain residual microorganisms, fat globules, and somatic cells (Blais, Ho et al. 2021), which allows the RO process to be carried out at higher temperatures (up to 50 °C), where permeate viscosity is significantly lower (0.55 at 50 °C *versus* 1.14 mPa·s at 15 °C), delivering higher flux and improved process efficiency.

Many numerical models have been developed to describe flux as function of time for nanofiltration (NF) or RO. Specific effects related to humic acid (Park, Jeong et al. 2019), sodium alginate (Hagihara, Ito et al. 2014) or bovine serum albumin (Seidel and Elimelech 2002) have been described. The proposed models often contain many parameters (and are not always validated), which complicates their use for other experiments than those for which they were set up.

To overcome this limitation Tong, Wu et al. (2020) reviewed the experimental data from 20 research groups and reported that both NF and RO processes can be described effectively by a normalized intermediate blocking model containing only two parameters: a normalized steady-state flux (normalized using the initial flux) and a fouling constant (membrane surface blocked per unit of permeate volume) ($R^2 > 0.89$, of which 80% were > 0.95). This model, considers that each foulant molecule seals one membrane pore, after which foulant stacking takes place. While this model was effective for relatively pure feed solutions, it is questionable whether it is applicable to complex feed solutions such as skim milk.

The objective of this study was to develop a model based on experimental results described in (Blais, Ho et al. 2021) to thus predict the performance of various RO plant configurations. After discretizing the RO membrane module, the local pressure drop and local permeate flow were simulated for each of the 100 segments, step by step. The local permeate flow values were subsequently summed to obtain the total permeate flow rate and by proxy, the total flux. Using the total permeate flow rate, transmembrane pressure and permeate viscosity, the fouling resistance was also calculated and correlated to the cumulative permeate volume with the two-parameter model of Tong, Wu et al. (2020), that they found described many RO and NF processes appropriately. To illustrate the rate at

which fouling accumulates per unit volume of permeate, the derivative of fouling resistance against cumulative permeate volume was calculated. Together with the energy consumption of the pumps and heat exchanger expressed per unit volume of feed processed, these flux simulations formed the basis for estimation of energy usage of various membrane process configurations.

4.2 Materials & methods

4.2.1 Experimental design

Experimental data (for filtration and energy consumption) were taken from chapter 3 (Blais, Ho et al., 2021). A MF (1.4 µm) pre-treatment was carried out at a volume concentration factor of 11, using three tubular ceramic membranes in parallel in continuous mode. Subsequently, skim milk was concentrated to 18% dry matter (VCF 2) by RO at 15 or 50 °C using two spiral-wound membrane elements in series, operated in continuous mode at a constant transmembrane pressure, at a volume concentration factor 2 (Figure 4-1). Each spiral-wound RO membrane element (Dairy AF3838C30, General Electrics) had a diameter of 9.6 cm, a length of 96.5 cm and a surface area of 7 m^2. In the hot RO process, a plate-and-frame heat exchanger was used upstream of the feed inlet.

Given the higher performance of the hot RO over RO and MF/RO processes carried out at 15 °C (see chapter 3), we focussed on optimization of RO performed at 50 °C. However, to provide the reader with a broader perspective on the efficiency gains (in addition to those from chapter 3), the performance of cold RO and/or MF/RO processes is sometimes provided in graphical representations, notably those referring to energy consumption per unit volume of permeate produced. Furthermore, these additional data points allow trends to be identified with regards to, e.g., the effect of recirculation flow rate on the rate of fouling

accumulation. Filtration processes were referred to as (i) RO for a single-stage reverse osmosis carried out at 15°C, (ii) MF-RO or (iii) MF-RO hot for combined MF-RO processes carried out at 15 or 50 °C respectively. Processing parameters relevant to the simulations are reported in Table 4-1.

4.2.2 Characterization of total flux and fouling resistance

The membrane module (Figure 4-1A and B) was first analysed as a whole unit, before subsequent evaluation thereof based on 100 discrete subdivisions.

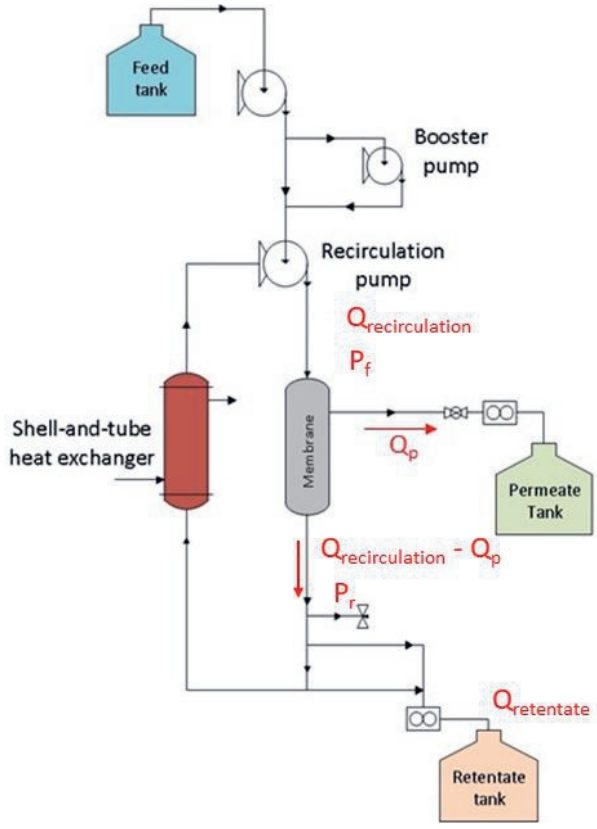

Fig. 4-1. (A) Schematic overview of the membrane filtration plant with Q_{recirc}, Q_p, $Q_{retentate}$: the recirculation, permeate and retentate flow, respectively.

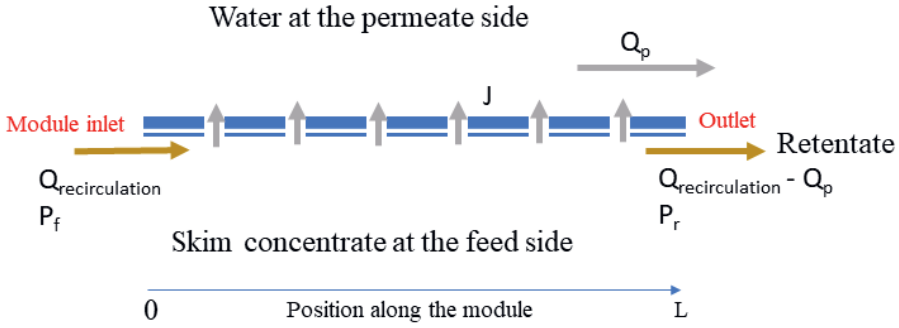

Fig. 4-1. (B) RO module with corresponding model parameters.

The pressure at the module inlet P_f and outlet P_r were kept constant over the filtration trial and the permeate pressure (approximately equal to atmospheric pressure), was assumed negligible relative to P_f and P_r (see Table 4-1 for parameter values). The effective transmembrane pressure (TMP) is therefore a function of the osmotic pressure difference $\Delta\pi$, and thus reduces along the module length with progressive water permeation. For one-dimensional flow through a body of variable permeability, the permeate flux, J ($m \cdot s^{-1}$), over the entire membrane module (Ethier and Kamm 1989) was calculated using:

$$J = \frac{\Delta P - \Delta\pi}{\eta \cdot (R_m + R_f)} = \frac{Q_p(t)}{A} \qquad (1)$$

with ΔP (Pa) the TMP, $\Delta\pi$ (Pa) the osmotic pressure difference, η (Pa·s) the permeate viscosity, R_m (m^{-1}) the membrane resistance, R_f (m^{-1}) the fouling resistance, $Q_p(t)$ ($m^3 \cdot s^{-1}$) the permeate flow over the entire module, and A (m^2) the membrane surface area of the module.

The membrane resistance R_m was determined when fouling was negligible (at the start of the experiment):

$$R_m = \frac{A(\Delta P - \Delta\pi)}{Q_{po} \cdot \eta} \quad (2)$$

with Q_{po} ($m^3 \cdot s^{-1}$) the permeate flow rate at the start of the experiment.

The fouling resistance R_f was expressed relative to the cumulative permeate volume F_c (rather than relative to time as described in chapter 3), following a non-linear expression derived by (Tong, Wu et al. 2020) that was shown to efficiently describe the twenty studies reviewed in their work:

$$R_f = \frac{A\left(\frac{P_f(t)+P_r(t)}{2} - P_p(t) - \Delta\pi(t)\right)}{Q_p(t).\eta(t)} - R_m = \frac{c_1 \cdot F_c}{c_2 + F_c} \quad (3)$$

with F_c ($L \cdot m^{-2}$) the cumulative permeate volume across the entire module, and c_1 (m^{-1}) and c_2 (L m^{-2}) model parameters (Table 4-1). As described in chapter 3, for each trial, the model parameters were determined by minimizing the sum squares of the resistance, using a non-linear script in Matlab (The Mathworks, Inc., Natick, USA). The averaged parameter value of both replicate trials was used to describe the fouling resistance R_f.

The accumulated fouling resistance, R_c (m^{-2}), was expressed as function of cumulative permeate volume F_c as:

$$R_c = \left.\frac{\partial R_f}{\partial F_c}\right|_{F_c=0} = \frac{c_1 \cdot c_2}{(c_2 + F_c)^2} \quad (4)$$

The permeability tensor K (m^4) of the module was calculated from the pressure at the module inlet P_f and outlet P_r, and the permeate flow recorded at the start of the experiment Q_{po} (Whitaker, 1986). In this study, K was assumed to be constant for a given trial temperature and expressed as:

$$K = \frac{\eta \cdot L \cdot (Q_{recirc} - Q_{po})}{P_f - P_r} \quad (5)$$

with L (m) the length of the membrane module.

4.2.3 Calculation of local permeate flow and pressure drop along the membrane length

To predict the permeate flow and pressure drop in membranes of different lengths and configuration (in-series *versus* in-parallel), the membrane module was discretized into 100 segments. The module used in the experiments (total length L =1.93 m) was thus discretized in segments of equal length dl and width W (= 0.096 m) as illustrated in Figure 4-2.

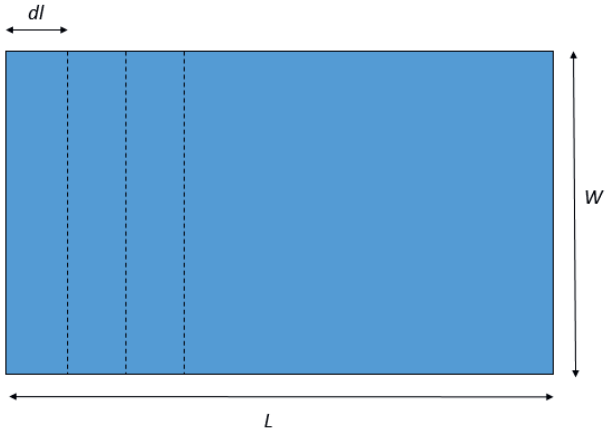

Fig. 4-2. Schematic of module discretization in segments of length *dl*.

The local permeate flow $dQ_p(l)$, ($m^3 \cdot s^{-1}$), i.e., the permeate flow calculated across each of these small membrane sections, can be expressed as:

$$dQ_p(l) = \frac{0.5 \cdot (P(l) + P(l+dl)) - \Delta\pi}{(\eta \cdot R_{tot})} \cdot W \cdot dl \qquad (6)$$

with R_{tot} (m^{-1}), the total resistance equal to $R_m + R_f$, $P(l)$ (Pa), and $P(l+dl)$ (Pa) the pressure at the inlet and outlet of a membrane portion, respectively.

In analogy to the equation described by Whitaker (1986), the local product (milk) flow $Q_{milk}(l)$ ($m^3 \cdot s^{-1}$) can be expressed as:

$$Q_{milk}(l) = -\frac{K}{\eta} \cdot \frac{\partial P(l)}{\partial l} \sim -\frac{K}{\eta} \cdot \frac{P(l+dl) - P(l)}{dl} \qquad (7)$$

with K (m^4) the permeability tensor, and $\frac{\partial P(l)}{\partial l}$ ($Pa \cdot m^{-1}$) the pressure drop between position l and $l+dl$ along the module.

Based on a mass balance principle, $Q_{milk}(l)$ can also be expressed as:

$$Q_{milk}(l) = Q_{recirc} - \int_0^l \frac{\partial Q_p}{\partial l}(u)du \quad (8)$$

with Q_{recirc} ($m^3 \cdot s^{-1}$) the ingoing recirculation flow at the module inlet (l=0) and $\frac{\partial Q_p}{\partial l}$ ($m^3 \cdot s^{-1}$) the permeate flow across one membrane section. The integral refers to the permeate flow measured from the module inlet (l=0) to position l.

Using equations (7) and (8), the pressure drop between position l and $l+dl$ along the module can be expressed as:

$$\frac{\partial P(l)}{\partial l} = -\frac{\eta}{K} Q_{milk}(l) = -\frac{\eta}{K}\left(Q_{recirc} - \int_0^l \frac{\partial Q_p}{\partial l}(u)du\right) \quad (9)$$

which implies, for the next position ($l+dl$) that:

$$Q_{milk}(l+dl) = Q_{recirc} - \int_0^{l+dl} \frac{\partial Q_p}{\partial l}(u)du$$

$$= Q_{recirc} - \int_0^l \frac{\partial Q_p}{\partial l}(u)du - \int_l^{l+dl} \frac{\partial Q_p}{\partial l}(u)du$$

The circled term corresponds to $dQ_p(l)$ in equation (6). Hence:

$$dQ_p(l) = Q_{recirc} - \int_0^l \frac{\partial Q_p}{\partial l}(u)du - Q_{milk}(l+dl)$$

$$= Q_{recirc} - \int_0^l \frac{\partial Q_p}{\partial l}(u)du + \frac{K}{\eta} \cdot \frac{P(l+dl) - P(l)}{dl}$$

$$\Leftrightarrow dQ_p(l) - \frac{K}{\eta} \cdot \frac{P(l+dl)}{dl} = Q_{recirc} - \int_0^l \frac{\partial Q_p}{\partial l}(u)du - \frac{K}{\eta} \cdot \frac{P(l)}{dl} \quad (10)$$

With equations (5) and (10), the following system is obtained, with two linear equations and two unknown variables $dQ_p(l)$ and $P(l+dl)$:

$$\begin{cases} dQ_p(l) - \frac{K}{\eta} \cdot \frac{P(l+dl)}{dl} = Q_{recirc} - \int_0^l \frac{\partial Q_p}{\partial l}(u)du - \frac{K}{\eta} \cdot \frac{P(l)}{dl} \\ dQ_p(l) - \frac{(P(l+dl) \cdot W \cdot dl) - \Delta\pi}{2 \cdot \eta \cdot R_{tot}} = \frac{(W \cdot dl)}{\eta \cdot R_{tot}} \cdot (0.5 \cdot P(l) - \Delta\pi) \end{cases} \quad (11)$$

The experimental ingoing recirculation flow Q_{recirc} and the pressure at the module inlet P_f were used as inputs for this system (i.e., the boundary conditions at l=0). The recirculation pressure P_r at the module outlet (l=L) was used together with P_f to calculate the permeability tensor K for the entire module. Subsequent local permeate flow and local pressure values were determined, step-by-step, using a model written and solved in Matlab (The Mathworks, Inc., Natick, USA).

