Journal of Membrane Science and Research 6 (2020) 138-146

Journal of Membrane Science & Research

journal homepage: www.msrjournal.com

Research Paper

Performance Evaluation of Ceramic Membrane on Ultrafiltration and Diafiltration Modes for Efficient Recovery of Whey Protein

Sama A. Al-Mutwalli [1], Mehmet Dilaver [2], Derya Y. Koseoglu-Imer [1,*]

[1] *Environmental Engineering Department, Istanbul Technical University, Istanbul, Turkey*
[2] *TUBITAK Marmara Research Center Environment and Cleaner Production Institute, Kocaeli, Turkey*

Article info

Received 2019-10-01
Revised 2019-12-10
Accepted 2019-12-29
Available online 2019-12-29

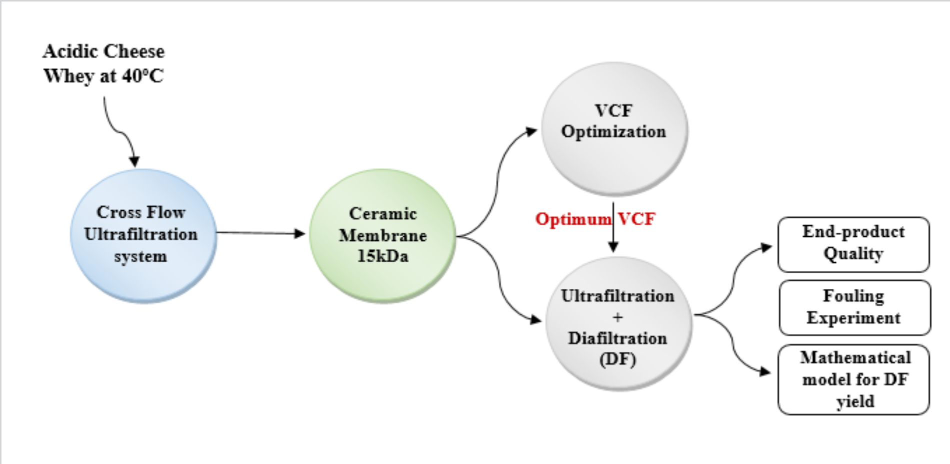
Keywords

Acid cheese whey
Ceramic membrane
Membrane fouling
Ultrafiltration
Diafiltration

Highlights

- Effect of VCF on the quality parameters of cheese whey
- Effect of diafiltration on the end product quality of the acidic cheese whey.
- Fouling analysis of ceramic membrane with different models
- Calculation of diafiltration yield with mathematical model

Graphical abstract



Abstract

The recovery of high-quality valuable end products from the whey is a very important industrial process. Ultrafiltration (UF) followed by diafiltration (DF) process improves the recovered protein content in powder and the washing lactose/minerals contents of the concentrate stream in the cheese whey filtration. The aim of this study is to investigate the UD ceramic membrane performance followed by DF with experimental and real-time model results. The experiments conducted by applying UF as the pre-concentration step and two intermittent feed diafiltration (IFD) cycles with disc ceramic membrane having 15kDa molecular weight. Firstly, at the pre-concentration step, the volume concentration factor (VCF) were performed at 1.4, 2.0 and 3.3 ratios. It was observed that the concentrations of whey components increased in the concentrate stream with the increasing of VCF during the UF process. Secondly, two IFD cycles were performed experimentally. The mathematical model for DF yield calculation was applied with real-time function. Thirdly, the fouling experiments were conducted during the overall process steps and three models were used for fouling parameters calculation. By applying the IFD process at the optimum VCF value, the protein percentage could be increased up to 33% in the concentrate stream.

1. Introduction

Cheese whey can be defined as a by-product of the cheese manufacturing consists of different components such as protein, lactose, minerals and fat [1]. Membrane technologies in the cheese whey processing lead to great benefits from its end products, especially the protein. Membrane processes are applicable for fractionation/separation of cheese whey components [2,3]. Ultrafiltration (UF) process are the most important membrane technology and have the ability to concentrate any substance with molecular weight between 1 to 1,000 kDa [4] especially for concentrating the whey protein. UF membranes are performed by applying a specific pressure in order to separate the particles according to their sizes [5] and molecular weight. In case of separation of whey components, by using UF process, the protein and fat can be recovered with accumulating on the surface or the pores of membrane as the retentate while lactose, minerals and water pass through the membrane pores as the permeate by using particular driven pressure [5]. The main applications of UF process in dairy industry are to separate protein from cheese whey and for cheese production after milk ultrafiltration process [4]. Whey protein concentrate (WPC) and whey protein isolate (WPI) are main products produced from whey by using membrane technologies [6]. These products have some great potential in dairy products as well as in nutritional foods, confectionery, processed meats, bakery products, dietetic foods, infant formula and pharmaceuticals products [7]. Volumetric concentration factor (VCF) is an important parameter at UF operation which should be control in

* Corresponding author: imerd@itu.edu.tr (D.Y. Koseoglu-Imer)

DOI: 10.22079/JMSR.2019.115152.1295

order to obtain the desired percentage of WPC. VCF can be defined as the ratio of feed volume of the whey to the remained volume from concentrated stream [8]. WPC with 35% protein content (WPC-35) can be obtained by operating the UF process with VCF as 4.5-7.0 while VCF should be increased in between 13-20 to produce whey protein concentrate with 60% protein content (WPC-60). On the other hand, WPC could be enhanced to 75-80 % of protein content by increasing VCF to a ratio of 30-35 by using combination of UF and DF [6]. On the other hand, the protein percentage in total solids of whey can be increased to reach 90% in order to produce WPI by using microfiltration as a pretreatment before UF and DF to treat the bacteria and to reduce the fat present in whey to ≤1.0% [6,7].

