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Processing and protein-fractionation characteristics of different polymeric membranes during filtration of skim milk at refrigeration temperatures

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ABSTRACT

Serum protein concentrates (SPCs) were generated from reconstituted skim milk (3.2% protein) using lab-scale tangential-flow filtration at 3–4 °C. The influence of membrane type on process performance (e.g., permeate flux) and protein-enrichment (e.g., protein profile) was assessed with polyvinylidene-difluoride membranes (0.1 μm and 0.45 μm pore-size), and a polyethersulfone membrane (1000 kDa cut-off). The 1000 kDa membrane exhibited the highest starting flux (6.7 L m^{-2} h^{-1}), followed by the 0.1 μm (5.4 L m^{-2} h^{-1}) and 0.45 μm (4.8 L m^{-2} h^{-1}) membranes. Flux decreased by >40% during filtration with the 1000 kDa and 0.1 μm membranes, while the decrease was lower (<20%) with the 0.45 μm membrane. β-Casein comprised >97% of casein in SPCs from the 0.1 μm and 1000 kDa membranes. SPCs from the 0.45 μm membrane had higher β-casein:α_s-casein ratios than the feed and higher levels of minor whey proteins (e.g., lactoferrin) relative to the other SPCs.

1. Introduction

In the manufacture of bovine milk-based first age infant milk formula (IMF) products, the protein component is formulated by reconstituting skim milk and whey powders in combination to yield a casein:whey protein ratio of approximately 40:60, which is equivalent to that of human milk (de Wit, 1998), and markedly different from that of bovine milk (80:20). Efforts to extend the humanisation of IMF typically involve increasing the levels of β-casein, α-lactalbumin and lactoferrin, while reducing levels of α-casein and β-lactoglobulin (Guo, 2014). Ingredients such as α-lactalbumin-enriched whey protein concentrates are already being incorporated into IMFs (Kuhlman, Lien, Weaber, & O'Callaghan, 2005). Similarly, the application of β-casein-enriched ingredients is expected to increase as manufacturers attempt to further bridge the gap between the protein profile of IMFs and human milk. However, industrial processes for the production of β-casein-enriched ingredients remain in the early stages of development commercially.

One of the most promising processes for the manufacture of β-casein-enriched serum protein concentrates (SPCs) is pressure-driven membrane filtration. Traditionally, filtration processes (e.g., ultrafiltration, microfiltration), are performed at high temperatures of 45–50 °C, where there is the advantage of a high flux (short processing time for a given volume of product) and limited growth of mesophilic bacteria (Gésan-Guiziou, 2013; Hurt, Zulewska, Newbold, & Barbano, 2010; O'Mahony & Tuohy, 2013; Zulewska, Newbold, & Barbano, 2009). For the enrichment of β-casein, filtration is performed at cold (typically 4–10 °C) temperatures (Christensen & Holst, 2014; Coppola Molitor, Rankin, & Lucey, 2014; Holland, Corredig, & Alexander, 2011; Le Berre & Daufin, 1994; O'Mahony, Smith, & Lucey, 2014; Seibel, Molitor, & Lucey, 2014; Woychik, 1992), under which conditions β-casein exists in its monomeric state in the serum phase (Payens & van Markwijk, 1963; Rose, 1968).

In the dairy industry, the term "cold", as applied to membrane separation processes, currently encompasses a relatively broad temperature range and can include any filtration process temperatures <20 °C. As low filtration temperatures may have additional benefits distinct from β-casein separation (e.g., reduction in the denaturation of whey proteins, reduced fouling

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of membranes by calcium phosphate and reduced growth of thermophiles), many manufacturers are currently transitioning from traditional "warm" (~40–50 °C) processes to cold processes (Lawrence, Kentish, O'Connor, Barber, & Stevens, 2008). However, the lower temperatures reduce diffusivity, and therefore the mass transfer coefficient, with a concomitant decrease in permeate flux (Le Berre & Daufin, 1994). This issue is exacerbated when polymeric membranes (e.g., polyvinylidene-difluoride, PVDF, and polyethersulfone, PES) are used instead of ceramic membranes, as the latter generally have considerably higher flux values (Beckman, Zulewska, Newbold, & Barbano, 2010; Zulewska et al., 2009). Ceramic membranes are used for membrane separation processes in the dairy industry, due to their excellent pH-, temperature- and cleaning-tolerance, in addition to high flux performance; however, in recent years, polymeric membranes have become increasingly popular due to their cost-effectiveness (O'Mahony & Tuohy, 2013).

The materials and conditions that have been described for the enrichment of β-casein using membrane filtration vary widely, and few researchers have provided a detailed analysis of processing performance. Woychik (1992) reported filtration of milk at temperatures of 2–8 °C using microfiltration membranes with pore sizes of 0.1 and 0.2 μm or an ultrafiltration membrane with a molecular mass cut-off of 100 kDa in a plate-and-frame configuration. Le Berre and Daufin (1994) separated β-casein from sodium caseinate at 4 °C using tubular ceramic membranes (ZrO_2 filtering layer on carbon supporting layer) with pore sizes ranging between 0.02 and 0.08 μm. Microfiltration of skim milk at 2–5 °C using 0.55 μm spiral-wound polymeric (PVDF) membranes has also been reported (O'Mahony et al., 2014). Holland et al. (2011) removed β-casein from skim milk using 80 kDa cut-off polymeric ultrafiltration (PES) membranes in a plate-and-frame configuration at 7 °C. More recently, Glas, te Biesebeke, Kromkamp, and Klarenbeek (2013) used different membranes with pore sizes of between 0.3 and 0.5 μm in a spiral-wound configuration for enrichment of β-casein from skim milk at much higher temperatures (10–20 °C), while Christensen and Holst (2014) reported using an 800 kDa cut-off membrane in a spiral-wound configuration to generate a β-casein-enriched permeate from micellar casein concentrate. Most of these researchers noted that the separation of β-casein had potential application in infant formula products.

