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Comparison between stirred and vibrated UF modules

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A B S T R A C T

Whey is used a nutritious protein source. The process of whey concentration was important historically, as the application of ultrafiltration (UF) in the dairy industry started with the separation and concentration of whey proteins from whey. In order to improve the performance of UF, it is beneficial to limit the extent of fouling of the membranes.

In this study, the performances of a vibratory shear-enhanced filtration process and a batch-stirred dead-end ultrafiltration process for the concentration of cheese whey were investigated with UF, C-30F regenerated cellulose and polysulfone 30 kDa nominal molecular weight limit membranes. The separations of protein and dry matter were examined by means of an IR technique and the Kjeldahl method. The turbidity and the chemical oxygen demand were also measured during concentration experiments. The volume of the pretreated (pasteurized) feed whey was decreased to 50% and 17.6% in the stirred and vibrated membrane processes, respectively.

Keywords: Whey; Ultrafiltration; Regenerated cellulose membrane; Polysulfone membrane; VSEP; Membrane resistance

1. Introduction

Whey is used mainly as animal feed or is released into the wastewater treatment process, although it is rich in valuable components [1]. It contains lactose, minerals and other nutritious proteins. Whey protein isolates are well known for their functional, nutritional and/or biological properties, with applications not only in the food industry, but also in the pharmaceutical and cosmetic industries [2]. The process of whey protein concentration is important: the application of ultrafiltration (UF) in the dairy industry started with the separation of the valuable proteins. In order to improve the performance of UF, it is beneficial to limit the extent of fouling of the membranes by selecting an appropriate flux or shear stress ratio. The high salt content of whey (8–20% in the dry matter) gives rise to numerous processing difficulties, a low lactose crystallization rate, and fouling in the microfiltration and UF performed in the manufacturing of whey protein concentrates [3].

Because of its high content of organic substances, whey can not be discharged into the environment without any clarification or concentration processes, even though these may be uneconomic. Moreover, when it is considered that, during cheese or casein-making, about 90% of the total milk finds its way into the whey, it is understandable that the processing of whey and in particular its organic constituents is regarded as very important [4]. Approximately 50% of the 115 million tons of a whey produced annually as a by-product of

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the dairy industry is disposed into the environment [5]. In view of its high organic content, with a huge chemical and biochemical oxygen demand (COD/BOD), this causes severe environmental and waste disposal problems [6]. UF membranes are often successful in reducing the COD/BOD content.

UF membranes are used extensively in the dairy industry. They have many applications, including the preconcentration of milk, the fractionation of whey, micellar casein enrichment for cheese-making, etc. However, an important disadvantage in the application of membrane technology in whey processing is the decline in the permeate flux (J) during the operation [7]. The decline in J during the UF of cheese whey is attributed to concentration polarization and membrane fouling [8].

Membrane fouling refers to the formation of deposits (a gel or cake layer) on the porous membrane surface and inside the pores of the membrane. This leads to blockage of the membrane and thereby reduces its permeability or J. Three separate stages of decline can in J be identified [9]. The initial rapid drop in J is principally due to concentration polarization. In the second stage, J continues to decline, but this is due to deposit formation. In the third stage, also called the steady-state period, J settles to a steady-state value.

It should be noted that a concentration polarization effect usually takes place in less than a minute, whereas fouling proceeds throughout the processing period. Fouling within the membrane pores causes changes inside the membrane, which reduce J. Fouling can be a serious problem, especially in those cases where biological fluids are handled. The fouling problem is manifested economically in the form of loss of productivity [10,11].

A vibratory shear-enhanced process (VSEP) module can be used to prevent deposition. This method increases the shear rate close to the membrane surface by vibrating the membrane. A notable feature is that the shear applied is independent of the cross-flow velocity [12]. Accordingly, a low cross-flow velocity can be applied, avoiding a decreasing trans-membrane pressure (TMP) along the membrane. Other means of increasing the shear close to the membrane surface are spacers, turbulence promoters, and inserts that create flow instabilities, such as Dean vortices or micro-turbulences [13].

