Concentration of whey by nanofiltration and Spray-drying

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ABSTRACT

For decades, whey was considered as a highly polluting industrial waste. Whey's treatment with the purpose of obtaining value-added products, such as protein concentrates, represents not only economic gains but also minimizes its serious environmental problems.
The primary objective of the present thesis is the concentration of whey samples using the following sequence of processes: nanofiltration, with and without diafiltration, vacuum evaporation and the drying of the protein concentrates by spray drying. We also pretend to study the influence of lipids in the flow permeation of whey. The NF process was carried out at 50 °C and 7 bar with a polyamide membrane, model H2521TF. It was observed a sharp decline in the flux of permeation of whey samples during the first 12 minutes. The skim milk whey showed higher permeate flux. The permeate flux of skim milk whey decreases from 23,3 to 4,8 $L.m^{-2}.h^{-1}$, while in the whole milk whey the decrease was from 15 to 4,3 $L.m^{-2}.h^{-1}$. The diafiltration step reduces the salt and lactose contents of the concentrate obtained by nanofiltration. For the resistances in series model was concluded that the major contribution to the mass transfer resistance is due to the concentration polarization at 98%. The Spray-drying of concentrates showed to be difficult and with a low yield. It was obtained 14 g, 30 g and 70 g of powder concentrates resultant of nanofiltration, nanofiltration/diafiltration and vacuum evaporation, per 1300 ml of concentrated whey, respectively.

Keywords: Whey, Nanofiltration, Vacuum evaporation, lipids, Spray-drying

1. Introduction

Whey is the main byproduct obtained from cheese production. Released during the precipitation of casein from milk by acid or enzymatic coagulation represents 85 to 95% of milk used in cheese production and contains 55% of solids components present in milk [1,2].

Whey is rich in valuable components, such as protein and lactose. For instance, β-lactoglobulin and α-lactoalbumin proteins compose 70% of total protein content of whey and are responsible for hydration and foaming process of whey solutions, which qualify whey as good raw material for ice cream manufacture or yoghurt [3,4,5].

The possibility of its recovery and treatment has been the subject of several studies, leading to improve the separation of its constituents, concentration, and purification [6,7,8,9].

The discharge of untreated whey in watercourses can lead to serious environmental damage, for example, the eutrophication of aquatic environment, due to high chemical oxygen demand (COD). This nutrients content causes the proliferation of microorganisms, responsible for the consumption of high amounts of oxygen. The COD pollutant load of whey can achieve between 60.000 and 80.000 $mgO_2.L^{-1}$.[8]

Brazil is the world's sixth largest producer of milk and one of the largest producers of cheese, with a production of 580.000 tons (2007). It is estimated that about 10 L of milk is used to make 1 kg of cheese, resulting in 8-9 L of whey. This is equivalent to 5 million tons of whey produced annually. In spite of the high organic matter content, cheese whey is mostly disposed as a wastewater, directly to the sewage or rivers and it's occasionally used for animal feed to avoid the waste treatment costs [10,11,12].

There is no much information available about the Portuguese production. However, according to 2001 data, it is estimated that whey production is about 500.000-560.000 tonnes per year. From the statistical analysis of production data and information provided by industry, it is estimated that the average production of whey powder, in continental part of the country, is about 6.000 tons per year [13].

In current days, the Nanofiltration has assumed an increasingly important role in the dairy industry. The growing application is related to its intermediate selectivity between ultrafiltration (UF) and the Reverse osmosis (RO), molecular exclusion rates between 200 and 1000 g/mol, which allow the separation and concentration of organic solutes and partial demineralization of whey. When used in the place of evaporation, electrodialysis and RO, to concentrate and demineralise the whey, it becomes possible to minimize the energy and total costs [14,15].

Nanofiltration (NF) is presented as an important process in the separation of small molecules and minerals. Its application has attracted the attention of researchers, in particular, the treatment of wastewater, purification and water demineralization, food processing and biological compounds separation [16,17,18,19,20].

Balannec et al. (2005) [21] studied the application of NF membranes and RO for the treatment of a solution of skimmed milk in order to reduce its COD. In all tests of concentration, the permeation flux decreased sharply early in the filtration. The membranes of RO were more effective in reducing the organic load. Retention of lactose was between 98 and 99%. However, permeate final COD values due mainly lactose, are very high compared to the permissible limit for human consumption of water.

Minhalma et al. (2007) [22] used the NF permeate from UF whey lactose to recover the whey resulting from Serpa cheese production. The concentration assay yielded a fraction of lactose with a concentration factor of five times and a recovery of 80% water with a high mineral salt content.

The efficiency NF process may be affected by the passage of lactose to permeate and nitrogen compounds [23] as well as by phenomena of concentration polarization and fouling of membranes [24]. The loss of nitrogen compounds and lactose to permeate is dependent on the characteristics of the membrane [25] and may also be influenced by pre-treating the food and the operating conditions of the process [14].

