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Concentration of proteinin fish mince wash water discharged from Surimi processing plant by ultrafiltration

A. Khatprathum[a,b], P. Siriwongpaisaan[b], W. Youravong[a,b*]

[a]*Membrane Science and Technology Research Center, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand*
[b]*Department of Food Technology, Faculty of Agro-Industry, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand*
Tel. +6674286321, Fax +6674212889; email: wirote.y@psu.ac.th

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ABSTRACT

Fish mince wash water, discharged from a surimi processing plant, has a major impact on wastewater treatment. It contains some valuable components such as proteins and enzymes. Therefore, recovery of these components is not only done to reduce environmental pollution but also to gain valuable components. In this work, protein in fish mince wash water was recovered and concentrated by ultrafiltration. The experiments were carried out using plate and frame regenerate cellulose membrane with a molecular weight cut off (MWCO) of 30 and 100 kDa, and the effect of MWCO and operating conditions on permeate flux and protein retention was investigated. It was found that protein retention was about 98% for both membranes while the crossflow rate and transmembrane pressure (TMP) did not affect protein rejection. The permeate flux at the same TMP of the 30 kDa membrane was higher than that of the 100 kDa membrane. Therefore, the 30 kDa membrane was used for the concentration of protein. It was also found that protein in fish mince wash water (0.27 $\pm$ 0.08% (w/v)) could be concentrated up to 10.92 $\pm$ 0.08% (w/v) at a volume concentration factor (VCF) of 40 and about 84% of chemical oxygen demand (COD) was reduced. In addition, the empirical equation based on a shear controlled model was developed to describe permeate flux during batch concentration.

Keywords: Fish mince; Protein concentration; Shear controlled model; Ultrafiltration

1. Introduction

Surimi produced from washed and dewatered fish mince is widely used as raw material for the production of a variety of food products such as meat balls and artificial crab. Washing and dewatering fish mince is one of the most important steps in surimi processing. It is done in order to remove fat and other water soluble substances, such as sarcoplasmic protein, and the enzymes lead to an increase in concentration of the remaining component, gel strengthened myofibril protein. As a result, a large volume of wash water containing high concentrations of organic materials is generated downstream of the washing and dewatering operation. It has been reported that about 29 liters of wash water is used to produce 1 kg of surimi [1]. The protein content in fish mince wash water is in between 0.4% and 2.3% (w/v) depending on the washing steps. In practice, solid waste from surimi processing plants is usually converted to animal feed or fish meal while liquid waste (including fish mince wash water) is generally discarded back in to the plant waste stream. This

*Corresponding author

leads to an increase in the load on the wastewater treatment system and the loss of some valuable components, especially proteins. Therefore, it would be beneficial to harvest these proteins and reduce the load on wastewater treatment.

The ultrafiltration process is one of the methods that have a great potential for the concentration, fractionation and purification of soluble and insoluble components in the food industry. Ultrafiltration offers several advantages over the traditional techniques, including low energy requirement and low temperature of operation. The crossflow ultrafiltration process is found to be suitable for large-scale operation and numerous studies of its commercial application to concentrate or purify solutions and in the extraction of solvents have been reported [2,3]. Studies of the application of ultrafiltration in the seafood industry are just beginning to emerge but an increase in the number of published papers and patents suggests that there will be a significant development in the near future. Protein from surimi processing wastewater could be harvested using ultrafiltration and microfiltration [1,4]. It has been found that most of protein could be recovered by ultrafiltration while microfiltration was suitable for recovery myofibrillar protein. The protein recovered by microfiltration showed highly functional food properties while the chemical oxygen demand (COD), protease activity and turbidity in the surimi wastewater processing plant were reduced greatly by ultrafiltration. In addition to protein, catheptic protease is also an important enzyme found in wastewater from surimi processing. This enzyme could be separated from the waste stream and purified using ultraflitration [5].

In general, the performance of ultrafiltration processes can be indicated by using at least two parameters including permeate flux and rejection. The limitation of the ultrafiltration process is that the permeate flux declines due to concentration polarization and fouling. The behavior of permeate flux depends on several factors including feed properties, membrane properties, membrane modules and operating parameters [2]. It has been reported that not only membrane pore size or molecular weight cut off (MWCO), but also membrane fouling, plays an important role in the determination of protein rejection [6].

