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Optimization of "Serpa" cheese whey nanofiltration for effluent minimization and by-products recovery

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Abstract

Second cheese whey (SCW) is a by-product of cheese and curd cheese production that is usually not recovered and therefore substantially contributes to the negative environmental impact of the cheese manufacture plants. Membrane technology, namely nanofiltration (NF), is used in this work for the recovery of SCW organic nutrients, resulting from "Serpa" cheese and curd production. The SCW is processed by NF to recover a rich lactose fraction in the concentrate and a process water with a high salt content in the permeate.

The permeation experiments were carried out in a plate & frame NF unit, where two NF membranes (NFT50 and HR-95-PP) were characterized and tested. The NF permeation experiments were performed accordingly with two different operation modes: total recirculation and concentration. In order to select the best membrane and operating pressure for the SCW fractionation, total recirculation experiments were carried out. The NF modeling was also performed, in terms of permeate fluxes and rejection coefficients using the resistances-in-series model and the solution-diffusion model, respectively. After the membrane selection, the concentration experiments showed that the selected membrane (NFT50) at 3.0 MPa allows a water recovery of approximately 80%, concentrating the SCW nutrients approximately 5 times. Therefore, the NF operation can successfully reduce the wastewater organic load and simultaneously contributes to the valorization of the cheese and curd cheese manufacture by-products.

Keywords: Second cheese whey; Wastewater treatment; Nutrients recovery; Nanofiltration

1. Introduction

"Serpa" cheese is made from ovine milk and has a very well-defined geographic origin and quality. Fig. 1 shows the diagram of an integrated process for the valorization of the by-products resulting from "Serpa" cheese manufacture. The cheese whey (CW) resulting from the cheese production can be defatted and filtered in an ultrafiltration (UF) unit. The separated fat (product 3, Fig. 1) can be used in the production of highly nutritive butter. The UF concentrate (product 1, Fig. 1) is very rich in proteins and can be purified for a wide range of applications, such as dietary proteins for functional foods and pharmaceuticals (Jayaprakasha and Brueckner, 1999; McIntosh et al., 1998; Atra et al., 2005).

The "Serpa" CW is currently used in the production of curd cheese. The effluent of the curd cheese production is called second cheese whey (SCW), being a by-product with a very high content in organic matter. The "Serpa" SCW has a very high lactose concentration and is very rich in mineral salts (essentially NaCl), vitamins and free amino acids. The very high salt concentration is due to the addition of NaCl during the production process of cheese and curd. Small amounts of fat and residual proteins are also present in the SCW composition. Nowadays, the majority of the "Serpa" cheese factories (if not all) treat the SCW as a common waste and mix it with the domestic sewage and other less pollutant wastewaters. Without a purification and recovery process like the one shown in Fig. 1, the SCW is a strongly polluting effluent. The negative environmental impact and the loss of this very

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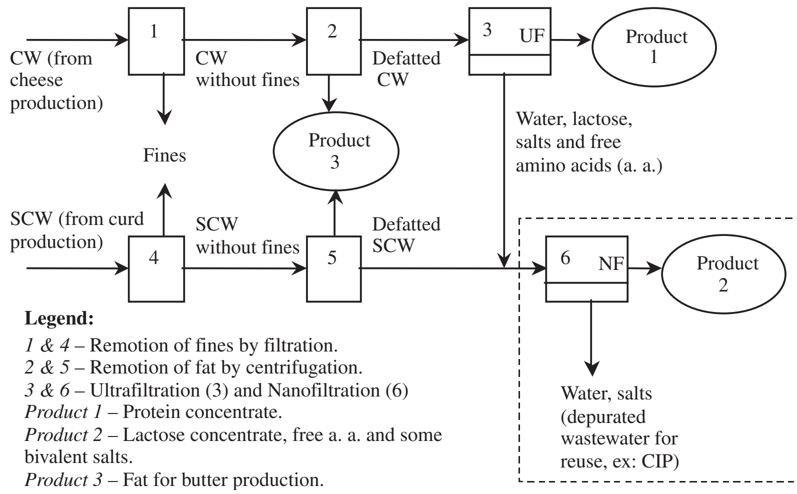

Fig. 1. Process for nutrients recovery and valorization of "Serpa" cheese by-products.

valuable product are the reasons for the implementation of a recovery and valorization process.