The membrane clogging results from interactions between the membrane and the various solutes present in feed, or between these and the already adsorbed solutes [26]. The most important components in the clogging of the membranes are proteins of whey, which can adsorb to the membrane surface or within the pores, lipids and minerals such as calcium and phosphate.

According Suarez et al. (2006) [27] from the whey NF the protein concentration near the membrane surface increases with pressure, due to the increased concentration polarization. If the concentration is high enough, can form a gel layer, representing an additional resistance to permeate flow. The solubility of proteins depends on various factors, including pH and temperature [28,29].

Yorgun et al. (2008) [8] studied the UF (3 bar), NF (5-8 bar) and RO (12 bar) samples of whey from the manufacture of cheese curd and white cheese with 0% and 0 2% lipids, respectively. The authors pretended to obtain a permeate stream with a low COD so that it could be discharged into the environment. The NF membranes used are polyethersulfone and polyamide. They observed that the process of the sample NF whey with 0,2% lipids results in initial permeation fluxes slightly lower (27,5; 25 and 17 $L.m^{-2}.h^{-1}$) other serum sample (30; 30,8; 20 $L.m^{-2}.h^{-1}$). The decrease in permeate flux was predictable due to the formation of the gel layer at the membrane surface, the extent that power is being processed and that increases the deposit of solid waste.

Luo (2012) [30] investigated the NF skim and whole milk with a polyamide membrane NF270 to evaluate the influence of lipids in the filtration process. Observed that for levels below 12g/L lipid their effects are negligible in NF. As justification feature shear stress and the hydrophilic of the membrane, which has a small contact angle and thus not deposited the lipid membrane surface. However, the decrease of permeation flux was more pronounced for higher lipid content and the flow permeation decreased by 3,1% compared to 7,6% without lipids to 12 g/L lipids.

The PSM has been considered as an alternative to traditional methods of processing fluids in the food industry, mainly in improving the competitiveness of the process or product.

Several papers apply UF process on the concentration of whey. Thus, the NF is presented as an alternative. However, it is need a greater understanding of whey NF, in terms of operation, materials, process control, rejection mechanism of solutes. The NF is widely used in industry and their properties allow enable new separations that are difficult or expensive to obtain through other separation methods.

The aim of the present work is the study of the influence of lipids content on the permeate flow resulting of whey NF. Moreover, the study of the spray-drying technique on the retentate stream is also addressed.

2. Materials and methods

2.1 Whey

The raw material consisted on two whey samples: whole whey (0,2 % lipids) and skim whey (not measurable lipids content considered 0%). The Brazilian company Dairy Cordilat Ltda, production unit of Palhoça, Florianópolis, Santa Catarina, Brazil, kindly provided these samples. The whey resulted from the manufacture of Mozzarella cheese and "*queijo prato*". The whey composition is shown in Table 1.

The whey samples were filtrated and then refrigerated at 3-4 ºC. Next step, they were heated until 75 ºC on a hot plate with agitation (40 rpm) for uniform heating and finally were cooled to 50ºC. The samples were stored under refrigeration (4ºC) until its use in the experiments.

Table 1
The composition of whey samples studied (average).

Component	Content (%)[1]
Water	93,4
Lactose	4,8
Mineral salts	1,0[2]
Protein	0,6
Lipids	0,2
pH	6,5

2.2 Schematic representation of the work developed

The different steps performed during the present work are shown in Fig. 1.

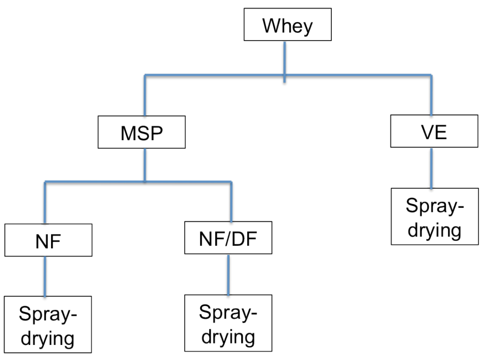

Fig. 1. Work steps. Legend: MSP-Membrane separations processes, NF-Nanofiltration, DF-Diafiltration, VE-Vacuum evaporation (Vacuum distillation).

2.3 Lactose determination

The lactose content was analyzed by the method of dinitrosalicilic acid (DNS) according to Miller (1959) [31]. A spectrophotometer was used in this analysis.

The measurements were performed with a spectrophotometer Lambda 45 – PerkinElmer at a wavelength of 540 nm.

2.4 Total protein determination

The total protein content was determined using the colorimetric method of Bradford (Sigma-Aldrich). The protein present in solution forms a complex with the dye Coomassie Brilliant Blue G-250 present in the Bradford reagent. This dye has a maximum absorbance at 465 nm. However, when combined with the protein displays a shift in absorbance of the band to 595 nm. The experimental procedure is followed according to that provided by the manufacturer. The absorbance measurements were performed with a spectrophotometer Lambda 45 (PerkinElmer).

2.5. Soluble Solids determination

The soluble solids content was determined with a refractometer, model Q667 (Quimis) measured at (20 ± 0.2) ° C. The results are given in ° Brix.