DF (diafiltration) can be defined as a modified UF process conducted by adding water to the feed solution in order to wash out the excess small particles that can pass through the UF membrane such as minerals and lactose in case of using the whey as a feed [5]. DF may be considered as water consumption process, so some parameters should be controlled in order to conserve the water for preventing the operation cost. The method of adding water during DF process is very important point in that purpose. The water should be added with less volumes repeatedly rather than a large volume once in order to enhance the separation performance and conserve the water used [8,9]. However, VCF ratio is another important parameter to be controlled by applying pre-concentration step as UF process before DF with a maximum acceptable level of VCF ratio in order to concentrate the whey to the most possible limit which leads to minimize the water used [9]. Furthermore, the number of DF cycles used after UF is very effective parameter in term of protein purification and concentration and for washing out minerals and low molecular weight particles [6,10]. Different modes could be used in order to apply DF process. Choosing the suitable mode depends on the volume and time needed to accomplish this process. The main DF modes are continuous and intermittent feed (discontinuous) DF. Furthermore, discontinuous DF can be classified into two types which are sequential dilution and volume reduction modes [10]. This mode is commonly used in laboratory scale because of its simplicity [10]. However, it has better performance when it applies with high number of DF cycles and small water volume addition [6]. Discontinuous diafiltration by using sequential dilution method conducts with adding water to dilute the feed solution to the required volume. Thereafter, ultrafiltration applies to the diluted feed solution in order to concentrate it to the initial volume. The same procedure is applied with multiple DF cycles to reach to the required removal efficiency of salts or low molecular weight particles as well as to reach the maximum protein purification. The main advantage of sequential dilution mode is to enhance the permeate flux by decreasing the feed solution viscosity through the dilution [10]. The main benefit of volume reduction mode is that the water using for DF process is about the half of that needed during sequential dilution mode. At this mode, UF process is used before DF which leads to reduce the initial volume [10]. Baldasso et al. [8] were used a pilot scale spiral polyethersulfone membrane with 10kDa MWCO to purify and concentrate the protein in whey by applying UF followed by discontinuous DF. They found that high VCF value with less DF cycles gives better results comparing with low VCF and high DF cycles, in term of purification and concentration of protein as well as decreasing lactose content. Continuous diafiltration is conducted by water addition to the concentrate or retentate with a flow rate equal to the permeate flow rate generated. Since the protein is the most important valuable component to be used in different food industries as well as in infant formulas, so it is necessary to improve the protein and decrease the lactose and minerals contents in the cheese whey. For this purpose, the aim of this study is to apply the UF followed by intermittent feed diafiltration (IFD) process at the optimum VCF to enhance the protein content and wash out the lactose in the concentrate stream to obtain good quality of end products from cheese whey. The required protein concentration in concentrate in this study is 30% (WPC-30) to be used as animal feed. The overall performance of process was evaluated with experiments and mathematical models.

2. Materials and methods

2.1. Ceramic disc ultrafiltration membrane

Commercial ceramic membrane with 15kDa molecular weight cut-off (MWCO) obtained from Sterlitech Corporation (WA, USA). The membrane has diameter as 90 mm, thickness as 2.5 mm and surface area as 52.8 cm^2. The active layer of 15kDa membrane is made of Zirconia (ZrO_2). Ceramic membrane holder with 90 mm diameter had been obtained from Sterlitech Corporation (CELLULEDIS90VT).

2.2. Whey properties

Acidic cheese whey in liquid form was obtained from real scale milk powder manufacturer in Turkey. The cheese whey was used after centrifuge process and fat extraction. It was ordered two periods with some differences of its characteristics. Table 1 illustrates the measured parameters of raw acidic cheese whey at two times during experiments. Firstly, the whey was used in VCF optimization experiments. Second whey sample was used in pre-concentration step (i.e. UF mode) and IFD experiments.

Table 1
Acidic cheese whey characteristics.

Parameters	Unit	Whey 1	Whey 2
pH	-	4.45 ± 0.04	3.64 ± 0.09
Electrical Conductivity (EC)	mS/cm	9.21 ± 0.05	8.40 ± 0.06
Chemical Oxygen Demand (COD)	g/l	65.5 ± 1.0	53.0 ± 1.0
Total Solids (TS)	g/l	54.0 ± 1.5	48.2 ± 0.2
Total Suspended Solids (TSS)	g/l	3.1 ± 0.04	2.3 ± 0.05
Protein	g/l	1.35 ± 0.3	3.64 ± 0.15
Lactose (LT)	g/l	33.0 ± 3.0	33.0 ± 2.0
Lactic Acid (LA)	g/l	4.3 ± 0.3	12.2 ± 0.5
Minerals (TDS)	g/l	5.89 ± 0.03	5.38 ± 0.04
LA/LT	-	0.1	0.2

2.3. Analytical methods

WTW series Inolab pH-EC meter was used for pH and electrical conductivity measurement. COD was measured by photometric method (COD cell test, Merck) with Merck Millipore SpectroquantProve 600 series UV/VIS spectrophotometer (Merck, Darmstadt, Germany) and Thermoreactor incubator (Spectroquant TR320, Merck) was used for the digestion step. Total solid and total suspended solids analysis were conducted by standard method (Code 2540 B. Total Solids Dried at 103–105°C; and Code 2540 D. Total Suspended Solids Dried at 103–105°C). Total protein was measured by using Lowry method. Liquid chromatography (HPLC) (DGU-20AS, SHIMADZU) was used for lactose and lactic acid measurement. Some chemicals were used for different analysis and cleaning purposes. Bovine Serum Albumin (BSA), Folin and Ciocalteu's phenol reagent (2N), di-Sodium Tartrate $C_4H_4O_6Na_2.2(H_2O)$, Copper (II) Sulfate pentahydrate $CuSO_4.5(H_2O)$, Sodium Carbonate Na_2CO_3 and Sodium Hydroxide NaOH were used for protein analysis. For chemical cleaning of membranes, Sodium Hydroxide NaOH and Phosphoric acid H_3PO_4 (85%) were used.

2.4. Experimental system

The experimental system in laboratory scale as shown in Figure 1 consists of disc type ceramic membrane cross flow filtration holder (Model CELLULEDIS90VT, Sterlitech Corporation, Kent, WA). In addition, the filtration system comprises of magnetic stirrer and hot plate (Heidolph, Hei-Tec), peristaltic pump (Filttec, FPP-1), pump head (Filttec, PH-II3), pressure valve and gauge and precision scale (AND, FX-5000i) connected to computer.

