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Effect of flow behaviour of skim milk on microfiltration performance and cleaning efficiency of polyethersulfone membranes

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Summary

The effect of milk rheology on membrane fouling remains a challenging problem for long-term microfiltration. This study aimed to investigate the effects of viscosity changes as a function of weight reduction factor (*WRF*) and temperature on the performance of commercial polyethersulfone membrane. The retentates were obtained from skim milk in batch concentration mode with *WRF* of 2.5, 3.5, 4.5 and 5.5, to investigate the effect of change in feed composition on polyethersulfone (PES) membrane performance. The performance of the PES membrane was evaluated with pure water before the microfiltration of milk and it was discovered that using low transmembrane pressure and pH levels above 5.0 resulted in more consistent water flux. The two-fold increase in the transmembrane pressure caused up to ten-fold increase in irreversible fouling resistance. At *WRF* greater than 2.5, the non-Newtonian pseudoplastic behaviour of the samples obtained became more pronounced, resulting in a more pronounced decrease in flux for the batch concentration mode at 55 °C compared to the total recycling mode. The rheological and chemical composition properties of the streams affected by varying microfiltration parameters are important for the dairy products in which they are used, as well as for innovative production processes where quality of whey proteins is required to be preserved.

Keywords

microfiltration; viscosity; rheology; fouling

The pressure-driven separating processes such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis, along with their several combinations, are used to extend the shelf life of milk, improve quality of the cheese produced from the milk, fractionate milk proteins, produce milk and produce whey powders [1].

The membrane filtration process, which varies according to the membrane material used, membrane pore size and target components, is a highly suitable and successful technology for separating and concentrating colloidal milk components consisting of various components from ions to large fat globules. Prior to cheese making, microfiltration and ultrafiltration techniques are used to produce from milk a stream containing colloidal and suspended particles (casein concentrate) and a filtrate stream containing whey proteins, lactose and minerals (ideal whey) [2]. The retentate is rich in casein and is called micellar casein concentrate [3]. Logan et al. [4] mentioned that the gross composition of milk protein will influence curd development during cheese making and the changes in milk fat and protein ratio, distribution of casein micelles, equilibrium of minerals and proteins between the colloidal and serum phase after the membrane filtration will affect the duration of the renneting process and cheese yield. The membrane filtration does not destroy the structure of casein micelles and industrially applicable technologies such as microfiltration can be used to obtain casein concentrates with various casein micelle size distributions [5]. Therefore, ideal whey obtained by processes such as microfiltration, where casein is separated by membrane filtration, has higher quality characteristics than whey produced by milk coagulation [6].

The removal of milk components before the manufacturing of cheese will provide new opportunities to enhance the usage area and ways of ideal whey to obtain value-added new products. As innovative research on the effects of whey proteins on structural modification, surfactants, emulsifying, thickening, gelling and foaming agents

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emerges, the most promising applications of whey proteins have been the development of edible films, coatings, nanoparticles and the production of bioactive peptides as potential nutraceuticals due to their biological properties such as antihypertensive, antioxidant, antimicrobial and immunomodulatory activities [7].

However, there are some concerns related to membrane performance in milk filtration. The main reason for this is fouling. Several fouling mechanisms, such as cake layer formation and pore blocking, negatively affect separation efficiency. They are related to changes in feed characteristics and flow behaviour with time as well as process conditions such as transmembrane pressure and temperature [8]. Membrane fouling is also a crucial phenomenon that affects the ideal whey composition (permeate) and rheology of the skim milk (retentate) in microfiltration [9]. Therefore, knowledge of the rheology of the retentate is very important for its processing and control of membrane filtration.

The casein micelles might be enriched in the retentate stream when the polymeric membrane materials having low fouling resistance such as polyethersulfone (PES) are used in microfiltration, which can be attributed to fouling. The rheological data play an important role in the analyses of flow conditions in microfiltration. Additionally, viscosity, a rheological property, is also considered an important physical characteristic related to the quality of a dairy product. Variations in the viscosity of milk affect the fouling mechanisms, the separation efficiency and the energy usage during microfiltration. Viscosity may become an important factor during the concentration of milk, especially in the production of high-density concentrates, due to the inefficiency of the operation when the product becomes highly viscous. Rheological properties of retentates are expected to be different from milk behaving like a Newtonian fluid. Flow behaviour can transit from Newtonian to non-Newtonian as viscosity increases due to the increasing milk concentration [10]. It has been reported in the literature that microfiltration retentates generally exhibit pseudoplastic behaviour. Pseudoplastic behaviour becomes more pronounced with increasing concentration and decreasing temperature [10]. This behaviour is thought to help explain the structure of products with a high casein rate and to obtain the necessary information during their processing [9, 11]. The rheological behaviour of milk and microfiltration retentate is important to understand the functional relationship of viscosity with temperature and concentration because it is subjected to varying temperatures and concentrations during transit, storage and various processing [12].

This relationship also affects the membrane performance and the route of membrane fouling. To the best of our knowledge, there are few fundamental studies on this topic using various food matrices. This study aimed to describe the effect of rheological variations on flux, membrane fouling and composition of permeate and retentate streams. The main goals of this study were (a) to evaluate the effects of viscosity changes as a function of the weight reduction factor (*WRF*) and temperature on the performance of commercial polyethersulfone membrane and its cleaning efficiency, (b) to determine the chemical composition of permeates and retentates obtained by microfiltration of skim milk and examine the effect of *WRF* on their chemical composition, (c) to examine their rheological properties in a range of concentrations, shear and temperature conditions and (d) to create a suitable mathematical model describing their rheological behaviour.