2. Materials and methods

2.1. Pretreatment of whey

The cheese whey was provided by Sole-Mizo Hungaria Ltd. Co. (Szeged, Hungary). It was pasteurized at 70°C with 2 min holding to eliminate microbes and to prevent pH decrease, and then skimmed by a milk separator at 8,000 rpm (ST-800 Milk Separator, Hungary) to decrease the fat content.

2.2. Membrane conditioning and cleaning

The flat-sheet membranes were submerged in deionized water overnight. Before the measurements, the membranes were treated by circulating deionized water at low pressure at a high recirculation flow rate for 1 h in order to remove the excess of preservation chemicals attached to the new membranes. After these conditioning steps, deionized water was permeated at same pressures as in the concentration processes (at 0.3 MPa for batch-stirred UF (BSUF) and at 0.4 MPa for VSEP), in order to measure the corresponding water permeation fluxes (J_W) and to establish the hydraulic permeability of the clean membrane. Membrane application in the food and dairy industries is faced with the important issue of membrane fouling by certain whey components, mainly proteins.

Furthermore, membrane cleaning is an important economic process. In our case, the procedure for membrane cleaning was as follows: (1) a rinsing step with deionized water, (2) exposure to pepsin enzyme solution (1 w/w%) for 30 min at 40°C, (3) a cleaning procedure with an alkaline (sodium dodecylsulfate, NaOH and EDTA [13]) 0.5 w/w% solution for 30 min at 50°C, and (4) a final rinse with deionized water. The cleaning procedures were repeated until at least 90% of the initial J_W was recovered.

2.3. Analytical methods

The COD was determined in test tubes (Lovibond, Germany) with an ET 108 digester (Lovibond, Germany) and a PC CheckIt photometer (Lovibond, Germany).

The turbidity of the permeate and that of the concentrate were determined with a HACH2100N turbidimeter. The dry matter content (expressed in m/m %) was determined by a standard gravimetric method by heating the sample to mass constancy in a hot air oven maintained at 105°C. The glass dish contained 5 mL of sample. The protein content was measured with Kjeldahl nitrogen determination equipment (Kjeltec Auto 2300 with a DS20 thermal digester block, Sweden).

2.4. Membrane processes

2.4.1. Batch-stirred ultrafiltration experiments

The UF experiments were carried out in a BSUF cell (Amicon 8200, Millipore, USA) and the whey was stirred at a constant speed of 200 rpm during the concentration tests. TMP was maintained at 0.3 MPa, using

a high-pressure nitrogen gas cylinder, and the temperature (T) was kept at 25 ± 2°C. The membranes used are manufactured by Millipore (Ultracel regenerated cellulose PLTK, (RC) and GE Osmonic (Sepa CF Polysulfone ER, (PS)); both membranes have a nominal molecular weight limit (NMWL) of 30 kDa and an effective filtration area of 40 cm^2, with a diameter of 76 mm. The feed volume (V_{FEED}) was 200 cm^3. UF experiments were stopped when the permeate volume reached 100 cm^3. J was calculated on the basis of the time (t) needed to collect five 20 mL samples of permeate corresponding to a volumetric reduction ratio (VRR) of 2. VRR is defined as

$$\mathrm{VRR} = \frac{V_{\mathrm{FEED}}}{V_{\mathrm{CONC}}} \tag{1}$$

where V_{FEED} and V_{CONC} are the volumes of solution in the BSUF cell initially and at the end of the test, respectively.

2.4.2. Vibratory shear-enhanced ultrafiltration experiments

The VSEP filtration module was a VSEP Series L (New Logic International, Emeryville, CA, USA) equipped with a single 27-cm outer diameter and 9.4-cm inner diameter annular membrane with an effective area of 503 cm^2, separated from the permeate by a support screen and a drainage cloth. The filtration module was situated in a circular housing placed at the tip of a 1.5 m vertical shaft. This shaft acts as a torsion spring, which transmits the oscillations created by an eccentric drive motor. The membrane oscillates azimuthally in its own plane with amplitude depending upon frequency (F). The resulting motion of the housing was indicated by the manufacturer to be 32 mm on the outer rim at the maximum F allowed of 60.75 Hz. Due to housing oscillations, the local membrane shear rate varies sinusoidally with t and proportionally to the radius.

