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Original article

The pre-concentration of milk by nanofiltration in the production of Quarg-type fresh cheeses

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Abstract — Milk pre-concentration by nanofiltration (NF) was proposed for fresh Quarg-type cheese manufacturing. NF process modelling by means of model solutions showed that transmembrane pressure and flow velocity had a clear effect on both permeation flux and lactose retention, that a rise in temperature resulted in an increase in permeate flux and a decrease in lactose retention, and that monovalent ion retention depended heavily on the concentration. Milk was concentrated 2 to 3 times by NF. Permeation fluxes were in a range of 10 to 41 $kg \cdot h^{-1} \cdot m^{-2}$ and solute retentions were in accordance with the results from model solutions. Quarg obtained using milk NF retentates was naturally sweeter (61.52 ± 4.30 $g \cdot L^{-1}$ lactose) than traditional fresh cheese and had a high calcium content (2.01 ± 0.33 $g \cdot L^{-1}$) and no bitter taste. Whey had a higher total solids and lactose content and, therefore, required an easier treatment than normal Quarg acid whey.

1. INTRODUCTION

Nanofiltration is a relatively new pressure-driven membrane process with growing applications to various fields such as food industry and water treatment. A peculiar feature of NF membranes is their low retention towards monovalent ions, whereas retention of higher ions and sugars is comparable to that obtained by reverse osmosis [7]. In addition, a lower transmembrane pressure (TMP) than that applied to RO can be used to obtain comparable fluxes. NF membranes wears ionogenic groups, and, consequently, their separation mechanisms involve both steric (sieving) and electrical (Donnan) effects. Partial loss of electrolytes is advantageous to several applications. A typical example is whey concentration: the use of NF yields partially demineralised

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whey of higher value than whole whey concentrate [6, 7]. NF has also been proposed for lactic acid/lactate separation [20] and amino acid and peptide recovery from β-lactoglobulin hydrolisates [19]. NF of milk has not been extensively investigated so far. Eckner and Zottola [3, 4] studied the effect of pH and temperature on flux and separation in HC50 membrane: permeation fluxes increased with temperature by 0.5–2.7%/°C and decreased with pH by 2.4%/ 0.1 pH unit decrease at pH 6.8 to 5.6. Lactose retention decreased on increasing the temperature, and ion retention has also been found to be pH dependent [3].

In this work NF is applied to the pre-concentration of milk, which is then used for the production of Quarg Cheese. Some properties (mainly the mineral content) of the cheese obtained by NF retentate are evaluated and compared with the traditional product. Experiments with model solutions containing salts or lactose are also reported.

2. MATERIALS AND METHODS

2.1. Membranes and equipment used

Two different flat sheet thin film composite polyamide membranes (200 $g \cdot mol^{-1}$ molecular weight cut-off) were purchased from Separem (Biella, Italy). NF20 and NF50 membranes had a nominal NaCl retention of 20 and 50%, respectively. The module used in the experiments was formed by several superimposed rectangular PVC sheets with comb diggings on the feed side (Fig. 1). Flow channels were rectangular in shape (1×10^{-3} m depth and 1.5×10^{-3} m width) and the length of the smodule was 0.254 m. The area of each membrane was 0.0168 m^2 and the module can locate up to 8 membrane sheets with an overall area of 0.1334 m^2. The batch system used in the experiments included a piston pump and a reservoir with jacket for temperature control.