With the increasing evolution and utilization of membrane technologies in the dairy industry since the late 1960s, nanofiltration (NF) is a possible economic option in the treatment of the SCW. The dashed line in Fig. 1 delimits the NF unit operation (part of the overall valorization process), on which this work is focused. NF membranes have low rejections (high permeability) of monovalent salts (NaCl, KCl) and have high rejections of the organic compounds and some bivalent salts dissolved in the SCW. The NF operation processes a combined feed of SCW and a CW UF permeate, since both streams have similar qualitative compositions. The NF processing of these streams has two major advantages. First, the production of a clean effluent and the reduction of wastewaters due to the possible reuse of some water in the process (ex: "cleaning in place", CIP). And secondly, the production of a lactose concentrate (product 2, Fig. 1) with potential application in pharmaceuticals, sugar-cellulose fibres (Fernandez et al., 2002) and food industry (Morr and Barrantes, 1998).

Typically, in industrial processes the CW or SCW demineralization is achieved in two steps. First the whey is concentrated by evaporation (EV) then the concentrated whey is demineralized using electrodialysis (ED) and/or ion-exchange (Sittig, 1975; van der Horst et al., 1995). With this kind of equipment, 50–95% of the dissolved ionized salts can be removed resulting in a substantial whey valorization (Sittig, 1975). NF is a good alternative to the combined process EV + ED. In fact, the NF operation has the advantage of simultaneously concentrating and demineralizing the whey, leading to a reduction of the total costs (equipment, energy, etc.) and to a reduction of the wastewater disposal (van der Horst et al., 1995; Nguyen et al., 2003; Atra et al., 2005; Muni et al., 2005; Vourch et al., 2005). Other studies related to the NF of CW and SCW have been made with model solutions (Alkhatim et al., 1998) and real solutions (Vasiljevic and Jelen, 2000; Hinrichs, 2001). These studies try to select the best NF membranes and the best operating conditions for a successful and economic fractionation of the CW and/or SCW. The aims of the present work are: (1) the characterization of the SCW NF permeation performance in total recirculation and concentration mode; and (2) the assessment of the influence of the recovery rates (RRs) on productivity and quality of NF products.

2. Materials and methods

2.1. Second cheese whey sample

The SCW sample was collected at "Ovelheira, Lda", a Portuguese cheese and curd factory. In the sample characterization, a total organic carbon (TOC) analyser (Dohrmann DC-85A), a Crison 2002 micro pH meter and a Crison 525 conductimeter were used. The total nitrogen concentration was also obtained using a Büchi Kjeldahl unit (Distillation unit model 315 and Digestor model 425). Table 1 presents the information from the SCW characterization.

2.2. Membranes and NF unit

Two types of NF membranes (NFT50 and HR-95-PP) supplied by DSS, Denmark were tested. They were subjected to compaction through permeation of pure water ($<1\,\mu S/cm$) at 3.6 MPa for 3 h. The membranes were characterized in terms of pure water permeability and in terms of apparent rejections of reference solutes. The apparent rejection coefficient, $R(i)$, is defined as $R(i) = (C_{bi} - C_{pi})/C_{bi}$, where C_{bi} and C_{pi} are the concentrations of solute i in the bulk concentrate and permeate, respectively. The information related to the characterization of the membranes is shown in Table 2.

All the permeation experiments (membrane characterization and SCW processing) were carried out in a plate & frame NF unit (Lab Unit M20 from DSS, Denmark), with flat sheet membranes and total membrane surface area of $0.072\,m^2$. In all permeation experiments, a feed circulation flow rate of 9.2 l/min and a temperature of 25 °C were kept constant.

2.3. Permeation experiments (total recirculation and concentration modes)

The NF permeation tests were carried out in total recirculation mode (for membrane and pressure selection) and in concentration mode. In the total recirculation mode, both concentrate and permeate are recirculated to the feed tank, while in the concentration mode only the concentrate is recirculated to the feed tank, the permeate being collected in a different vessel. The total recirculation mode experiments were performed at three transmembrane pressures (1.5, 2.5 and 3.0 MPa). The concentration mode experiments were carried out only with the NFT50 membrane (selected membrane) at 3.0 MPa (selected pressure). Again note that in all cases, the feed circulation flow rate is 9.2 l/min and the temperature is 25 °C. For all the samples taken during the NF of the SCW (concentrate and permeate samples), both TOC and total nitrogen concentration, the pH and the specific conductivity were determined.