MATERIALS AND METHODS

Microfiltration unit

A laboratory-scale microfiltration system consisting of a cross-flow membrane filtration module (Vivaflow 50; Sartorius, Göttingen, Germany) which is composed of PES material with a pore size of 0.2 μm, a peristaltic pump, a pressure controller and a water bath was used to perform filtration operations.

Microfiltration of the skim milk

Commercial pasteurized skim milk was obtained from a local market in Edirne (Turkey). Microfiltration experiments were carried out in the total recycle mode and the batch concentration mode. In the former case, the permeate and retentate streams were continuously recycled to the feed tank as described by CASSANO et al. [13]. In the latter case, the permeate stream was collected in a separate tank. Each run was performed at trans-membrane pressure (*TMP*) of 28 kPa, axial feed flow rate of 36 l·h^{-1} and temperature of 55 °C. Weight reduction factor (*WRF*), which is a concentration factor that is defined as the ratio between the initial feed weight and the weight of the resulting retentate, was the independent variable in the second process. *WRF* was calculated as:

$$WRF = \frac{W_i}{W_i - W_p} \quad (1)$$

where W_i is the initial weight of skim milk and

W_p is the weight (in grams) of permeate collected during the microfiltration process [14] by an electronic balance AX4202 (Ohaus, Parsippany, New Jersey, USA). Each microfiltration process was terminated when *WRF* reached 2.5, 3.5, 4.5 and 5.5 separately under batch concentration mode. During the process, the permeate was collected in a container and its amount was measured every 10 min. Each process was replicated twice. The retentate and the permeate samples were kept at –25 °C for a maximum of 1 month until the chemical analyses were performed.

Cleaning procedure and resistance analysis

After each run, the module was cleaned with ultrapure water (18.2 MΩ-cm resistivity; Purelab Option-Q, Elga, High Wycombe, United Kingdom) at 25 °C firstly. The first step was in total recycle mode using zero *TMP*, axial feed flow rate of 72 $l \cdot h^{-1}$, and duration of 30 min. Then, 0.5 $mol \cdot l^{-1}$ HCl for 60 min, 70% (v/v) ethanol for 30 min and 10% (v/v) ethanol for 10 min were applied at the same hydrodynamic conditions to finish the cleaning procedure. Eventually, the module was rinsed with ultrapure water at 25 °C and then it was kept at +4 °C with 10% (v/v) ethanol until the next use for a maximum of six months. Before the start of the ongoing run, the membrane fouling degree was checked based on the decrease in initial permeate flux. The initial steady state permeate flux of the clean membrane was 31.2 $kg \cdot m^2 \cdot h$.

Hydraulic permeability values of the clean membrane (Lp_0), the membrane after microfiltration of skim milk (Lp_1), the membrane after cleaning by ultrapure water (Lp_2) and the membrane after chemical cleaning with 0.5 $mol \cdot l^{-1}$ HCl (by dissolution of analytical grade 37% HCl; Merck, Darmstadt, Germany) (Lp_3) were obtained from the slopes of *TMP* versus water flux graphs and generated straight lines. The fouling resistance values were calculated by using these values according to the resistance-in-series model based on Darcy's law as stated in our previous study [15]. In this model, total fouling resistance (R_t) is the sum of the intrinsic membrane resistance (R_m), the cake layer resistance (R_c), reversible fouling resistance (R_{frev}) and irreversible fouling resistance (R_{firr}).

Measurements and chemical analyses

The pH values of the samples were measured in a 50 ml beaker using a portable pH meter (Seven2Go; Mettler Toledo, Columbus, Ohio, USA) equipped with an InLab Expert Pro-ISM-IP67 electrode (Mettler Toledo). Each sample was mixed thoroughly before analysis and the measurement was carried out at 21.5 ± 0.1 °C. Total solids were determined using the forced-air oven drying method [16]. Total nitrogen was determined by the Kjeldahl method and the results were expressed as a protein equivalent using a conversion factor of 6.38 [16].

Colour measurement

The colour was measured by using a chroma meter CM-5 (Konica Minolta, Tokyo, Japan) to determine whiteness (L^*), red/greenness (a^*), and yellow/blueness (b^*) values of milk (feeding), retentate and permeate samples. Before measurements, the instrument was calibrated with a white reference tile. For the colour measurement of feeding and retentate samples, the tube cell CR-A502 and target mask CM-A195 were used, while for the colour measurement of permeate samples the rectangular cell CM-A98 was used.

Analysis of mineral content

The mineral content of the samples was determined by inductive coupled plasma-mass spectroscopy (ICP-MS) according to the method presented by da Silva et al. [17] with slight modifications. For the microwave-assisted closed vessel wet digestion of the samples by Mars 6 One Touch digestion system (CEM, Matthews, North Caroline, USA), 0.5 ml sample and 10 ml nitric acid (analytical grade, 65%; Merck) were mixed into 25 ml microwave digestion tubes (MARSXpress; CEM, Matthews, North Carolina, USA). After a one-hour burning operation at 180 °C, samples were diluted with ultrapure water (100-fold dilution in total) and were analysed by 7800 ICP-MS System (Agilent Technologies, Santa Clara, California, USA). The mineral content was quantified using a calibration line based on the ratio between the signal of the element and the signal of the associated standard. After each reading, the device automatically carried out the washing process with ultrapure water and 20 $ml \cdot l^{-1}$ nitric acid. The analyses were performed in duplicate.

