

Diafiltration Based Cow's Milk Partial Demineralization by Membrane Filtration Process – Parameter and Technology Estimations

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Abstract. Milk and dairy products contain a number of biological materials that are essential for the human body, for example proteins, lipids, vitamins and minerals. In this study the application of membrane filtration based milk partial demineralization is detailed. The main point of the partial demineralization is to reduce the monovalent ions (Na^+ , K^+) but to keep the divalent ions (Ca^{2+} , Mg^{2+}) content. The experiments were carried out using laboratory ultra- and nanofiltration units. Comparing the separation behavior of the membranes it was found that the investigated membranes are suitable for the partial demineralization. The result of the Lowry test showed that the protein concentration is higher in the retentates of all membrane filtrations than in the permeates.

Keywords: partial demineralization of milk, membrane separation, protein concentration, conductivity

1. Introduction

The milk is a complex lipid, carbohydrate and protein matrix which contains a number of biologically active components (Csapo, Csapone, 2002). Developments in the filtration technology have created the opportunity for an entirely new approach to partial milk demineralization. Among the most common procedures for demineralization we find ion exchange-based, nanofiltration and electro dialysis-based technologies. Depending on the pore size we can distinguish four types of filtration membranes, namely microfiltration, ultrafiltration, nanofiltration and reverse osmosis. The membrane is a selective barrier which allows some components to pass through but not others. The pore size of an ultrafiltration membrane varies between 10 and 100 nm, these pores are

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only permeable for the water, salts and the lower molecular weight components. The nanofiltration membranes pore size is between 1 and 10 nm, smaller than that of the ultrafiltration and microfiltration membranes. Nanofiltration membranes are widely used in the dairy industry and the partial demineralization (Baker, Martin, 2007; Suárez et.al. 2009). The membrane separation processes are selective and during the separation chemical changes do not happen, nonetheless, the membrane filtration techniques have disadvantages, such as concentration polarization and membrane fouling, which can result in flux decrease (Mulder, 1996; Strathmann et.al. 2006). To reduce the membrane fouling it is necessary to optimize the transmembrane pressure and the cross-flow velocity, or to use some other turbulence promoters like vibrating modules (Hodúr et.al. 2013) or static mixers (Gáspár, 2016; Nath et.al. 2017). The UF membranes are suitable to separate proteins from sugars and minerals, as it is planned in the first step. The demineralization of whey can be very efficient, when the nanofiltration is followed by a batch diafiltration step.

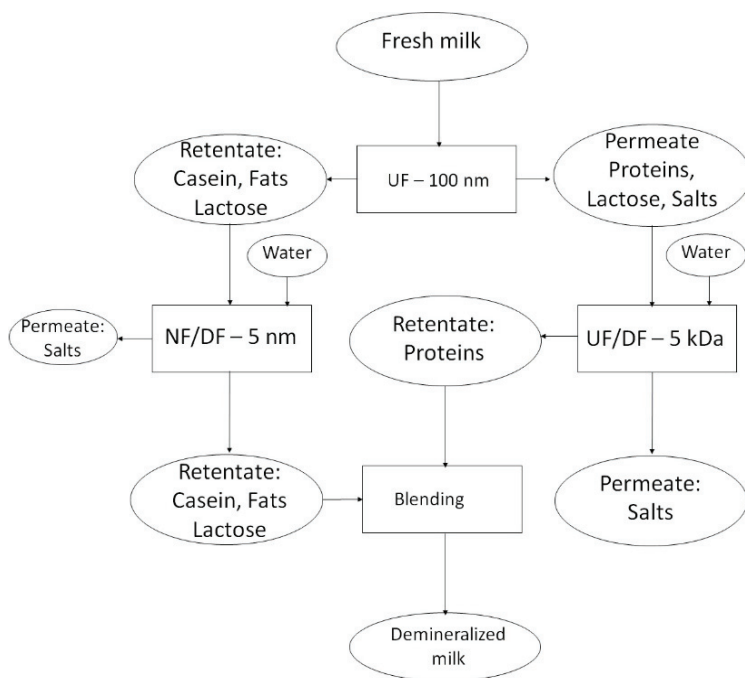


Fig. 1. Flow diagram of milk partial demineralization by using UF and NF membrane diafiltration