From equation (3), the local fouling resistance $R_f(l)$ at time t and position l can be written as:

$$R_f(l) = \frac{c_1 \cdot \int_0^t \frac{\partial Q_p}{\partial l}(l)\, dt}{c_2 + \int_0^t \frac{\partial Q_p}{\partial l}(l)\, dt} \qquad (12)$$

The local pressure drop, local permeate flow (equation 11) and the local fouling resistance (equation 12) along the one-dimensional membrane module were numerically solved for time steps of 30 seconds using a finite difference method to determine the non-linear fouling resistance behaviour. The simulations were used to evaluate performance of different membrane plant configurations.

4.2.4 Energy consumption

The energy consumed per unit volume of RO permeate produced, E_{ROperm} (kJ·L^{-1}), was calculated as follows:

$$E_{ROperm} = \frac{E_{pF} + E_{pR} + E_{pB} + E_{he}}{Q_p} + 2 \cdot E_{MFperm} \qquad (13)$$

with E_{pF}, E_{pR} and E_{pB} (J·s^{-1}) energy consumption of feed, recirculation and booster pumps, respectively, E_{he} (J·s^{-1}) energy consumption of heat exchanger and E_{MFperm} specific energy consumed during MF pre-treatment (20.6 kJ·L^{-1} permeate). The factor 2 relates to the volume concentration factor during RO. The feed and recirculation flows dictate the energy consumed by the pumps, and were used to calculate the energy for other module configurations (Figure 4-3).

Table 4-1. Processing parameters recorded or calculated based on experimental data from RO trials (post-MF treatment) carried out by Blais, Ho et al. (2021).

	RO at 15°C	RO at 50°C
Recirculation flow rate ($L \cdot h^{-1}$)	7000	8400
Feed pressure P_f (kPa)	300.5	
Recirculation pressure P_r (kPa)	283.0	
Permeability tensor K (m^4)	$1.22 \cdot 10^{-9}$	$7.66 \cdot 10^{-10}$
Permeate flux Q_p ($L \cdot m^{-2} \cdot h^{-1}$)	5.86	10.5
Turgor pressure (kPa)	16.44	18.26
Transmembrane pressure (kPa)	2920±10	
Viscosity of the retentate (mPa.s)	5.33±0.07	3.46±0.01
Viscosity of the permeate (mPa.s)	1.14±0.05	0.55±0.05
Osmotic pressure of the retentate (MPa)	1.60±0.06	1.78±0.05
Parameter c_1 (m^{-1})	$20.6 \cdot 10^{13}$	$120 \cdot 10^{13}$
Parameter c_2 ($L \cdot m^{-2}$)	26.3	504.0
Membrane surface area (m^2)	14.0 (or 7 m^2 per element)	

4.2.5 Module arrangement

Pressure drop limited the number of elements that could be placed in series to 5 (Figure 4-3; configuration A); a maximum of 10 was achieved by placing an additional series of 5 in parallel (configuration B). Simulations were performed for 15 and 50 °C for 18 hours duration, representative of commercial operation.

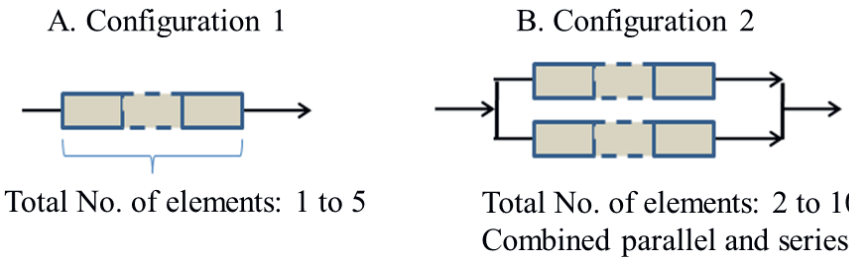

Fig. 4-3. RO plant with an in-series (A) and in-parallel (B) membrane cascade.

4.3 Results and discussion

4.3.1 RO performance: permeate flux and fouling accumulation

Most of the following results are for RO operated at 50 °C given its better performance compared to RO or MF-RO at 15 °C as described in chapter 3.

Using the permeability tensor K and the local pressure drop simulated along an RO module of two elements in-series, operated at 50 °C, the local permeate flow $dQ_p(l)$ was calculated (equation 11). Subsequently, its values for the discrete membrane portions of length dl were summed to obtain the total permeate flow, and by corollary the total flux. The resulting permeate flux is presented in Figure 4-4, at a recirculation flow Q_{recirc} = 8.2 $m^3 \cdot h^{-1}$, over a period of ~8.3 h. The R^2 value between experimental and simulated values was 0.99, indicative of a good fit.

Due to the head loss along the module length as well as to increasing osmotic pressure difference and viscosity associated with progressive water permeation (Shrivastava and Stevens 2018), the pressure difference along the module decreased from P_f ~3005 kPa at the inlet to P_r ~2830 kPa at the module outlet with a concomitant flux decline over time due to foulant accumulation and concentration polarization (Fortunato 2020). For RO of skim milk, Kulozik and Kessler (1988) have shown that the decline in permeate flux is caused by both an

increased osmotic pressure due to the accumulation of soluble materials, e.g. salts and lactose, as well as to a deposit layer of milk proteins.

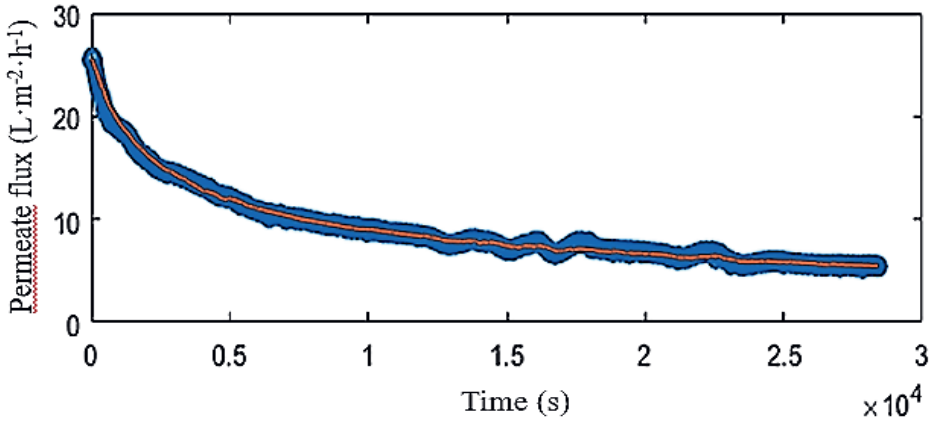

Fig. 4-4. Experimental data (blue symbols) and model prediction (red line) of RO flux performance at 50°C, with a recirculation flow rate Q_{recirc} = 8.2 $m^3 \cdot h^{-1}$, P_f~3005 kPa and P_r ~2830 kPa.

In Figure 4-5, the accumulation rate of fouling resistance R_c was plotted against time and position along two membrane elements in series (of total length 1.93 m) operated at 50 °C, for recirculation flows Q_{recirc} of 8.2 or 8.6 $m^3 \cdot h^{-1}$. The rate of accumulation was strongest in the first two hours of filtration (as indicated by the dark and light blue colours) when the permeate flux was highest. The time scale represented is from 0 to 4.3 h, after which the flux reached a steady-state and variations of R_c in the latter stages of the process cycle were negligible.

Due to the pressure drop along the membrane, R_c slightly decreased with increasing distance from the inlet. An increase in recirculation flow by ~5% (8.6 *versus* 8.2 $m^3 \cdot h^{-1}$) reduced the accumulation rate of fouling resistance by ~17%, highlighting the critical role of recirculation flow rate and by proxy the cross-flow velocity in controlling fouling build-up.

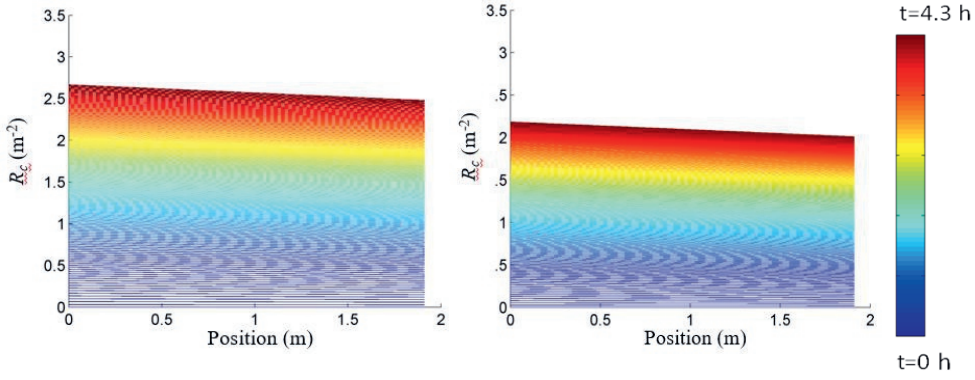

Fig. 4-5. Accumulation rate of fouling resistance R_c along two RO membrane elements in series, operated at 50 °C and exposed to different recirculation flow rates: Q_{recirc} = 8.2 (A) or 8.6 $m^3 \cdot h^{-1}$ (B).

The effect of fluid velocity on fouling accumulation along a spiral-wound membrane was compared among all RO processes reported in chapter 3 ($RO_{15°C}$, MF-$RO_{15°C}$ and MF-$RO_{50°C}$) by plotting the accumulation rate of fouling resistance R_c against the average recirculation flow (Figure 4-6); duplicate trials were distinguished ('Trial 1' & 'Trial 2'). When considering all data as a whole, R_c decreases (linearly) with increasing cross-flow velocity (Choi, Zhang et al. 2005), and seems independent of the temperature used. Numerous studies have shown a positive effect of cross-flow velocity on fouling mitigation (Belfort, Davis et al. 1994, Chong, Wong et al. 2008, Subramani and Hoek 2008); in fact, it is the main strategy used to maintain highe fluxes. The impact of cross-flow velocity on fouling accumulation is dependent on the component considered; particles are for instance transported through different mechanisms as molecular components, as reported by e.g., Radu, van Steen et al. (2014). This has led to critical flux and uniform low transmembrane concepts, and other hypotheses focusing on particle migration, as reviewed by Schroën, van Dinther et al. (2017).

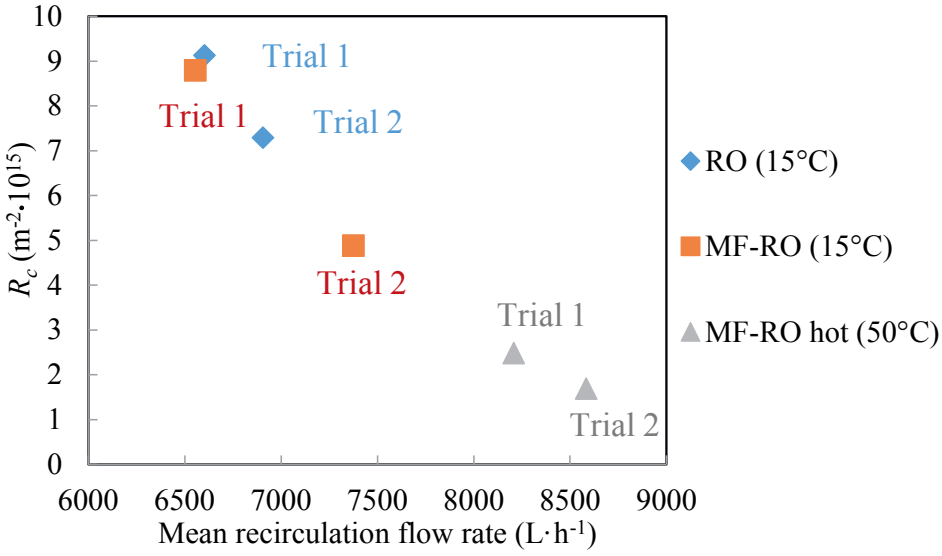

Fig. 4-6. Accumulation rate of fouling resistance R_c relative to mean recirculation flow rate for the three RO processes carried out experimentally by Blais, Ho et al. (2021).

4.3.2 Energy consumption during RO of skim milk

The feed, booster and recirculation pumps as well as the heat exchanger are responsible for the energy consumed by the filtration plant. The multistage centrifugal high-pressure booster pump consumed the most energy with a range of 3.67 to 3.87 kW, compared to 0.52-0.56 kW and 1.23-1.27 kW for the feed and recirculation pumps, respectively. At both 15 and 50 °C, the combined specific energy consumption of the feed and booster pumps per unit volume of permeate had limited correlation with feed flow variations (Figure 4-7), the latter being an artefact of the increased permeation caused by a concomitant higher recirculation flow rate and thus lower rate of fouling accumulation (Figure 4-5).