Rheological analyses

Rheological analyses were performed using the Haake Mars III rheometer (Thermo Fisher Scientific, Waltham, Massachusetts, USA). The rheometer was equipped with a coaxial cylindrical rotor CC25 DIN Ti (Thermo Fisher Scientific) and cup CCB25 DIN (Thermo Fisher Scientific). The gap between the rotor and the cup was 5.3 mm for all samples. The amount of sample used in the analyses was 16.1 ml. The temperature of the samples was set with a Peltier temperature module TM-PE-C (Thermo Fisher Scientific), which is suitable for cylindrical measurement geometries. Rheological analyses were performed using two different methods. In the first method, viscosity was measured in the shear rate range of 6.05–200 s^{-1} at 20 ± 1 °C. Flow curves were drawn based on results of the measurement and the data were modelled according to the power law equation. In the second method, viscosity was measured at 200 s^{-1} shear rate at 7 different temperatures (20, 30, 40, 50, 60, 70, and 80 ± 1 °C). Before the measurements, the samples were kept at each temperature for 120 s to stabilize their temperatures. Viscosity curves versus temperature were drawn based on the results of the measurement.

The power law equation for pseudoplastic behaviour is described by Eq. 2:

$$\sigma = K\gamma^n \ (0 < n < 1) \qquad (2)$$

where σ is shear stress (in Pascals), K is the consistency coefficient, γ is the shear rate (in reciprocal seconds) and n is the flow behaviour index. The flow behaviour index is dimensionless and reflects the closeness to Newtonian flow [18].

Statistical analysis

Statistical analysis of data was performed using SPSS 16.0 software (SPSS, Chicago, Illinois, USA). The differences between means were analysed by one-way ANOVA with Tukey's test at the 5% significance level.

RESULTS AND DISCUSSION

The presence of a long-term decline in the filtrate flux is not necessarily the conclusive evidence for membrane fouling. Such a long-term flux decline could also reflect an alteration in the feed stream or a slow physical or chemical alteration of the membrane structure or composition, as stated by Makardij et al. [19].

Permeate flux of milk is often less than the ideal value because of boundary layer formation, concentration or fouling effects as stated by Tomasula and Bonnaillie [20]. As can be seen from both Fig. 1A and Fig. 1B, the initial permeate flux of the skimmed milk was 5-fold lower than that of the pure water for the operation at 28 kPa. An increase in *TMP* caused an increase in the initial pure water flux when the comparison was made at the constant pH range of 7.2–7.6. This pattern was also seen in the hydraulic permeability graph (Fig. 1C), which shows the high linearity of the relation between *TMP* and the water flux. According to Darcy's law [20], the flow rate of per-

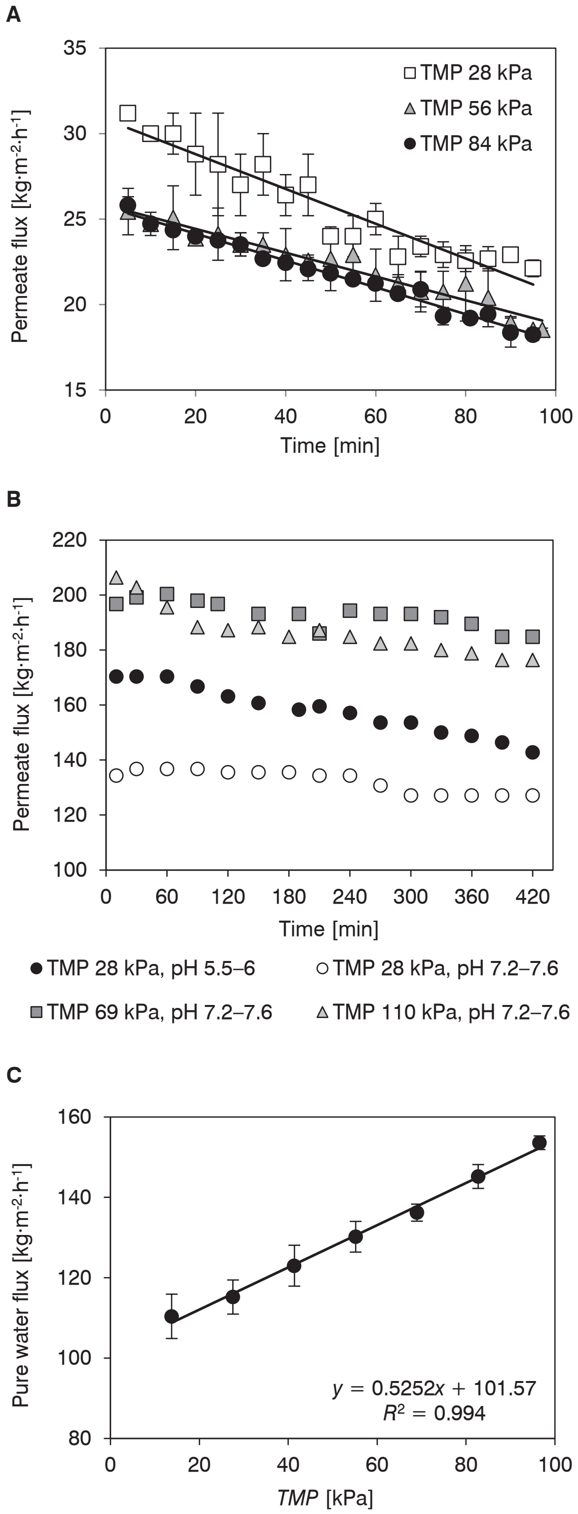

Fig. 1. Fouling of the polyethersulfone membrane during microfiltration in batch concentration mode.