As the above examples illustrate, studies on the enrichment of β-casein have involved the use of a multitude of membrane materials, pore sizes and cut-offs, configurations and processing temperatures. Presently, the optimal materials and conditions for the filtration of skim milk at refrigeration temperatures are unclear. Le Berre and Daufin (1994) performed a thorough analysis of processing characteristics during their β-casein enrichment experiments; however, the researchers used a 1% (w/w) sodium caseinate solution as the feed and ceramic membranes for the separation. In industrial applications for the development of infant formula ingredients, skim milk is more likely to be used as the feed material for β-casein enrichment, as it facilitates co-enrichment with whey proteins and the generation of a separate "native" functional retentate stream enriched in casein micelles (O'Mahony et al., 2014; Seibel et al., 2014).

In this study, membrane filtration at refrigeration temperatures (≤4 °C) was performed using polymeric microfiltration membranes (0.1 μm and 0.45 μm pore-size PVDF) and a polymeric ultrafiltration membrane (1000 kDa cut-off PES), with detailed analysis undertaken of the filtration process itself, in addition to the composition, physicochemical properties and protein profile of the process streams generated, with a view to developing a protein base for IMF manufacture.

2. Materials and methods

2.1. Materials

Low-heat skim milk powder (SMP) was supplied by the Irish Dairy Board (Fermoy, Ireland). Reconstituted SMP was prepared in deionised water under constant magnetic stirring at 22 °C to attain a 3.2% (w/w) true protein suspension. Reconstituted SMP was then stored at 4 °C for ~23 h to ensure complete rehydration.

2.2. Membrane filtration: processing parameters, process analysis and cleaning

Filtration experiments were performed at lab-scale using a pressure-driven, tangential-flow filtration device (Pellicon 2 mini-holder; Merck-Millipore, Tullagreen, Carrigtwohill, Ireland), as described by Crowley, O'Callaghan, Kelly, Fenelon, and O'Mahony (2015), who reported using the unit for ultrafiltration of reconstituted SMP and IMF, with the following modifications: in the present study, both PES (Biomax, Merck-Millipore) and PVDF (Durapore, Merck-Millipore) membranes were used in individual trials (Table 1); the heat-exchanger (plate and frame) was used to control temperature at between 3 and 4 °C; an equilibration time of at least 30 min was allowed to ensure stable conditions (e.g., temperature and flux). Reconstituted SMP was concentrated to a volume concentration factor (VCF) of 3 by removing permeate, with the retentate being continuously recirculated back to the feed. Samples of the retentate and permeate were taken for analysis when VCF = 3, while the feed was sampled before concentration (VCF = 1). Critical flux was determined as described by Crowley et al. (2015).

The filtration system was cleaned fully after each concentration process and critical flux determination using flushing and recirculation steps with water, sodium hypochlorite and phosphoric acid for PVDF membranes and water and NaOH for the PES membrane. The contribution of the membrane, reversible fouling and irreversible fouling to hydraulic resistance were determined for each membrane by resistance-in-series modelling of water flux data at 25 °C on clean and fouled membranes, according to Darcy's law (Beckman & Barbano, 2013); viscosity of water was taken as 8.91×10^{-4} Pa s, water flux was determined at a TMP of 0.1 bar, and a cross-flow velocity of 0.16 m s^{-1} was used. The degree of fouling was determined as described by Beckman et al. (2010).

Table 1
Geometric and hydrodynamic properties of membranes used for filtration of reconstituted skim milk.

Membrane code	PES1000	PVDF0.1	PVDF0.45
Molecular mass cut-off (kDa)[a]	1000	n.a.	n.a.
Pore-size (μm)[a]	n.a.	0.1	0.45
Spacer present[a]	Yes	Yes	Yes
Channel length (m)[a]	0.16	0.16	0.16
Channel height (m)[a]	0.001	0.001	0.001
Channel width (m)[a]	0.04	0.04	0.04
Total active membrane width (m)[a]	0.625	0.625	0.625
Membrane area (m^2)[a]	0.1	0.1	0.1
Number of feed channels[a]	12	12	12
Number of permeate channels[a]	13	13	13
Total hydraulic diameter (m)[b]	0.021	0.021	0.021
Water permeability (L m^{-2} min^{-1} bar^{-1})[b]	1666	2057	2006
Volumetric flow rate (L m^{-2} min^{-1})[b]	3	3	3
Cross-flow velocity (m s^{-1})[b]	0.14	0.14	0.14

[a] Values taken from documentation received from, or personal communication with, Merck-Millipore technical representatives; n.a. = not applicable.
[b] Values calculated as described by Crowley et al. (2015).