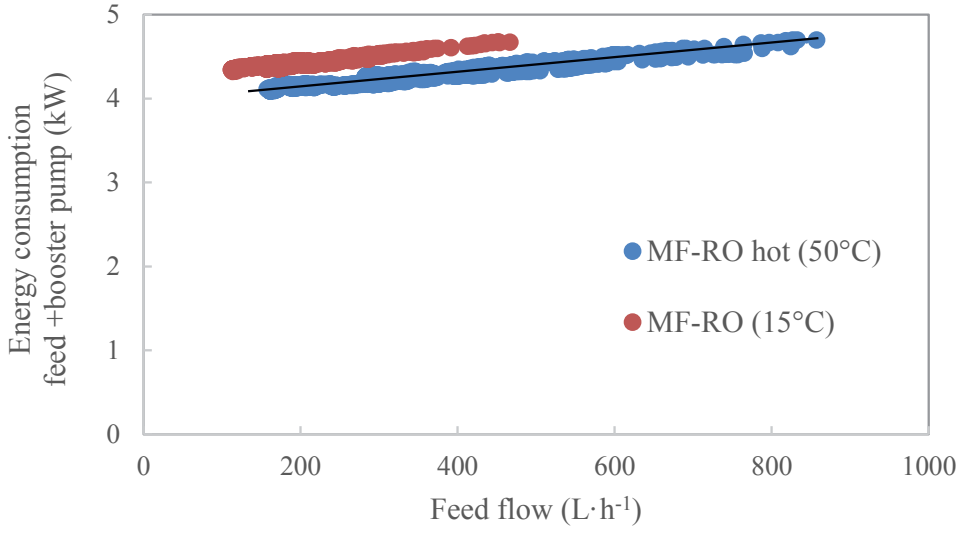

Fig. 4-7. Energy consumption of the feed and booster pump *versus* feed flow during RO at 15 or 50 °C. Symbols indicate experimental values and the line the linear model (cold) $y = 8.5 \cdot 10^{-4} \cdot x + 4.2$ and (hot) $y = 8.4 \cdot 10^{-4} \cdot x + 4.0$.

Likewise, the energy consumption of the recirculation pump increased from 1.1 to 1.3 kW when increasing the recirculation flow from 6.6 to 8.6 $m^3 \cdot h^{-1}$, at 15 and 50 °C respectively, resulting in a lower energy consumption per unit volume of skim milk processed (Figure 4-8) because of the higher flux due to lower fouling accumulation at 50 compared to 10 °C. The sensitivity of pump energy consumption to flow rates was low, i.e., for an increase of the feed flow rate of ~55%, the combined pump energy consumption only increased by ~5%. This implies that additional membranes may be connected in series at limited additional energy consumption, given the limitations of the modules such as the mechanical strength of the membrane; as outlined in the next section. The energy consumption for the different configurations (described in Figure 4-3) were calculated based on the empirical equations derived from Figures 4-7 & 4-8.

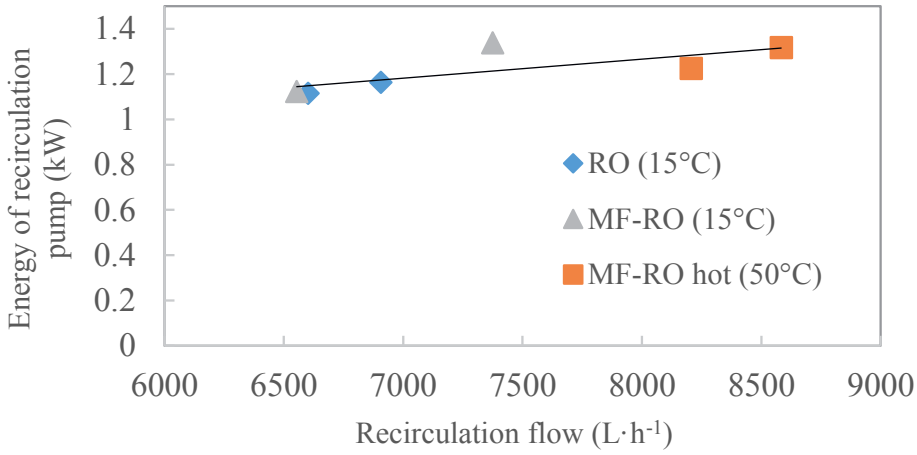

Fig. 4-8. Energy consumption of the recirculation pump versus the recirculation flow during RO. Symbols indicate experimental values and the line the linear model ($y = 8 \cdot 10^{-5} \cdot x + 0.6$).

4.3.3 Effect of module configuration on flux and energy consumption

The performance of RO processes with different module configurations, based on the parameters in Table 4-1, is presented in Figures 4-9 & 4-10. Assuming a constant feed pressure of 3000 kPa, the mean permeate flux and associated pressure drop of an RO plant comprising one to five elements in series, operated during 18 hours (similar to commercial runs) at 50 °C, were plotted in Figure 4-9. To put these flux values into perspective relative to the total energy consumption of an RO plant, the energy requirements for a multi-element RO plant to concentrate skim milk at a volume concentration factor of 2 was calculated according to equation 13, and presented in Figure 4-10. To be complete, the energy consumed during a MF pre-treatment (20.6 $kJ \cdot L^{-1}$ permeate) was included.

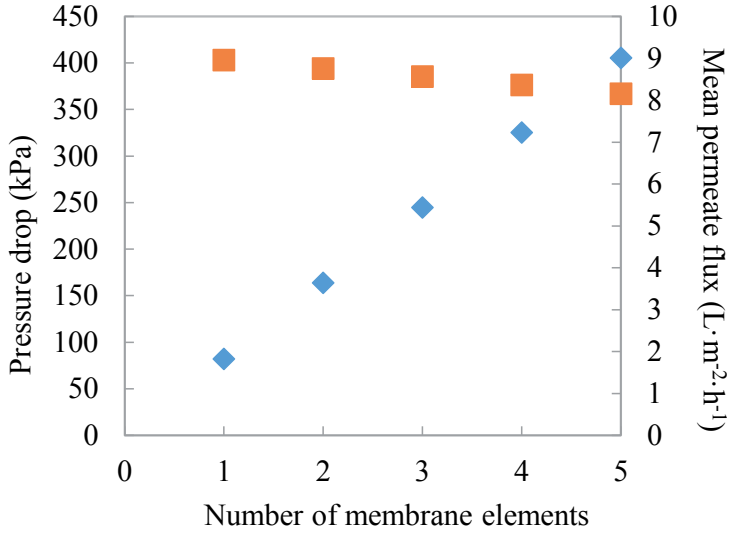

Fig. 4-9. Simulation of mean permeate flux (orange squares) and associated pressure drop (blue diamonds) of an RO plant with one to five membrane elements operated in series (Q_{recirc}= 8.6 $m^3 \cdot h^{-1}$ and T= 50°C).

At both 15 and 50 °C, it was found that increasing the number of elements (up to 5 in one series, or 2 x 5 in two parallel series (Figure 4-3)) and altering the configuration (in-series or in-parallel) considerably reduced the overall energy consumption per unit volume of permeate removed. As outlined before, this efficiency gain was associated with a limited loss of flux when increasing the number of membrane elements while keeping feed pressure the same as for one element (while ensuring manufacturer limitations are not exceeded).

Furthermore, the performance of two parallel series of five elements each was markedly higher than that of a single series (with half the amount of elements totally), whereby the energy consumption per litre of permeate was reduced by ~31% at 15 °C (from 261 to 180 $kJ \cdot L^{-1}$ permeate) or by 21% at 50 °C (from 104 to 82 $kJ \cdot L^{-1}$ permeate) respectively. The observed efficiency gain is associated with the reduced pressure drop influence when spreading membrane elements

over two parallel modules as compared to one single long series that is much more affected by a higher pressure drop. In itself it is interesting to compare higher numbers of modules in series; however, pressure drop limitations from the manufacturer do not allow operation of modules longer than 5 elements.

Finally, below a certain module length (hardly applicable at commercial scale), the specific energy consumption was comparable when the same total number of elements was used (e.g., four in series or two in two parallel). For such short modules, pressure drop was low and its effect on permeate flow negligible; hence performance correlated linearly with the total membrane surface area.

The total energy consumption per litre permeate was considerably lower at 50 compared to 15 °C due to the lower (permeate) viscosity and the fact that energy did not need to be removed from the system by the heat exchanger. At 15 °C, the specific energy consumption of the heat exchanger, expressed as a negative, was higher to compensate for the pump heat. When using 5 elements in two parallel series operated at 50 °C, the energy consumption was reduced to ~82 kJ per litre of water removed compared to 302 $kJ \cdot L^{-1}$ for a single element. While this configuration would imply higher initial capital costs, the associated performance gains would soon compensate for these. In fact, due to the relatively high flux performance for the extended surface area (associated with high cross-flow velocity at 50°C, reduced viscosity and lower pressure drop influence in this parallel configuration), it would result in a ~54% lower energy consumption per litre permeate removed compared to the operation of two elements in series as in the study of Blais, Ho et al. (2021). Compared to a 7-stage falling-film evaporator equipped with thermal vapour re-compression that uses ~300 kJ per litre of water removed (Ramírez, Patel et al. 2006), the present configuration would compare favourably, saving 72% energy albeit at a concentration factor of 2.

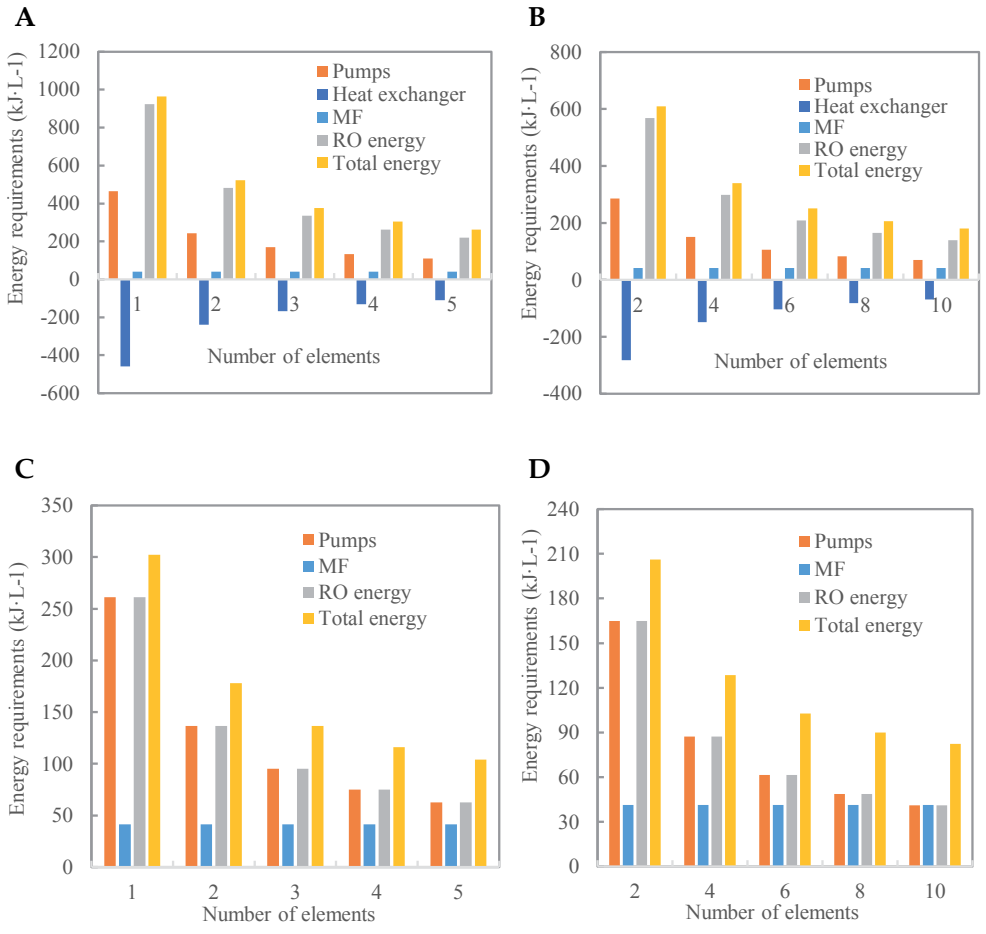

Fig. 4-10. Calculated energy requirements for RO processes performed at 15 °C (A & B) or 50 °C (C & D), for in-series 1-5 (A & C) and in-parallel 2 x 1-5 (B & D) membrane configurations as defined in Fig. 4-3.

Several studies highlight the use of multiple membranes in series to reduce operation costs. Specific strategies dedicated to spreading membrane elements over several stages, with intermediate booster pumps connected in series, to make use of the outlet pressure and cross-flow rate already generated, have been suggested (Kishizawa, Tsuzuki et al. 2015, Li 2020). By using a first stage of 6-

8 elements, and boosting the pressure before a second stage of 2-4 elements, the overall hydraulic pressure needed for desalination was reduced from 6.0-7.5 to 4.5-6.0 MPa for a similar performance (0.3 $m^3 \cdot m^{-2} \cdot day^{-1}$). This leads to a more even distribution of the flux over the process because of reduced fouling build-up early on, thereby increasing the overall recovery rate from 45 to 60%, with energy savings of ~20% compared to a conventional system (i.e., parallel modules operated in a single-stage fashion) (Kishizawa, Tsuzuki et al. 2015).

4.4 Conclusion

RO performance was modelled based on semi-empirical approaches and used to calculate energy consumption associated with skim milk concentration. The pressure drop along various module configurations, and associated flux and energy consumption per volume permeate were calculated. It was found that ten membrane elements connected in two parallel series of five each, resulted in the lowest energy consumption of 82 $kJ \cdot L^{-1}$ of water removed (50 °C). This was mostly attributed to the reduced pressure drop in the parallel *versus* single-series configuration, thereby limiting flux decrease across the entire surface area. Further research trials on multistage and low-pressure RO processes, coupled with pump energy consumption at higher feed flow rate, are needed to confirm RO performance. Finally, in order to translate the outcomes of the model to commercial settings, the pressure drop over a series of modules would need to be experimentally determined, and possibly related to the use of an intermediate booster pump (Kishizawa, Tsuzuki et al. 2015). It is expected that a similar approach can be used in other RO applications such as seawater desalination.

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Chapter 5

Concentration of skim milk by forward osmosis using delactosed permeate as an innovative draw solution

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Abstract

Forward osmosis (FO) is proposed as a sustainable alternative to evaporation and reverse osmosis but its commercial application is limited by energy-intensive draw solution recovery and solute permeation through the membrane. To mitigate this, the dairy by-product delactosed permeate has potential as a draw solution for concentration of dairy products, where permeation of solutes and draw solution recovery are not a concern. In this study, skim milk was concentrated from 9 to 18% dry matter by FO using delactosed permeate as the draw solution. The influence of temperature on filtration performance was assessed whereby average fluxes of 3.6 and 4.8 $kg \cdot h^{-1} \cdot m^{-2}$ were obtained at 10 and 30 °C, respectively. Energy savings of ~67% per kg of water removed compared to reverse osmosis were observed. This, together with the absence of undesirable solute permeation during FO, highlights the potential of delactosed permeate as a draw solution for concentration of dairy streams.