A – effect of transmembrane pressure on the permeate flux, B – effect of the pH value of feed on the pure water flux, C – change in hydraulic permeability.
Process conditions were temperature 55 °C and axial flow rate 36 l·h^{-1}.
TMP – transmembrane pressure.

meate stream was proportional to *TMP*, viscosity and intrinsic membrane resistance for pure water. However, for the microfiltration of skimmed milk, the highest initial permeate flux was obtained at the lowest *TMP* (Fig. 1A). This result was probably due to the quick formation of a cake layer and the increased irreversible fouling resistance with an increase in *TMP* (Tab. 1). These results are in agreement with the explanation of GRANDISON et al. [21] that fouling is mainly controlled by hydrodynamic factors and was also the evidence of sharp pore clogging when higher *TMP* was used. Moreover, the decreasing trend in the permeate flux with time was higher at *TMP* of 28 kPa than that of the other operations at 56 kPa and 84 kPa, which can be attributed to the higher adsorption of foulant particles causing the reversible fouling resistance (Tab. 1). The reversible fouling layer was indicated by a slow decline in the permeate flow as stated by TOMASULA and BONNAILLIE [20]. The rate of decline in the flux, determined by calculating the slope of the flux and time profiles (Fig. 1A), was highest at *TMP* of 28 kPa, followed by 56 kPa and 84 kPa. Additionally, at an increase in *TMP*, the capacity of the membrane was saturated by total fouling and the flux became independent of the membrane pore size. This phenomenon appeared gradually for the operation at 28 kPa. Consequently, membrane fouling, the important part of which is irreversible fouling, was more severe when the milk microfiltration was operated at higher *TMP* values (Tab. 1).

Also, membrane fouling is dependent on the temperature and pH of the feed contacting the polymeric membrane material. FRANCE et al. [22] showed that an increase of 8 °C in process temperature caused a 41% increase in irreversible fouling. They stated that greater fouling occurred at microfiltration of skimmed milk when 50 °C process temperature was used, although higher initial permeate flux values could be obtained. As stated by TOMASULA and BONNAILLIE [20], temperature affects the viscosity term of Darcy's law equation. Permeate flow at milk microfil-

Tab. 1. Effect of transmembrane pressure on the fouling resistance for milk microfiltration in batch concentration mode.

TMP [kPa]	Resistance [$\times 10^{12}$ m^{-1}]				
	R_t	R_m	R_c	R_{frev}	R_{firr}
28	18.0 ± 0.3^{a}	10.3 ± 1.7	5.6 ± 0.4^{a}	1.5 ± 0.1^{a}	0.6 ± 0.3^{a}
56	23.2 ± 0.5^{b}	10.3 ± 1.7	5.7 ± 0.4^{a}	1.2 ± 0.2^{a}	6.1 ± 1.1^{b}
84	24.0 ± 0.5^{c}	10.3 ± 1.7	6.9 ± 0.7^{b}	0.4 ± 0.2^{b}	6.5 ± 1.0^{b}

Process conditions were temperature 55 °C and axial flow rate 36 l·h^{-1}.
Means with same letters in superscript in a column within the category data are not significant at $p > 0.05$.
TMP – transmembrane pressure, R_t – total resistance, R_m – membrane resistance, R_c – cake layer resistance, R_{frev} – reversible fouling resistance, R_{firr} – irreversible fouling resistance.

Tab. 2. Gross composition of skim milk, permeate and retentate obtained from milk microfiltration in batch concentration mode.

Sample code	pH	Total solids [%]	Mass balance [%]	Protein [%]	Mass balance [%]	Lactose [%]	Mass balance [%]
SM	6.65 ± 0.00^{a}	8.7 ± 0.0^{e}	100.0	3.4 ± 0.1^{e}	100.0	4.7 ± 0.0^{a}	100.0
R2.5x	6.59 ± 0.01^{ab}	11.7 ± 0.5^{d}	53.5	6.1 ± 0.1^{d}	70.8	3.9 ± 0.1^{b}	32.7
R3.5x	6.59 ± 0.00^{ab}	16.3 ± 0.1^{c}	53.9	10.7 ± 0.2^{c}	89.8	3.6 ± 0.2^{cd}	22.1
R4.5x	6.51 ± 0.04^{b}	18.5 ± 0.3^{b}	46.4	12.7 ± 0.3^{b}	82.2	3.2 ± 0.0^{h}	14.7
R5.5x	6.50 ± 0.00^{b}	21.3 ± 0.0^{a}	45.1	16.8 ± 0.2^{a}	90.2	3.0 ± 0.0^{i}	11.6
P2.5x	6.57 ± 0.02^{ab}	5.2 ± 0.1^{h}	36.0	0.2 ± 0.0^{f}	3.0	3.4 ± 0.1^{g}	43.5
P3.5x	6.58 ± 0.01^{a}	5.4 ± 0.1^{f}	44.7	0.1 ± 0.0^{f}	2.9	3.7 ± 0.0^{c}	55.6
P4.5x	6.56 ± 0.04^{ab}	5.3 ± 0.1^{g}	47.1	0.1 ± 0.0^{f}	2.7	3.6 ± 0.1^{e}	59.6
P5.5x	6.56 ± 0.00^{ab}	5.5 ± 0.0^{f}	51.7	0.1 ± 0.0^{f}	3.4	3.5 ± 0.2^{f}	61.2

Process conditions were transmembrane pressure 28 kPa, temperature 55 °C and axial flow rate 36 l·h^{-1}.
Means with same letters in superscript in a column within the category data are not significant at $p > 0.05$.
SM – skim milk; R2.5x, R3.5x, R4.5x and R5.5x – retentates having 2.5, 3.5, 4.5 and 5.5 fold concentration factor; P2.5x, P3.5x, P4.5x and P5.5x – permeate samples having 2.5, 3.5, 4.5 and 5.5 fold concentration factor.