2.4. Membrane cleaning

After the permeation experiments with the SCW, the membranes have to be cleaned in order to restore the initial permeation water fluxes (after membrane compaction). The cleaning of the membranes is CIP-wise and is performed in accordance with the manufacturer instructions. Typically, cleaning the membranes with a solution of Ultrasil 11 is enough to restore the initial water fluxes. Table 3 presents more detailed data about the cleaning procedure.

Table 1
Second cheese whey characterization

Parameter	Value
pH	6.2
Specific conductivity	23.3 mS/cm
Total organic carbon (TOC)	31.2 g C/l
Lactose	50.6 g/l
Total nitrogen by Kjeldahl method	1.74 g N/l
Proteins and free amino acids	8.3 g/l

3. Theory

Permeate fluxes and rejection coefficients were estimated using the resistances-in-series model and the solution-diffusion model, respectively.

3.1. Resistances-in-series model

The resistances-in-series model considers that besides the intrinsic membrane resistance the adsorption of solutes into the membrane surface can add an additional resistance to the permeation; the permeate fluxes are described by

$$J_{\mathrm{p}} = \frac{(\Delta P - \Delta \Pi)}{\mu(R_{\mathrm{m}} + R_{\mathrm{a}})}, \tag{1}$$

where R_{m} is the intrinsic membrane resistance, given by $1/L_{\mathrm{p}}$ and R_{a} is the resistance due to the adsorption of solutes.

3.2. Solution-diffusion model

The solution-diffusion model allows that the solutes and solvent of a given mixture dissolve in the polymeric matrix of a membrane (active layer), and are then independently transported by diffusion through the membrane due to different chemical potential or concentration gradients, and are desorbed in the membrane–permeate interface.

The diffusive flux of a solute i through the membrane is given by the Fick's first law

$$J_i = -D_{i\mathrm{m}} \frac{\partial C_i'}{\partial x}, \tag{2}$$

where $D_{i\mathrm{m}}$ is the solute i diffusivity, C_i' is the solute concentration in the membrane and x is the distance to the active layer of the membrane.

The relation between the solute concentrations in the fluid phases adjacent to the membrane (feed and permeate side) and the solute concentrations in the membrane next

Table 2
Characteristics of HR-95-PP and NFT50 membranes

Membrane	HR-95-PP	NFT50
Material	Thin film composite on polypropylene	Thin film composite on polyester
Pure water permeability, Lp (m)	8.20×10^{-15}	1.82×10^{-14}
Rejections (R) to reference solutes, % (pressure = 1.0 MPa; T = 25 °C)		
NaCl	97.3	69.0
Na_2SO_4	99.1	99.0
Glucose	98.5	94.5
Sucrose	98.6	98.5

Table 3
Membrane cleaning data

Step	Description	pH	Pressure (MPa)	T (°C)	Time (min)
1	Water flushing for complete removal of the SCW	—	Minimum allowed	Room temperature	—
2	Solution containing Ultrasil 11	11	0.5	40	15
3	Water flushing till complete pH normalization is achieved	—	Minimum allowed	Room temperature	—

to these interfaces, is defined as the partition coefficient, given by the expression

$$\Phi = \frac{C_i'}{C_i}. \tag{3}$$

The integration of Eq. (2) through the membrane, is carried out considering the following boundary conditions

$$x = 0, \quad C_{im}' = \Phi C_{\text{im}}, \tag{4}$$

$$x = L, \quad C_{ip}' = \Phi C_{\text{ip}} \tag{5}$$

and results in

$$J_i = \frac{D_{\text{im}}\Phi}{L}(C_{\text{im}} - C_{\text{ip}}) = B(C_{\text{im}} - C_{\text{ip}}), \tag{6}$$

where L is the membrane thickness and B is a characteristic constant of a given membrane/solution system, given by

$$B = \frac{D_{\text{im}}\Phi}{L}. \tag{7}$$

In steady state, the solute flux through the membrane is given by

$$J_i = J_{\text{p}} C_{i\text{p}}, \tag{8}$$

where J_{p} is the permeate flux and $C_{i\text{p}}$ is the solute concentration in the permeate.