5.1 Introduction

Milk concentration and drying processes are used to prepare dairy products with reduced transportation and storage costs, as well as an extended shelf-life (Petrotos and Lazarides 2001). But this comes at a cost: evaporation and spray drying account for ~96% of the total energy consumed during milk powder manufacturing (45 and 51%, respectively (Ramírez, Patel et al. 2006)), and are the most energy-intensive operations performed in dairy plants (Hasanoğlu and Gül 2016, Chen, Artemi et al. 2019). As an alternative to evaporation or reverse osmosis (RO) which requires generation of hydraulic pressures up to 10 MPa (Kowalik-Klimczak 2017), forward osmosis (FO) has emerged as a low-energy technology to increase dry matter (DM) content without the need for high energy input (Chung, Li et al. 2012, Ge, Ling et al. 2013, Chen, Artemi et al. 2019).

FO is driven by the osmotic pressure difference between a feed and a draw solution separated by a semi-permeable membrane. This osmotic gradient leads to water transfer from the low to the high osmotic pressure liquid while eliminating almost completely the need for high hydraulic pressures. These mild operating conditions provide FO with another advantage with regards to the preservation of physical, organoleptic and nutritive properties of sensitive components (Lin and Ho 2003, Zhao, Zou et al. 2012). Heat treatment (62 °C x 30 min) was for instance found to impair bioactive proteins such as lactoferrin or lactadherin by triggering their denaturation and aggregation thus altering their functionality (Zhang, Boeren et al. 2016, Brick, Ege et al. 2017). Furthermore, the absence of high hydraulic pressures during FO limits fouling accumulation compared to reversed osmosis, thus reducing the need for frequent aggressive chemical cleaning (Chung, Li et al. 2012, Chekli, Phuntsho et al. 2016).

During the FO filtration process, the draw solution is diluted by movement of water from the feed side of the membrane, which necessitates a concentration step in recirculation mode for which evaporation, RO or nanofiltration may be used, which reduces potential energy savings (Cath, Childress et al. 2006, McGinnis and Elimelech 2007, Chung, Li et al. 2012, Altaee, Zaragoza et al. 2014). Alternatively, high osmotic pressure by-products can be considered as draw solutions, such as delactosed permeate (DLP) that do not require recovery and can form part of a sustainable concentration/stabilisation strategy in an integrated dairy factory.

DLP is derived from milk or sweet/acid whey from which proteins are removed by ultrafiltration. The permeate thereof is then concentrated to 65-70% DM (Wong and Hartel 2014) by evaporation, after which ~70% of the lactose is removed by crystallisation. The remaining liquid is termed DLP or mother liquor (Keller 2017) and is not well-defined (Burrington 2010). It typically contains 25-34% dry matter (Liang, Bund et al. 2009), of which 47-68% is lactose and 9-20% minerals, the rest is organic acids and non-protein nitrogen compounds (Liang, Bund et al. 2009, Oliveira, Puri et al. 2019). The composition of the solution and the relatively low concenteration of components therein do not support additional isolation of individual compounds, thus DLP is used as animal feed, field spread or disposed of by effluent treatment (Kellam and Wansbrough 1998, Friend, Kaiser et al. 2004, Wong and Hartel 2014).

The low-molecular weight components in DLP contribute to a high osmotic pressure which makes it attractive for use as a draw solution in FO. Additionally, its dairy origin prevents cross-contamination by components from the draw solution, as would be the case for more commonly used draw solutions (e.g., high fructose corn syrup or polyethylene glycol). The dilute DLP resulting

from the FO process could be fermented to produce lactic acid or ethanol (Aydiner, Sen et al. 2014), incorporated into other food products as a salt substitute (Smith, Metzger et al. 2016), used as an ingredient in ice cream (Bund and Hartel 2013, Levin, Burrington et al. 2016), or disposed of as described earlier. In some applications where a low concentration DLP is specifically required, e.g., for the production of renewable biofuel (Summers, Ledbetter et al. 2015), the dilution of the DLP resulting from this process may be desirable, eliminating one of the major issues (i.e., solution recovery) in identification of a sustainable draw solution.

While FO has been investigated for concentration of fruit or vegetable juice (Zhao, Zou et al. 2012), and for milk (Beldie and Moraru 2021), application of a dairy by-product as draw solution has not been reported previously. This study used DLP to concentrate skim milk from 9 to 18% DM using a proprietary FO membrane. This implies removal of 50% of the water in skim milk under conditions at which viscosity development is unlikely to be rate limiting. The effect of temperature (10 or 30 °C) on water flux and solute transfer (proteins, minerals and lactose) through the membrane was evaluated, and physicochemical properties (viscosity, osmolality, density, conductivity, DM, lactose and mineral content) of both feed and draw solutions were measured before, during and after FO. The energy consumption was compared to literature values for an RO process operating at an equivalent concentration factor (CF).

5.2 Materials and methods

5.2.1 Preparation of the draw and feed solutions:

DLP was sourced from a local dairy processor commercially manufacturing lactose. On receipt it was pasteurized using a tubular heat

exchanger (MicroThermics, USA), operated at a flow rate of 2 $L \cdot min^{-1}$. DLP (36.4% DM, (w/w)) was pre-heated at 50 °C, held for 15 s at 72 °C, and cooled to 45 °C. The initial/final product exiting the plant was discarded to avoid dilution with process water. The pasteurized DLP was centrifuged (20,000 g, 20 min, 30 °C) (Sorvall Lynx 6000, Thermo Scientific, USA) to remove residual lactose and salt crystals, and the supernatant was aliquoted and frozen.

The DLP composition was 33.7% (w/w) DM, 22.4% (w/w) lactose, 8.6% (w/w) minerals, and 0.3% (w/w) crude protein. Before each trial, the DLP was thawed at 35-40 °C or 15-20 °C for 1 h in a water bath (Grant, UK), cooled to 30 or 10 °C and centrifuged (15,000 g x 10 min at 30 or 10 °C) to remove lactose/salt crystals. Commercially available pasteurized skim milk (4.8% (w/w) lactose, 3.5% (w/w) protein, 0.4% (w/w) fat) was sourced locally and equilibrated at the required processing temperature for 1-2 h prior to FO.

5.2.2 Forward osmosis process

5.2.2.1 FO system

The lab-scale FO (Figure 5-1. A) consists of a crossflow hollow-fibre membrane (Aquaporin, Nymøllevej, Denmark) containing 13800 fibres with internal diameter of 0.2 mm and a surface area of 2.3 m^2. The membrane had an Aquaporin Inside® coating on the lumen side with a negatively-charged active layer and a fibre wall thickness of 35 µm. Two gear pumps (Iwaki, France) were used to pump the feed and draw solutions in batch recirculation mode. The draw solution tank was placed on a weighing scales to monitor changes in mass during processing, which was used to determine the permeate water flux. All water used for trials, analysis and cleaning was ultrapure water (resistance of 18.2 mΩ, Purelab flex, Elga, UK) or reverse osmosis water (conductivity of <43 µS/cm) unless stated otherwise.

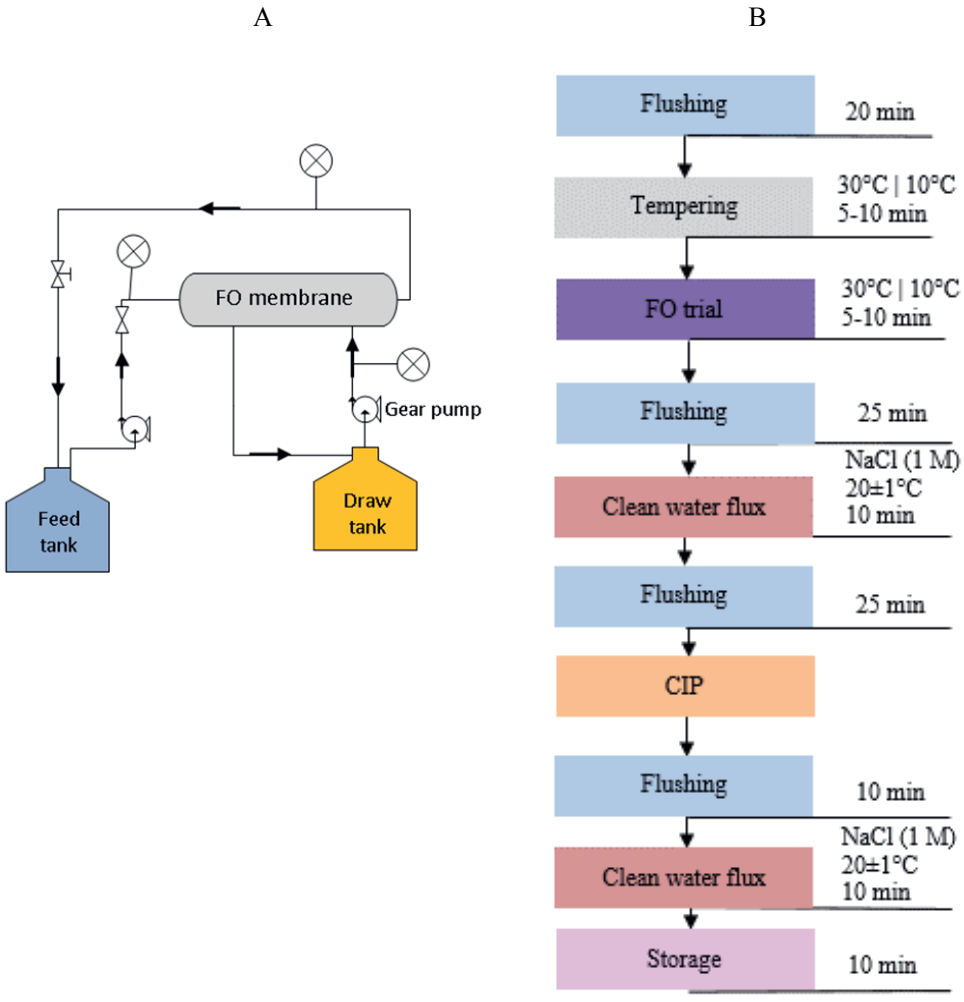


Fig. 5-1. Schematic of the lab-scale FO membrane system (A) and overview of the process steps involved (B).

5.2.2.2 Cleaning-in-place (CIP), water flux, and membrane permeability

Before each trial, the storage solution was flushed from the system with RO water for 15 min. After each trial, a 2-step clean in place (CIP) procedure was carried out as follows: (1) circulation of 2.5 L 0.3% (v/v) Ultrasil 78 solution

(Ecolab, UK) at 45 °C for 30 min, followed by flushing with RO water for 15 min; (2) circulation of 2.5 L 0.8% (v/v) Ultrasil 115 solution at 45 °C for 30 min, followed by flushing with RO water for 15 min.

To ensure the consistency of cleaning and membrane integrity during successive filtration trials, the time for a given amount of water to be drawn from the feed to draw side was measured before each trial (t_{ref}) and after each trial, both before ($t_{ref,}$BC) and after ($t_{ref,}$AC) cleaning. Water fluxes were determined using 5 L of RO water as feed and 5 L of a 1 M NaCl (20±1 °C) draw solution; with the time for all the water to move to the draw side recorded. After clean water flux measurements (t_{ref} and $t_{ref,}$AC) the system was flushed with RO water for 15 min and the membrane was removed and stored in a 0.25% (w/v) sodium metabisulfite preservative solution at 4 °C. To evaluate the reversibility of fouling, if any, a dimensionless cleaning efficiency coefficient ε was defined as follows:

$$\varepsilon = 1 - \frac{t_{ref}}{t_{ref,AC}} \quad (1)$$

Low ε-values correspond to effective cleaning. Membrane permeability was determined using the method of Chen, Artemi et al. (2019): transmembrane pressure (TMP) was varied in six steps between 43±4 kPa and 147±0 kPa in a random order, at 14.1±0.2 °C. The water flux was determined over 20 min from the change in mass of the draw solution. A linear relationship between water flux and TMP was assumed and permeability of the membrane, B ($m \cdot s^{-1} \cdot Pa^{-1}$), was calculated as a proportionality factor in equation 2 (assuming $\Delta\pi = 0$).

$$J_w = B \cdot \Delta P \quad (2)$$

with J_w ($L \cdot m^{-2} \cdot s^{-1}$) the water flux and ΔP (Pa) the hydraulic TMP.

5.2.2.3 FO trials

Each temperature condition (10 or 30 °C) was evaluated in triplicate following the procedure outlined in Figure 5-1. B. Before each trial, RO water at the required temperature was recirculated. Given the relatively short trial duration (20 min), no temperature adjustment was needed. Next, the system was fully drained, after which 5 and 0.55 L of temperature-adjusted feed and draw solution were added to the respective tanks. Based on preliminary tests a feed:draw mass ratio of 9:1 was chosen to achieve a concentration factor of 2 at close to osmotic equilibrium. Each trial was performed in batch-mode, using a counter-current flow, with the active and support layers facing the feed and draw sides, respectively. At the start of the trial, feed inlet and outlet pressures were adjusted to 120 and 20 kPa, respectively, and the draw inlet to 30 kPa, yielding an average TMP of 55 kPa. The mass of the draw solution tank, feed inlet/outlet pressure, draw solution inlet pressure, feed/draw solution temperature, conductivity and refractive index were recorded during filtration. Samples were taken from the feed outlet or the draw solution tank.

Flux through the membrane, J_w ($L \cdot m^{-2} \cdot h^{-1}$), was determined as follows:

$$J_w = \frac{\Delta M}{\rho \cdot A_m \cdot \Delta t} \quad (3)$$

with ΔM (kg) the difference in mass of the draw solution within a time interval Δt (h), ρ ($kg \cdot L^{-1}$) the density of the feed solution at 10 or 30 °C and A_m (m^2) the membrane surface area. Mass balance calculations were conducted using solute concentrations (crude protein, non-protein nitrogen (NPN), lactose and minerals) in the feed and (dilute) DLP in time on a dry matter basis:

$$\%\ \text{recovery} = \frac{[solute]_{concentrate} \cdot 100}{[solute]_{skim\ milk}} \text{ or } \frac{[solute]_{diluteDLP} \cdot 100}{[solute]_{DLP}} \quad (4)$$

5.2.2.4 Statistic analysis

The data derived from the DSC, water holding capacity, and protein solubility measurement was analyzed using SPSS software (IBM statistical analysis Version 25.0). Univariate general linear model with LSD test was performed to investigate significant differences for apparent CGA-protein molar ratios of 1:10, 1:5, 1:1, 5:1, and 10:1 and reference pure protein samples receiving similar pH-treatment. Differences were considered significant if $P < 0.05$.