These advantages were observed in ricotta cheese production technology, improving characteristics like color, rheology, microstructure, etc, while the protein and total solids (TS) content did not change (Prudencio et al. 2014; Mohammad et al. 2015). In this study membrane filtration (UF, NF) combining common batch concentration and diafiltration has been carried out for milk partial demineralization using our previous laboratory experiences in demineralization of whey (Román 2010).

The major purpose of this study is the partial demineralization of milk to decrease the monovalent ions from the matrix. To remove the monovalent ions complex membrane separation processes were used as it is presented in the flow diagram in *Fig. 1*.

The main idea was to separate casein and fats from the proteins, salts and lactose treating the retentate of large pore size UF membrane with the 5 nm pore size NF membrane washing out the monovalent salts by dialization solvent.

On the other hand, the permeate of the UF was diafiltered using a small nominal molecular weight cut-off (NMWCO) UF membrane to wash out the salts from the permeate.

2. Material and Methods

For the experiment the average composition milk was purchased in the local supermarket. In this study two ultrafiltration and one nanofiltration membranes were used. The first ultrafiltration membrane (Schumasiv 100nm, UF1) was used for milk pre-concentration. The next steps were the UF1 permeate and UF1 retentate diafiltration by using different pore size membranes, Schumasiv type 5 nm pore size nanofiltration membrane for treatment of the UF1 retentate and the Membralox type 5 kDa, exactly a small pore size ultrafiltration membrane was used for diafiltration of the UF1 permeate.

For the characterization of the membrane filtration and diafiltration the usual procedure has been used, the permeate flux was calculated from the permeate volume:

$$J = \frac{V}{A * t}$$

where J - pure water flux [$L/(m^2 \cdot h)$], V - volume (m^3), A - membrane surface (m^2) and t - filtration time (h).

The Volume Concentration ratio (VCR) was calculated as follows:

$$VCR = V_f / V_c$$

where V_f - volume of feed (cm^3) and V_c - volume of retentate (cm^3).

The rejection coefficient of certain solutes was calculated using the formula:

$$RF = (1 - C_p / C_r) * 100$$

where C_p - solute concentration in the permeate (g/l) and C_r - solute concentration in the retentate (g/l).

In the Ultrafiltration of Milk, the effective area of the UF1 ultrafiltration membrane was 0.005 m^2 . During the experiment the milk was circulated from a feed tank, and the experiment was performed at room temperature ($25 \text{ }^\circ\text{C}$), which was maintained by using a thermostat bath. The volume of permeate and the time were measured during the experiment. In this experiment the transmembrane pressure was 1.5 bar and the recirculation flow rate was 150 l/h, chosen on the basis of earlier experiments (Csighy et.al. 2016). These parameters were controlled by regulation valves. The protein content in the UF1 permeate and in the UF1 concentrate fractions were determined by taking samples from these fractions during the experimental runs, which were analyzed by LOWRY method.

In the *Diafiltration of UF1 permeate (UF/DF)*, the active area of the membrane was 0.005 m^2 . The experiment was performed at room temperature ($25 \text{ }^\circ\text{C}$), which was maintained by using a thermostat bath. During the experiment the transmembrane pressure was 4 bar and the recirculation flow rate was 200 l/h. To control the process parameters, regulation valve and adjustable circulation pump were used.

During the *Diafiltration of UF1 retentate (NF/DF)*, the experiment was carried out at the optimal transmembrane pressure and recirculation flow rate values. In this case these parameters were the same as in the case of the diafiltration of UF1 permeate (4 bar, 200 l/h). As a result of this, the process time was reduced significantly and better mixing effect was achieved. The active area of the membrane was 0.005 m^2 and the temperature was $25 \text{ }^\circ\text{C}$.