2.6. pH

A microprocessor pH meter (model Q-400MT, Quimis) was used in this analysis.

2.7. Ash

The ash content was determined using the method described by the Adolfo Lutz Institute [32].

2.8 Minerals determination

The content of sodium and potassium salts was analyzed by atomic emission spectrometry flame, with a flame photometer Micronal B462 and proceeding according to the method of the Adolf Lutz Institute [32]. The Atomic Absorption Spectrometry with Atomic Absorption spectrophotometer with flame atomization, Hitachi - Z8230, determined the content of magnesium and calcium.

2.9 Membrane concentration

Whey samples were concentrated using a tangential filtration system on a pilot scale, with a nanofiltration membrane as seen in the schematic diagram shown in Fig 1. The experiments were performed on pilot equipment that permits the batch circulation mode, which means that both permeate and concentrate could be carried back to the feed tank.

The nanofiltration module is equipped with a NF90 membrane (GE Osmonics, Minnetonka, USA) which is composed of polyamide with 0,9 m^2 of filtration area.

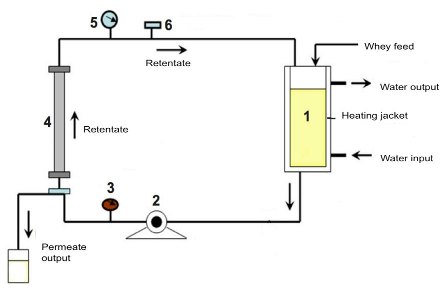

Fig. 2. Schematic diagram of the nanofiltration unit. 1 - feed tank, 2 - pump, 3 - thermometer, 4 - membrane module, 5-manometer, 6 - valve.

In order to evaluate the influence of temperature and pressure on whey permeate flux, it were carried out experiments at different temperatures (30-55 ºC) and pressures (1-8 bar). In these experiments, both permeate and retentate were maintained under recirculation in closed systems. The permeate flux was calculated according to the Eq. 1.

[1] Mass percentage

[2] Maybe to calcium addiction.

$$J_p = \frac{V_p}{A_p . t} \text{ (Eq.1)}$$

Where V_p is the permeate volume collected during the time interval t and A_p is the membrane surface area of permeation [33].

Approximately 6,0 L of which whey sample (whole and skim whey) permeated through the membrane over 45 min, this being the time necessary to complete the concentration in an open system, which means that the permeate was removed from the process. In the trials permeate was removed and the retentate re-circulated until a concentration factor of around 3,2. The volumetric concentration factor (VCF) is calculated according to Eq. 2.

$$VCF = \frac{V_{feed}}{V_{feed} - V_{permeate}} \text{ (Eq. 2)}$$

Where V_{feed} is the total volume used in the feed, $V_{permeate}$ is the volume collected in the permeate fraction and VCF is the concentration factor [33].

The quality of the filtration process was measured according to lactose, protein, minerals salts content present in permeate, evaluated as described in Sections 2.3, 2.4 and 2.8, and the efficiency was measured according to the flux of permeate and the retention index. This index measures the relation between the amounts of the compound of interest in permeate and in the concentrated solution, which demonstrates the ability of the membrane to retain this compound under the experimental conditions. The index is calculated according to Eq. 3.

$$R' = \frac{C_{Aa} - C_{Ap}}{C_{Aa}} = 1 - \frac{C_{Ap}}{C_{Aa}} \text{ (Eq. 3)}$$

Where R' is the retention index, C_{Ap} is the concentration of the compound of interest in permeate and C_{Aa} is the concentration of the same compound in the feed [33].

It is important to know the rate of fouling that occurs in the membrane process, and one way of measuring this is to compare the permeate flux of the solution under study with the permeate flux when water is used as feed solution, under different pressures. Usually a variation in system pressure will cause a change directly proportional to the permeate flux. The fouling influence was measured by comparison of the permeate flux of the whey samples (whole and skim) with the flux of distilled water, increasing the pressure from 1,0 to 7,0 bar.

2.10 Transport model: the resistance in series model [34]

The intrinsic membrane resistance (R_M) was determined by the flow of water (J_{iw}) measured with the membrane clean before starting the whey nanofiltration **(Eq. 4).** The viscosity of water (μ_w) is considered to be 1,003 x10^{-3} Pa.s [35] and the viscosity of the permeate (μ_p) equals to 1,4 × 10^{-3} Pa.s [10].

$$J_{initial.water} = \frac{P_T}{\mu_p . R_M} \text{ (Eq. 4)}$$

The total resistance (R_T) was determined with the definition of permeate flux, knowing the final flow permeation of whey (J_{fp}), the permeate viscosity (μ_P) and pressure (P_T) **(Eq. 5).**

$$R_T = \frac{P_T}{\mu_p . J_{final.permeate}} \text{ (Eq. 5)}$$

The resistance due to fouling or membrane colmatation (R_F) was determined by knowing the permeated water flow after processing and cleaning with water ($J_{final\ water}$) **(Eq. 6).**

$$R_F = \frac{P_T}{\mu_p . J_{water.before.washing}} \text{ (Eq. 6)}$$

The resistance due to the phenomenon of concentration polarization (R_{PC}) was determined with the knowledge of the resistances: R_T, R_M, R_F (Eq. 7).