5.2.3 Energy calculations

The energy consumption of the system, E_{tot} (Wh) was determined based on the electric power drawn by the feed and draw pumps, E_f and E_d, respectively:

$$E_{tot} = (E_f + E_d) \cdot \Delta t \quad (5)$$

with E_f and E_d (W) the capacity of the feed and draw pumps respectively and Δt (h) the trial duration.

5.2.4 Analysis of the physicochemical properties of the samples

5.2.4.1 Dry matter, total protein nitrogen (TPN), non-protein nitrogen (NPN), lactose, ash and mineral content

DM content was measured folowing the ISO5537-IDF26 method (ISO 2004). TPN and NPN concentrations were measured by the Kjeldahl method ISO 8968-3/IDF 20-3:2004. Lactose content was determined by HPLC (Waters Alliance 2695, USA) with a fixed ion-resin column (Aminex HPX 87C), using a Waters 2414 refractive index detector. Prior to the measurements, the column was calibrated using lactose solutions (10, 20, 50 and 100 $\mu g \cdot ml^{-1}$). Samples were diluted with distilled water to fit the measurement range and filtered through a 0.2 µm Chromafil Nylon filter (Labquip, Ireland). Distilled water was used as the mobile phase and a 0.009 N solution of H_2SO_4 as the eluent at 0.5 $ml \cdot min^{-1}$. A

standard buffer LGG (lactose, glucose, galactose) (Supelco Inc., Bellefonte, PA 16823, USA) used as reference. All samples were analysed twice by HPLC.

Chloride content was measured via reagent free ion chromatography (Dionex ICS-5000+, Dionex Corporation, Sunnyvale, USA). Prior to analysis, samples (1.0±0.2 g) were ashed using a gravimetric oven (TGA 701, LECO, Michigan, USA). The temperature for moisture and ash determination was set to 104 and 550 °C, respectively. The ashed samples were dissolved in 1 mL of nitric acid (1 M) and transferred to 100 mL volumetric flasks (Isolab, Germany) using nitric acid (2 mM). The volumetric flasks were mixed thoroughly and sonicated for 25 min at 30 °C (VWR international, Oud-Heverlee, Belgium) to ensure dissolution. The diluted ash samples were passed through 2 µm PTFE filters into PPE vials. Samples were prepared in triplicate and each replicate was injected three times. Only plastic ware and ultrapure water were used for sample preparation and analysis. Plastic ware was rinsed twice with 2 mM nitric acid prior to use. The system software used for instrumentation control, data acquisition and processing was Chromelian (Version 7.2 SR5, Thermofisher, UK). Other mineral contents were measured via inductively coupled plasma-optical emission spectrophotometry by an external company (FBA Laboratories Ltd., Waterford, Ireland).

5.2.4.2 Microscopic observations

To check for lactose and salt crystals, polarized light microscopy images (60x) (Olympus BX 51, Japan) of DLP were taken.

5.2.4.3 Density conductivity, viscosity, pH, osmolality, osmotic pressure

Density was measured using DMA 35 (Anton Paar, Austria) at the trial temperature. Conductivity of the feed solution was measured with HI 8733

(Hanna instruments, USA) at the trial temperature. The pH was measured with the portable device (Seven Compact, Mettler Toledo, USA) at 25 °C.

Osmolality was measured using an osmometer (Cryoscopic Osmomat030, GONOTEC, Germany). A volume of 50 µL of solution was pipetted into an Eppendorf tube and the thermistor probe was placed in solution. Concentrated samples were diluted to fit the calbration range. Osmotic pressure π of an aqueous solution was determined as follows:

$$\pi = C_{osm} \cdot \rho \cdot R \cdot T \quad (6)$$

with C_{osm} (osmol·kg^{-1}) the osmolality, ρ the solution density at 10 or 30 °C, R the ideal gas constant (8.314 m^3·Pa·K^{-1}·mol^{-1}) and T (K) the temperature.

5.2.4.4 Statistical analysis

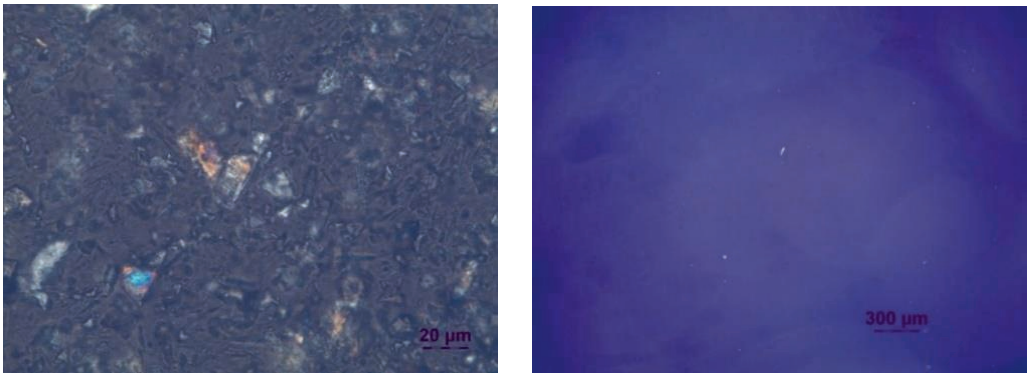
Physicochemical properties of skim milk, DLP, skim concentrate and dilute DLP were analyzed using SPSS software (SPSS v.24, IBM, New York, USA) and excel. Differences between triplicate trials were analyzed for variance using two-sample F-test and significant differences were tested with independent sample T-test at $p < 0.05$.

5.3 Results & discussion

5.3.1 Membrane water permeability and optimization of the DLP

Membrane permeability (B) was found to be 2.80±0.21·10^{-6} m·s^{-1}·MPa^{-1}, which is similar to literature values (1.38·10^{-6} to 6.93·10^{-6} m·s^{-1}·MPa^{-1}) for spiral-wound (Chen, Artemi et al. 2019) and flat-sheet (Ren and McCutcheon 2014) membranes, respectively. When using the same FO module as in our study, Sanahuja-Embuena et al. (2019) obtained 4.42±0.13·10^{-6} m·s^{-1}·MPa^{-1} for deionized water at 25 °C; the difference probably caused by higher crossflow velocities used compared to our study resulting in a higher water diffusivity.

Centrifugation was used to remove larger insoluble particles (salt and lactose) from DLP to prevent membrane damage (Figure 5-2). The resulting supernatant had DM of 33.7±0.4% which is slightly lower as the starting liquid (36.4±0.1%). There was no significant difference when DPL was centrifuged at 10 or 30 °C except for a slightly higher lactose concentration (p-value=0.03) at 10 °C (229.8 versus 218.9 $mg \cdot mL^{-1}$, respectively).



A B

Fig. 5-2. Polarized light microscopy images of DLP before (A) and after (B) centrifugation at 60 X.

The DM, lactose and mineral content of DLP (Table 5-1) are similar to Liang et al. (2009), whereas protein concentration was lower at 0.31 compared to 1.9% w/w_{DM}, but in line with Oliveira et al. (2019). Calcium was ~20% of that reported by Liang et al. (2009), while sodium and chloride were higher at 152 and 110% respectively, likely due to differences in the manufacturing process.

5.3.2 Forward osmosis results

5.3.2.1 Water flux

The flux during concentration of skim milk at 10 and 30 °C as function of time, osmotic pressure difference and concentration factor are presented in Figures 5-3 and 5-4.

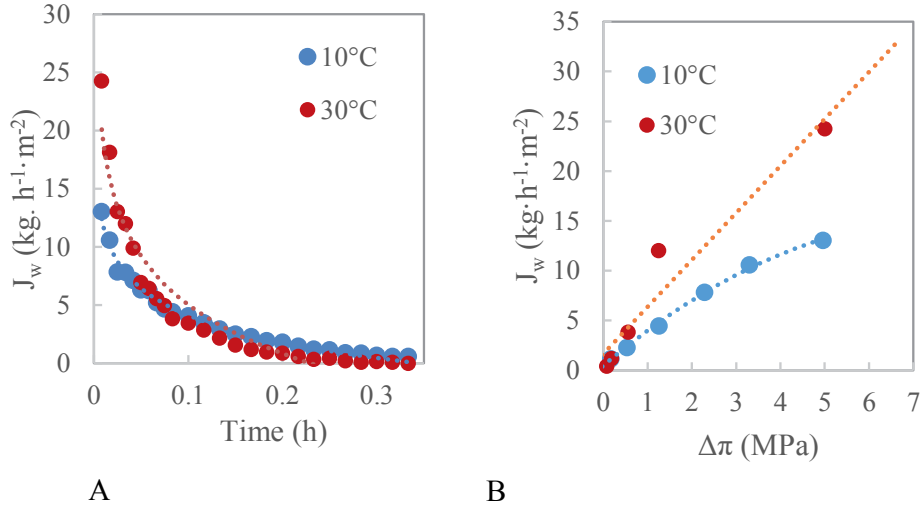


Fig. 5-3. Flux as function of (A) time and (B) osmotic pressure difference at 10 or 30 °C during FO concentration of skim milk. The lines are there to guide the eye.

At both temperatures, the flux rapidly declined within the first 5 min, and continued to decline until a value close to osmotic equilibrium was reached where the flux neared zero, as expected. The rapid decline at the start was caused by the high dilution rate of the draw solution (9-fold lower initial mass compared to feed). Average water fluxes of 4.8 and 3.6 kg·m^{-2}·h^{-1} were obtained at 30 and 10 °C, respectively, with a higher initial water flux at 30 °C, due to lower feed viscosity (p-value=0.04) and increased diffusivity at higher temperature.

This also follows from:

$$J_w = \frac{\Delta P}{R \cdot \eta} \qquad (7)$$

with ΔP (Pa) transmembrane pressure, R (m^{-1}) resistance (membrane and possible foulants), and η (Pa·s) permeate viscosity. McCutcheon and Elimelech (2006) observed similar temperature effects for sodium chloride solutions used as feed and draw in a flat-sheet module operated in counter-current and FO mode.

Table 5-1. Composition of milk and DLP before and after FO (blue: trial at 10 °C; red: trial at 30 °C).

Compound	Unit	Skim milk	DLP	Concentrate	Concentrate	Dilute DLP	Dilute DLP
DM	%w/w	9.28±0.06	33.72±0.37	18.00±0.05	18.50±0.15	6.48±0.03	6.17±0.06
Ash	%w/w	0.74±0.15	8.88±0.16	1.49±0.01	1.52±0.02	1.60±0.04	1.61±0.02
Protein	%w/w	3.79±0.06	0.31±0.00	7.18±0.02	7.46±0.02	0.03±0.00	0.03±0.00
NPN	%w/w	0.03±0.00	0.39±0.01	0.05±0.01	0.06±0.00	0.08±0.00	0.08±0.00
Lactose	%w/w	3.22±0.04	22.43±0.29	6.28±0.01	6.60±0.09	3.61±0.05	3.39±0.07
Minerals*	%w/w	0.57±0.00	7.24±0.18	1.07±0.00	1.14±0.01	1.32±0.00	1.34±0.01
Ca	%w/w	0.13±0.00	0.06±0.00	0.24±0.01	0.26±0.03	0.01±0.00	0.01±0.00
Mg	%w/w	0.01±0.00	0.05±0.00	0.02±0.00	0.02±0.00	0.01±0.00	0.01±0.00
P	%w/w	0.10±0.00	0.38±0.02	0.18±0.01	0.21±0.03	0.06±0.00	0.07±0.00
K	%w/w	0.14±0.00	2.16±0.07	0.25±0.00	0.24±0.01	0.36±0.01	0.39±0.02
Na	%w/w	0.05±0.00	1.66±0.05	0.09±0.00	0.10±0.00	0.27±0.01	0.28±0.01
Cl	%w/w	0.11±0.00	2.84±0.03	0.23±0.00	0.24±0.01	0.60±0.01	0.57±0.01
SO_4	%w/w	0.03±0.00	0.09±0.00	0.06±0.00	0.06±0.01	0.01±0.00	0.01±0.00
pH	–	6.75±0.00	4.77±0.00	6.35±0.02	6.29±0.00	5.24±0.33	5.05±0.39
π	10^5 Pa	6.49±0.28	75.14±2.84	14.40±1.49	14.44±0.83	14.88±1.12	14.64±0.18

* sum of determined minerals

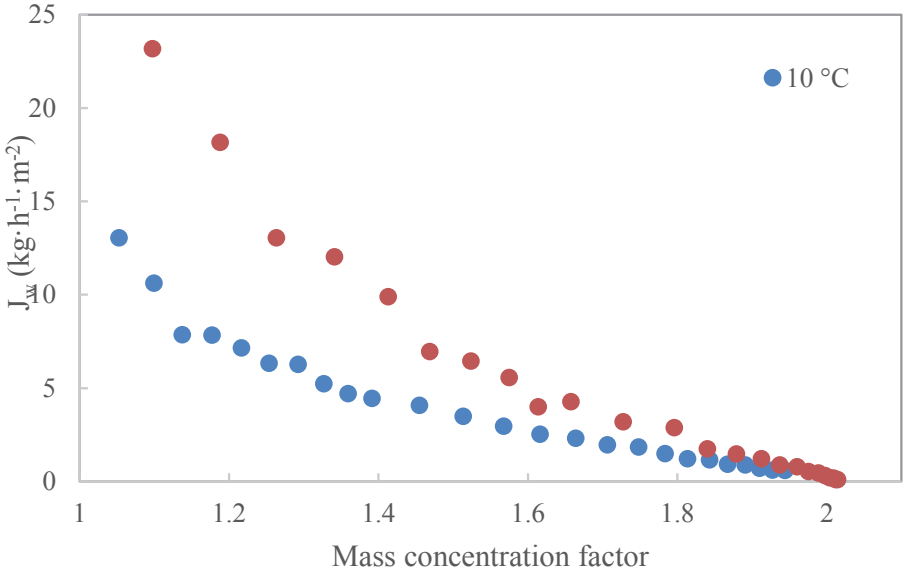


Fig. 5-4. Water flux as function of concentration factor of the feed solution at 10 or 30 °C during concentration of skim milk by FO.