2.5. Filtration procedure

During the all experiments, the feed (i.e. cheese whey) temperature was set at constant value (40±2ºC) with hot plate and temperature controller. Trans membrane pressure (TMP) was set as 3 bar throughout the experiments. The samples were taken from the feed at the beginning of experiment, the permeate which is collected separately and the concentrate which is returned to the feed tank. The flux was calculated by collecting the permeate on digital balance with time interval of one-minute by the following equation:

$$J = \frac{(\frac{\Delta m}{\rho})/1000}{A * (\frac{\Delta t}{60})} \quad (1)$$

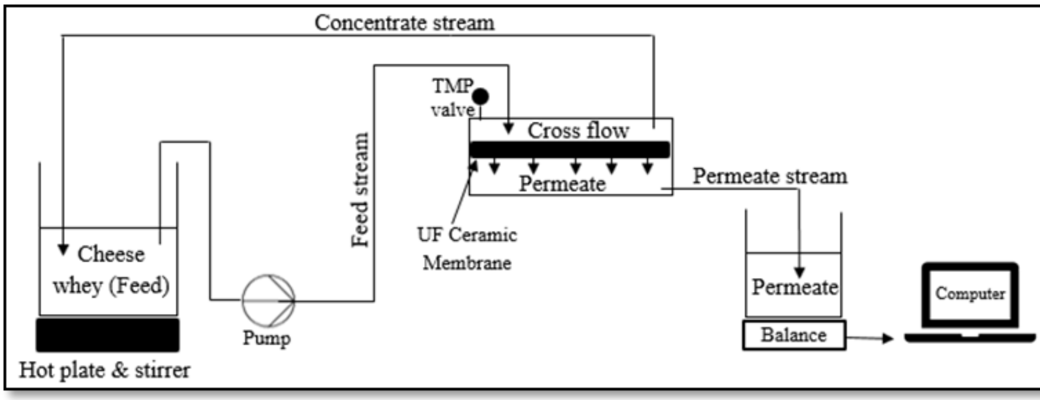


Fig. 1. A general scheme of the cross flow filtration system.

where J (L/m^2.h) is the permeate flux, Δm (g) is the amount of permeate collected at particular time interval, ρ (g/cm^3) is the feed density, A (m^2) is the membrane surface area and Δt (minute) is the particular time interval.

2.6. Diafiltration Experiment

Firstly, three different VCF values (1.4, 2.0 and 3.3) were operated at UF mode for obtaining the maximum protein. The permeate sample was collected separately for each VCF step in order to avoid any accumulation might be happened and could affect the permeate quality. After optimum VCF selection, the IFD experiments were operated in order to enhance end product quality of the whey. Diafiltration concept is to start with pre-concentration step with the required VCF value, followed by number of DF cycles by discontinuously adding specific amount of distilled water to the feed stream. The permeate stream was collected separately while the concentrated stream was returned to the feed tank. Samples were taken from feed, permeate and concentrate stream for each step (UF, DF1 and DF2). Flux was calculated by using the Eq. 1 mentioned previously.

Secondly, the yield of IFD process was calculated according to the model study done by Wang et al. [11]. Three steps of filtration were determined by microsolute concentration change in concentrate stream and volumetric change of permeate. In the pre-concentration step, the interaction between C and V is calculated with Eq. 2 at different P values (Eq. 3).

$$C = C_o\left(\frac{V_o}{V_o - V}\right)^{1-P} \tag{2}$$

$$P = \frac{C_p}{C_0} \tag{3}$$

C_o, C_p and C are the initial concentration of microsolute in the feed (g/L), the concentration of microsolute in the permeate (g/L) and the concentration of microsolute in the concentrate (g/L), respectively. V and V_o are the accumulated volume of permeate (L) and the initial volume of feed (L), respectively. P is the permeation/passage coefficient of microsolute (%). In the IFD steps, the relationship between C and V is calculated with Eq. 4.

$$C = C_o(1+b)^{-mP}\left(1 + mab - \frac{V}{V_o}\right)^{P-1} \tag{4}$$

m, a and b values are the times of feed washing solution, volume concentration ratio in pre-concentration step (L/L) and volume dilution ratio in DF (L/L), respectively. a is calculated with V_d/V_o and V_d is the retentate volume at the end of pre-concentration step. b is calculated with V_w/V_d and V_w is the washing solution volume fed to retentate every time.

The real-time relationship of yield (ξ) and V is obtained from Eq. 5 and Eq. 6 at pre-concentration step and IFD cycles, respectively.

$$\xi = 1 - \left(1 - \frac{V}{V_o}\right)^P \tag{5}$$

$$\xi = 1 - \left[(1+b)^{-m}\left(1 + mab - \frac{V}{V_o}\right)\right]^P \tag{6}$$

At the end of filtration, the overall yield (ξ) is calculated with Eq. 7.

$$\xi = 1 - [ac(1+b)^{-n}]^P \tag{7}$$

n is the overall times of feed washing solution in DF step.

Fouling experiment with resistance in series model, MFI and UMFI models were performed for IFD mode. Firstly, the resistance in series model was applied according to Darcy's law and by follow Eq. 8 below [12].

$$J = \frac{\Delta P}{\mu * R} \tag{8}$$

where J is the flux (m/sec), P is the transmembrane pressure (Pa), μ is the dynamic viscosity (Pa.sec) and R is the membrane resistance (m^{-1}).

Five steps were followed sequentially to conduct the fouling experiment depending on resistance in series model. Firstly, the distilled water was filtered throw a fresh ceramic membrane for 30 min. at room temperature. Secondly, UF of cheese whey was applied for 60 min. after heating it to 40±2 ^{o}C followed by DF with VCF=2 for each cycle by adding distilled water with volume equal to remained volume in concentrate stream. Number of cycles applied were depending on stability of experimental flux which was two cycles. In the third step, distilled water was filtered for 30 min. at room temperature before membrane cleaning. Fourth step was filtering the distilled water at room temperature for 30 min. after physically cleaning of the membrane. In the last step, filtration of distilled water was applied at room temperature for 30 min. after chemically cleaning of the membrane.

The chemicals used during the chemical cleaning of the fouled membranes were 0.1N NaOH as a base chemical to remove the organic substances and 0.04N of 85% H_3PO_4 as an acid chemical to remove the inorganic substances. Cleaning the fouled membranes with NaOH was applied for 30 min. at 85 ^{o}C while H_3PO_4 was applied for 15 min. at 50 ^{o}C. The distilled water was used after each base and acid chemical cleaning of the membranes to neutralize pH. However, before using the cleaned membranes in any filtration experiment, they should be kept overnight in distilled water. Two other models were used to investigate the fouling mechanism which are Membrane Fouling Index (MFI) and Unified Membrane Fouling Index (UMFI). MFI model was calculated by following the procedure of Farizoglu and Keskinler [13] who they mentioned Eq. 9 in their study in order to calculate specific cake resistance

$$MFI = \frac{(\alpha.\mu.C_{TS})}{2.\Delta P} \tag{9}$$

where α (m/kg) is specific cake resistance, μ is dynamic viscosity (Pa.sec), C_{TS} (mg/l) is total solids concentration of feed, ΔP (kPa) is transmembrane pressure.