$$R_{PC} = R_T - R_M - R_F \text{ (Eq. 7)}$$

2.11. Nanofiltration/Diafiltration concentration

Skim milk whey was concentrated by nanofiltration with an identical procedure presented in subsection 2.9. It was fed 8 L. Diafiltration (DF) consists in water addiction, equal volume of the permeate NF. This volume was added to the collected NF retentate. It was added 5.5 L of water corresponding to the volume of permeate relating the first NF (VCF: 3,2).

2.12. Vacuum distillation

Primarily, the whey sample (skim whey milk) was filtered and the temperature of the hot water bath was set to 80 °C and the cold water bath to 10,5 °C. Then 1L of sample was introduced in the balloon equipment, the drum rotation equipment started (60 rpm), the vacuum pump was turned on, the speed and vacuum were adjusted (80-120 rpm) until condensation has occurred. It was necessary to pay attention to rotation speed; vacuum and temperature of the hot bath to prevent the sample boiling and the occurring of reflux to the collecting permeate balloon. The experiments were finished when a volume of 690 ml of water corresponding to a VCF of 3,2 was collected.

2.13. Spray-drying

The concentrates were dried with a spray-dryer Büchi B290. The operating conditions are shown in Table 2.
Büchi B290. The experimental procedure is followed according to that provided by the manufacturer [36].

Table 2
Operating conditions for drying whey retentates by using Spray-drying. Legend: NF – Nanofiltration, NF/DF – Nanofiltration/Diafiltration, VE- Vacuum evaporation.

Parâmetros	NF	NF/DF	VE
T air inlet (ºC)	174	175	176
T air output (ºC)	71	60	52
T room (ºC)	17	22	24
Aspirator (%)	100	100	100
Pump (%)	25	25	25
Flow (%)	25	25	25

3. Results and discussion

3.1 Effects of lipid on fouling and filtration behaviors

In the whey concentration were used low pressures (2-8 bar). Therefore, this process can be assumed to be viable mainly because of the reduced energy requirements necessary to generate the lower pressure. Fig. 2 shows that the permeate flux changed linearly with the pressure in the interval studied and for both samples. Initially, at 3 bar, the values of permeate flux, for both samples, presented a difference of 1,3 $Lm^{-2}.h^{-1}$ between each other. After this pressure is observed that the permeate flux values begin to show a greater difference between them, and the sample of skim whey has always values higher flow relative to the other sample. At 7 bar, the difference between the values of the permeate fluxes is 15,3%, while at a pressure of 8 bar this difference is smaller and equal to 9,4%. The difference between the samples tends to decrease.

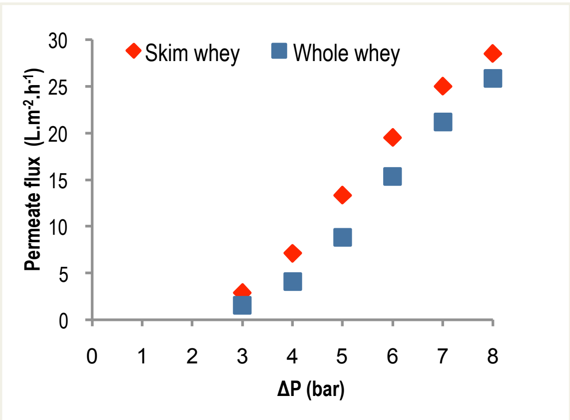

Fig. 2. Influence of pressure on the permeate fluxes whey samples (◆-Skim whey and ■-Whole whey). Operating conditions: T = (40 ± 2) °C; $v_{tangential}$ = 0,68 m/s; ΔP = 2 - 8 bar.

The Fig. 3 shows the values determined for the retention of lactose with the pressure increase. Initially, it is observed that the membrane rejects at 4 bar 96,6% of lactose that exists in the whole milk whey sample. This rejection increases with the increasing of pressure (8 bar) until 98,6 %.

For instance, skim milk whey at 4 bar the membrane rejects 95% lactose and undergoes an increase to 98.5% at 8 bar. With the pressure increase may have been greater compression of the membrane, leading to a higher retention of lactose.

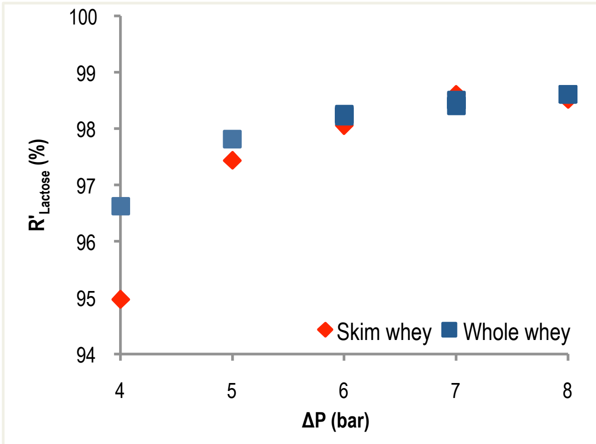

Fig. 3. Apparent rejection factor of lactose ($R'_{lactose}$) as function of pressure. (◆ - Skim whey and ■ - Whole whey). Operating conditions: vtangential = 0,68 m.s-1; T = (40 ± 2) °C; P = 4 - 8 bar.