For comparison with studies using other operating conditions, the initial water flux of the trials was expressed relative to osmotic pressure difference (Table 5-1). The $J_w/\Delta\pi$ (10 °C) = 2.6±0.1 kg·m^{-2}·h^{-1}·MPa^{-1} and $J_w/\Delta\pi$ (30 °C) = 4.8±0.3 kg·m^{-2}·h^{-1}·MPa^{-1} were within the range reported in other studies with the same membrane module: $J_w/\Delta\pi$ (15 °C) = 1.3-5.1 kg·m^{-2}·h^{-1}·MPa^{-1} (Sanahuja-Embuena, Khensir et al. 2019) and $J_w/\Delta\pi$ (20 °C) = 2.5-2.9 kg·m^{-2}·h^{-1}·MPa^{-1} (Ren and McCutcheon 2018). These values were slightly higher than those reported for flat-sheet membranes in literature; $J_w/\Delta\pi$ (23 °C) = 1.3-4.5 kg·m^{-2}·h^{-1}·MPa^{-1} (Achilli, Cath et al. 2009) and $J_w/\Delta\pi$ (20 °C) = 1.9-2.6 kg·m^{-2}·h^{-1}·MPa^{-1} (McCutcheon and Elimelech 2006).

Apart from the module configuration (flat-sheet as opposed to hollow-fibre), these differences may arise due to varying temperature and the differences

in feed and draw solution composition (a synthetic organic solution was used by Achilli, Cath et al. (2009) and a sodium chloride solution by McCutcheon and Elimelech (2006)), which affects viscosity and water diffusivity. Furthermore, given the impact of viscosity on flux, a more accurate comparison would require correlation of the measured flux with solution properties, which was not possible with the aforementioned studies as viscosity was not reported. In general, the current literature regarding FO provides useful information regarding achievable concentration factors relative to osmotic pressure difference, assuming fouling propensity and concentration polarisation are not impacted by the nature of both feed and draw solutions.

Both feed and draw flow conditions were laminar (p-value=0.5 and 0.4 for feed and draw respectively), with a corresponding Reynolds number below the critical value for turbulent flow (see Table 5-2 and supporting information). In larger scale spiral wound and tubular membrane systems turbulence will more easily be achieved (Cath, Childress et al. 2006).

Table 5-2. Reynolds number (Re) for feed and draw solution, using fluid properties (ρ – density, η – dynamic viscosity), module geometry (A_{cs} – cross-sectional area, L_{ch} – characteristic length) and process conditions ($\dot{V}$- volume flow rate, v – cross-flow velocity). Critical Reynolds numbers are shown in the last column.

	$\dot{V}$	S_{cs}	v	ρ	η	L_{ch}	Re	Re_{crit}
	($m^3 \cdot s^{-1}$)	(cm^2)	($m \cdot s^{-1}$)	($kg \cdot m^{-3}$)	(mPa·s)	(mm)	(–)	(–)
10 °C concentrate	$5.3 \cdot 10^{-5}$	9.7	0.05	1073	8.9	0.20	1.3	2300
10 °C DLP	$3.1 \cdot 10^{-5}$	7.0	0.04	1032	3.3	0.24	3.4	300
30 °C concentrate	$5.3 \cdot 10^{-5}$	9.7	0.05	1068	3.8	0.20	3.1	2300
30 °C DLP	$3.2 \cdot 10^{-5}$	7.0	0.04	1025	1.9	0.24	6.0	300

As illustrated in Figure 5-3.A, the flux was zero at 30 °C after ~17 minutes, and neared this value after 20 min of processing at 10 °C, indicating that further concentration would have been possible if the trial had continued for an extended period, albeit at very low flux. After 20 min the residual osmotic pressure differences were 47 or 20 kPa, at 10 or 30 °C, respectively (Figure 5-3.B). The J_w~4.8 $kg \cdot h^{-1} \cdot m^{-2}$ and faster concentration at 30 °C makes this temperature preferable to 10 °C (J_w~3.6 $kg \cdot h^{-1} \cdot m^{-2}$), that is if bacterial growth is not an issue. The difference in flux is linked to viscosity as the osmotic pressure of the DLP was not influenced by temperature, and the milk was identical in all trials.

In a commercial process reaching osmotic equilibrium would not deliver an efficient process solution due to the very low fluxes involved. However, various options to reach the desired concentration are available such as an adjusted feed/draw solution ratio to increase overall flux. Another option could be temperature modulation, whereby a feed solution at low temperature to ensure product quality by reducing the risk of microbial growth, could be coupled with a higher draw solution temperature to improve flux. Feng et al. (2018) reported that increasing NH_4HCO_3 draw solution temperature from 20 to 40 °C had a more significant impact on FO performance than the same temperature change when applied to the feed (NaCl) solution.

5.3.2.2 Fouling and mass balance calculations

In this study, fouling accumulation was expected to be low but, if any, was expected to be either: i) organic fouling caused by lactose, non-protein nitrogen, proteins, organic acids or ii) inorganic fouling by minerals (scaling; Hiddink, De Boer et al. 1980). Scaling and organic fouling can be interrelated, for instance, calcium phosphate nanoclusters are an integral part of casein micelles, contributing to gelation at elevated concentrations (Walstra, Wouters et al. 2005).

The relatively linear correlation between flux and effective osmotic pressure difference at both temperatures (Figure 5-3.B) indicates that little fouling or concentration polarization occurred, which was further supported by a ratio $t_{ref,AC}$ to $t_{ref,BC}$ of ~0.8-0.9 indicating minimal deposition. The similarity in duration for water to be drawn from the feed to draw side before and after concentration (and cleaning), indicated that any accumulation was reversible as expected for the low transmembrane pressure applied.

These results align with those of Nyborg Nielsen (2019) who employed the same membrane module with whey and cheese brine as feed and draw solutions, respectively, and found low fouling. Comparison among trials in our study based on $t_{ref,BC}$ indicated low levels of fouling irrespective of operating temperature. This minimizes chemical cleaning requirements, and apart from environmental and economic benefits, this extends the operational life of the membrane. Additionally, turbulent flow conditions may be considered for longer operational cycles, as suggested by Singh and Das (2014).

When assessing the retention behaviour of feed/draw solution components on a mass balance basis (Table 5-3), using values measured for concentrated skim and dilute DLP relative to the initial skim milk and DLP on a dry matter basis (Table 5-1), it can be concluded that most components are accounted for fully when considering experimental error. On a DM basis, the concentrations of all components are similar when comparing diluted DLP and concentrate for the two temperatures used (Table 5-3). There are small differences, but these are well within experimental variation, with the exception of NPN in the concentrate (10 °C), which is most probably caused by the very low concentration in combination with high variability between measurements. Obviously the composition of the DLP and the feed are quite different, given their different overall composition.

When doing a more detailed statistical analysis on the composition of skim milk and concentrate at 10 °C, lactose (p-value=0.0003) was lower in skim milk compared to the concentrate suggesting some transfer from draw to feed, which is supported by a corroborating difference in DLPs (p-value=0.001). For 30 °C, similar effects were found for lactose in DLPs (p-value=0.001), whereas this effect was not found for feed and concentrate. When comparing DLP with dilute DLP for significant differences at 10 °C, calcium (p-value=0.03), phosphorus (p-value=0.02), sodium (p-value=0.048), sulphur (p-value=0.005), and protein (p-value=0.009) were higher, whereas at 30 °C, NPN was significantly lower (p-value=0.04) while protein (p-value=0.02) and sodium (p-value=0.047) were significantly higher. It is good to point out that all concentrations were low, and conclusions may be affected by measurement accuracy.

It was expected that sodium may permeate through the membrane; however, there was no significant difference in % recovery of sodium in the feed solution at 10 or 30 °C (p-value=0.91 and 0.12 respectively). In general, if permeation takes place, it is minimal and due to the dairy origin of both the feed and draw solutions, it should not impact product quality.

5.3.2.3 Energy consumption

The power consumption of the feed and draw pumps was 260 and 46 W, respectively. The energy consumed to reach a given mass concentration factor was plotted in Fig 5.5. Performing the trials at 30 °C was more energy-efficient than at 10 °C, especially for concentration factors $\leqslant$1.9 when osmotic pressure difference is substantial. For operating temperature 30 °C and a concentration factor of 2, the average specific energy consumption was 32.6 $Wh \cdot kg^{-1}$ or 117 $kJ \cdot kg^{-1}$ water removed. At lower concentration factors ($\leqslant$1.9) at 30 °C, the energy consumption was as low as 58.5 $kJ \cdot kg^{-1}$.

Table 5-3. Mass balance relative to skim milk and DLP composition before FO, on a dry matter basis (blue: trial at 10 °C; red: trial at 30 °C).

	DM	Lactose	Protein	NPN	Ash	Cl^-	SO_4^{2-}	P	Na^+	K^+	Mg^{2+}	Ca^{2+}
	$\%w/w_{DM}$	$\%w/w_{DM}$	$\%w/w_{DM}$	$\%w/w_{DM}$	$\%w/w_{DM}$	$\%w/w_{DM}$	$\%w/w_{DM}$	$\%w/w_{DM}$	$\%w/w_{DM}$	$\%w/w_{DM}$	$\%w/w_{DM}$	$\%w/w_{DM}$
Concentrate	97±0	101±1	98±2	69±22	104±1	103±2	96±8	100±2	100±8	93±5	96±7	95±8
Concentrate	100±1	103±2	99±2	92±4	103±1	109±7	101±9	108±5	111±3	87±6	95±5	101±12
Dilute DLP	99±0	84±2	43±5	103±2	94±3	111±2	75±5	91±3	88±4	90±4	89±4	88±4
Dilute DLP	94±2	83±2	48±1	107±2	99±2	109±2	83±9	90±1	88±5	96±7	93±7	94±9

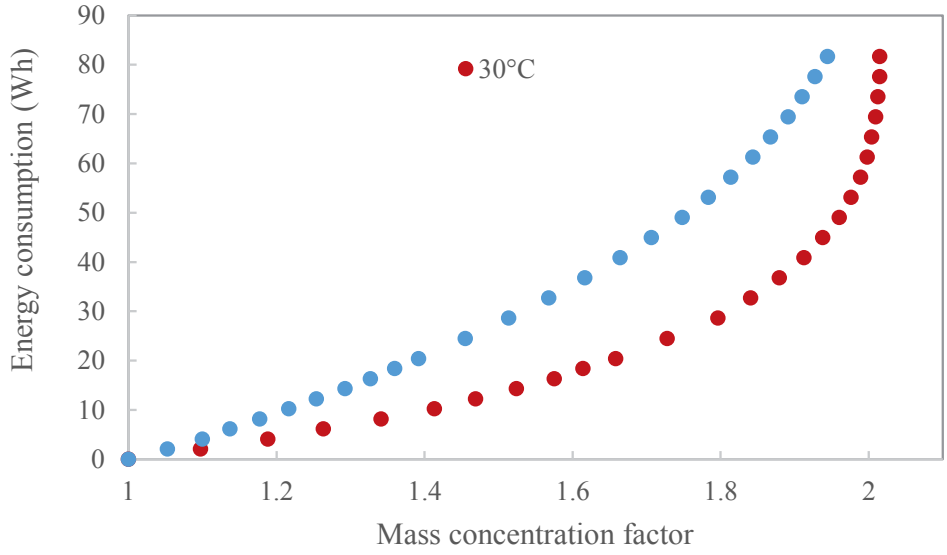


Fig. 5-5. Energy consumption of feed and draw pumps as a function of concentration factor at 10 or 30 °C during concentration of skim milk by FO.

The average pump energy consumption of an RO plant concentrating skim milk by a factor 2 at 50 °C was 178.5±25.4 kJ·kg^{-1} of water removed (Blais, Ho et al. 2021). Compared to that, using the FO approach an energy reduction of ~60% is possible in absence of the need for recovery of the DLP draw solution.

5.4 Conclusions

Delactosed permeate was successfully used in FO to concentrate skim milk from 9 to 18% DM, at a feed:draw ratio of 9:1. Over 20 minutes of operation at 30 °C, the average flux was ~4.8 compared to ~3.6 kg·h^{-1}·m^{-2} at 10 °C, due to lower feed solution viscosity and increased water diffusivity. Hardly any solute transfer and fouling/concentration polarization occurred leading to ~60% less energy usage compared to equivalent concentration by RO at pilot-scale. DLP has high osmotic pressure, low cost and does not require recovery, while any

permeation is unlikely to be deemed a contaminant in dairy products, and is of interest for products sensitive to thermal loads, e.g., protein- or vitamin-enriched dairy streams. In the future, modulation of draw and feed solution temperatures may be used to further enhance process efficiency, also outside the dairy field.

5.6 References

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5.5 Supporting information

The hydrodynamic conditions present on both the feed and the draw side of the membrane (Table 5-2) were determined by calculation of the Reynolds number (equation A.1). For that, the cross-flow velocity was first calculated using equation (A.2); symbols are explained in Table 5-2.

$$\mathrm{Re} = \frac{\upsilon \cdot L_{ch} \cdot \rho}{\eta} \qquad \text{(A.1)}$$

$$\upsilon = \frac{\dot{V}}{A_{cs}} \qquad \text{(A.2)}$$

The obtained values, as well as fluid viscosity and density, the relevant geometry of the module and the critical Reynolds number are reported in Table 5-2. For the feed solution, flow through a pipe with tube diameter equal to the inner diameter of hollow fibres was assumed. For the draw solution, flow through a bed with hydraulic diameter d_h was assumed (equation (A.3) (Kraume 2020):

$$d_h = 4 \cdot \frac{A_{cs}}{L_{circ}} \qquad \text{(A.3)}$$

with L_{circ} (m) the wetted circumference, i.e., the sum of all outer hollow fibre diameters.