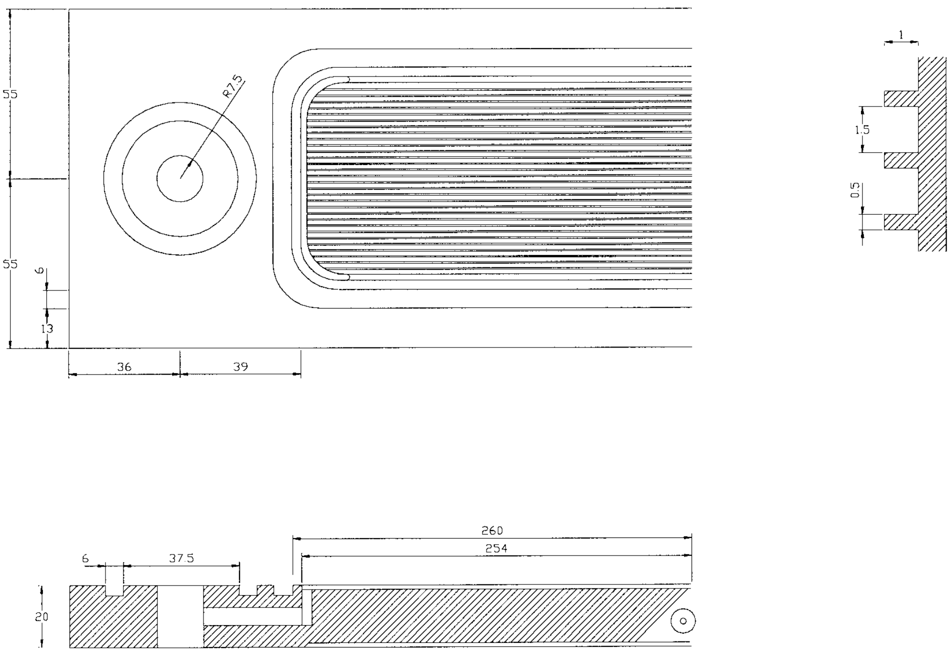

Figure 1. View of a plate of the NF module: feed side (upper) and cross section (lower).

2.2. Model solutions and milk NF experiments

Several experimental runs were performed with model solutions of either single components (NaCl, $CaCl_2$, Na_2SO_4, $MgSO_4$ and lactose) or mixed solutes, mainly salts with common anions or cations as well as whole or skim milk. Both permeate and retentate were recycled to the feed reservoir during the experiments. Flux and solute retentions were measured as a function of temperature, TMP (9 to 15 bar), flow velocity (1.49 to 5.95 $m \cdot s^{-1}$), and solute concentration. Instant retention R of a given component was calculated according to the following equation: $R = 1 - C_P/C_F$, where C_P and C_F are the permeate and feed concentrations, respectively. These experiments were carried out with only one membrane sheet in the module, and the pressure drop along the membrane varied from 0.084 to 1.26 bar depending on the flow velocity.

Milk pre-concentration by NF was carried out with eight membrane in the module. Milk pre-concentration was performed at 48 ± 1 °C using 5 kg of whole milk in each run at TMP of 12 or 19.5 bar and VCR in a range of 2 to 3. The partition of milk components between the permeate and the retentate was characterised by an overall retention defined as $R_0 = 1 – C_{Pav}/C_0$, where C_{Pav} is the concentration of a given component in the permeate collected during the operation and C_0 is the initial concentration of that component in the milk.

The effect of diafiltration on ion removal was tested by adding 1.5 kg of demineralized water to the NF retentate (VCR = 2.1) and removing 1.5 kg of additional permeate.

2.3. Cheese-making trials

Five cheese-making trials were performed using 2 kg of milk NF retentate (VCR = 2.1x) for each trial. The NF retentate was heated to 70 °C in a water bath for 5 min and chilled at 25 °C. After addition of a direct to vat mesophilic starter (Chemiferm, Livraga, Lodi, Italy) and, subsequently, of calf rennet (1 mL per 100 kg retentate) (Clerici, Cadorago, Como, Italy), the retentate was kept at 25 °C for 18 ± 1 h. The acid curd (pH 4.5 ± 0.1) was gently stirred and separated from whey by means of a linen cloth. Filtration was performed at 5 °C for 24 h. The drained whey and the resulting cheese were weighed. A control cheese was made from whole milk not concentrated by NF using the same technical procedure.

2.4. Analytical methods

Analyses were performed on milk, NF permeate, cheese and whey. Lactose, lactic acid and ion contents of the samples were determined by high performance liquid chromatography (HPLC) [1, 11]. Total solids were determined according to the 4A/1982 IDF standard. The Chemical Oxigen Demand (COD) of NF permeates was determined according to Standard Methods [15]. Total lactococci and citrate fermenting lactic acid bacteria present in NF Quarg cheese were determined after incubation at 25 °C for 3 days, using M17 (Difco, Detroit, Michigan, USA) and M17 + 20 $g \cdot L^{-1}$ of Na-Citrate (Difco, USA) as culture media.

Sensorial analysis of NF Quarg was performed by a trained panel composed by ten people, requested to express its opinion about the presence or not of a bitter taste. The evaluation was made twice, the day after the production and after one week of cold storage.