The protein content in the permeate, resulted from nanofiltration of whole milk whey sample was evaluated and it was found that the obtained values are very small and the errors associated to their determination are quite high.

Fig.4 shows that increasing the temperature from 30 to 55 ºC, maintaining the pressure at 7 bar, it was possible to determine the relationship between the temperature and the permeability of the membrane. Permeate flux increased proportionally for both whey samples. Initially at 30 ºC, the permeate flow of skim milk whey is equal to 16,7 $L.m^{-2}.h^{-1}$ while for other sample is smaller and 12,4 $L.m^{-2}.h^{-1}$.

Concerning the whole milk whey, the permeate flux increases linearly with temperature until 45 ºC (16,2 $L.m^{-2}.h^{-1}$) and remaining stable at 16,5 $L.m^{-2}.h^{-1}$ for the others temperatures. For skim milk whey it was observed that the permeate flux also increases with temperature until 50 ºC and then remains ate 21,2 $L.m^{-2}.h^{-1}$.
For the temperature range studied, it can be seen that skim milk whey has always permeate flux values higher than the other sample.

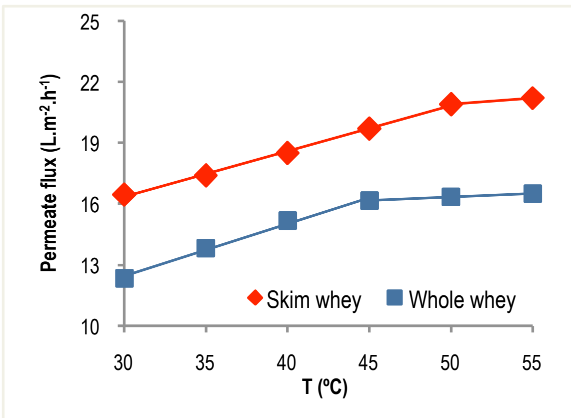

Fig. 4. Permeate flux of whey samples (J_p) as function of temperature (T). Operating conditions: T = (30-55) °C; $t_{angential}$ = 0,68 m/s; P = 7 bar.

Fig. 5 demonstrate that an increase in temperature corresponds to a decrease in the apparent retention coefficient of lactose. In the temperature range studied was observed that the whole milk whey has a superior apparent retention coefficients of lactose when compared with skim milk whey. Concerning 30 and 50 °C there is a decrease in rates of rejection between 99% and 97% for whole milk whey and 98,6% to 97,2% in the case of skim milk whey. After a temperature of 50 °C, the apparent rejection coefficient of lactose for whole milk whey remains stabilized at 97%. Whey samples analyzed have similar retention values between them, and the whole milk whey shows values above the skim whey. The greatest difference observed corresponds to a temperature of 50 ° C.

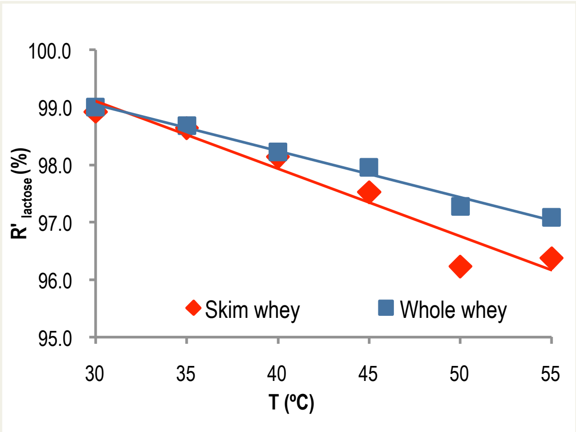

Fig. 5. Apparent rejection factor of lactose ($R'_{lactose}$) as function of temperature. Operating conditions: vtangential = 0,68 m.s-1; T = (30-55) °C; P = 7 bar.

Fig. 6 presents the evolution of the permeate flow samples of whey over the experiments of nanofiltration in concentration mode. The experiments in concentration mode took place over 45 minutes. It is found that the permeate flow of skim milk whey decreases sharply up to the first 12 minutes, from 23,3 $Lm^{-2}.h^{-1}$ to 4,8 $Lm^{-2}.h^{-1}$. In the case of whole milk whey is observed a marked reduction in the first 6 minutes, decreasing from 15 to 4,3 $Lm^{-2}.h^{-1}$ corresponding to an average flow of 3,2 $Lm^{-2}.h^{-1}$. In literature, there are several studies on the evolution of the permeate flow of whey solutions. The permeation fluxes exhibit a typical for this type of process behaviour, in which the phenomena of concentration polarization and fouling of the membrane leading to a gradual reduction in the flow of membrane permeation.