TMP was set to 0.4 MPa at 25 ± 2°C and the amplitude of the oscillation was set to 1.9 cm (3/4 inch) and F to 54.8 Hz. The whey from the tank was pumped to the inlet of the VSEP system. The flat membrane used here was the RC UF membrane (C-30F), with a NMWL of 30 kDa.

2.4. Determination of resistances

In order to investigate the membrane fouling, the different fouling resistances were calculated. The rate and extent of membrane fouling and its effect on J for any given system depends on various parameters, such as the specific interactions between the membrane surface and various fouling species, hydrodynamic forces exerted by the flowing process fluid and process parameters such as the cross-flow velocity, TMP, feed concentration, pore size and T.

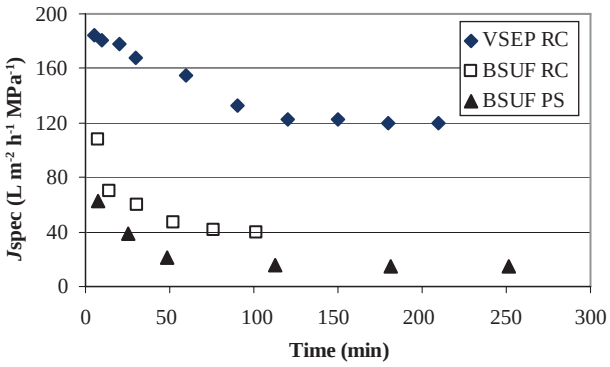

Fig. 1. J_{spec} versus t during the concentration of whey with the VSEP and BSUF systems (VSEP parameters: TMP = 0.4 MPa, T = 25°C, volumetic flow rate (q_V) = 680 L h^{-1}, F = 54.7 Hz; BSUF parameters: TMP = 0.3 MPa, T = 25°C, stirring rate (n) = 200 rpm).

The resistance of the gel layer (R_G) was determined from the resistance of the porous fouling layer (R_F), determined after rinsing with deionized water to remove any whey residue layer from the surface of the membrane [14], by subtracting the resistance of the clean membrane (R_M):

$$R_{\mathrm{G}} = \frac{\mathrm{TMP}}{\eta \times J} - R_{\mathrm{M}} - R_{\mathrm{F}} \quad (\mathrm{m}^{-1}) \tag{2}$$

where η is the viscosity of water at 25°C.

The fouling resistance thus accounts for the increase in resistance due to both internal membrane fouling and the formation of a cake/gel layer on the membrane surface. The resistance of the polarization layer (R_T) was evaluated from the steady-state flux by using the resistance-in-series model:

$$R_{\mathrm{T}} = R_{\mathrm{M}} + R_{\mathrm{F}} + R_{\mathrm{G}} \quad (\mathrm{m}^{-1}) \tag{3}$$

The membrane resistance was calculated as

$$R_{\mathrm{M}} = \frac{\mathrm{TMP}}{J_{\mathrm{W}} \times \eta} \quad (\mathrm{m}^{-1}) \tag{4}$$

R_F can be measured by washing the gel layer from the membrane. R_F can be calculated as

$$R_{\mathrm{F}} = \frac{\mathrm{TMP}}{J_{\mathrm{W}} \times \eta} - R_{\mathrm{M}} \quad (\mathrm{m}^{-1}) \tag{5}$$