The intrinsic rejection coefficient, $R'(i)$, is defined as

$$R'(i) = \frac{C_{\text{im}} - C_{i\text{p}}}{C_{i\text{m}}}. \tag{9}$$

Combining Eqs. (6), (8) and (9), results

$$R'(i) = \frac{J_{\text{p}}}{J_{\text{p}} + B}. \tag{10}$$

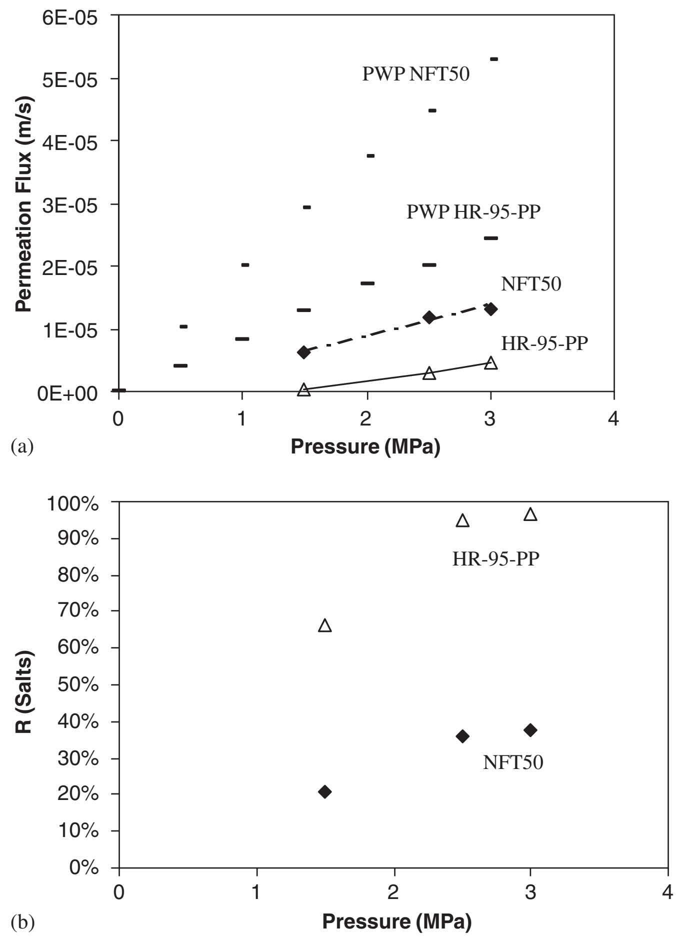

Fig. 2. Variation of the permeation fluxes (a) and salts rejections (b) with the applied pressure—total recirculation mode.

4. Results and discussion

4.1. Experiments in total recirculation mode

The permeation results obtained in total recirculation mode for the two membranes tested, show that the permeate fluxes for both membranes decrease considerably when SCW is treated (Fig. 2(a)). These results are due to the high content in terms of salts of the SCW, leading to important osmotic pressure, and to adsorption phenomena.

A comparison of permeate fluxes between the two membranes shows that the NFT50 membrane is the one that presents higher productivities and that the fluxes vary linearly with the increase of the transmembrane pressure. Regarding the salts rejection, Fig. 2(b) presents a rejection increase with increasing pressure for both membranes. NFT50 membrane has much lower salts rejection ($<40\%$) than the HR-95-PP membrane ($>65\%$).

One can see in Fig. 3(a) and (b) that both TOC and nitrogen rejections are high and similar for both membranes, the TOC rejection always higher than 98% and the nitrogen rejection always higher than 86%.

The results presented in Figs. 2 and 3 show that the NFT50 membrane has higher permeation fluxes and lower salts rejections than the HR-95-PP membrane, keeping high rejections of TOC and Nitrogen. Therefore, this membrane is more suitable for the fractionation of the

SCW, producing an organic matter concentrate and a permeate with very low concentrations in terms of TOC and nitrogen. For the NFT50 membrane, the optimal operating pressure is the higher pressure tested, i.e. 3.0 MPa, due to the fact that in the studied pressure range there is a linear dependence between the permeation flux and the pressure applied.