3. RESULTS AND DISCUSSION

3.1. NF of model solutions

The behaviour observed with single salt solutions, is shown in Figure 2 for NF50 membrane: retention is almost complete for multivalent anions, like SO_4^{2-}, and quite

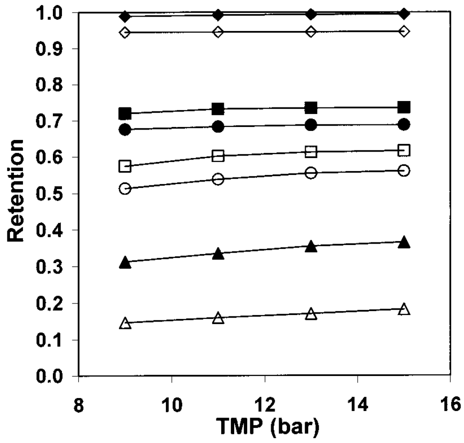

Figure 2. Nanofiltration of single salt solution through NF 50 membrane: retention vs. transmembrane pressure for different concentrations (mol·L^{-1}). (△) NaCl 0.5 mol·L^{-1}; (▲) NaCl 0.05 mol·L^{-1}; (○) NaCl 0.01 mol·L^{-1}; (●) NaCl 0.001 mol·L^{-1}; (□) $CaCl_2$ 0.1 mol ·L^{-1}; (■) $CaCl_2$ 0.01 mol·L^{-1}; (◇) $MgSO_4$ 0.1 mol·L^{-1}; (◆)Na_2SO_4 0.1 mol·L^{-1}.

poor for monovalent anions, like Cl^-. For the latter retention was highly concentration dependent. When both sulphate and chloride ions were present in the feed, chloride retention decreased: for high sulphate to chloride ratios negative chloride retention was observed. The behaviours above are typical of nanofiltration membranes with negative fixed charge, as reported by several authors [6, 7, 12].

The results obtained from lactose solutions are summarised in Table I. Retention in the order of 0.95 can apparently be easily obtained for dilute solutions (45 g·L^{-1}). Conversely, higher pressures than 15 bar were required to approach 0.90 retention for concentrated solutions (100 g·L^{-1}). In addition, retention, as well as the flux, appeared to be strongly dependent on the flow velocity, showing heavy concentration polarisation effects.

The permeate flux of a lactose solution (45 g·L^{-1}) increased with temperature by 2.81% ± 0.17/°C at 25 to 49 °C. Similar values have been reported for NF of milk [19]. However, instant retention decreased on increasing the temperature. For example, during NF of the same lactose solution (45 g·L^{-1}) at 15 bar, retention was 0.974 at 25 °C and 0.933 at 49 °C.

NF20 membrane showed a nearly 30% larger flux than NF50 membrane, although retention appeared to be quite poor. In addition, preliminary tests on milk showed that the NF20 membrane was susceptible to fouling and difficult to clean. The NF50 membrane was thus preferred for the application considered.

3.2. Nanofiltration of milk

A TMP increase from 9 to 15 bar resulted in an increase in the flux of whole milk permeate from 15 to 19.5 kg·h^{-1}·m^{-2} at a flow velocity of 1.49 m·s^{-1}, and from 22 to 37 kg·h^{-1}·m^{-2} when the flow velocity was 5.95 m·s^{-1}. The fluxes observed for whole milk were generally 15–20% lower than those measured by nanofiltering skim milk. However, in both cases, flux dependence on TMP and flow velocity was similar.

The average permeate flux obtained during whole milk NF at VCR 2.1x, performed at 12 bar TMP and 1.49 m·s^{-1} flow velocity, was about 10 kg·h^{-1}·m^{-2}. An increase in the TMP applied and flow velocity to 19.5 bar and 2.98 m·s^{-1}, respectively, resulted in a flux increase to 41 kg·h^{-1}·m^{-2}.

Table II shows compositions of the permeates collected in the various runs and the overall retention calculated as described in the Materials and Methods section. The lactose content of the permeate apparently depended largely on the TMP applied. NF conditions also influenced mineral retention. Ca and Mg ions were highly retained in all cases, while the overall retention of Na and K ions increased from 0.3 to 0.4 as TMP increased from 12 to 19.5 bar. This behaviour is according to the increase of salt rejections with increasing permeation flux observed

Table I. Nanofiltration of lactose solutions at 25 °C: flux (J, $kg \cdot h^{-1} \cdot m^{-2}$) and lactose retention (R) as a function of transmembrane pressure, concentration and flow velocity.