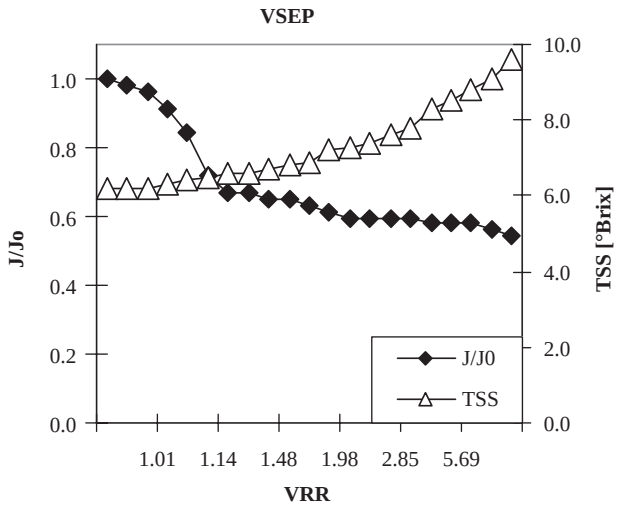

Fig. 2. J/J_0 and TSS content of retentate vs VRR during UF of whey with the VSEP (VSEP parameters: TMP = 0.4 MPa, $T = 25°C$, $q_V = 680$ L h^{-1}, $F = 54.7$ Hz).

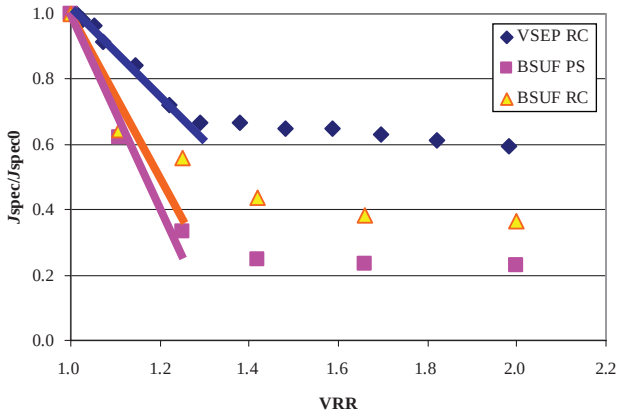

Fig. 3. J_{spec}/J_{spec0} versus VRR during the process of whey concentration for the VSEP and BSUF systems (VSEP parameters: TMP = 0.4 MPa, $T = 25°C$, $q_V = 680$ L h^{-1}, $F = 54.7$ Hz; BSUF parameters: TMP = 0.3 MPa, $T = 25°C$, $n = 200$ rpm).

where η is the viscosity of the filtered solution at 25°C.

The selectivity of a membrane for a given solute was expressed by the average retention (R) [15]:

$$R\% = \left(1 - \frac{c}{c_0}\right)100 \quad (\%) \tag{6}$$

where c is the average concentration of the solute in the permeate phase (m/m %), and c_0 is the concentration of the solute in the bulk solution (m/m %).

3. Results and discussion

3.1. Fluxes in concentration tests

The concentration fluxes of the VSEP and BSUF systems during whey concentration tests are illustrated in Fig. 1. Since the TMP applied was different in the different tests, we calculated the normalized or specialized flux (J_{spec}) referred to unit TMP (L m^{-2} h^{-1} MPa^{-1}). It is clear that, during whey concentration, the VSEP system yields a higher flux than the BSUF system. The initial flux (J_0) values, the steady-state J values, and the decline in the ratio J/J_0 differed considerably. At the beginning, a milder decrease in J was observed for the VSEP system. The initial difference between the J_0 values was about 50% (184.11 L m^{-2} h^{-1} MPa^{-1} for the VSEP RC, 107.9 L m^{-2} h^{-1} MPa^{-1} for the BSUF RC and 38.9 L m^{-2} h^{-1} MPa^{-1} for the BSUF PS); J decreased very rapidly in the first few minutes for the BSUF systems, followed by a slower fall, until finally quite constant steady-state values were observed (to 119.5 L m^{-2} h^{-1} MPa^{-1} for the VSEP RC, 39.5 L m^{-2} h^{-1} MPa^{-1} for the BSUF RC and 13.9 L m^{-2} h^{-1} MPa^{-1} for the BSUF PS). This means that the concentration polarization and deposit or gel layer formation was formed in all cases but with different speeds. The initial fall was caused in both cases by concentration polarization, which is generally unavoidable in membrane processes. The gradual cake or gel layer build-up of solute particles on/near the membrane surface affects J in various ways. It may lead to the formation of a layer of higher density. The solute particles may also block the membrane pores and thus alter the sieving characteristics and permeability.