The ion content in the permeate and in the retentate fractions were determined by taking samples from these fractions during the experimental runs, which were analyzed by conductivity method. During the ultrafiltration and diafiltration processes the ion content is somehow related to the ion concentration, which is based on the anion and cation concentration, but when we are washing out the cations and/or anions by diafiltration, it can be detected by changing in the conductivity in the permeate and/or retentate (Román, 2010). In order to determine the optimal

parameters for the membrane separation processes (pre-concentration, diafiltration) it was important to prepare the factorial experimental design. These settings and the results of this and experiments are presented in details elsewhere (Csighy, 2015), but for the experimental runs with different membranes, the optimal transmembrane pressure and recirculation flowrate values were used.

3. Results and Discussion

Ultrafiltration of milk. The influence of the volume concentration ratio (VCR) at optimal operation parameters settings during the experimental runs of milk ultrafiltration (UF1) and diafiltration steps of the UF1 permeate and retentate are shown in Figs 2–4, for different membranes. From these results it is obvious that in all cases the measured fluxes are economically feasible, because in the whole range of the experiments, the permeate fluxes are over 20 l/(m²h) (Mulder, 1996). The volume concentration factor (VCR) and flow rate significantly influenced the permeate flux. Reaching the target volume concentration ratio value (VCR = 2) the flux becomes permanently constant.

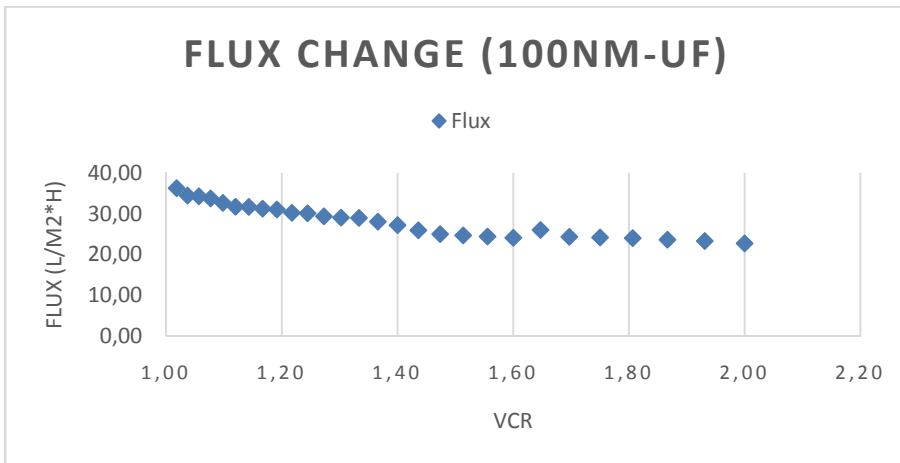


Fig. 2. Milk concentration by ultrafiltration – UF1 (100 nm) membrane

Concentration of UF1 permeate by diafiltration (UF/DF). The small pore size ultrafiltration membrane was used for the elimination of the

monovalent ions from the UF1 permeate. The membrane had lower pore size (5 kDa) where the macromolecules like proteins and partially the lactose were rejected. The influence of the volume concentration ratio on permeate flux during the diafiltration of UF1 milk permeate is shown in Fig. 3. During the ultrafiltration process the flux was decreasing similarly as in the UF1 ultrafiltration process.