tration at 53 °C was shown to be by approximately 85% greater than that at 6 °C due to the decreased viscosity. Protein diffusivity increases with an increase in temperature, which causes lesser concentration polarization and fouling despite greater internal fouling of membranes. In this study, no change in the viscosity of skimmed milk in a temperature range of 20–80 °C was observed (Fig. 2). Therefore, it is possible to say that the starting permeate flux at 55 °C was near the highest value that can be achieved. The clean PES membrane was affected by the pH change of the pure water (Fig. 1B). The operation at 28 kPa showed that a shift in the pH to an acidic region caused an increase in the initial flux. Similar to our results, DENG et al. [23] showed that hydrophilic modification of PES material caused an increase in flux at acidic pH values, while there was no observable change in a broad pH range for pristine PES. However, a higher flux decrease was observed for the pure water microfiltration at 28 kPa and pH in the range of 5.5–6.0. This result can be attributed to re-orientation of the side chains of the polymers and the increased interaction of polymer chains at acidic pH values causing a decrease in the pore size [23]. Relatively more stable water flux was obtained at pH in the range of 7.2–7.6 during conditioning of the PES membrane. Although the relation between *TMP* and the initial flux was linear up to 100 kPa (Fig. 1B), the declining trend in the flux increased with a further increase in *TMP*. Therefore, lower flux values were obtained after 100 min than at *TMP* of 69 kPa. Finally, it has emerged that a steadier water flux was obtained for the operations using lower *TMP* at a pH range of 7.2–7.6, which is near to pH of the retentate streams during milk microfiltration (Tab. 2). Because there was no significant difference in pH among the retentate streams ($p > 0.05$), it could be thought that pH change due to concentration factor might affect the flux decline slightly. However, pH values of the R4.5x and the R5.5x samples were significantly different from the skim milk ($p < 0.05$). KULOZIK [24] showed that even slight variations in milk pH induced significant changes in the flux. This explanation, which can be valid for *WRF* greater than 3.5, was attributed to less repulsion of deposited proteins due to reduced charge and possible variations in molecular size.

Another reason for the increase in the flux decline for the operation at 28 kPa could be the faster concentration of the skimmed milk due to high initial permeate flux values. In comparison with milk, it was stated before that flux declines steadily with time for feeds containing less proteins, while it is initially lower but remains constant in microfiltration of milk. This explanation was attributed to concentration polarization as a controlling mechanism of membrane fouling [25]. As can be seen from Fig. 3A, *WRF* close to 3 was reached at the end of 100 min operation at 28 kPa. However, at the same time, lower *WRF* for higher *TMP* values were reached due to lower permeate fluxes (Fig. 1A). As can be seen from Fig. 3A, in 100 min period of the milk microfiltration, the slope of permeate flux decline was greater than that at *WRF* greater than 3.5. Besides fouling, the changes in viscosity and rheological behaviour of the milk could be also the other factors that affected the trend of flux decline (Tab. 3). Therefore, the results obtained for the operation in batch concentration mode was also compared with the operation in total recycle mode, which is the milk microfiltration causing no concentration change during the process at the same conditions (Fig. 3C). The viscosity of the skim milk exhibiting Newtonian behaviour was determined as 2.1 $mPa{\cdot}s^{-1}$ from the model as reported by TOBIN et al. [26]. Similarly, it could be said that the retentate with *WRF* of 2.5 exhibited virtually Newtonian behaviour because the flow behaviour index was determined as 1.02 when the power law equation was used to examine non-Newtonian pseudoplastic behaviour due to a decrease in viscosity at low shear rates. The Newtonian behaviour is reflected by $n = 1$ and the pseudoplastic behaviour is reflected by $n < 1$ [18]. Therefore, the viscosity of the retentate with *WRF* of 2.5 was determined as 3.33 $mPa{\cdot}s^{-1}$. The logarithmic function of permeate flux versus time graph showed that the difference in the trend of flux decline of both operations

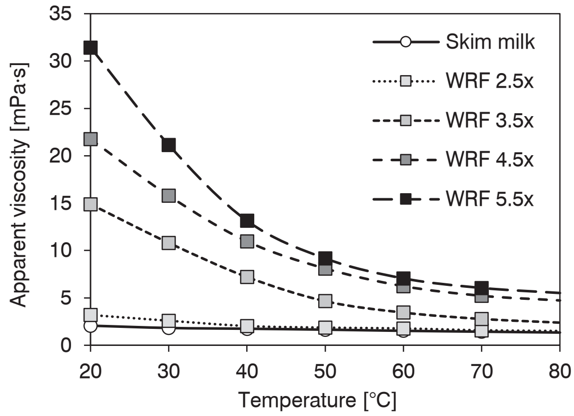

Fig. 2. Dependence of viscosity of the samples on temperature.

WRF 2.5x, WRF 3.5x, WRF 4.5x, WRF 5.5x – retentates having 2.5, 3.5, 4.5 and 5.5 fold weight reduction factors.