TMP bar	Lactose $g \cdot L^{-1}$	Flow velocity ($m \cdot s^{-1}$)							
		1.49		2.98		4.47		5.95	
		J	R	J	R	J	R	J	R
9	45	27.5	0.882	33.5	0.919	34.1	0.934	36.4	0.942
9	*60*	*22.0*	*0.854*	*24.3*	*0.904*	*28.7*	*0.935*	*34.7*	*0.948*
9	*100*	*11.5*	*0.687*	*12.9*	*0.658*	*13.5*	*0.736*	*14.7*	*0.775*
12	45	40.0	0.908	46.8	0.936	50.1	0.948	53.8	0.956
12	*60*	*33.6*	*0.890*	*36.4*	*0.925*	*39.1*	*0.946*	*43.9*	*0.953*
12	*100*	*18.6*	*0.708*	*21.8*	*0.728*	*23.8*	*0.815*	*25.6*	*0.820*
15	45	52.5	0.926	56.3	0.944	63.8	0.958	71.0	0.963
15	*60*	*41.8*	*0.903*	*48.1*	*0.938*	*51.2*	*0.950*	*55.6*	*0.957*
15	*100*	*26.8*	*0.797*	*30.6*	*0.804*	*34.8*	*85.7*	*38.5*	*87.6*

during UF-whey permeate nanofiltration [17]**.** Chloride retention was negative, as previously verified for NF of $NaCl/Na_2SO_4$ mixtures and observed for nanofiltration of acid casein whey added of 0.02 $mol \cdot L^{-1}$ trisodium citrate [6]. As a consequence of the higher retention of monovalent cations, negative chloride retention decreased as TMP increased.

Diafiltration (DF) was applied to increase permeation of monovalent ions and, consequently, to improve Ca to Na and Ca to K ratios in the retentate. However, this technique did not appear to be particularly appealing because additional lactose was also lost, and both volume and COD of the permeate to be processed as a waste substantially increased. The COD of the permeate stream changed from 4.86 to 17.5 $g \cdot L^{-1}$ depending on the pressure, VCR and whether DF had been used.

3.3. Quarg cheese-making

NF retentates (VCR = 2.1x) were used for Quarg cheese production. NF Quarg composition (Tab. III) shows that it is naturally sweeter than traditional fresh cheese, the lactose content in Creamed Quarg, Thermo-Quarg (18% TS) and UF Quarg being approximately 2.5–3.4% [5, 10]. In order to improve the sweeter taste of Quarg, lactose hydrolysis has been proposed [14], and some trials are currently being carried out by applying this technique to NF milk.

The average calcium content (2 $g \cdot kg^{-1}$) of NF Quarg was higher than the values ranging from 0.03 to 1.9 $g \cdot kg^{-1}$ found in traditional, separator and UF Quarg, as well as in other fresh cheeses [5]. The calcium level of NF Quarg was comparable to that found in Quarg made by fermentation of milk UF retentates [8, 9], although no bitter taste formation, which is often associated with this latter cheese variety, was observed. Also, the control Quarg resulted no bitter. The absence of bitter taste may depend on a combined masking effect of the high lactose concentration and the different multivalent to monovalent ions ratio characteristic of NF Quarg, as compared to UF Quarg. Other trials at pilot scale are currently in progress with the aim to confirm these results obtained at lab scale.

Table II. Nanofiltration of whole milk: average values for permeate composition and single component retention in the various runs.

TMP bar		VCR	COD $mg \cdot L^{-1}$	Lactose		Ca		Mg		Na		K		Cl	
				$g \cdot L^{-1}$	R	$g \cdot L^{-1}$	R	$g \cdot L^{-1}$	R	$g \cdot L^{-1}$	R	$g \cdot L^{-1}$	R	$g \cdot L^{-1}$	R
19		2	4 860	3.33	0.934	0.010	0.991	0.001	0.986	0.259	0.443	0.930	0.374	1.209	–0.164
		3	6 220	4.78	0.905	0.010	0.990	0.001	0.984	0.273	0.413	0.985	0.337	1.236	–0.190
12	mean	2.07	11 895	12.50	0.738	0.027	0.968	0.006	0.926	0.298	0.335	1.119	0.261	1.194	–0.196
	sd	0.10	4 304.8	1.22	0.013	0.011	0.004	0.001	0.001	0.028	0.066	0.100	0.051	0.072	0.103
12 + DF	mean		15 339	14.31		0.034		0.007		0.256		0.968		1.086	
	sd		3 056.1	2.72		0		0.000		0.007		0.006		0.112	

Table III. Average composition of fresh Quarg-type cheese and whey obtained from milk preconcentrated by NF as compared to the conventional process.