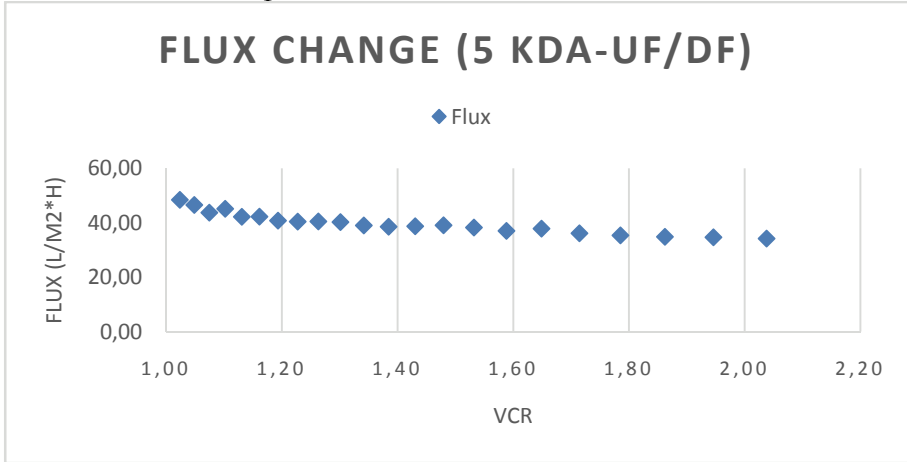


Fig. 3. Concentration of ultrafiltration permeate (UF1) by diafiltration (5 kDa) membrane

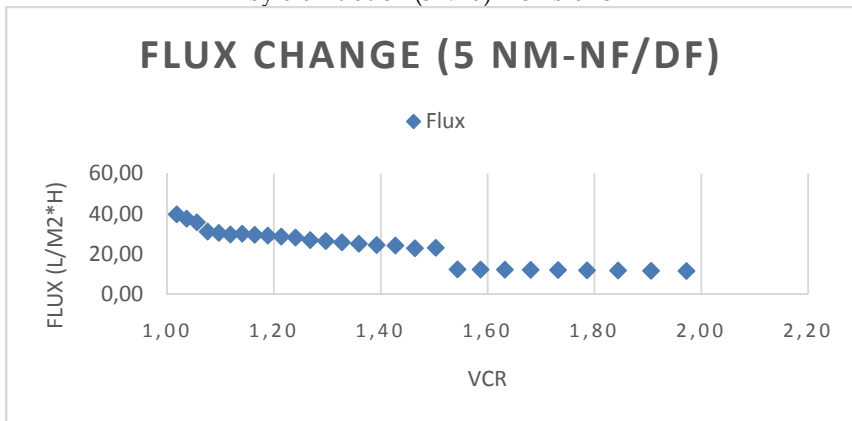


Fig. 4. Concentration of ultrafiltration (UF1) retentate by diafiltration (5 nm) membrane

Concentration of ultrafiltration (UF1) retentate by diafiltration (NF/DF). As in the case of diafiltration of milk permeate the flux of the permeate also decreased with an increase of the VCR as it is shown in Fig. 4. During the diafiltration of retentate the nanofiltration membrane pore size was 5 nm.

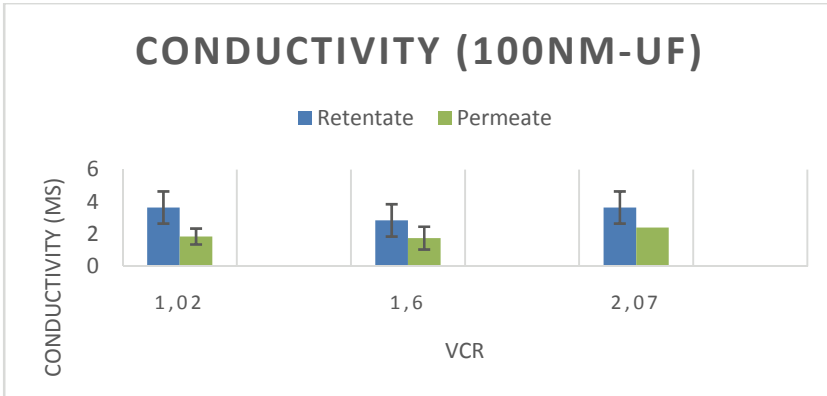


Fig. 5. Conductivity in the UF1 permeate and retentate (UF 100 nm)

The effect of membrane filtration and diafiltration on the conductivity can be seen in Figs 5–7. During the first ultrafiltration process (UF1) the permeate side of conductivity values are lower than the retentate side values. The average value of conductivity in the permeate was 1.7 mS and 3.7 in the retentate. Therefore the ultrafiltration is a useful method for reducing ion content in the permeate.