Although ultrafiltration has been employed for the recovery of protein from surimi processing plants but no data have been reported of permeate flux and the quality of permeate during the concentration of protein using ultrafiltration. The objectives of this present research were: (1) to study the effect of membrane MWCO and operating conditions on permeate flux and protein retention; (2) to concentrate protein and reduce COD in fish mince wash water using the most suitable membrane MWCO; and (3) to develop empirical equations based on a shear controlled model to describe permeate flux during batch concentration.

2. Materials and methods

2.1. Sample collection and preparation

Fish mince wash water was collected from a local surimi processing plant of the MANA Company, Songkhla, Thailand. The sample was kept at 4°C and used within 48 h. The sample was filtrated through cotton filter to remove suspended particles before being introduced to the membrane system.

2.2. Ultrafiltration experiments

A crossflow plate and frame unit with regenerated cellulose membranes (MWCO 30 and 100 kDa) (Millipore, USA) were used. The membrane surface area was 0.5 m^2. All experiments were operated at temperature of 15 ± 2°C. Ultrafiltration experiments were performed according to two types of operating modes: the total recycle mode and the batch concentration mode. In the total recycle mode, the experimental trials were devoted to study the effect of the MWCO, the crossflow rate and transmembrane pressure (TMP) on the permeate flux and protein retention. The range of TMP and crossflow rates were 0.5–4.5 bars and 180–360 l/h, respectively.

In the batch concentration mode, the concentration of the feed increased as the volume concentration factor (VCF) increased. The VCF can be expressed as

$$\mathrm{VCF} = \frac{V_\mathrm{f}}{V_\mathrm{f} - V_\mathrm{P}}, \tag{1}$$

The best MWCO membrane, TMP and crossflow rate obtained from the total recycle mode experiments were used to concentrate protein in the fish mince wash water up to a VCF of 40. The data obtained was used to develop empirical equations to describe permeate flux using a shear controlled model.

2.3. Analytical methods

The samples of fish mince wash water, permeate and retentate (concentrate) were collected during ultrafiltration for physical and chemical analysis. The total solid was determined gravimetrically after drying the samples in an incubator at 105°C and measuring the weight of the residue. The COD was determined using the procedure described by American public health

Table 1
Some properties of fish mince wash water, permeate (accumulate) and retentate (concentrate at VCF = 40)

Properties	Fish mince wash water	Permeate (accumulate)	Concentrate (at VCF = 40)
pH	6.75 ± 0.05	6.75 ± 0.05	6.25 ± 0.05
Protein (%w/v)	0.27 ± 0.08	0.012 ± 0.01	10.92 ± 0.08
Total solid (%w/v)	0.43 ± 0.06	0.02 ± 0.01	16.22 ± 0.06
Viscosity (mPa.s at 15 °C)	0.9987 ± 0.0058	–	4.1139 ± 0.2312
COD (mg/l)	3648 ± 128	768 ± 58	–

association (APHA), American water works association (AWWA) and Water pollution control federation (WPCF) [7]. The pH was measured using a pH meter (Toshniwal instruments, Germany) at 15 ± 2°C. Viscosity was determined by using a glass Oswald capillary viscometer (Schott Geräte, Hofheim/Ts, Germany) at constant temperature of 15 ± 2°C. The total protein content was measured by the Kjeldahl method [8]. All measurements were done in triplicate. The mean comparison of permeate flux and protein retention, obtained by using 30 and 100 kDa membranes were carried out using *t*-test, calculated by the spread sheet program (Microsoft Excel). The molecular weight of protein was determined by gel electrophoresis. The electrophoresis was performed according to the method of Laemmli [9] with some modification using the Mini-Protein II Dual Slab Cell (Model 1000-500, Bio-RAD Inc, USA).