Chapter 6

General discussion

6.1 Introduction

In this thesis, various options are discussed to make better use of milk and its ingredients as starting materials for various applications. In some cases, a minimum purity is needed to ensure a controlled and repeatable process e.g., during cheese-making with milk casein concentrates (Gésan-Guiziou 2007). Conversely, a high purity is sometimes needed e.g., for the formulation of pharmaceutical products (Guo 2004). In order to tailor to the entire breadth of applications, a wide range of fractionation techniques can be employed to achieve various levels of purity. In this thesis, membrane filtration is the method of choice and even more specifically, its use in a cascaded fashion. This is investigated in the light of cost and energy reduction, while some attention is paid to enrichment in terms of nutritional value and technical functionality.

6.2 Main findings

In chapter 2, a review of membrane filtration processes documented in the literature is provided, highlighting that when used for concentration purposes, membrane filtration preserves the native state of milk proteins better compared to conventional evaporative treatments (Fox, Akkerman et al. 2010, Verruck, Sartor et al. 2019). This has been reported to be of particular importance for application in edible coatings for which mechanical strength, sensory properties and mass transfer regulation are key (Mishra, Mann et al. 2022). Compared to thermal concentration techniques like evaporation, membrane filtration consumes less energy per unit mass of water removed for dry matter contents <27% due to the absence of phase change (Hiddink, De Boer et al. 1980, Gésan-Guiziou 2007, Castel and Favre 2018).

Another conclusion from the review is that filtration techniques can be used to obtain various product fractions when used in cascaded fashion, unlike centrifugation, chromatography, supercritical fluid extraction or pressurized liquid extraction. This allows isolation of relatively pure components in their native state and at high quantity, which considerably lowers their production costs and therefore facilitates their use in a wider range of applications. For instance, such fractions include casein proteins that are used as replacement of synthetic adhesives in water-based glues or as a basis for water-resistant and versatile plastics (Audic, Chaufer et al. 2003).

Cascaded membranes have two main advantages: reduction of energy consumption as well as increased product purity, and this holds for micro- to nanofiltration (Brans, Schroën et al. 2004). While membrane concentration reduces the feed volume and corresponding energy usage, product purity can be optimized by upstream microorganism removal, allowing subsequent processes to be carried out at higher temperatures to enhance flux and reduce operating time

This latter effect is illustrated in chapter 3, in which skim milk is subjected to a cascade of microfiltration and reverse osmosis to remove microorganisms upstream, which allows a higher processing temperature during RO. This significantly increased the flux compared to single-stage RO due to a lower permeate/retentate viscosity (Blais, Ho et al. 2021), and lowered energy usage per volume water removed to reach a given concentration factor. Furthermore, the evaporated RO concentrates showed similar whey protein nitrogen index as a skim milk control. This makes the cascaded process a promising alternative for production of skim milk powder at lower economic and environmental costs. To further optimize energy use, we systematically investigated the influence of operating parameters on filtration performance through modelling (chapter 4).

Taking chapter 3 as a basis, in chapter 4 the local pressure drop and permeate flow along discretized module configurations (different number of elements, in series or in parallel) were simulated, allowing determination of mean permeate flux and, by corollary, energy usage. For the same feed pressure applied as for one element, a configuration consisting of two parallel series with five membrane elements each increased process efficiency per liter water removed. This was associated with limiting pressure drop among parallel modules compared to a single series, therewith maintaining a relatively high flux across the entire membrane surface area. When carried out at 50 °C the lower viscosity led to reduction of energy needed per kg of water removed to 82 $kJ \cdot L^{-1}$, which is an indication that improvements compared to 178 $kJ \cdot L^{-1}$ (Chapter 3) may be possible, although this would still need to be validated in practice.

In chapter 5, forward osmosis was explored as a way to reduce energy use during concentration of skim milk compared to evaporation, which represents the industry standard. It was shown that skim milk can be concentrated by a factor of 2 using 84% less energy per unit mass of water removed compared to evaporation. This is achieved by making use of a concentrated dairy waste effluent that utilises an osmotic pressure effect, rather than thermal energy thereby reducing the energy needed. The effluent, delactosed permeate has high osmotic pressure (mineral and lactose content) and is available at negligible cost. The components present in it are the same as in milk, thus preventing cross-contamination. After the forward osmosis process, the diluted draw solution can be used for bioethanol or lactic acid production (Oliveira, Puri et al. 2019), thus circumventing the need for reconcentration and reducing the energy costs (Shon, Chekli et al. 2015). Forward osmosis is an efficient technique to concentrate dairy streams, as well as other food and non-food streams of low osmotic pressure.

6.3 Next steps and further interpretation

Production of dairy products and ingredients will more and more need to be carried out at lower energy input. The current thesis has put forward some options to concentrate or fractionate dairy streams more efficiently using less energy. In addition to these, other options can be envisioned when considering the dairy production chain in a broader perspective. For instance, the animal from which milk originates, and even fermentation of dairy-like proteins through advanced techniques as alternatives to milk which will be discussed relative to food and some non-food applications.

6.3.1 Improved fractionation of dairy streams

6.3.1.1 Processing conditions

Process conditions determine process efficiency, and options that are specific to the membrane can be used to reduce energy usage. To prevent microbial growth, milk is traditionally pasteurized, or, for storage at ambient temperature, sterilized or high-heat-treated. This effectively inactivate microbes; but triggers protein denaturation, in particular near-complete denaturation of valuable immunoglobulins. Alternatively, high pressure processing can be used to inactivate microorganisms while preserving most of biological functionality of immunoglobulins (Huppertz 2016). The relative pressure stability of proteins may thus be exploited to isolate them in their native state, which is particularly relevant given their high economic value. Other components affected by heat treatment include vitamins; e.g., folate of which sterilization and ultra-high heat treatment are known to trigger highest losses (Witthöft and Jägerstad 2002). MF holds benefits over heat treatment, removing >99% of bacteria from milk (using for instance a 1.4 µm cut-off) at low temperature (Daufin, Escudier et al. 2001).

Other operating parameters that have not been investigated in this thesis can alter membrane selectivity. For instance, during NF of glucose solutions or effluents from a paper pulp plant, an increase in temperature until a critical value (55-65 °C) was found to reduce the retention of neutral solutes, without affecting charged components (Mänttäri, Pihlajamäki et al. 2002). It is important to point out that a permanent alteration to membrane selectivity was found for high temperatures, which highlights the need for careful monitoring of membrane properties. These findings are key for fractionation of charged ions from lactose in whey, prior to downstream lactose concentration (Rice, Barber et al. 2009).

The membranes used in this thesis had a neutral charge according to the manufacturer specifications. The use of charged membranes offers additional possibilities to fractionate milk components, in particular high-value proteins. For instance, the use of a positively-charged 100 kDa cellulose UF membrane at pH 5 allowed an almost complete separation of lactoferrin (retentate) and bovine serum albumin (permeate) from a binary protein mixture. At pH 5, there is a slight electrostatic repulsion between the membrane and lactoferrin whereas the negatively charged bovine serum albumin can permeate rather freely. In contrast, at pH 9, the membrane was negatively charged which led to retention of bovine serum albumin whereas lactoferrin passed through the membrane (Valiño, San Román et al. 2014). These findings, obtained with model solutions, show that separation of similarly sized proteins (66.5 and 78 kDa for bovine serum albumin and lactoferrin, respectively) is possible. Whether this would also hold for more complex dairy solutions as they occur in practice requires further investigation, since charge screening may occur readily in the presence of ions.

In another study, grafting of a 100 kDa polyethersulfone UF membrane resulted in five-fold higher rejection of β-lactoglobulin over α-lactalbumin

compared to the unmodified membrane. This was associated with both the reduction in membrane pore size (favouring size-exclusion of β-lactoglobulin) and higher electrostatic repulsion between the membrane and β-lactoglobulin at pH~7.2, compared to α-lactalbumin (Cowan and Ritchie 2007). It is good to point out that the experiments were carried out for single-protein solutions and not for more complex dairy liquids.

Membrane characteristics may change over time e.g., because of exposure to cleaning products (alkaline, acidic, enzymatic), and are essential to monitor to ensure process stability. For instance, alkaline cleaning was found to reduce retention of neutral solutes in model glucose solutions (Mänttäri, Pihlajamäki et al. 2002) while a combined enzymatic-alkaline cleaning improved membrane permeability as compared to enzymatic cleaning alone when filtering process water from the paper industry (Rudolph, Schagerlöf et al. 2018). From this, it is clear that membrane monitoring and timely replacement are essential for smooth operation, and overall process cost calculation.

When comparing techniques, for instance pre-concentrating skim milk by a cascade MF-RO or by single-stage RO rather than evaporation (as done in Chapter 3), the additional costs associated with membrane purchase and operation must be balanced by the energy savings of the filtration processes, and better preservation of native protein properties. Therefore the choice of an operating temperature of 50 °C to enhance RO performance, which is the maximum temperature tolerated by polyamide membranes, must be evaluated in view of their lifetime of ~5-10 years, replacement (15-25% of operational costs) and recycling/disposal (Senán-Salinas, García-Pacheco et al. 2019).

6.3.1.2 Choice of dairy animals

Milk composition is dependent on stage of lactation, age and parity, but also differs greatly between ruminants and non-ruminants. Milk from the former, particularly of sheep, buffalo and yak, is richer in total solid, protein, fat and ash while lactose concentration is higher in horse and donkey milk (Alichanidis, Moatsou et al. 2016). The composition of the milk will influence choices made for fractionation processes (apart from the available amounts and costs of the milk). To isolate lactose from horse or donkey milk, it would be recommended to start with a MF treatment to remove protein and fat, operated at a high volume concentration factor due to the lower solid content, followed by NF to optimise lactose purity and yield. On the other hand, ruminant milk is desirable for cheese-making or yogurt production for which a high protein content is required.

Casein is the main protein of ruminant milk with a casein:whey protein ratio of ~80:20, which is favourable for cheese yield, whereas non-ruminant milk have proportionally higher serum protein content. Casein composition varies within types of milk; e.g., β-casein is dominant in goat and camel milk, which is relevant for polyphenol encapsulation (van der Schaaf, Crowley et al. 2022), and α_s- and β-casein are the main subtypes found in horse milk (Malacarne, Martuzzi et al. 2002). While β-lactoglobulin is the major protein in the milk of most mammals, it is absent in camel milk, giving this milk low allergenicity (relevant for infant formulae). Lactoferrin also varies within milk types, with a concentration in horse milk nearly 6 times as high as in cow milk (Alichanidis, Moatsou et al. 2016), making the former a good candidate for exploitation of lactoferrin's anticancer and anti-inflammatory properties (García-Montoya, Cendón et al. 2012).

6.3.1.3 Protein fermentation

Membrane filtration is employed for the recovery of alternative proteins, including 'molecularly-identical' dairy proteins, produced by fermentation of plant-based sugars in a bioreactor. With a drastically different approach than the aforementioned fractionation techniques focusing on downstream processes, this method is becoming more and more popular due to its lower carbon footprint associated with the sole production of the targeted ingredient as compared with conventional dairy farming , thereby minimizing organic resources employed for the animal body parts.

By corollary, all undesirable components typically found in milk e.g., hormones, lactose or cholesterol are absent which considerably simplifies downstream processes and thereby reduces economic and environmental costs; last but not least no animal suffering is involved. In practice, using a technique called precision fermentation, fungi are genetically-modified to produce e.g., casein and whey proteins similar to those found in cow milk. The latter are then ultrafiltered and spray-dried prior to use in cheese or ice cream, a process already commercialized in e.g., the US and Hong Kong (Nay 2021).

Following the same principle, fungi or bacteria hosts are used to produce other proteins such as enzymes, vitamins or rennet for cheese as well as several non-dairy related proteins (Hinds 2020). Interestingly, this method could be highly beneficial with regards to milk protein allergies, known to be life-threatening in some cases (Burris, Burris et al. 2020), whereby a total absence of caseins could be guaranteed in a whey protein supplement or *vice versa*. Large-scale developments of these alternative dairy-like proteins are so far hampered by regulatory considerations (Lähteenmäki-Uutela, Rahikainen et al. 2021) as well as by their higher price compared to traditional dairy products. Yet, whenever

possible, larger scale commercialization could invert this trend due to the considerably lower production costs: up to ~60% reduced energy costs and 99% lower water consumption per unit protein content produced compared to those from cows, based on an ISO-conformant study (Day 2021).

6.3.2 Application of novel fractionation set-ups to non-dairy streams

6.3.2.1 Other applications for the MF-RO cascade

In production of water, many steps are needed of which some (e.g., bactericide and other components addition) can be detrimental to the final RO treatment step by e.g., reducing the membrane lifetime (Yamamura 2001). In order to retain microorganisms and the largest foulants from seawater while suppressing the need to add chemicals and simplifying the chain, the addition of an MF step before the RO desalination process could be considered, as was demonstrated in chapter 3 for removal of microorganisms from skim milk. It would ensure compliance with safety regulations while the subsequent RO may be carried out at higher temperature than the typical 20-25 °C used in desalination process to enhance its flux. Whether this is economic, will need to be determined.

Also non-dairy food streams could benefit from concentration by an MF-RO cascade to reduce microbial load (or other undesirable components) as well as their transport and storage costs. Wine, cider, vinegar and fruit juice industries employ MF for simultaneous clarification and sterilization (Gan, Howell et al. 2001). Beer is clarified using diatomaceous earth and pasteurized (dos Santos Bernardi, Magro et al. 2019), yet, environmental regulations motivate brewers to move away from the use of diatomaceous earth (Gan, Howell et al. 2001), making membranes an interesting alternative. Pasteurization (60 °C for 15 min) is known to alter beer flavour, colour, bitterness, chill haze and protein sensitivity (Buzrul,

Alpas et al. 2005), and filtration is more and more applied (van der Sman, Vollebregt et al. 2012). Given the size of yeast cells (5-10 µm), microbiological stability could be achieved by microfiltration, while protein retention needs to be guarded closely for foam stability (Esmaeili, Peivasteh Roudsari et al. 2015).

Following clarification, concentration of beer, wine and cider has been reported to be possible using a two-pass, low-temperature (2 °C) RO system patented by Alfa Laval in order to remove ~70% of the initial water content (Laval 2021). Most of the water is removed during the first pass while the second one is used to recover residual alcohol (~30% of initial alcohol content) and aromas that permeated during the first pass. RO does not require degassing (which leads to flavour loss), and compared to single-pass FO, the two-pass RO process retains aromas better at lower energy costs.