The difference was much more characteristic and easily visible when J/J_0 and the total soluble solid (TSS) content of the retentate were plotted as a function of VRR. Fig. 2 reveals that, during UF with increasing VRR, J/J_0 decreased and the TSS content increased, in the VSEP system, while VRR increased from 1 to 5.7 for the retentate of the whey proteins, it rose from the initial 5.9°Brix to 9.6°Brix. However, in the BSUF system the TSS content of the retentate reached 6.3°Brix for the RC and PS membranes by the end of the tests. The reason why only the VSEP system is shown in Fig. 2 is that, in the BSUF system, it was not possible to measure the TSS content of the retentate during the experiment, but only at the end of the tests.

The main difference between the two systems was in the initial part of the J/J_0 curves (Fig. 3). At the beginning of the processes higher decreases were observed for the BSUFs than for the VSEP. The slope of the curves for VSEP RC was 0.0033, for BSUF RC was 0.0105 and for BSUF PS was 0.0207. The steady-state flux for VSEP was observed at 120 min (at 1.3 VRR), while that for BSUF PS was at 113 min (at 1.25 VRR)

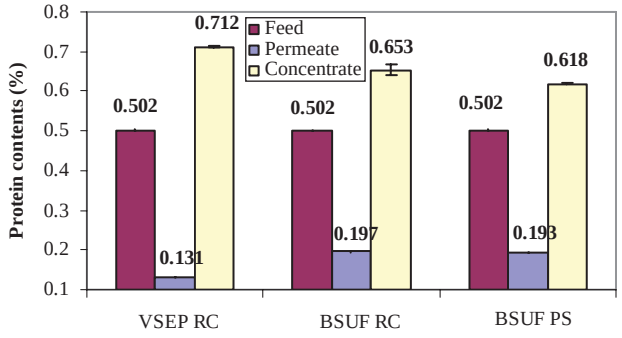

Fig. 4. Protein contents of feed, permeate and retentate for the VSEP and BSUF systems.

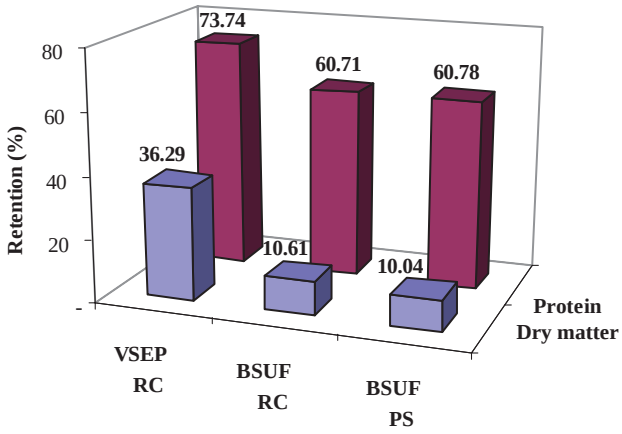

Fig. 5. Comparison of retentions of protein and dry matter.

and that for BSUF RC at 250 min (at 1.7 VRR). The initial rapid decrease in J_0 for the BSUFs was greatly enhanced for the BSUF PS system. This was mainly due to the higher concentration polarization that can arise in the PS membrane. In the second part of the curves, a lower J/J_0 value was observed for the BSUF PS system (0.23) than for BSUF RC (0.38).

3.2. Retentions

Since the feed was the same pretreated whey in all concentration tests (Fig. 4), the protein content of the feed was in all cases 0.502%. The differences in protein content of the permeates of the different system were not significant, whereas the differences between the retentates were significant. The protein content of the permeate was 0.131%, 0.197% and 0.193% for VSEP RC, BSUF RC and BSUF PS, respectively. Slightly lower permeate (0.131%) and higher protein concentrate values (0.712%) were observed for the VSEP system, which reflects a higher membrane rejection, as Fig. 5 shows a protein retention of 73.7% as compared with 61%.