3. Results and discussion

3.1. Effect of membrane MWCO on permeate flux and protein retention

The total solid, protein content, viscosity, pH and COD of fish mince wash water are shown in Table 1, and the molecular weight of protein in fish mince wash water, determined by using SDS–PAGE, is shown in Fig. 1. The COD of fish mince wash water was relatively high and could not be directly discharged to the environment. The protein content in fish mince wash water was about 0.27 % (w/v) and its molecular weight was in the range of 14–97 kDa. Table 2 shows the average of permeate fluxes and protein retention (at TMP 3.5 bar and a crossflow rate of 360 l/h) during the ultrafiltration of fish mince wash water. It was found that the average permeate flux at filtration time of 60 min for 30 kDa membrane was significantly higher than that of 100 kDa membrane ($P < 0.05$) while the average protein retention of 30 kDa membrane was significantly higher than that of 100 kDa membrane ($P < 0.05$). These results suggest that 30 kDa membrane was more suitable than 100 kDa membrane for the concentration of protein in fish mince wash water. Thus the membrane with MWCO 30 kDa was used for the following study.

3.2. Effect of TMP and crossflow rate on permeate flux and protein retention

The permeate flux and protein retention (R_j) versus TMP with varying crossflow rates in the total recycle mode using 30 kDa membrane are shown in Fig. 2. The permeate flux was increased as TMP increased until it reached a pressure independent region. The limiting flux at a crossflow rate of 180 (TMP = 2.5 bar) and 360 l/h (TMP = 4.5 bar) were about 60 and 90 l/m^{2}h, respectively. This result was expected since increasing the crossflow rate led to an increase in mass transfer of

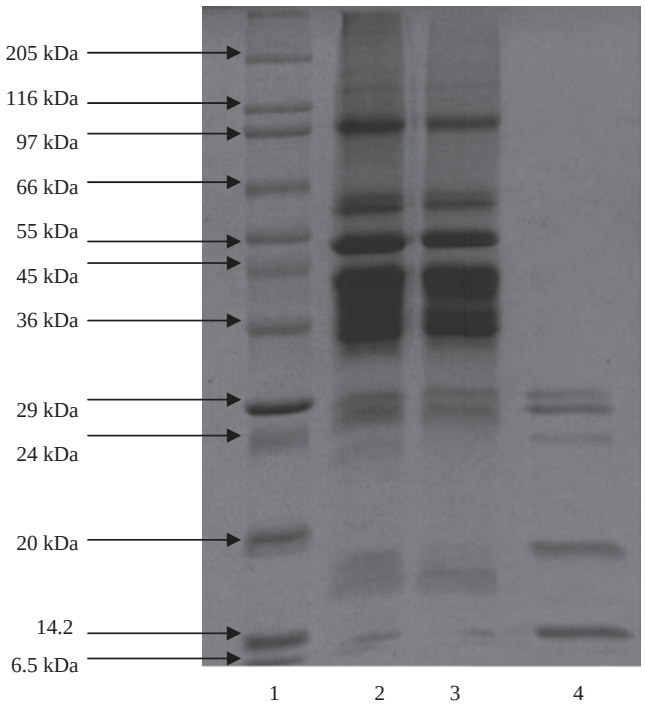

Fig. 1. SDS–PAGE pattern of fish mince wash water: (1) standard protein, (2) original, (3) concentrate (at VCF = 40) and (4) permeate.

Table 2
Average permeate flux and protein retention after ultrafiltration of fish mince wash water for 60 min (at constant crossflow rate 180 l/h, TMP 3 bar and temperature 15°C)

Membrane	Flux* at $t = 60$ min (l/m^2h)	Average protein retention* (%)
Regenerate cellulose membrane with MWCO 30 kDa	56.6 ± 0.5	98.4 ± 0.1
Regenerate cellulose membrane with MWCO 100 kDa	51.5 ± 0.5	96.3 ± 0.1

*Statistically significant difference: $P < 0.05$.

the solute back to the bulk solution. In addition, it was also possible that increasing in crossflow rate could also reduce the external fouling. Fig. 2 also shows that the retention of protein slightly increased as TMP increased. This could be due to formation fouling and the consolidation of a fouling layer on the top of membrane [6]. Increasing crossflow rates, however had no significant effect on protein retention ($P < 0.05$). According to these results, a TMP of 3.5 bar and a crossflow rate of 360 l/h were selected for operating conditions in batch concentration mode.