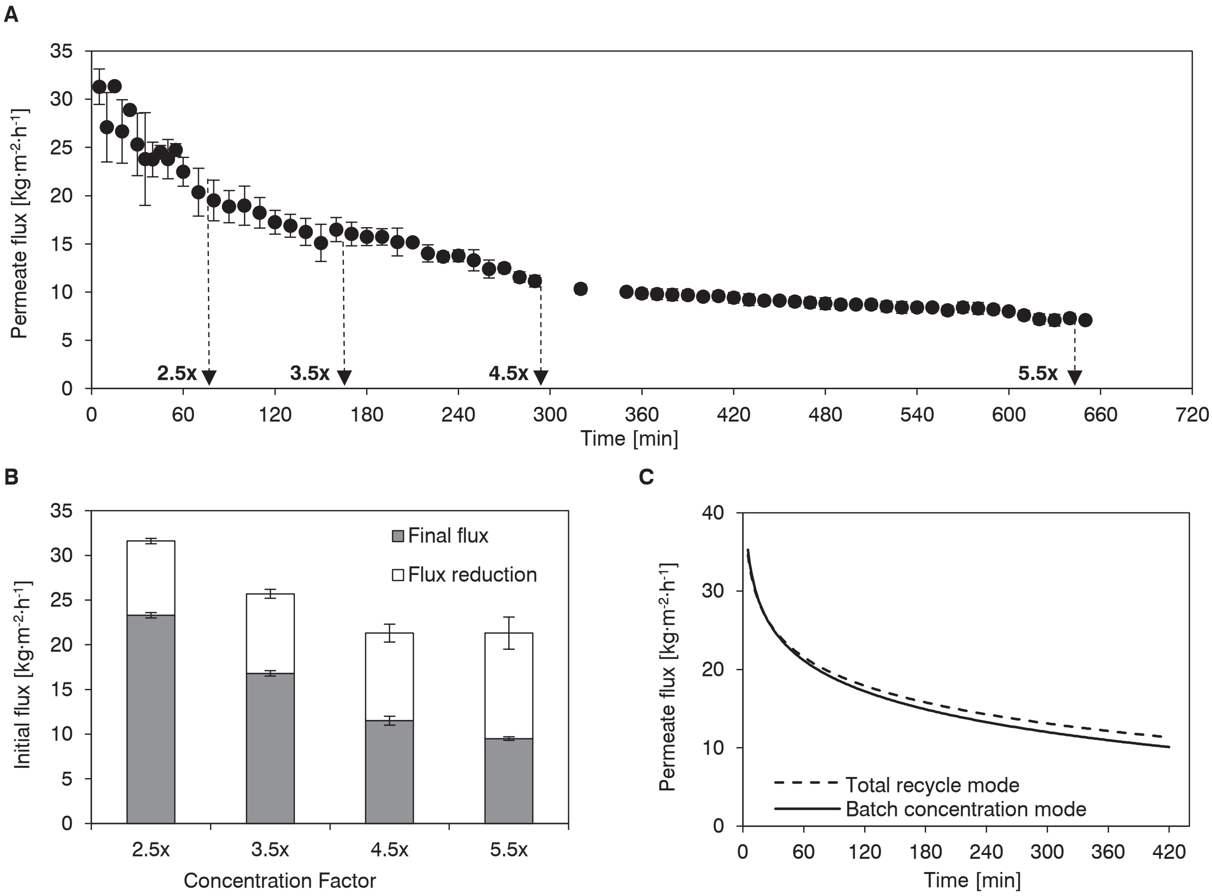

Fig. 3. Fouling in the polyethersulfone membrane during microfiltration.

A – change in the permeate flux for microfiltration in batch concentration mode, B – change in flux reduction according to the concentration factor, C – comparison of the two operation modes.
Process conditions were transmembrane pressure 28 kPa, temperature 55 °C and axial flow rate 36 $l \cdot h^{-1}$.

appeared after approximately 60 min. This was the time when the temperature-dependent viscosity started to increase in the skimmed milk (Fig. 3). Therefore, it could be said that the primary reasons for the decline in flux at *WRF* lower than 2.5 were membrane material and solid-surface interaction causing faster decrease and unstable fluxes because the effect of viscosity on the permeate flux was more pronounced at *WRF* greater than 2.5 at 55 °C.

As the concentration factor increased further, the concentration of total solids and protein contents of the retentates increased, while the amount of lactose decreased (Tab. 2). It was reported previously that the main enriched protein in the milk microfiltration retentate stream is casein, and its concentration increases as the concentration factor is increased [3, 27]. As the concentration of total solids (in particular casein) in the skimmed milk increased, the distance between casein micelles decreased and this caused an increase in electrostatic repulsion. As two particles with the same charge try to avoid each other, they change their flow paths. This causes increased resistance to the flow of a liquid in which they are suspended, and their viscosity increases [10].

The concentration of minerals also increased in the retentates and this phenomenon was more distinctive for calcium followed by phosphorus, magnesium, copper and zinc (Tab. 4). However, potassium and iron levels of the retentates decreased with longer filtration time. The increased concentration of colloidal calcium phosphate due to the increase in the concentration of casein was the main reason for the enrichment of calcium in all the retentates [28]. The mass balances for proteins, lactose and total solids showed that steady conditions have not yet occurred during the operation time, causing *WRF* to be 2.5. This result could be attributed to the solids contributing to the reversible fouling layer causing a rapid decline in the flux at *WRF* of up to 3.5, as shown in Fig. 3. This phenomenon was valid for all time regarding lactose separation. Increased fouling layer acted as a second membrane probably causing the change in membrane selectivity. This might be also responsible for the enrichment of whey proteins and several minerals in the retentate streams. Components such as serum proteins, lactose or mineral substances don't have much effect on viscosity, but they may interfere with the interaction of casein micelles with each other, thus causing a decrease in viscosity [9, 29]. Higher increase in the milk consistency was observed at *WRF* greater than 2.5 due to effective separation of these substances.

As the effect of casein on the viscosity of the skim milk is more than that of other components, the viscosity of the retentate with *WRF* of 3.5, 4.5 and 5.5 changed with shear rate and decreased with increasing shear rate. Therefore, it could be said that the retentates exhibited non-Newtonian pseudoplastic behaviour. As the concentration factor increased, pseudoplastic behaviour became more evident (Tab. 3) as reported by Solanki and Rizvi [14]. These observations were also in agreement with the study by Sauer et al. [9], who reported that micellar casein concentrates showed two different flow behaviours. They reported that skim milk and retentates with low casein concentrations exhibited Newtonian behaviour and retentates with high casein concentrations exhibited non-Newtonian pseudoplastic behaviour. Viscosity effects at *WRF* greater than 3.5 became more important on the permeate flux besides membrane fouling and it caused more steady flux behaviour (Fig. 3).