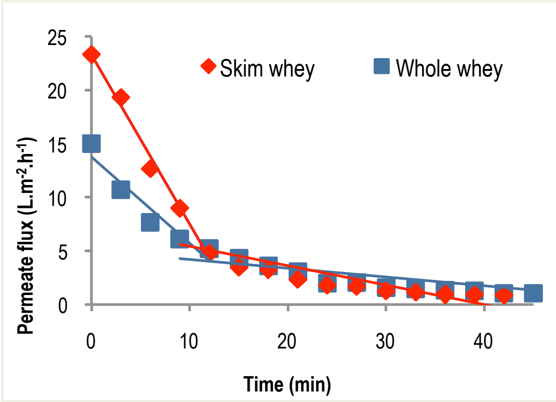

Fig. 6. Permeate flux of nanofiltration as a time function. Operating conditions: P = 7 bar; T = 50 °C; v tangential = 0,68 m.s-1.

3.2 Comparison between the concentrates obtained by the different processes: NF, NF/DF and VE

Initially, the skim milk whey sample has a total soluble solids content of (6,4 ± 0,1) ° Brix. Through its concentration is expected that occurs the increasing of the solids content in the retentates. Of all three processes the VE concentrate has the highest value of solids (16,4 ± 0,1) °Brix. During vacuum evaporation process occurs the formation of foam and the accumulation of fat in the walls of the roto-evaporator balloon.

By comparison of the values for concentrated NF and DF, it appears that the first has a higher solids content (12,1 ± 0,1) ° Brix, up 2 ° Brix relative to DF. These results can be explained considering that in a DF process, the protein concentrate is subjected to a further washing with water, the loss occurring solutes and salts due to the following procedure.

It is observed that the lactose content increases with increasing sample concentration, increasing to 49, 79 and 130 g / L, to processes NF/DF, NF and VE, respectively. Although the value obtained for the concentrated DF is the smallest of the three concentrates produced, this represents an increase of 13% compared to the initial rate. The highest value corresponds to the VE process and represents an increase of 65% compared to the NF concentrate.

Table 3
Concentrates of nanofiltration (NF); Nanofiltration/diafiltration (NF/DF) and vacuum evaporation (VE) of the skim milk whey sample (Final Volumetric concentration factor 3,2).

	Retentate		
Compound	**NF**	**NF/DF**	**VE**
Soluble solids (ºBrix)	(12,2 ± 0,1)	(10,2 ± 0,1)	(16,4 ± 0,1)
Lactose (g/L)	79	49	130
Protein (g/100g)	1,46	0,96	2,74
Protein (g/L)	14,94	9,82	28,03

In the sample of skim milk whey, potassium (1306,6 ± 40,4) mg/L and sodium (551,6 ± 13,5) mg/L are presented as the major minerals. Analyzing the values of monovalent ions sodium and potassium, it is possible to conclude that through DF protein concentrates are obtained with lower levels relative to the initial sample. With DF cycle is obtained a protein concentrate with a content of potassium (425,2 ± 12,7) mg/L, representing a reduction of 67% compared to the initial sample. For the sodium and observed that the DF and its content less than 58% of the concentrate in the initial serum sample of skimmed milk, decreasing (551,6 ± 13,5) to (229,7 ± 12,8) mg/L. It is concluded that the NF concentrate has a higher content of sodium 537,9 mg/L, with respect to the NF/DF sequence.

For divalent ions Magnesium and calcium it is not observed the same reduction than the one observed for monovalent ions. The NF/DF allows the obtantion of concentrates with a lower content of divalent ions, although that is not so pronounced as in the case of monovalent ions. Between NF and NF/DF concentrates there is a difference between them of 26% and 41% in calcium and magnesium ions, respectively.

When analyzing the values obtained VE and NF/DF processes, it appears that for VE retentate the contents in calcium and magnesium salts are higher: 159,4 mg/L and 292,5 mg/L, respectively, than NF/DF retentate.

Table 4
Powder retentate. Mineral content: Sodium, Calcium, Potassium, Magnesium; in retentates obtained by nanofiltration (NF), diafiltration (DF) and vacuum evaporation (VE) (Final Volumetric concentration factor 3,2).

	Powder retentate		
Compound / Processe	***NF***	***NF/DF***	***EV***
Ash (% m/m)	5,93	2,00	8,29
Lactose (g/100g)	69,4	67,3	69,9
Protein (g/100g)	12,94	12,78	13,52

3.3 Spray-drying

The drying of VE process concentrate VE apresents the highest yield 70 g of concentrated powder. The main differences observed between yields should be associated to water and solids contents present in concentrate.