Sample		Total solids	Lactose	Lactic acid	Ash	Ca	Mg	Na	K	Cl	Ca/ash	Ca/Na	Ca/K
		$g \cdot L^{-1}$											
Milk	mean		49.170		6.980	1.077	0.093	0.430	1.499	0.989	0.148	2.489	0.712
	sd		1.310		0.250	0.034	0.001	0.030	0.088	0.052	0.008	0.182	0.023
NF Quarg	mean	311.795	61.518	10.428	10.948	2.007	0.166	0.432	1.544	0.394	0.193	4.735	1.317
	sd	12.434	4.304	1.900	1.599	0.326	0.024	0.072	0.320	0.250	0.029	1.087	0.202
Control Quarg		nd	nd	nd	6.980	0.966	0.095	0.404	1.400	0.438	0.138	2.391	0.690
Whey	mean	130.333	82.863	12.370	11.098	2.054	0.167	0.446	1.553	0.255	0.188	4.350	1.233
	sd	16.337	11.543	1.798	0.735	0.581	0.045	0.077	0.232	0.062	0.051	0.608	0.262
Control Whey		nd	nd	nd	7.420	0.988	0.089	0.456	1.345	1.126	0.133	2.167	0.734

The Ca to ash ratio (0.193 ± 0.29) of NF Quarg was also higher than the value of 0.138 found in the control Quarg, that resulted similar to that (0.144) reported for separator Quarg [9]. The selective mineral concentration induced by NF allowed us to obtain higher Ca to Na and Ca to K ratios (4.73 ± 1.09 and 1.32 ± 0.2, respectively) than the values (2.39 and 0.69) found in the control Quarg made without salt addition (Tab. III). In Quarg obtained by fermentation of milk UF retentate [8] the calcium to sodium ratio was similar to, though lower than that found in NF Quarg (3.7 vs. 4.7). A nutritional study on Ca bioavailability from fresh cheese enriched with calcium to 1.6 $g \cdot L^{-1}$, as compared to traditional cheese containing 0.72 $g \cdot L^{-1}$ calcium, evidenced that Ca absorption was not significantly different. The authors concluded that, since the higher Ca concentration in the enriched fresh cheese did not alter Ca bioavailability, consumption of this cheese would probably provide more Ca than the standard one [18].

NF Quarg exhibited a lactococci content of 2.3E + 7 $cfu \cdot g^{-1}$ and a citrate fermenting bacteria content of 3.8E + 6 $cfu \cdot g^{-1}$. Coliform counts never exceeded 10 $cfu \cdot g^{-1}$. These figures were lower than those found in traditional Italian fresh cheese [13] and higher than those found in UF Quarg [2]. In the latter case the difference may be due to a combined acidity - high UF temperature effect on the viability of starter bacteria during UF Quarg production [18], as evidenced also by Tamine [16] during Labneh production by UF.

Milk solids recovery in NF Quarg was 70.6%, and the relevant yield was about 28%. For skim milk Thermo-Quarg and UF-Quarg production (18% TS) a yield of 23.8% and 27%, respectively, is usually reported [10], while for traditional whole milk Quarg (25% TS) a yield of 34.1% has been shown [14]. A higher NF Quarg yield may be obtained by improving the heat treatment of NF concentrates and/or replacing traditional cloth whey separation with successive UF of fermented NF pre-concentrated milk.

3.4. Whey characteristics

The acid whey derived from NF Quarg showed a high TS and lactose content as a result of both the higher TS content of NF milk used for Quarg cheese-making and its reduced volume (Tab. III). Whey from traditional Labneh, separated using a cloth bag, showed a TS and ash content of 57.8 and 7.2 $g \cdot L^{-1}$, respectively [13]. Mineral (11.1 $g \cdot L^{-1}$) and Ca (2.05 $g \cdot L^{-1}$) contents of whey derived from NF Quarg were higher than those present in whey derived from the control Quarg (Tab. III) and those derived from both separator Quarg and Quarg made from milk UF retentates (8.0 and 5.5 $g \cdot L^{-1}$ ash, and 1.2 and 0.3 $g \cdot L^{-1}$ Ca, respectively) [9]. These characteristics improve the feasibility of whey processing, as compared to traditional acid whey, which may be considered an additional advantage of the process proposed.

4. CONCLUSION

NF milk pre-concentration may be considered a suitable technique for making fresh Quarg-type cheese characterised by sweet taste and a high Ca content, without perception of bitter taste. Operating conditions of milk NF are fundamental to improve flux permeation and to obtain the highest lactose retention. The various ions are differently influenced by NF conditions as a function of their electrical charge and size. The degree of NF pre-concentration of milk directly affects the lactose content of cheese, and additional lactose hydrolysis can further improve its sweetness. NF Quarg may be interesting as a basis for production of fresh cheese with added fruit obtained by lowering the sugar content present in fruit preparation. This process makes also effluent treatment easier because it leads to a double effluent stream: an NF permeate with a reduced organic load, and a pre-concentrated whey with a TS and mineral content more suitable for further utilisation and treatment.

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