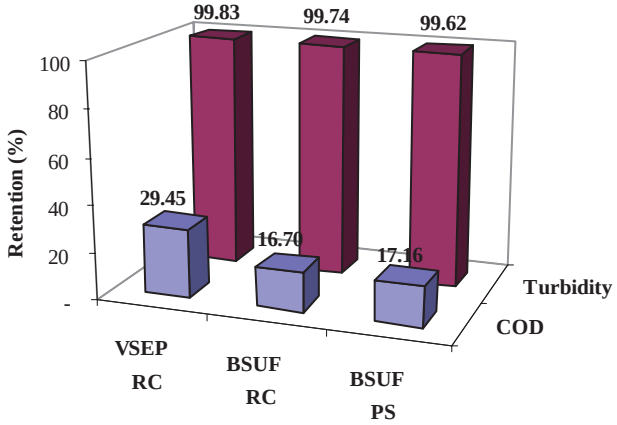

Fig. 6. Comparison of retention of COD and turbidity.

All the applied membranes had the same cut-off values, but the measured retentions of proteins and dry matter were different (Fig. 5) for the VSEP and BSUF membranes. The retentions of the BSUFs were quite close to each other, but the retention of VSEP RC was much higher. This could be explained by the protein layer that developed on the membrane in the BSUF methods. For the VSEP system, the data rather show that the solute particles may block the membrane pores, thereby altering the sieving characteristics and the pore distribution. Around 13% higher retention was observed for the protein, and around 26% higher retention for the dry matter when the VSEP system was used.

Fig. 6 illustrates the retentions of turbidity and the COD. There was no considerable difference between the turbidity levels, i.e. protein rejection, though VSEP RC had the highest value (99.83%). The retention of COD in the VSEP system was almost twice as high as for the BSUF systems, which means that much more organic components remained in the concentrate during the vibration method, i.e. the permeate was clearer.

3.3. Resistances

The total resistance (R_T) of membrane filtration is made up of the membrane resistance (R_M) itself and the resistances of the membrane transport phenomena, i.e. porous fouling (R_F) and concentration polarization/gel layer formation. The gel layer resistance (R_G) refers to the concentration polarization, and the formation of a gel layer on the surface of the membrane. This leads to blockage of the membrane, thereby reducing the membrane permeability or J. R_M is much higher for the PS membrane than for the RC membranes. As may be

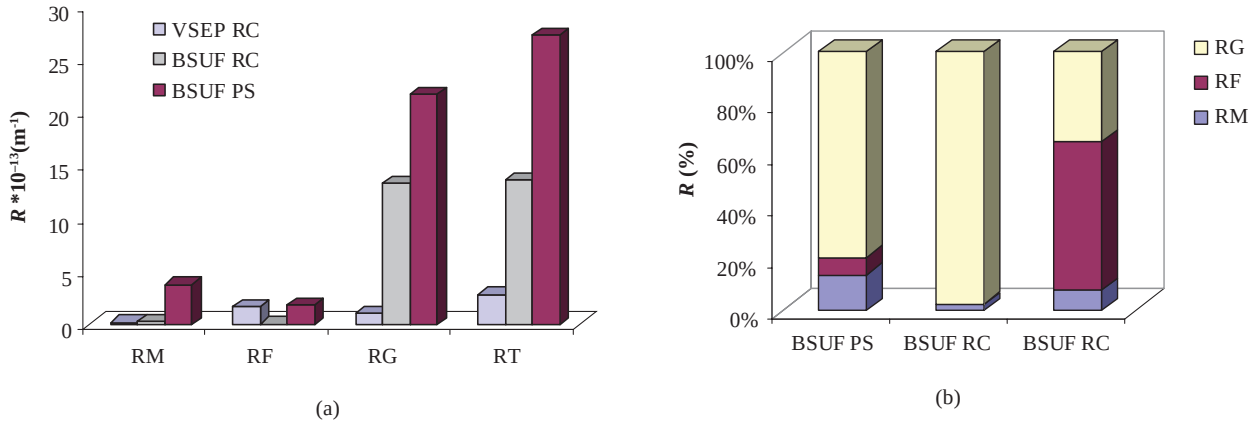

Fig. 7. Resistances (in terms of real values (a) and percentages (b)) in the VSEP and BSUF systems.

seen in Fig. 1, the RC membrane has a higher flux than the PS membrane, and hence a lower R_T (Fig. 7a).