3.3. Concentration of protein with batch concentration mode

The permeate flux and protein retention versus VCF during ultrafiltration with 30 kDa membrane using the batch concentration mode is shown in Fig. 3. It was found that protein retention was in the range of 97–98% and was not affected by VCF. The initial permeate flux was 87.5 l/m^2h and decreased to about 2.1 l/m^2h at a final VCF of 40. The permeate flux profile could be divided into two periods. In the initial period, the permeate flux rapidly decreased from 87.5 to 4.3 l/m^2h at VCF of 6. After that the permeate flux slightly decreased and was about 2.1 at a VCF of 40. The viscosity of the concentrate also increased as VCF increased (Fig. 4). The permeate flux declined due to the concentration polarization and membrane fouling always observed during ultrafiltration of protein solution [6,10,11]. Fish mince wash water is a complex system. It contains suspended and soluble proteins. Thus severe fouling both in the pore and on the top of the membrane surface was expected. In addition, since the viscosity of the concentrate increased significantly during the concentration mode, this led to a decrease in mass transfer rate of solute back to bulk solution and therefore reduced the permeate flux. In addition, it was also observed that the average protein retention over the concentration operation mode was in the range of 97–99%. The protein retention was slightly decreased as VCF increased ($R_j = 99.1\%$ at VCF =1.1 and $R_j = 97.5\%$ at VCF = 40).

3.4. Shear controlled model

In the ultrafiltration with batch concentration mode, concentration of the solute increase as the VCF increase

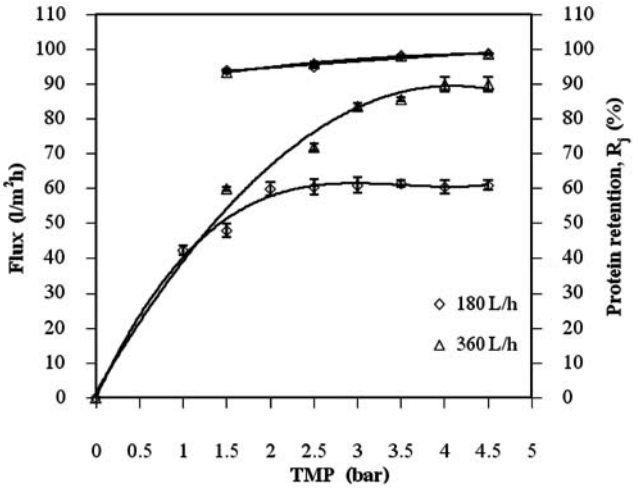

Fig. 2. Permeate flux and protein retention during ultrafiltration of fish mince wash water.

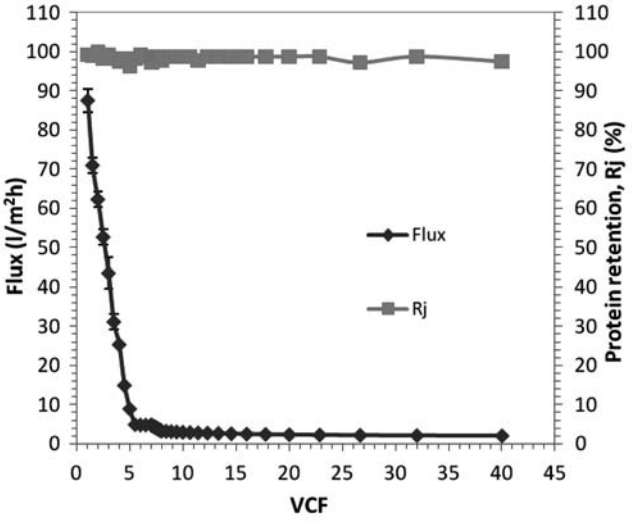

Fig. 3. Permeate flux and protein rejection versus VCF during ultrafiltration of fish mince wash water.