The NF modelling was carried out in terms of permeation fluxes and in terms of TOC rejection coefficients through the use of the resistances-in-series model and solution-diffusion model, respectively. For the permeate fluxes prediction Eq. (1) was used. The osmotic pressure ($\Delta\Pi$) was assessed by extrapolating the permeate flux line to the value zero. The adsorption resistance (R_a) was determined numerically. These results are shown in Table 4 and in Fig. 2a. Fig. 2a shows that the predicted permeate fluxes (lines) are in very good agreement with the ones obtained experimentally. It is also shown that the osmotic pressure phenomenon is more severe for the HR-95-PP membrane and that the ratio between the membrane resistance and adsorption resistance is higher for the

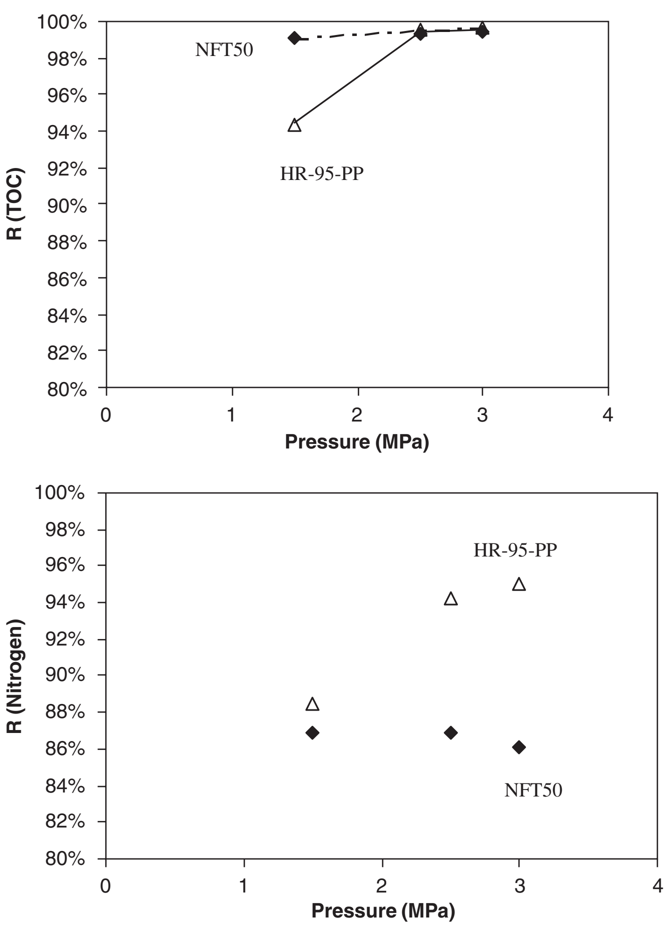

Fig. 3. Variation of the TOC rejection (a) and total nitrogen rejection (b) with the applied pressure—total recirculation mode.