The microfiltration process caused a slight decrease in the lightness values of the skim milk retentates (Tab. 5), but this effect was independent of the concentration factor and was not significant ($p > 0.05$). Also, it caused an increase in the lightness values of the permeate streams, which was the evidence of effective removal of casein micelles from the skim milk. The concentration factor had no significant effect on the lightness again ($p > 0.05$). However, significant decrease in a^* (a negative value indicates green colour)

Tab. 3. Apparent viscosity, consistency coefficient and flow behaviour index of samples.

Sample code	η_{200} [mPa·s]	K [Pa·s^n]	n	R^2
SM	–	0.0015 ± 0.0000	1.07 ± 0.00	1.00 ± 0.00
R2.5x	–	0.0030 ± 0.0001	1.02 ± 0.00	1.00 ± 0.00
R3.5x	13.72 ± 0.24	0.0272 ± 0.0012	0.87 ± 0.00	1.00 ± 0.00
R4.5x	21.49 ± 1.38	0.0607 ± 0.0097	0.80 ± 0.02	1.00 ± 0.00
R5.5x	30.69 ± 0.09	0.0645 ± 0.0011	0.86 ± 0.00	1.00 ± 0.00

η_{200} – apparent viscosity, K – consistency coefficient, n – flow behaviour index.
SM – skim milk; R2.5x, R3.5x, R4.5x and R5.5x – retentates having 2.5, 3.5, 4.5 and 5.5 fold concentration factor; P2.5x, P3.5x, P4.5x and P5.5x – permeate samples having 2.5, 3.5, 4.5 and 5.5 fold concentration factor.

Tab. 4. Mineral content of samples obtained from milk microfiltration in batch concentration mode.

Sample code	Ca [mg·kg^{-1}]	P [mg·kg^{-1}]	K [mg·kg^{-1}]	Mg [mg·kg^{-1}]	Cu [mg·kg^{-1}]	Fe [mg·kg^{-1}]]	Zn [mg·kg^{-1}]
SM	1 139 ± 44 ^{d}	819 ± 38 ^{d}	1 629 ± 86 ^{ab}	106 ± 5 ^{d}	0.05 ± 0.04 ^{e}	1.75 ± 0.00 ^{c}	4.00 ± 0.02 ^{e}
R2.5x	1 746 ± 74 ^{c}	1 171 ± 51 ^{c}	1 724 ± 64 ^{ab}	133 ± 7 ^{c}	4.64 ± 0.03 ^{d}	1.02 ± 0.01 ^{g}	9.03 ± 0.04 ^{d}
R3.5x	3 211 ± 113 ^{b}	2 113 ± 66 ^{b}	1 737 ± 54 ^{a}	214 ± 8 ^{b}	5.92 ± 0.04 ^{c}	1.51 ± 0.00 ^{d}	17.29 ± 0.05 ^{c}
R4.5x	4 297 ± 119 ^{a}	2 878 ± 76 ^{a}	1 764 ± 81 ^{a}	263 ± 9 ^{a}	6.15 ± 0.06 ^{b}	2.53 ± 0.01 ^{b}	24.02 ± 0.07 ^{b}
R5.5x	4 477 ± 21 ^{a}	2 974 ± 65 ^{a}	1 788 ± 48 ^{a}	265 ± 4 ^{a}	9.84 ± 0.05 ^{a}	3.00 ± 0.03 ^{a}	26.2 ± 0.07 ^{a}
P2.5x	319 ± 22 ^{e}	329 ± 64 ^{e}	1 479 ± 54 ^{b}	68 ± 7 ^{e}	0.16 ± 0.00 ^{e}	1.13 ± 0.00 ^{f}	0.51 ± 0.01 ^{g}
P3.5x	358 ± 13 ^{e}	397 ± 42 ^{e}	1 784 ± 71 ^{a}	82 ± 5 ^{e}	0.07 ± 0.01 ^{e}	1.29 ± 0.01 ^{e}	0.68 ± 0.01 ^{f}
P4.5x	312 ± 35 ^{e}	336 ± 41 ^{e}	1 564 ± 72 ^{ab}	74 ± 2 ^{e}	0.05 ± 0.01 ^{e}	0.69 ± 0.01 ^{h}	0.33 ± 0.01 ^{h}
P5.5x	307 ± 15 ^{e}	340 ± 55 ^{e}	1 531 ± 38 ^{ab}	76 ± 2 ^{e}	0.07 ± 0.01 ^{e}	0.48 ± 0.01 ^{i}	0.38 ± 0.01 ^{h}

Process conditions were transmembrane pressure 28 kPa, temperature 55 °C and axial flow rate 36 l·h^{-1}.
Means with same letters in superscript in a column within the category data are not significant at $p > 0.05$.
SM – skim milk; R2.5x, R3.5x, R4.5x and R5.5x – retentates having 2.5, 3.5, 4.5 and 5.5 fold concentration factor; P2.5x, P3.5x, P4.5x and P5.5x – permeate samples having 2.5, 3.5, 4.5 and 5.5 fold concentration factor.

Tab. 5. Colour characteristics of samples obtained from milk microfiltration in batch concentration mode.