During whey UF with the BSUF systems, R_G was higher than R_F in both systems, but for the RC membrane the main part of R_T was due to the gel layer and the effect of fouling could be neglected (Fig. 7b). The concentration polarization can be minimized by appropriate selection of the TMP or/and the whey feed tangential velocity, i.e. the shear stress.

When the VSEP system was used for the concentration of whey, R_T was found to be reduced by 89.5% as compared with the BSUF PS system and by 50.2% as compared with the BSUF RC system. R_F for VSEP RC was larger than R_G. The measured R_G was 92.5% and 95.4% of that measured for the BSUF RC and PS system, respectively (Fig. 7b). The greater proportion of R_F in the overall resistance distribution explains the higher COD retention (see Fig. 7).

4. Conclusions

The performance of the 30 kDa RC and PS UF membranes was investigated during the membrane processing of cheese whey. It is clear that, during whey concentration tests, the VSEP UF system yields a higher flux than the classical BSUF systems. The protein layer that developed on the membrane could more visibly reduce J in the BSUF methods during the concentrations.

For the VSEP system, the data rather show that the solute particles may block the membrane pores, thereby altering the sieving characteristics and the pore distribution. R_T was much lower for the VSEP system and the proportions of R_G and R_F also differed. R_T for the VSEP was reduced by 89.5% as compared with the BSUF PS system and by 50.2% as compared with the BSUF RC. The measured R_G was 92.5% and 95.4% of that measured for the BSUF RC and PS system, respectively. R_F for VSEP RC was larger than R_G. Consequently, for the BSUF systems, the membrane suffered more significant fouling.

Our data demonstrated that the VSEP system outperforms the conventional BSUF systems in UF in terms of permeate COD, protein and dry matter reduction. The retention values of the BS membrane systems were quite close to each other, but the retentions of VSEP RC were in all cases higher.

A comparison of the data measured with the two systems indicated a definite advantage for the VSEP system operating with the same membrane and at the same pressure and temperature.

In view of the better performances of VSEP, we conclude that the VSEP system could be a viable alternative for the concentration of cheese whey.

Acknowledgments

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Symbols

BOD	biochemical oxygen demand (mg L^{-1})
BSUF	batch-stirred ultrafiltration
c	concentration of the solute in the permeate phase (m/m %)
c_0	concentration of the solute in the bulk solution (m/m %)
CH	convective heating
COD	chemical oxygen demand (mg L^{-1})
EDTA	ethylenediaminetetraacetic acid
F	frequency (Hz)
J	permeate flux (L m^{-2} h^{-1})

J/J_0	flux reduction ratio
J_{spec}/J_{spec0}	normalized flux reduction ratio
J_{spec}	normalized/specialized flux (L m^{-2} h^{-1} MPa^{-1})
J_w	pure water flux of the clean membrane (L m^{-2} h^{-1})
MW	microwave
n	stirring rate (rpm)
NMWL	nominal molecular weight limit (kDa)
NaOH	sodium hydroxide
η	viscosity (Pas)
PS	polysulfone
q_V	volumetric flow rate (L h^{-1})
R	average membrane retention (%)
R_G	resistance of the gel/cake layer (m^{-1})
R_F	internal porous fouling resistance (m^{-1})
R_M	resistance of the clean membrane (m^{-1})
R_T	total resistance of the system (m^{-1})
RC	regenerated cellulose
t	time (h)
T	temperature (°C)
TMP	trans-membrane pressure (bar)
TSS	total soluble solid (Brix)
UF	ultrafiltration
V_{CONC}	volume of solution at the end of the test (retentate) (dm^3)
V_{FEED}	volume of feed solution (dm^3)
VRR	volumetric reduction ratio
VSEP	vibratory shear-enhanced process

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