Another application of membranes is related to the production of alcohol-free beer, using either reverse osmosis or dialysis (Catarino, Mendes et al. 2007). Among the two, RO is usually preferred (Jackson 2014); water and ethanol permeate through an RO membrane whereas other components, including aromas and flavour compounds, are (mostly) retained and concentrated. An optimal ethanol removal and rejection of flavour compounds was obtained in diafiltration mode (López, Alvarez et al. 2002). It must be noted that these membrane processes are only effective to remove alcohol down to 0.45% v/v as lower contents are not economically achievable (Catarino, Mendes et al. 2007, Wenten and Khoiruddin 2016). Compared to thermal dealcoholisation (e.g., vacuum distillation or water vapour stripping), membrane processes use less energy and preserve thermosensitive compounds from chemical alteration or physical losses as they are carried out at temperatures below 15 °C (Brányik, Silva et al. 2012).

6.3.2.2 FO concentration of labile components

For the concentration of components labile to pressure or thermal treatment, FO is a suitable alternative to RO or evaporation. However, its commercial application is limited by the energy-consuming recovery of the draw solution, typically carried out by evaporation, or RO. To improve process performance, a variety of so-called responsive draw solutes have been investigated which can, for instance, be recovered upon heat or electromagnetic stimuli. However, these remain too expensive to be employed at large scale (Cai and Hu 2016). As in chapter 5 of this thesis, the use of a waste effluent as draw solution can be a solution due to its availability and negligible related costs as long as it can be disposed of at no higher environmental or economic cost than the initial effluent.

Orange juice is traditionally concentrated via evaporation; however, this results in altered organoleptic properties: loss of volatile fragrances, colour degradation, self-oxidation and cooked taste (Rastogi 2018). While compensating strategies including essence recovery from peel oil and blending are developed, they are not perfect and have triggered citrus industries to opt for concentration techniques such as freeze or sublimation concentration (Jiao, Cassano et al. 2004, Rastogi 2018). However, these methods are currently not economically viable (e.g., capital costs many times that of an evaporation plant or limited to only clarified juices) (Herron, Beaudry et al. 1994). For fruit/vegetable juices, the use of the aforementioned cascade MF-RO at 50 °C would not be a suitable alternative either. While MF or UF treatments are successfully used to retain the largest suspended solids, bacteria, pectins, moulds and yeasts from fresh juice (Girard and Fukumoto 2000), RO triggers the accumulation of polypeptides,

pectins and polysaccharides on the membrane, and besides, RO must be run at ~10 °C in order to preserve flavour compounds, which increases energy use.

FO-concentrated orange juice has been found to be of superior quality compared to its evaporated counterpart (Hameed 2013). When heating the draw solution only (e.g., high fructose corn syrup or polyethylene glycol solution (Haupt and Lerch 2018)), the osmotic pressure difference can be increased while preserving thermolabile components in the juice. Alternatively, waste effluents produced by juice industries would be logical draw solutions that are expected to prevent cross-contamination. Based on the literature, wastewaters originating from juice industries are low in osmotic pressure when compared to e.g., the delactosed permeate that we used for milk concentration in Chapter 5. For instance, the dry matter content of orange bagass is typically 22% of which 3.4% is ash (Cypriano, da Silva et al. 2018) compared to 34% dry matter in DLP with 26.3% ash. Furthermore, the sugar content in orange juice is ~8.5 g per 100 mL of juice (Chanson-Rolle, Braesco et al. 2016), while delactosed permeate has a lactose content of 20.3 g per 100 mL solution, which leads to favourable chemical gradient for FO concentration (ignoring other components).

The potential migration of sugars from any draw solution (e.g., a concentrated sugar solution such as high fructose corn syrup) to fruit and vegetable juices was investigated by Herron, Beaudry et al. (1994) by monitoring the stable carbon isotope ratios in both solutions; and in all cases, sugars did not cross the FO membrane. Cross-contamination of juice (sucrose, glucose and fructose) by delactosed permeate (mostly lactose with some galactose, glucose) can therefore reasonably be neglected. To date, such a draw solution has not been used to concentrate fruit or vegetable juice; yet, its food-grade status makes it a

promising alternative to NaCl or sugar solutions (Sant'Anna, Marczak et al. 2012, Blandin, Ferrari et al. 2020).

Similarly to the applications outlined above, wastewater from the coffee industry could be employed to concentrate coffee by FO rather than being directly disposed of in the nearby water bodies, causing amongst other eutrophication. For instance, coffee mucilage is a residue mainly composed of simple sugars including ~36 g of glucose, 38 g of galactose and 1 g of lactose per L of solution together with 0.12 g of protein per L of solution (Pérez-Sariñana, León-Rodríguez et al. 2015). In comparison, typical drinking coffee with ~3% dry matter (Paiva, Ranocchia et al. 2018) has concentrations of ~0.02 g sucrose, 0.03 g protein and 0.01 g ash per L of solution (Pinheiro, Pinheiro et al. 2021) which suggests a favourable chemical gradient for FO concentration using the former residue. Post-FO, the dilute by-product could be used to produce various bioproducts including biogas, bioethanol and vinegar (Rattan, Parande et al. 2015) or, in the least preferred case, disposed of on condition that solute concentrations comply with recommended guidelines (Dadi, Mengistie et al. 2018).

The numerous fractionation approaches discussed in this thesis demonstrate the complexity of reconciling low energy consumption to high yield and purity. To these operational criteria, ethical considerations regarding, e.g., genetical modifications, add another dimension to the achieving commercial objectives. Combination of several (membrane) fractionation processes currently surpasses any technique operated individually in terms of process efficiency and it is certain that the diversity of their industrial application e.g., including non-food streams, will accelerate further optimization thereof.

6.4. References

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Summary

Membrane filtration is an efficient technology to concentrate or isolate dairy fractions, among other food streams. As compared with thermal concentrative techniques, membrane filtration better preserves thermosensitive components while reducing the energy costs per unit mass water removed. It is used as pre-treatment, often in combination with a classic evaporation step due to viscosity and osmotic pressure limiting its performance at high concentration factors. In contrast to classical fractionation techniques such as centrifugation, decantation, or chromatography that are characterized by a trade-off between yield and purity, membrane filtration separates targeted component(s) based on a molecular sieving approach. These fractions can be employed in various industrial sectors including food and pharmaceutics. In this thesis, we pay special attention to the interplay of membranes that are used in series or in a cascaded form, as well as to the use of by-product in innovative filtration set-ups, to thus reduce operation costs.

Chapter 1 defines the general terms of this thesis, i.e. the targeted dairy components, the membrane filtration platforms and their performance with regards to fractionation of dairy components. **Chapter 2** focuses on the advantages of cascade membrane filtration processes over single-stage processes for the isolation of high-value dairy fractions. The yield, purity and process efficiency of these processes are compared to identifyinnovative solutions. The role of processing parameters on fractionation outcomes is also discussed to facilitate translation of lab-scale studies, often found in the literature, into commercial-scale operations.

Chapter 3 reports the enhanced performance and energy savings allowed by a combination of microfiltration and reverse osmosis over a single-stage

reverse osmosis process for concentration of skim milk by a factor 2. The microfiltration process virtually retained microorganisms and fat globules upstream, allowing subsequent reverse osmosis to be carried out at a higher temperature while complying with food safety considerations. This increased temperature improved process performance by reducing retentate and permeate viscosity and increasing diffusivity, as observed through a higher flux and altered fouling dynamics on a cumulative permeate volume basis. Furthermore, the cascade membrane configuration operated at high temperature consumed less than half of the energy per unit volume of water removed compared to the low-temperature approach. Changes of physicochemical properties in the final skim milk concentrates were also monitored after low, medium and high heat treatments to provide insights into likely performance in downstream manufacturing processes.

Chapter 4 describes mathematical models to predict the performance of reverse osmosis employed for skim milk concentration using numerical simulation. Based on experimental data from **chapter 3**, pressure drop was simulated along various module configurations to predict permeate flow rate and fouling resistance. It was found that spreading ten membrane elements among two parallel series of five resulted in a more energy-efficient process than either aligning them in a single series due to pressure drop influence, or employing shorter parallel series not utilizing pump capacity at its best.

In **chapter 5**, the potential of delactosed permeate as draw solution to concentrate skim milk by a factor 2 by forward osmosis was evaluated. At this concentration factor, each kg of delactosed permeate had the potential to draw 4.5 kg of water from skim milk when osmotic equilibrium was reached. Furthermore, employing a dairy by-product as draw solution suppressed any risk of migration

of undesirable components from draw to feed, thereby alleviating one of the main challenges of forward osmosis as a concentration technology for food. Through this innovative approach, skim milk was concentrated at lower energy costs as compared with reverse osmosis or evaporation, indicating the potential of delactosed permeate as a sustainable alternative to thermal techniques, also to concentrate other dairy streams.

In the **General Discussion**, optimization of concentration and fractionation processes of dairy streams is evaluated in a broader context than through membrane filtration, whereby upstream animal selection and production of the very ingredients themselves are discussed. Finally, applications of innovative filtration set-ups to other food or non-food streams are provided to enhance efficiency of other fractionation processes.

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Author

About the author

About the author

Herehau Blais was born on January 15th, 1996 in Tahiti, French Polynesia. She studied in Raiatea until the age of 15-years-old where she moved to France to finish high school in a military institution, the Prytanée National Militaire, in view of becoming a doctor in the army. Following a discovery internship in a military hospital, she finally chose to broaden her knowledge in biology by pursuing engineering studies in molecular biology at the Université de Technologie de Compiègne. As part of these studies, she went to the Sino-European School of Technology of Shanghai University and to the Norwegian University of Science and Technology for study semesters. She also carried out an internship at the Ecole Polytechnique Fédérale de Lausanne on type-2 diabetes occurrence in mouse models, and finally an internship on phosphate interactions with milk proteins at Royal FrieslandCampina.

She started her PhD in September 2018 in the laboratory of Food Process Engineering, as a collaboration between Wageningen University and Research and Teagasc Moorepark Research Centre. This thesis entitled 'Innovative energy efficient membrane separation approaches for milk' is the result of that PhD project.

List of publications

This thesis:

Blais, H., Ho, Q. T., Murphy, E. G., Schroën, K., & Tobin, J. T. (2021). A cascade microfiltration and reverse osmosis approach for energy efficient concentration of skim milk. *Journal of Food Engineering*, *300*, 110511.

Blais, H. N., Schroën, K., & Tobin, J. T. (2022). A review of multistage membrane filtration approaches for enhanced efficiency during concentration and fractionation of milk and whey. *International Journal of Dairy Technology*.

Blais, H. N., Schroën, K., & Tobin, J. (2022). Concentration of skim milk by forward osmosis using delactosed permeate as an innovative draw solution. *International Dairy Journal*, 105510.

Blais, H. N., Ho, Q. T, Schroën, K., & Tobin, J. T. (2022). Modelling reverse osmosis performance during skim milk concentration. *Considered for submission.*

Other publications:

McCarthy, W. P., Blais, H. N., O'Callaghan, T. F., Hossain, M., Moloney, M., Danaher, M., ... & Tobin, J. T. (2022). Application of nanofiltration for the removal of chlorate from skim milk. *International Dairy Journal*, 128, 105321.

Conference abstracts

Blais H.N.L, Schroën K., Tobin J.T. Combination of microfiltration, reverse osmosis and evaporation to reduce energy consumption and enhance performance of skim milk concentration. In: Institute of Food Science and Technology of Ireland (IFSTI) 48th conference, Limerick, Ireland, 16 December 2019.

Blais H.N.L, Schroën K., Tobin J.T. Combination of microfiltration, reverse osmosis and evaporation to reduce energy consumption and enhance performance of skim milk concentration. In: International Conference on Membranes and Membranes processes (ICOM) 12th conference, England (online), London, December 6th – 11th 2020.

Blais H.N.L, Schroën K., Tobin J.T. *Concentration of skim milk by forward osmosis using delactosed permeate as an innovative draw solution*. In: European Federation of Food Science and Technology (EFFoST) 35th, Lausanne, Switzerland, November 1st – 4th 2021.

Blais H.N.L, Schroën K., Tobin J.T. *Concentration of skim milk by forward osmosis using delactosed permeate as an innovative draw solution*. In: Network Young Membrains Meeting (NYM) 18th, Lund, Sweden, November 25th – 27th 2021.

Blais H.N.L, Schroën K., Tobin J.T. *Concentration of skim milk by forward osmosis using delactosed permeate as an innovative draw solution*. In: Euromembrane 48th conference, Copenhagen, Denmark, November 28th - December 2nd 2021.

Overview of completed training activities

Discipline specific activities	
Courses	
Han-Sur-Lesse winterschool (Han-sur-lesse, Belgium)	2019
PhD writing Essentials (Professional Writing Academy Ltd, virtual online)	2020
Matlab Onramp course (MathWorks, virtual online)	2020
Machine Learning Onramp (MathWorks, online)	2020
Online Presentation skills (WGS)	2021
Practical thesis writing (WGS)	2019
Conferences	
47th Institute of Food Science and Technology conference (Cork, Ireland)	2018
48th Institute of Food Science and Technology conference (Cork, Ireland)	2019
Starting a Food Business seminar (Kilkenny, Ireland)	2020
12th International Conference on Membranes and Membranes processes (Virtual online)[a]	2020
35th European Colloid & Interface Society conference (Athens, Greece)	2021
35th EFFoST International Conference (Lausanne, Switzerland)[a]	2021
Network Young Membrains Meeting (Lund, Sweden)[a]	2021
Euromembrane conference (Copenhagen, Denmark)[b]	2021
General courses	
PhD week (VLAG)	2018
Model Thinking (Coursera)	2018
Leadership skills for the Agri-Food researcher (AFGDP)	2019
Europe Geopolitics (Sciences Po)	2020
Introduction to Negotiation (Yale University)	2020
VLAG Online Lecture series (VLAG)	2019
PhD Carousel workshops (WGS)	2019
Transformative dialogues workshops (WGS)	2020
LaTex workshop (WGS)	2022
Ethics and Animal sciences (WGS)	2022
Assisting in teaching and supervision activities	
Supervision of 4 students	2018-2021
Other activities	
Preparing PhD research proposal	2018
FPE weekly meetings & Group days[a,b]	2018-2022

[a] *Oral presentation;* [b] *Poster presentation.*

VLAG: Advanced Studies in Food Technology, Agrobiotechnology, Nutrition and Health Sciences; WGS: Wageningen Graduate Schools; AFGDP: Agri-Food Graduate Development Program

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