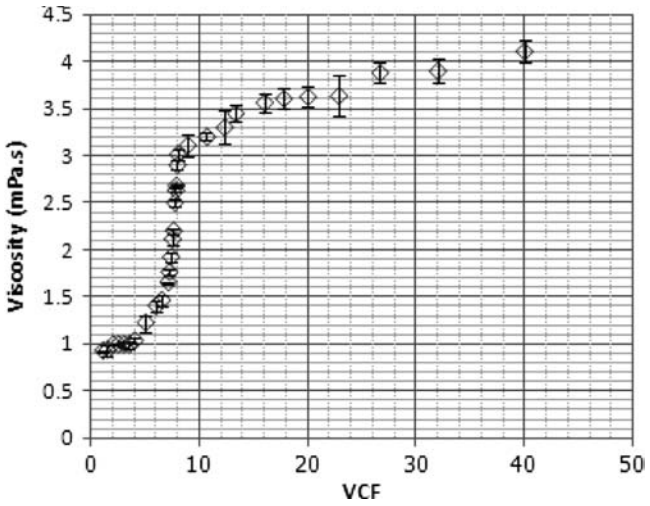

Fig. 4. Viscosity of retentate versus VCF during ultrafiltration of fish mince wash water.

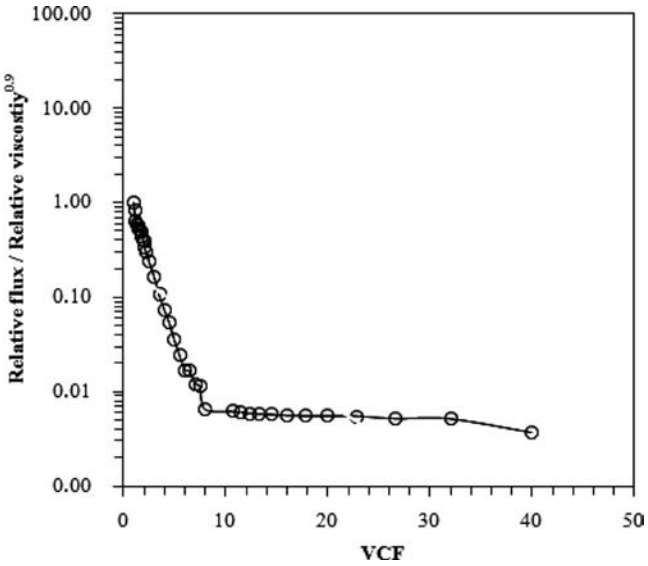

Fig. 5. Development of shear controlled model for ultrafiltration of fish mince wash water

led to an increase in viscosity of the feed (bulk) solution. Thus the reversible fouling, e.g. labile gel layer, play a major role in flux behavior. Wall shear stress (τ_w) at the membrane surface is a significant variable in minimizing the thickness of the gel layer and preventing the deposition of the solute onto the foulant layer [12]. For the system where the foulant layer is the major resistance, it was proposed that the relative flux is dependent on the relative shear stress (τ_r) at the membrane surface and the negative exponential of concentration. This relative flux (J_r), the ratio of the flux at a given concentration (J) to the flux at the initial feed concentration (J_i), can be expressed as a shear controlled model as follows:

$$J_r = \tau_r^n a e^{-bC}. \quad (2)$$

For the systems with a fixed cap between the plates and operated at a constant crossflow rate or crossflow velocity, the relative shear stress reduces to the relative bulk viscosity (μ_r), the ratio of bulk viscosity at given concentration (μ) to the bulk viscosity at the initial feed concentration (μ_i). In the concentration mode, solid concentration (C) directly links to VCF. Thus it can be replaced by VCF and the shear controlled model becomes:

$$J = J_i \left(\frac{\mu}{\mu_i}\right)^n a e^{-b\mathrm{VCF}}. \quad (3)$$

The viscosity of fish mince wash water during batch concentration versus VCF is shown in Fig. 4. It was observed that the viscosity of the feed increased as VCF increased and it was about 0.9 mPa s (at VCF =1) and about 4 mPa s (at VCF = 40). The ratio of relative flux and viscosity^n (J_r/μ_r^n) was plotted versus VCF as shown in Fig. 5. It was observed that the correlation developed was divided into two regions, the falling-flux region (VCF 1 to 8) and the constant-flux region (VCF 8 to 40). The correlation coefficients (R^2) were 0.99 and 0.89 for the falling-flux region and the constant-flux region respectively with an optimal value n of 0.9. For the falling-flux region, the correlation developed was:

$$J = 2.4654 J_i \left(\frac{\mu}{\mu_i}\right)^{0.9} e^{-0.6358(\mathrm{VCF})}. \quad (4)$$