During diafiltration stage (5 kDa) the process showed a decreased trend, furthermore this trend is minimal in the target value (VCR = 2) linearly as it is illustrated in Fig. 6. This inverse proportion can be seen in these diafiltration (5kDa) experiments. The permeate values are decreasing continuously, but the retentate side values are growing.

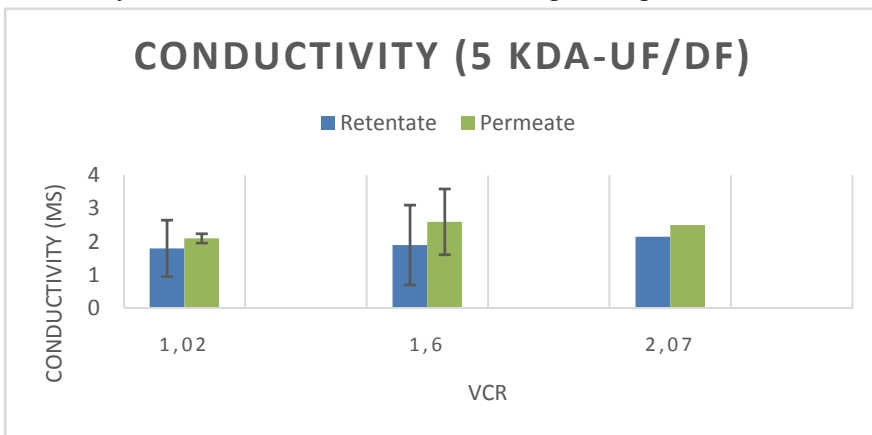


Fig. 6. Conductivity in the permeate and the retentate in UF/DF (5 kDa)

It can be seen that the conductivity during the diafiltration process (5 nm) is decreasing both in the permeate and the retentate.

The effect of diafiltration (retentate) on the conductivity can be seen in Fig. 7. In the third point the retentate and permeate values become nearly constant, which are 1.5 mS (retentate) and 1 mS (permeate).

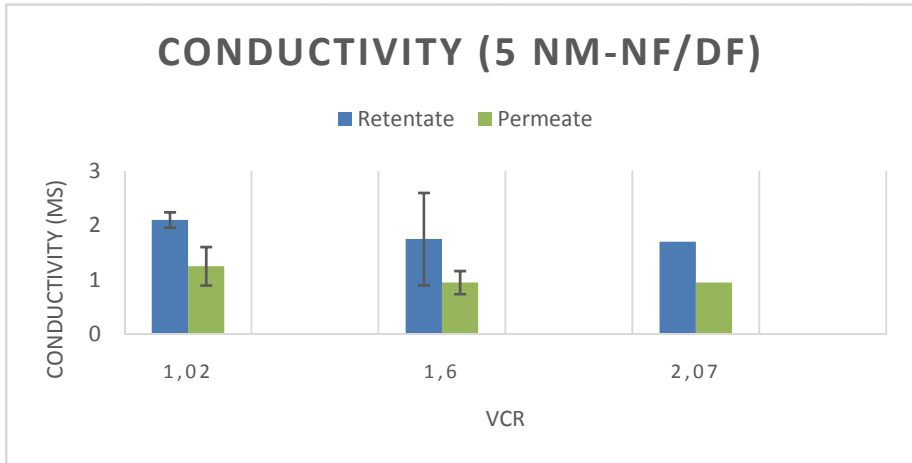


Fig. 7. Conductivity in the permeate and the retentate in NF/DF (5 nm)

The effect of membrane filtration and diafiltration on the protein concentrations in the permeates and retentates are shown in Figs 8 and 9.