UMFI model is the revised version of Hermia model which was improved to determine the membrane fouling mechanism. In order to calculate UMFI model, the procedure from Huang et al. [14] had been followed with Eq. 10 where $J's$ (J/J_o) is normalized specific flux.

$$\frac{1}{J'_s} = 1 + UMFI.V_s \tag{10}$$

3. Results and discussions

3.1. Optimum VCF selection

Figure 2 shows the permeate volume collected during the experiment with 15kDa MWCO of the membrane at three VCF values. During the filtration period, the permeate volume increased with time or with increasing of VCF. It was observed that the time needed to reach the required VCF of 15kDa is near to 6 h. In Rezaei et al. [15] study, they showed that the permeate volume of whey increased with the increasing the time period throughout the microfiltration experiment by using polymeric membrane. According to the slope value for each stage of the filtration process, it was observed that the permeate volume increased faster at the first VCF value (VCF=1.4) as the accumulation of the whey ingredients on the membrane surface still in the initial step. On the other hand, the permeate volume collection started to slow down at the final stage of the filtration process as the membrane was fouled with the whey compounds especially with the protein.

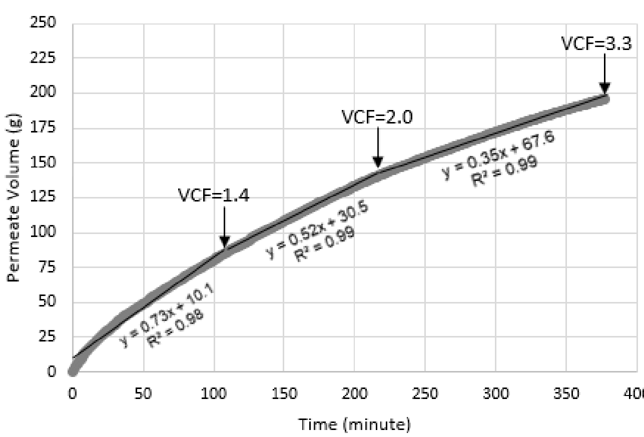


Fig. 2. Permeate volume curve for different VCF values of 15kDa membrane.

The concentrations of cheese whey in the concentrate stream at different VCF ratios are shown in Figure 3 (a-e). The VCF=1 refers to the feed at the beginning of the experiment while the other VCF refer to the concentrate stream of the cheese whey during the ultrafiltration process. Whey protein could be maximized in the concentrate part by increasing VCF value during the filtration process [16]. Increasing the protein content in the concentrate stream is one of the main purposes in this study to be reached in order to achieve the good separation performance of the cheese whey components. Referring to Figure 3-a, protein concentration in concentrate stream is increasing with the increasing of VCF value and reach to the maximum concentration as 9.9 g/l at VCF equal to 3.3 while the lower concentration value was observed at VCF of 1.4 for 15kDa membrane. In Baldasso et al. [8] study, they found that the concentration of protein increased throughout the time of the experiment in ultrafiltration process which in turns leads to increasing of total solids content.

In terms of lactose as shown in Figure 3-b, its concentration in concentrate stream increased with the increasing of VCF from 1.4 to 3.3. However, there was a decreasing in lactose concentration between the feed and the first VCF value (VCF=1.4) which can be explained as the most of the lactose flow to the permeate stream as the membrane pores are still opened at the beginning of the experiment. The lactose concentration increasing from 35.3 g/l at VCF of 1.4 to 39.2 g/l at VCF of 3.3 in concentrate stream. This increasing may occur as the lactose was accumulating more on the surface or inside the membrane during the filtration period. This increase is the same as the protein behavior which is affecting the total solids content during the ultrafiltration experiment [8].

Figure 3-c shows the total solids behavior with the VCF value during ultrafiltration process. It is clear that the total solids concentration is increasing with the increasing of the VCF value throughout the experiment. This expected increasing of total solids because of increasing the protein and lactose concentration which are the main components of the total solids.

In terms of COD, Figure 3-d shows the COD concentration of the cheese whey at feed (VCF=1) and concentrate stream with three different VCF value. It was observed that the COD value in the concentrate stream is increasing with the increasing of the VCF value. The COD increased from 65 g/l at feed to 79 g/l at VCF=3.3 in the concentrate stream. As the lactose is the main sources of COD in the cheese whey [17], the rejection of the lactose on the membrane surface could be the reason of COD increasing in the concentrate stream as Cuartas-Uribe et al. [18] study proved this increasing.

Referring to Figure 3-e, the electrical conductivity showed a slight increasing with the increasing of the VCF (i.e. increasing experiment time). The EC increased from 9.4 mS/cm to 10.2 mS/cm after 6 h of the ultrafiltration experiment or when the VCF reached to 3.3. The increasing of the electrical conductivity was not significant and this result is in line with Iltchenco et al. [19] study as they found that the electrical conductivity of whey in feed and concentrate stream after ultrafiltration experiment was almost the same.

As a final result from this step, VCF=3.3 showed better results in terms of high protein in the concentrate stream which is suitable to be used in the DF experiment for flux behavior and end product quality studies.

3.2. Diafiltration Experiment with IFD mode

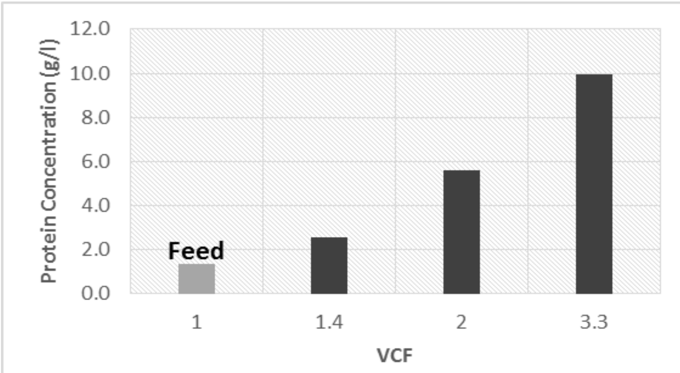
3.2.1. Flux curve

Figure 4 shows the flux curve during pre-concentration step and two DF cycles experiment by using 15kDa ceramic membrane. Pre-concentration step was conducted with VCF of 3.3 while for DF(1) and DF(2) the VCF was 2. The experiment started with UF mode at VCF of 3.3 and it was observed that the experiment started with a flux value of 14.7 $L/m^2.h$ and reached to 1.9 $L/m^2.h$ at the end of step which was taken 984 min. A significant increasing in flux occurred with the starting of first DF cycle once distilled water added and it reached to 3.0 $L.m^2/h$. This could be explained as TS concentration in the concentrate stream decreased with the adding of distilled water which will leads to decrease the membrane fouling and increase the flux [20]. For the second DF, there was not an increasing in flux after adding water. At the end of DF(1), the flux started to be in a steady state with a value of 1.7 $L/m^2.h$ at the end of DF(2) or end of the experiment. The experiment took around 26 h to accomplish UF and two DF cycles. The same behavior of flux in the first DF was observed in Tremblay-Marchand et al. [20] study, when they found that the flux decreased in the beginning of filtration experiment while it increased once they added tap water to the skim milk during DF step.