According Gernigon et al. (2010) [37], whey is a product of hard drying, due to the presence of lactose and other solutes in its composition, the interactions of these with water, or even among themselves, leading to a low yield. Drying of the Mozzarella cheese whey by spray-drying is a difficult process and results in unsatisfactory values. The milk products of hydrolyzed lactose are difficult to dry due to the high hygroscopic characteristic of glucose and galactose. Mineral salts may also increase the difficulty of drying. For example, the acid whey is particularly difficult to dry because it has a small pH and high salt content.

Table 5 shows that whey powder has an high mineral content. The resulting powder concentrate EV shows a content of 8,3% ash. There is a significant difference between the values of dehydrated whey NF and DF, 5,9 and 2%, respectively. These values are indicative of a lower mineral content in the concentrate obtained by DF and greater elimination of salts throughout the process. It is observed that the mineral content is higher for the VE concentrate, remaining 8,3% mineral content. In the NF concentrate the salt content is equal to 6%. Predictably the NF/DF concentrated powder has the lowest mineral content, 2%. It is observed that whey powder is a significant source of protein, with a content of approximately 13% in all three cases. It is possible to verify that the values obtained are very close, however, the highest values were found for the process of EV of 13,5%.

Table 5
The concent of lactose, protein and ash in retentate powders, resulting from nanofiltration (NF), nanofiltration/diafiltration (NF/DF) and vacuum evaporation (EV) of skim milk whey (final volumetric concentration factor 3,2) with subsequent spray-drying.

	Retentates		
Minerals	***NF***	***NF/DF***	***VE***
Sódio (mg/L)	767,6	(229,7 ± 12,8)	(2295,3 ± 84,6)
Potássio (mg/L)	1776,7	(425,2 ± 12,7)	(5670,8 ± 84,3)
Cálcio (mg/L)	520,6	387,5	680,0
Magnésio (mg/L)	140,6	83,0	231,3

By comparison between NF and DF processes, there is lower mineral content in the process of DF. Between EV and DF there is a reduction in the sodium content of (41,60 ± 3,08) mg/L to (16,53 ± 0,89) mg/L, representing a decrease of 60%. In the case of potassium ion, the content in th EV was (86.16 ± 6.25) and DF (34.90 ± 1.88) mg/L, also a reduction of approximately 60%. From the comparison of NF with DF, we observe a reduction in salt content from (27,16 ± 1,37) to (16,53 ± 0,89) mg/L in sodium, NF and DF processes respectively, representing a decrease of 40%. In the case of the potassium content, this one decreased from (61,08 ± 2.62) to (34,90 ± 1,88) mg/L, for the NF and DF processes, representing 43%.

Table 6
Mineral content in powders concentrates, resulting of nanofiltration (NF), nanofiltration/diafiltration (NF/DF) and vacuum evaporation (EV) of the skim milk whey (final volumetric concentration factor 3,2) with subsequent spray-drying.

	Powder concentrates		
Minerals	***NF***	***NF/DF***	***EV***
Sodium (mg/L)	27,16 ± 1,37	16,53 ± 0,89	41,60 ± 3,08
Potassium (mg/L)	61,08 ± 2,62	34,90 ± 1,88	86,16 ± 6,25
Calcium (%)	0,55	0,54	0,65
Magnesium (%)	0,14	0,12	0,18

3.4 Resistances in series model

In table 7 are presented the parameters and the necessary fluxes values to determine the different resistances to whey milk permeation.

Table 7
Parameters and permeate flux results, used to calculate the different resistances to mass transfer. μ_p – permeate viscosity, $J_{initial\ water}$ – permeate flux of pure water with clean membrane, $J_{p\ initial}$ – permeate flux in the beginning of whey nanofiltration, $J_{p\ final}$ – permeate flux in the end of whey nanofiltration, $J_{final\ water}$ – permeate flux after the concentration of nanofiltration and subsequent cleaning with water.

Skim milk whey	Whole milk whey
T = 50 ºC	T = 50 ºC
P = 7 bar	P = 7 bar
μ_p = 1,40 mPa.s [14]	μ_p = 1,40 mPa.s [14]
$J_{initial\ water}$ = 74,67 $L.m^{-2}.h^{-1}$	$J_{initial\ water}$ = 62,67 $L.m^{-2}.h^{-1}$
$J_{initial\ permeate}$= 23,33 $L.m^{-2}.h^{-1}$	$J_{initial\ permeate}$ = 15,00 $L.m^{-2}.h^{-1}$
$J_{final\ permeate}$ = 0,87 $L.m^{-2}.h^{-1}$	$J_{final\ permeate}$ = 0,67 $L.m^{-2}.h^{-1}$
$J_{water\ before\ washing}$ = 74,67 $L.m^{-2}.h^{-1}$	$J_{water\ before\ washing}$ = 52,67 $L.m^{-2}.h^{-1}$

Table 8 shows that the resistances to the permeation of the two whey milk samples have a difference of 0,62 x 10^{15} m^{-1}. For the whole milk whey sample, the resistance due to fouling is lower when compared to the resistance due to the membrane. The skim milk whey not presented resistance due to the fouling. This may provide a justification for the difference between the permeate flux observed in experiments through concentration of NF, in which it was found that the permeation flux of skim milk whey is higher than the observed permeate flux of whole milk whey sample.