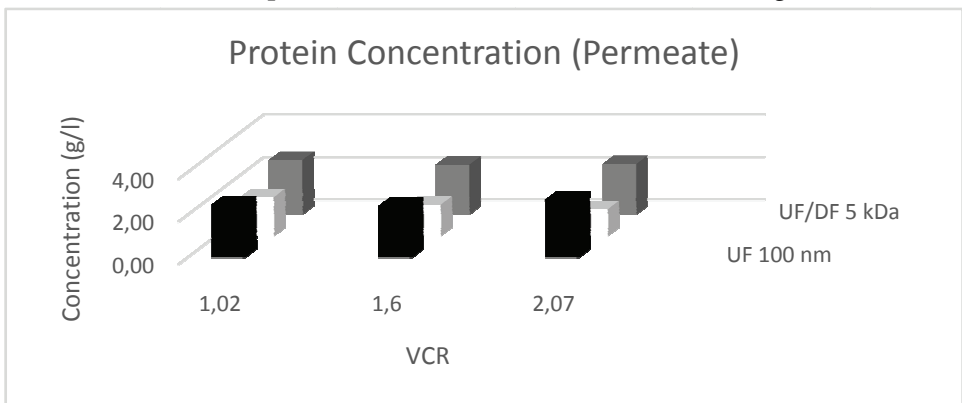


Fig. 8. Protein concentration changes in the permeates in the case of all applied membrane filtration processes

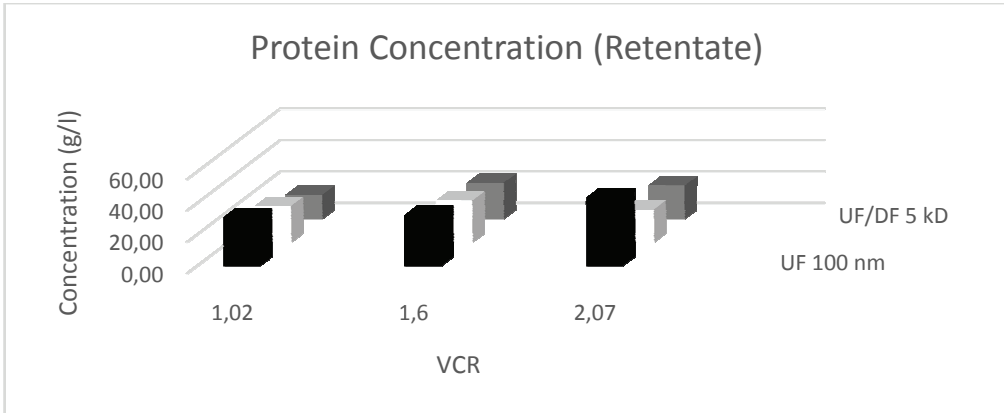


Fig. 9. Protein concentration changes in the retentates in the case of all applied membrane filtration processes

On the basis of the diagrams it is obvious that the proposed multistep membrane technology is suitable for partial demineralization of milk, because the protein concentrations are quite low in the permeates (Fig. 8), between 1 and 2.2 g/l, even at highest VCR values (2.07), which means that the protein losses during the UF1 concentration step and diafiltration steps are less than 10%, because of good average protein retention (90%) of all membranes (Csighy, 2015).

4. Conclusions

From the results of the experiments it can be concluded that the first step ultrafiltration (UF1) and also the diafiltration of the UF1 permeate and retentate by ultrafiltration and nanofiltration can be successfully achieved by the investigated membranes (100 nm UF, 5 nm NF, 5 kDa UF). The protein rejection of the membranes (100 nm UF, 5 nm NF, 5 kDa NF) reached 83–98%, the flux in the end of the process was between 11.5–33 l/(m²h). The results of the conductivity measurement showed that the ion concentration increased in the concentrate and decreased in the permeate in the case of 100 nm and 5 nm membranes.

Inverse behavior was detected with the 5 kDa UF membrane because in this section the permeate had higher conductivity, i.e. ion concentration due to washing out of the ions, mostly monovalent by diafiltration (Román, 2010). Overall it can be concluded that this technology is suitable to reduce the ion concentration in milk, keeping the other main components (protein,

lactose, fat) concentrations near to the initial levels, detecting approximately less than 10% losses of the above mentioned components.

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