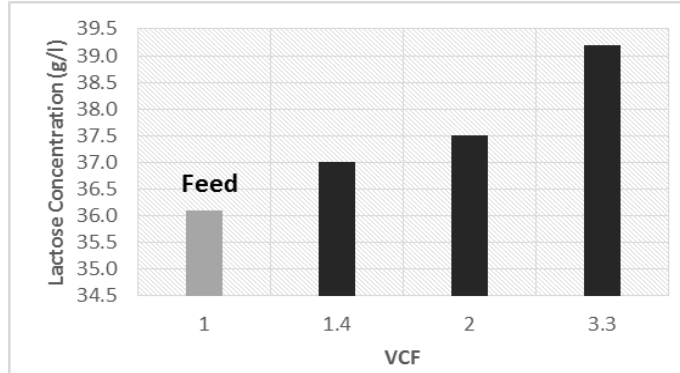
3.2.2. The model of yield of IFD process

The curves C/Co-V/Vo of pre-concentration step and DF steps is given in Figure 5. The a value was found as 0.3 and b values were calculated as 0.67 and 0.5 at DF(1) and DF(2), respectively. The reason of different b values was the volume reduction between DF cycles. The C/Co-V/Vo graph was formed as related with different P values. As seen from Figure 5, the filtrate volume reached to 0.7Vo, 0.9Vo and 1.03Vo at the pre-concentration step, DF(1) and DF(2) respectively. At pre-concentration step, C/Co in concentrate stream reached 1.0 for P value=100%. It means that all microsolutes passed to permeate stream and C_P was equivalent to Co. Therefore, as experimentally, the ratio of lactose concentration in permeate stream (C_P) and initial lactose concentration (Co) was found as 1.15. It means that the real permeation coefficient of 15kDa ceramic membrane was 94% at pre-concentration step. The ceramic membrane can provide this high permeation value. At the end of DF cycles, the real C/Co ratios were calculated as 0.81 and 0.71 for DF(1) and DF(2), respectively. It means that the ultrafiltration can wash the great ratio of lactose at pre-concentration step however two DF cycles were not enough for washing all lactose concentration. The permeation ratio reached to theoretically almost 80% (as shown in Figure 6) at each cycle.

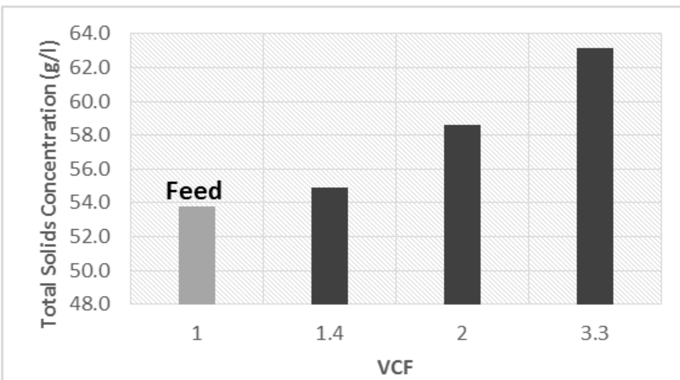
The interaction of ξ and V with different P values is shown in Figure 7. The maximum yield was found as 88% for P value=100% in DF(2). The yield reached to maximum increase trend at DF (2) cycle.



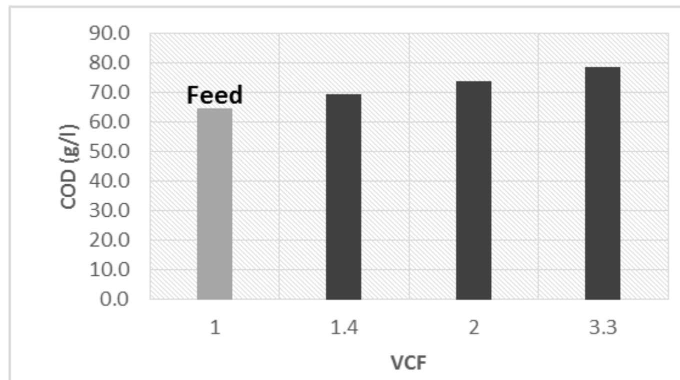
(a)



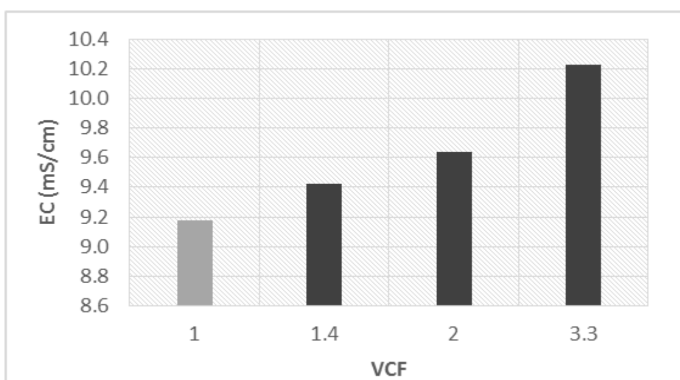
(b)



(c)



(d)



(e)

Fig. 3. Concentration in concentrate stream of (a) Protein (b) Lactose (c) Total solids (d) COD (e) Electrical conductivity with different VCF values for 15kDa MWCO.

According to end product quality, percentage of cheese whey component was investigated in concentrate stream and good quality of cheese whey end product was observed in terms of high protein and low lactose when VCF of UF was equal to 3.3 and the DF cycles was 2 by using 15kDa ceramic membrane and accomplished under feed temperature of 40 ºC. The lactose content was partially washed out after DF experiment. On the other hand, the required percentage of protein in the concentrate stream was achieved with 33% at the end of DF(2) (i.e. protein increased by 4.8 folds from its original content in the feed). In Baldasso et al. [8] study, they applied VCF=6 in UF experiment and 4 DF cycles when they could increase the protein percentage to reach 71% and decrease the lactose to 29% in the concentrate stream by using pilot scale polymeric membrane. In terms of fat content, by having fats in the feed, it could be concentrated with the protein as it has a large molecule size and could negatively affected the end product quality. In that case, the feed should be fat free as much as possible by applying centrifugation process as a pretreatment step. For minerals content, as a concentration, it could be washed out by almost the half of its original concentration by applying DF. However, more washing out might be reached by increasing the DF cycles as much as possible. Minerals percentages were almost stable during the diafiltration experiment. Generally, in DF mode, minerals could be reduced by 99% but it needs higher DF cycles and higher distilled water volume to be added. Theoretically, the percentages for cheese whey components after diafiltration experiment might be the same percentages after spray drying process in the powder form of whey. However, spray drying results need to be checked in order to know the exact quality of the end product of the whey.