It is found that the largest contribution to total resistance of permeate flux for comes from the phenomenon of concentration polarization, constituting 2,65 x 10^{15} m^{-1} and 2,04 x 10^{15} m^{-1} for whole milk whey and skim whey, respectively. The resistance derived from the membrane itself is the second largest contribution to total resistance and values were higher in the case of whole milk whey.

Table 8
Resistances to the permeation of skim milk whey by nanofiltration, obtained by the model of resistance in series. R_T represents total resistance; R_M is the intrinsic membrane resistance, R_F the resistance due to fouling and R_{CP} the resistance resulting of concentration polarization.

Amostra	R_T x 10^{-15} (m^{-1})	R_M x 10^{-13} (m^{-1})	R_F x 10^{-12} (m^{-1})	R_{CP} x 10^{-15} (m^{-1})
Whole milk whey	2,70	4,01	7,61	2,65
Skim milk whey	2,08	3,36	0,00	2,04

The concentration polarization is presented as the largest contributor to the resistance of permeates flow. This may occur due to the presence of macromolecules, protein, lipids, lactose. In the study of the influence of pressure variation in permeate flow, this increases with pressure, but does not increase proportionally due to existence of solutes. As the pressure is increased, it can be seen the deposition of solutes on the membrane surface, thereby increasing the thickness of the polarization layer increases the resistance to associate itself [39,40]. According Suaréz et al. (2006) [28] when performing nanofiltration the whey protein levels near the surface of the membrane increases with pressure, due to the formation of a concentration polarization layer. If the concentration is high enough it forms a gel layer can be formed which represents one additional permeation resistance to flow.

Conclusions

In the pressure range studied, 2-8 bar, the permeation flux of the samples of whole and skim milk whey, increased linearly with increasing pressure. The permeate flux of the whole milk whey passes of 0,53 $L.m^{-2}.h^{-1}$, at a pressure of 2 bar, until a value of 25,8 $L.m^{-2}.h^{-1}$ at 8 bar. For the skim milk whey the permeate flux at a pressure of 2 bar is 0,41 $L.m^{-2}.h^{-1}$ and at 8 bar is 28,5 $L.m^{-2}.h^{-1}$. At a pressure value of 4 bar it is observed a difference between apparent rejetion coefficients of lactose ($R'_{lactose}$) of 3,5%, with the higher value corresponding to whole milk whey. With the increase of pressure there is an increase rejection by the membrane of lactose, with the highest values for serum sample from whole milk. After a pressure of 7 bar R'lactose values are coincident for both samples milk whey.

In the temperature range studied of 30-55 °C it is found that the permeate flux of whey milk samples increased linearly with the increasing temperature. The permeate flow of skim milk whey increases linearly until a temperature of 50 ºC, while for the whole milk whey the linear increase occurs up to 45 ºC. Initially, the permeate flux is 16,7 $L.m^{-2}.h^{-1}$ and 12,3 $L.m^{-2}.h^{-1}$ to skim and whole milk whey, respectively.

NF experiments in concentration mode were conducted in 45 minutes. By studying the influence of temperature and pressure, it is observed that the most favorable operating conditions are 50 °C and 7 bar. Initially, the permeate flow of skim milk whey is 23,3 $L.m^{-2}.h^{-1}$ and markedly decreased until

12 minutes to 4,8 $L.m^{-2}.h^{-1}$. In the case of whole milk whey sample, the initial value is $L.m^{-2}.h^{-1}$ and after 15 minutes is 3,2 $L.m^{-2}.h^{-1}$. The permeate flux of the lean solution are higher than the values obtained for the whole milk whey, however, an average flow of 1,3 $L.m^{-2}.h^{-1}$ was obtained after 24 minutes of laboratory experiments.

It is found that the process of DF allows the reduction from 79 g/L to 49 g/L the content of lactose in the concentrate resulting from NF. It is noted that the concentration of mineral salts is also reduced through the diafiltration step. The sodium content in NF concentrate is reduced from 767,6 mg/L to 229,7 mg/L, the potassium content is reduced from 1776,7 mg/L to 425.2 mg/L and the calcium from 520 mg/L to 387,5 mg/L.

The drying of liquid concentrates by spray-drying proved to be very difficult, 70, 30 and 14 g of concentrate powder produced by VE, NF/DF, NF, from a start volume of 1300 ml of liquid concentrate.

There was an overall resistance to mass transfer of 2,70 x 10^{15} and 2,08 x 10^{15} m^{-1}, for the whole and skim milk whey, respectively. And to point out that 98% of the total resistance results from the phenomenon of concentration polarization for both samples analyzed. The second greatest resistance corresponds to the membrane, representing 1,5% and 1,6% of the total resistance to permeation of skim and whole milk whey, respectively. Finally it should be noted that the resistance due to fouling was only observed for whole milk whey, representing 0,3% of the total resistance.

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