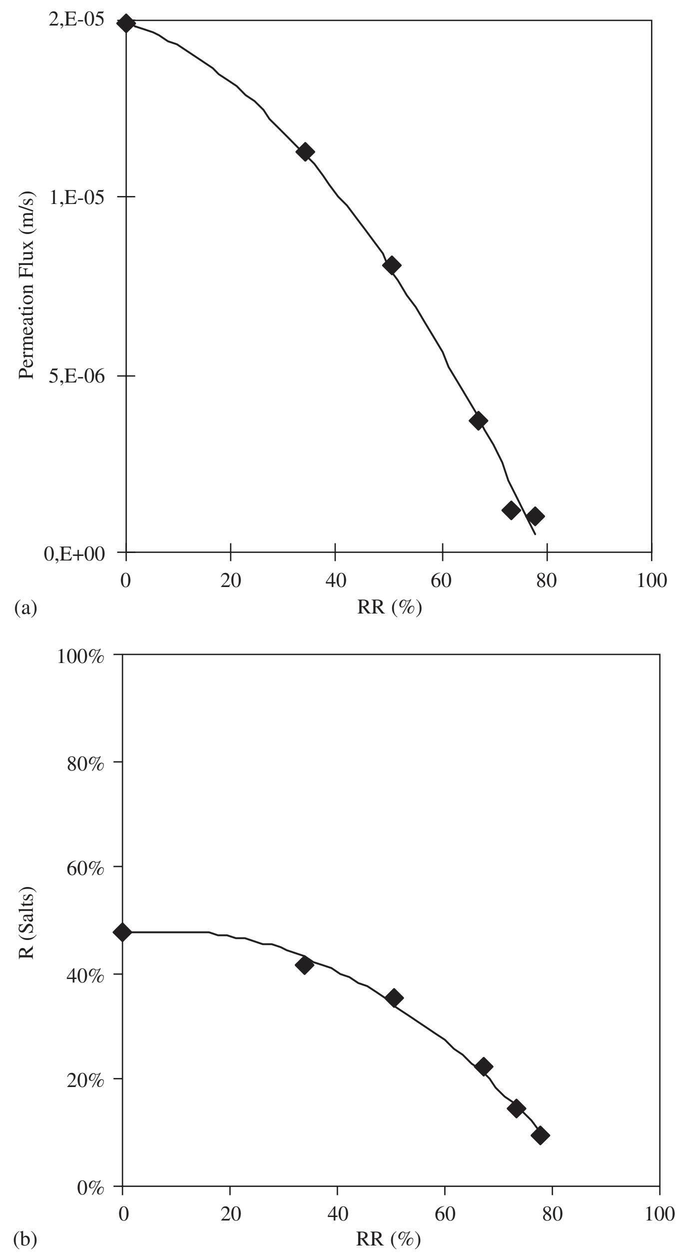

Fig. 4. Variation of the permeation fluxes (a) and salts rejections (b) with the water recovery rate—concentration mode. Membrane: NFT50, pressure: 3.0 MPa.

Table 4
NF modeling results

	$\Delta\Pi$ (MPa)	R_m (m^{-1})	R_a (m^{-1})	R_a/R_m	B (m/s)
HR-95-PP	1.39	1.2×10^{14}	2.39×10^{14}	2.0	1.82×10^{-8}
NFT50	0.12	5.51×10^{13}	1.52×10^{14}	2.8	6.56×10^{-8}

NFT50, this result is expected as membranes with higher permeabilities usually have higher fouling/adsorption problems.

The rejection coefficients prediction was carried out through the used of the solution-diffusion model (Eq. (10)), leading to the determination of the B parameter. The results are presented in Table 4. Having in mind the concentration polarization minimization the permeation experiments were carried out at the highest feed flow rate, allowed by our permeation equipment, and at a transmembrane pressure of 3.0 MPa, where the permeate flux linearity with pressure is still observed, and therefore it is assumed that the apparent rejection coefficients (R) are equal to the intrinsic rejection coefficients (R'). Table 4 shows that the B parameter found for membrane NFT50 is higher than the one determined for the HR-95-PP, and this shows, as expected, that the organic matter permeation is higher for the NFT50 membrane.