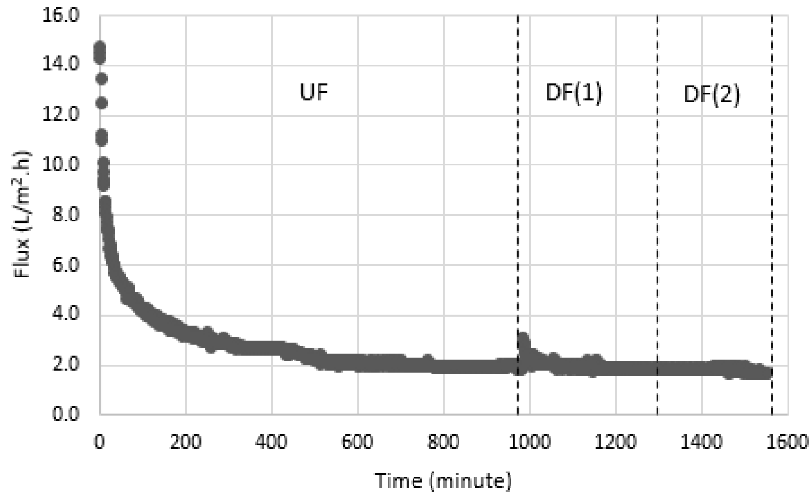


Fig. 4. Flux curve of DF experiment with two DF cycles and 3.3VCF of UF.

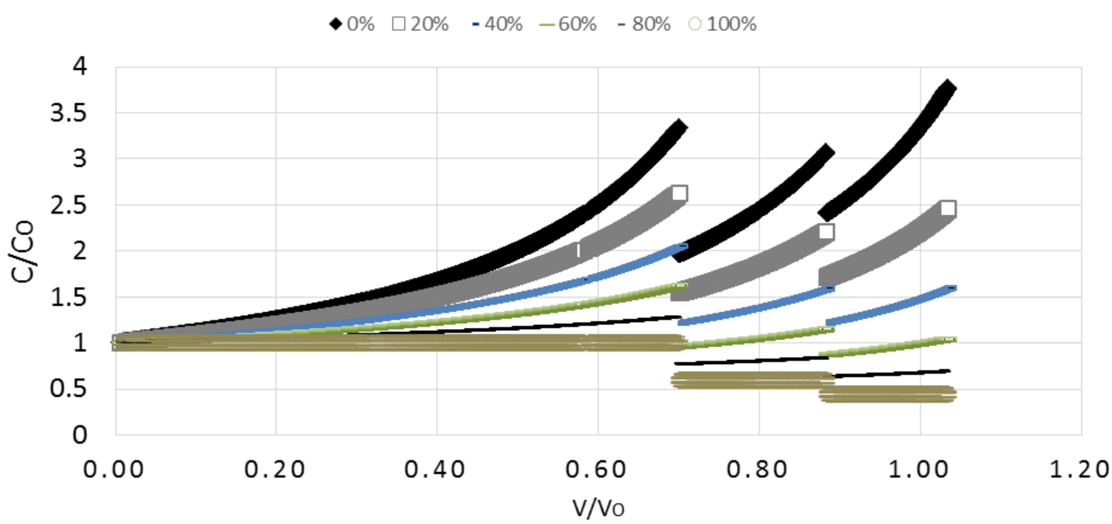


Fig. 5. The relationship between C/Co and V/Vo.

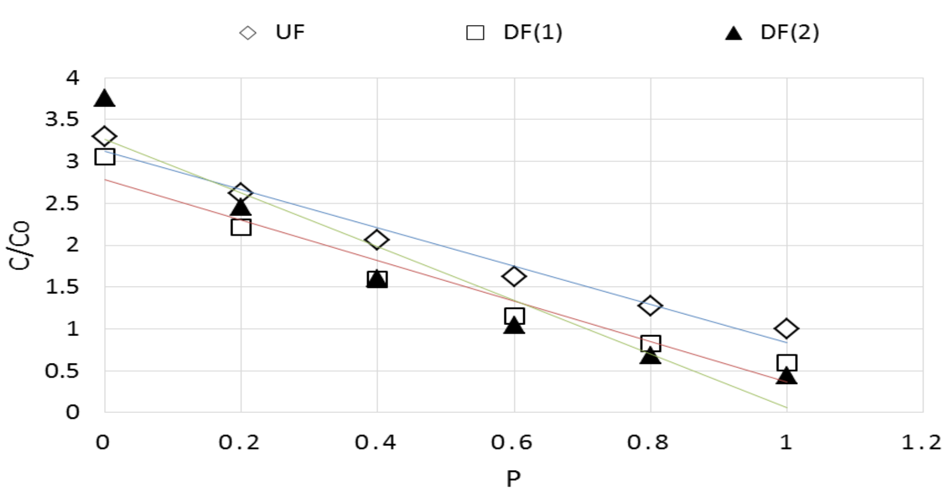


Fig. 6. The graph of last C/Co values related with different P value.

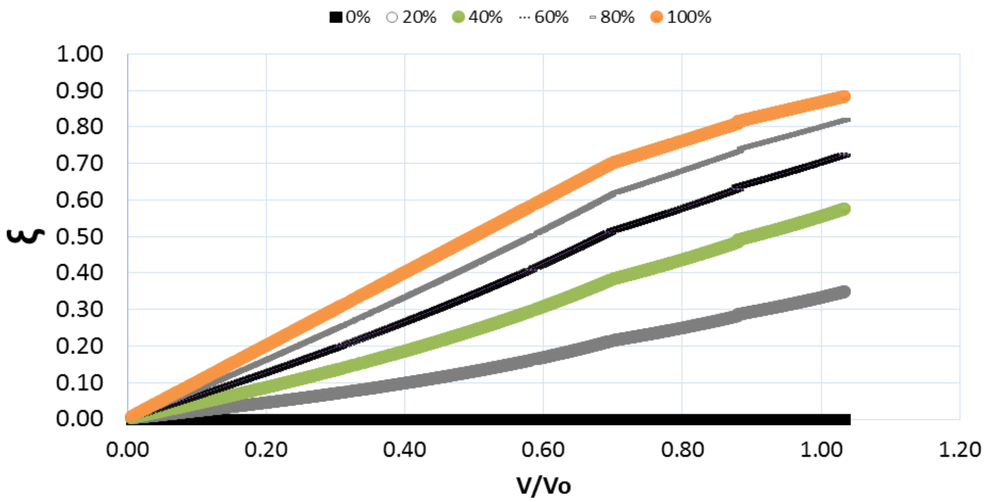


Fig. 7. ξ and V/Vo relationship graph at different P values.