Sample code	L^*	a^*	b^*
SM	90.26 ± 0.02 ^{b}	–1.76 ± 0.01 ^{e}	11.07 ± 0.13 ^{a}
R2.5x	89.58 ± 0.21 ^{b}	–1.86 ± 0.01 ^{d}	6.66 ± 0.05 ^{e}
R3.5x	89.71 ± 0.10 ^{b}	–1.96 ± 0.02 ^{c}	7.95 ± 0.00 ^{d}
R4.5x	89.38 ± 0.42 ^{b}	–2.62 ± 0.01 ^{b}	8.27 ± 0.02 ^{c}
R5.5x	89.36 ± 0.25 ^{b}	–3.03 ± 0.14 ^{a}	9.15 ± 0.01 ^{b}
P2.5x	99.68 ± 0.04 ^{a}	–0.79 ± 0.09 ^{g}	3.22 ± 0.32 ^{h}
P3.5x	99.63 ± 0.05 ^{a}	–1.14 ± 0.11 ^{f}	4.51 ± 0.20 ^{g}
P4.5x	99.62 ± 0.04 ^{a}	–1.20 ± 0.30 ^{f}	4.62 ± 0.72 ^{f}
P5.5x	99.58 ± 0.08 ^{a}	–1.22 ± 0.01 ^{f}	4.66 ± 0.04 ^{f}

Process conditions were transmembrane pressure 28 kPa, temperature 55 °C and axial flow rate 36 $l \cdot h^{-1}$.
Means with same letters in superscript in a column within the category data are not significant at $p > 0.05$.
SM – skim milk; R2.5x, R3.5x, R4.5x and R5.5x – retentates having 2.5, 3.5, 4.5 and 5.5 fold concentration factor; P2.5x, P3.5x, P4.5x and P5.5x – permeate samples having 2.5, 3.5, 4.5 and 5.5 fold concentration factor.

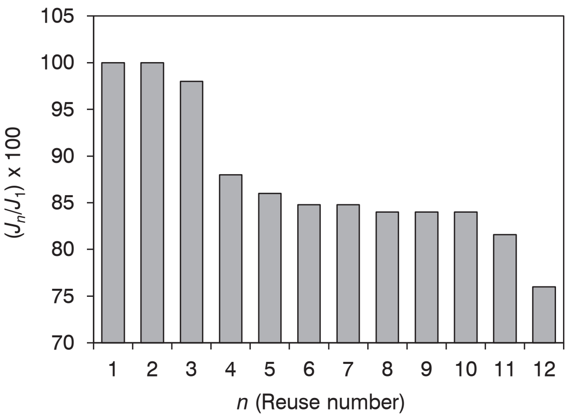

Fig. 4. Change in the performance of polyethersulfone microfiltration membrane with repeated use.

Process conditions were transmembrane pressure 28 kPa, temperature 55 °C and axial flow rate 36 $l \cdot h^{-1}$.
J_n – initial permeate flux at each use, J_1 – initial permeate flux at the first use of the membrane.

and b^* (a positive value indicates yellow colour) values of the retentates ($p < 0.05$) were observed in comparison with the skimmed milk. This effect became more pronounced with an increase in *WRF*. The greenish-yellow colour is related to whey proteins and riboflavin content of the milk as stated in our previous study [30]. Removal of them from the milk by microfiltration caused a significant decrease in these values for the retentates ($p < 0.05$), while this effect was opposite for the permeate streams. The effect of the increased *WRF* on the retentate colour was more significant than that of the permeate streams. As *WRF* increased, the b^* value of the retentates was increased again, while this effect was not observable for the permeate streams. This can be attributed to the second membrane layer changing the selectivity.

Finally, the reuse potential of the PES membrane in the production of casein concentrates at a constant transmembrane pressure of 28 kPa, the temperature of 55 °C and axial flow rate of 36 $l \cdot h^{-1}$, which led to *WRF* of 5.5, were evaluated (Fig. 4). The processed membrane was exposed to the cleaning procedure and the initial permeate flux for each usage (J_n) was compared with the initial permeate flux for the first use of a clean membrane (J_1). It was observed that three uses of the membrane were possible comprising the initial permeate flux. After that, additional seven cycles could be processed with approximately 85 % of the initial permeate flux. After 12 times of usage, 25 % of the initial flux was lost due to increased irreversible fouling resistance.

CONCLUSIONS

A shift in the basic pH range to the acidic range increased the initial permeate flux of the PES membrane. *TMP*, shear rate and viscosity effects had greater effect on the membrane performance in skim milk microfiltration without pH change. The use of low *TMP* caused higher permeate flux and lower membrane fouling. An increase in *TMP* caused an increase in irreversible fouling, which limited the reusability of the PES membrane. Cleaning allowed to use the PES membrane twelve times with 75 % of the initial permeate flux of the clean membrane after the operations at a constant transmembrane pressure of 28 kPa, temperature of 55 °C and axial flow rate of 36 $l \cdot h^{-1}$, with *WRF* of 5.5. An increase in the concentration factor caused the enrichment of the retentates by proteins, minerals such as calcium, and total solids except for lactose. *WRF* of 3.5 was critical to pronounce pseudoplastic behaviour more importantly due to the increased consistency coefficient. For microfiltration of skim milk at 55 °C, an increase in viscosity was important at *WRF* greater than 2.5 only. Below that point, the key factor to affect membrane performance was the interaction of feed and membrane material rather than hydrodynamic factors such as viscosity. The results of this study also showed that microfiltration of skim milk was operated successfully at *WRF* of up to 5.5 at 55 °C to enrich the total solids of retentates and to obtain ideal whey rich in lactose. These two separate fractions of skim milk have great potential to produce traditional cheese such as Sirene (white brine cheese) and to produce prebiotic whey beverages.

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