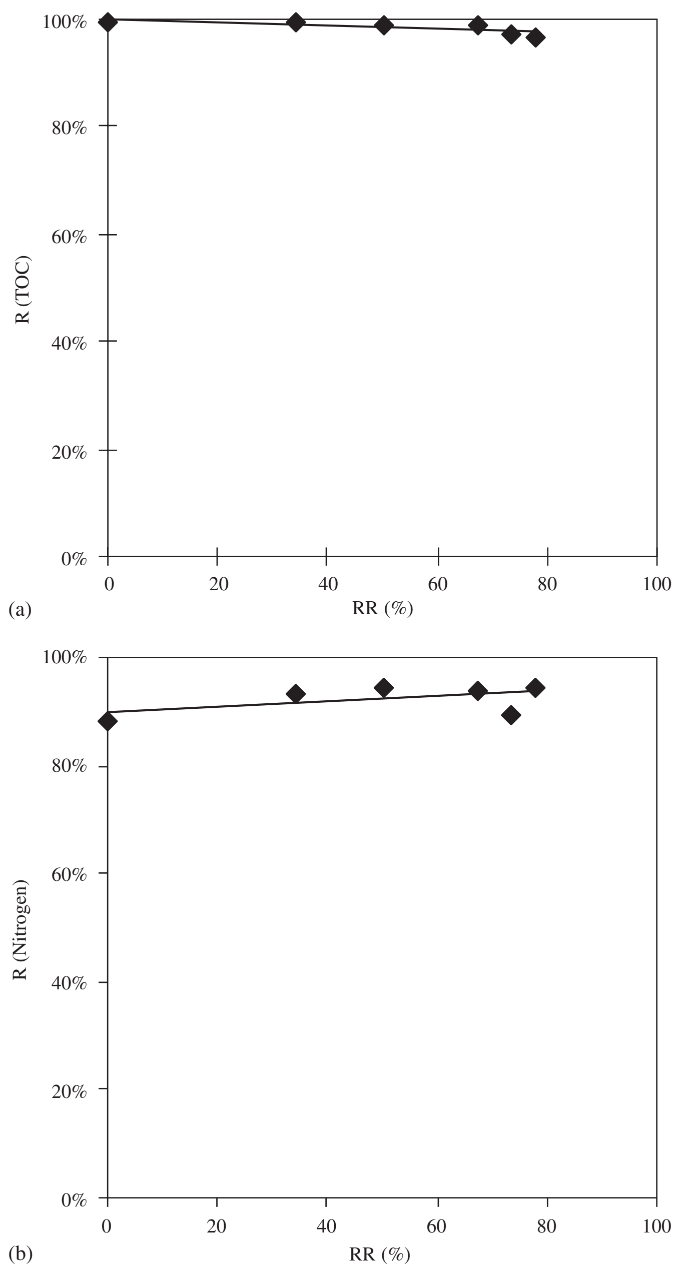

Fig. 5. Variation of the TOC rejection (a) and total nitrogen rejection (b) with the water recovery rate—concentration mode. Membrane: NFT50, pressure: 3.0 MPa.

4.2. Experiments in concentration mode

Using the selected membrane (NFT50) at the selected operating pressure (3.0 MPa), the experiments in concentration mode were performed. Fig. 4 presents the permeation fluxes (a) and salts rejections (b) for the fractionation and concentration of the SCW. The RR is defined as RR (%) = (total permeate volume/initial feed volume) $\times$ 100.

Fig. 4(a) shows a steep flux decline with increasing RR. At the beginning of the concentration experiment the permeate flux was 1.49×10^{-5} m/s and decreased till a value of 1.03×10^{-6} m/s when an RR of 77% was reached. Fig. 4(b) shows that with the RR increase there is a strong decrease in the salts rejection. The salts rejection decreases from 50% (at the beginning of the experiment) to 10% at an RR of 77%. Fig. 5(a) and (b) shows that the TOC and nitrogen rejections remain practically constant with the RR variation and are around 98% and 92%, respectively.

Analysing the combined results, one can say that for higher RRs, the SCW fractionation (separation of the organic matter from salts) is improved, but the process productivity (permeation flux) has a sharp decline.

Table 5 presents the variation of the organic and nitrogen content in the concentrate with the RR. The total organic matter, mainly lactose, is concentrated about 5 times, thus obtaining a lactose concentrate depleted of salts.

5. Conclusions

In this work, two NF membranes were tested envisaging the secondary CW fractionation in two different streams, allowing the valorization of the separated products—a lactose concentrate and a permeate water that can be used upstream in the process or in CIP.

Table 5
Concentration of total organic carbon (TOC) and total nitrogen in the NF concentrate during the nanofiltration of the SCW—concentration mode

RR (%)	Initial: 0.0	34.0	50.5	67.2	73.5	Final: 77.8
TOC (g C/l)	29.06	46.21	63.24	96.67	122.8	140.1
Total nitrogen (g N/l)	1.46	2.16	2.86	4.14	5.38	7.73

The NFT50 membrane showed, in a preliminary set of permeation experiments, the best results in terms of SCW fractionation and productivity. The optimal operation conditions were found to be: operating pressure of 3.0 MPa, temperature of 25 °C and feed circulation flow rate of 9.2 l/min. NF modeling showed that the NFT50 membrane is less affected by osmotic pressure and more affected by adsorption than the HR-95-PP membrane.

The final concentrate stream obtained in the concentration mode experiment is a lactose-enriched solution with a lactose concentration approximately five times higher than the initial value. This lactose enrichment is due to the very high NFT50 rejection of organic matter (>98%). The salts rejection decreases with the RR increase, presenting values always lower than 40%. In fact, these results allow the SCW fractionation into a salt depleted lactose concentrate, than can be used as a raw material in the pharmaceutical, food or paper industries, and a salt enriched permeate almost free from organic matter, that can be reused in the process.

The NF operation, using the selected membrane and the optimal operating conditions, can therefore minimize the wastewater environmental impact and at the same time contributes to the valorization of the cheese and curd cheese making by-products.

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