3.2.3. Determination of fouling parameters

Figure 8 shows the changing of total resistance (R_T) with the time during the diafiltration experiment with 15kDa ceramic membrane. The total resistance started to increase during the experiment as the membrane started to be fouled with the cheese whey throughout the time. This can be explained according to increasing of concentration polarization which in turns leads to solids deposition on the surface or inside the pores of the membrane results in increasing of the polarized layer thickness causing a permeation resistance [8,21,22]. Total resistance was observed as $2.4x10^{14}$ m^{-1} for 15kDa membrane at the end of UF experiment. At the end of experiment (i.e. after two DF cycles), the total resistance was increased to $5.15x10^{14}$ for 15kDa membrane.

On the other hand, the results from MFI and UMFI models showed that there is an effect of the fouling mechanism on the ceramic membrane. Table 2 illustrated the values of α, MFI and UMFI for 15kDa membrane after second diafiltration experiment. In Barukcic et al. [23] study, they found that the total resistance was increasing throughout the microfiltration process time whatever the pore size of the membrane.

Figure 9 shows the changing of flux decline ratio (FDR) with the time during the diafiltration experiment with 15kDa membrane. The FDR was started as 1 from the beginning of the experiment with the first minute. During the experiment, FDR value started to decrease as the membrane started to be fouled with the cheese whey throughout the time due to deposition of the total solids. There was a sharp decreasing in the first hour of the UF experiment as most of the solids in the whey especially the protein accumulating inside the membrane. On the other hand, after 2 diafiltration cycles the FDR was almost steady. FDR was observed as 0.24 for 15kDa at the end of UF after 60 minutes. However, the FDR was decreased to 0.11 for 15kDa at the end of the experiment.

Table 2
α, MFI, UMFI values after DF (2) with 8kDa and 15kDa MWCO.

MWCO	DF (2)		
	α (m/kg)	**MFI**	**UMFI**
15kDa	$3.86x10^8$ (r^2=0.996)	$25x10^6$	344

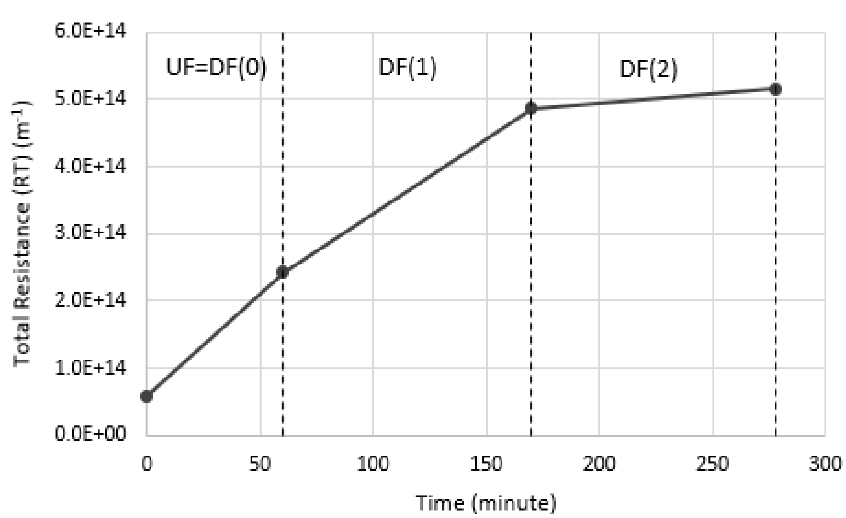


Fig. 8. Total resistance values at different stage of DF experiment for 15kDa membrane.

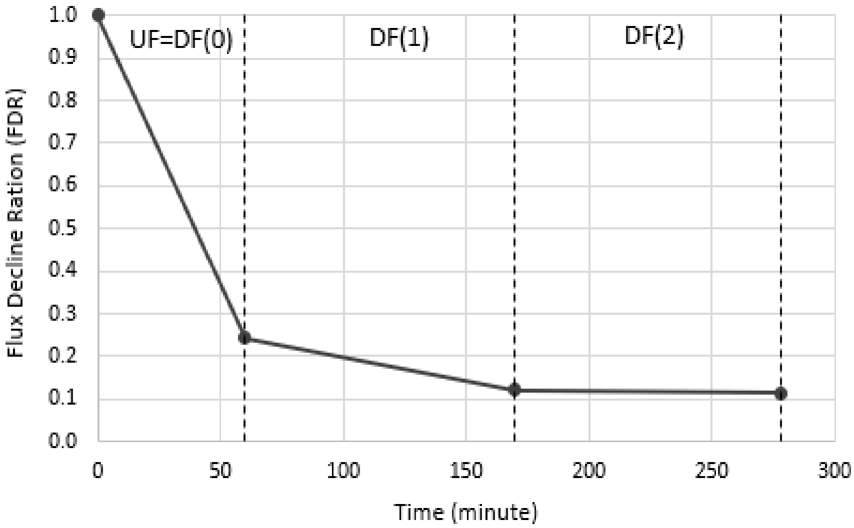


Fig. 9. Flux decline ratio at different stages of DF experiment for 15kDa membrane.

4. Conclusions

During this study, different findings were obtained in terms of VCF optimization by ultrafiltration process and the yield calculation of UF+DF cycles and fouling mechanism after diafiltration process. It was found that increasing of VCF for 15kDa ceramic membrane leads to increasing protein concentration in the concentrate stream. By applying filtration experiment with VCF of 3.3 with 15kDa membrane, maximum protein concentration of 9.9 g/l was reached in the concentrate stream. Furthermore, apply higher VCF values to get higher end product quality in term of whey components is one of the future studies to be improved.

In the diafiltration experiment, increasing in the flux was observed once distilled water added in the first DF cycle while the flux remained stable in the following DF cycle. On the other hand, the percentage of protein increased with the increasing of diafiltration cycles while the percentage of lactose decreased in concentrate stream. By applying VCF of 3.3 in the UF before diafiltration and conducting two diafiltration cycles, promising quality in terms of protein and lactose was obtained. Using of diafiltration mode, minerals presents in the whey could be partially washed out in this study as low number of diafiltration cycles were used. In addition, fouling mechanism models explained the occurrence of membrane fouling because of the presence of total solids including protein and lactose which in turn affected the permeability performance. However, the filtration of cheese whey using ceramic membranes (i.e. inorganic membranes) showed low fouling properties of the ceramic membrane as well as less water needed with ceramic membrane during DF experiment which is an important point in terms of water conservation.

Acknowledgements

Special thanks to Prof. Dr. Ahmet Karagunduz and Philip Omwene for HPLC analysis from Gebze Technical University, Department of Environmental Engineering.

List of abbreviations

FDR	Flux Decline Ratio
HPLC	High Performance Liquid Chromatography
IFD	Intermittent Feed Diafiltration
J	Whey permeate flux
J_0	Whey initial flux
J/J_0	Normalized specific flux (Flux decline)
kDa	Kilo Dalton
MFI	Membrane Fouling Index
MWCO	Molecular Weight Cut Off
R_T	Total Resistance
TMP	Trans Membrane Pressure
UF	Ultrafiltration
UMFI	Unified Membrane Fouling Index
VCF	Volumetric Concentration Factor
WPC	Whey Protein Concentrate
WPI	Whey Protein Isolate

References

[1] A. R. Prazeres, F. Carvalho, J. Rivas, Cheese whey management: A review, J. Environ. Manage. 110 (2012) 48-68.

[2] F. Lipnizki, Cross-flow membrane applications in the food industry, in: K.V. Peinemann, S. Pereira, L. Giorno (Eds.), Membrane Technology: Membranes for food applications, Volume 3, 1st Ed., Willey-VCH, Weinheim, 2010, pp. 1-23.

[3] E. Polom, Research on flux decline in nanofiltration of lactic acid solutions with ZRIV/PAA membranes application, Pol. J. Chem. Technol. 18 (2016) 17-21.

[4] R. Atra, G. Vatai, E. Bekassy-Molnar, A. Balint, Investigation of ultra-and nanofiltration for utilization of whey protein and lactose, J. Food. Eng. 67 (2005) 325-332.

[5] F. E. El-Gazzar, E. H. Marth, Ultrafiltration and reverse osmosis in dairy technology: a review, J. Food. Protect. 54 (1991) 801-809.

[6] P. Kelly, Manufacture of Whey Protein Products: Concentrates, Isolate, Whey Protein Fractions and Microparticulated, in: H. C. Deeth, N. Bansal (Eds.), Whey Proteins: From Milk to Medicine, Academic Press, 2019, pp. 97-122.

[7] J. N. De Wit, Lecturer's handbook on whey and whey products, 1st Ed., Brussels, 2001.

[8] C. Baldasso, T. C. Barros, I. C. Tessaro, Concentration and purification of whey proteins by ultrafiltration, Desalination. 278 (2011) 381-386.

[9] D. Barba, F. Beolchini, D. Cifoni, F. Veglio, Whey protein concentrate production in a pilot scale two-stage diafiltration process, Sep. Sci. Technol. 36 (2001) 587-603.

[10] L. Schwartz, Diafiltration: A fast, efficient method for desalting, or buffer exchange of biological samples, Pall Scientific & Technical Report, 2003.

[11] L. Wang, G. Yang, W. Xing, N. Xu, Mathematic model of the yield for diafiltration processes, Sep. Purif. Technol. 59 (2008) 206-213.

[12] S. Azimah, A. M. Mimi Sakinah, Resistance in Series Model for Ultrafiltration Betacyanin from Hylocereus polyrhizus Peels, J. Appl. Sci. 14 (2014) 1343-1346.

[13] B. Farizoglu, B. Keskinler, Sludge characteristics and effect of crossflow membrane filtration on membrane fouling in a jet loop membrane bioreactor (JLMBR), J. Membrane. Sci. 279 (2006) 578-587.

[14] H. Huang, T. A. Young, J. G. Jacangelo, Unified membrane fouling index for low pressure membrane filtration of natural waters: principles and methodology, Environ. Sci. Technol. 42 (2008) 714-720.

[15] H. Rezaei, F. Z. Ashtiani, A. Fouladitajar, Effects of operating parameters on fouling mechanism and membrane flux in cross-flow microfiltration of whey, Desalination. 274 (2011) 262-271.

[16] J. Hinrichs, Incorporation of whey proteins in cheese, Int. Dairy. J. 11 (2001) 495-503.

[17] M. I. Gonzalez Siso, The biotechnological utilization of cheese whey: a review, Bioresour. Technol. 57 (1996) 1-11.

[18] B. Cuartas-Uribe, M. I. Alcaina-Miranda, E. Soriano-Costa, J. A. Mendoza-Roca,

M. I. Iborra-Clar, J. Lora-García, A study of the separation of lactose from whey ultrafiltration permeate using nanofiltration, Desalination. 241 (2009) 244-255.

[19] S. Iltchenco, D. Preci, C. Bonifacino, E. F. Fraguas, C. Steffens, L. A. Panizzolo, R. Colet, I. A. Fernandes, C. Abirached, E. Valduga, J. Steffens, Whey protein concentration by ultrafiltration and study of functional properties, Cienc. Rural. 48 (2018).

[20] D. Tremblay-Marchand, A. Doyen, M. Britten, Y. Pouliot, A process efficiency assessment of serum protein removal from milk using ceramic graded permeability microfiltration membrane, J. Dairy. Sci. 99 (2016) 5230-5243.

[21] M. D. Caric, S. D. Milanovic, D. M. Krstic, M. N. Tekic, Fouling of inorganic membranes by adsorption of whey proteins, J. Membrane. Sci. 165 (2000) 83-88.

[22] F. A. Glover, Principles of Ultrafiltration and the Concentration and Fractionation of Cow's Milk, in: Nestle Nutrition: Human Milk Banking, 1st Ed., Raven Press, New York, 1984, pp. 1-16.

[23] I. Barukcic, R. Bozanic, U. Kulozik, Effect of pore size and process temperature on flux, microbial reduction and fouling mechanisms during sweet whey cross-flow microfiltration by ceramic membranes, Int. Dairy. J. 39 (2014) 8-15.