For the constant-flux region the correlation was expressed as follows:

$$J = 0.0129 J_i \left(\frac{\mu}{\mu_i}\right)^{0.9} e^{-0.0202(\mathrm{VCF})}. \quad (5)$$

The effectiveness of these equations is also shown in Fig. 6. These results suggested that the shear controlled model was successfully employed to describe the flux behavior during concentration of fish mince wash water as evidence by the reasonable value of R^2. The value n of 0.9 suggested that the wall shear stress had more significant effect on permeate flux compared to those found for homogenized soy extract ($n = 0.7$) and unhomogenized soy extract ($n = 0.5$) [12]. This could be due to the difference in the properties of the external fouling layer.

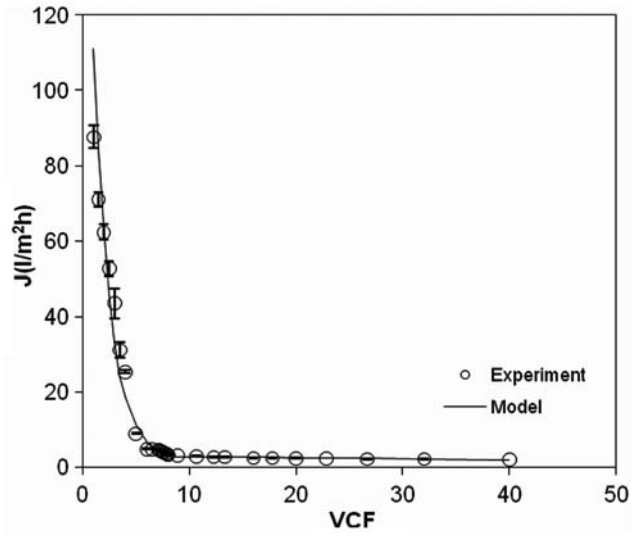

Fig. 6. Shear controlled model for fish mince wash water concentration by ultrafiltration.

3.5. Properties of permeate and concentrate

The major compositions of concentrated fish mince wash water including total solid and protein is shown in Table 1. It was found that protein concentration increased from 0.27% to 10.92% (w/v) and the total solid increased from 0.43% to 16.22% (w/v) at a VCF of 40. The COD of fish mince wash water was significantly reduced (about 82%) by ultrafiltration with 30 kDa membrane. This result indicated that ultrafiltration was successfully employed to concentrate protein and to reduce COD in fish mince wash water discharged from surimi processing plant. The molecular weight of protein obtained by ultrafiltration, analyzed by SDS–PAGE is shown in Fig. 1. It can be seen that the molecular weight of protein in fish mince wash water and concentrate protein were similar. The molecular weight of protein was in the range of 14–60 and 100–110 kDa and about 75% of concentrated protein had a molecular weight of 14–60 kDa. For the permeate, the molecular weight of protein was in the range of 14–30 kDa, indicating that most of the larger molecular weight protein was retained in the concentrate. The functional properties of protein concentrate should be studied for their possible application.

4. Conclusion

Ultrafiltration was successfully employed for the concentration of fish mince wash water. The permeate flux and protein retention of 30 kDa membrane was higher than those of 100 kDa membrane thus the membrane with MWCO 30 kDa was more suitable for the concentration of protein in fish mince wash water. In the batch concentration mode, the protein retention of 30 kDa membrane was in the range of 97–98% and protein could be concentrated from 0.27 up to 10.9% (w/v) at VCF of 40. The molecular weight of the concentrated protein was in the range of 14–110 kDa. About 82% COD of the fish mince wash water was reduced by ultrafiltration. A shear controlled model was successfully employed to describe the permeate flux during the batch concentration mode. It is very important to note that the permeate flux during ultrafiltration (VCF > 6) was relatively low therefore the membrane module and technique that improves permeate flux or reduces fouling must be considered and studied. For example, critical flux concept can be employed to reduce external fouling. In addition, the use of techniques those promote mass transfer of the solutes moving away from the membrane surface. These potential techniques include gas sparging and use of vibrated membrane module.

Acknowledgement

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List of symbols

a, b, n	parameter in shear controlled model
C	bulk concentration (wt %)
J	permeate flux (l/m^{2}h)
J_i	permeate flux at initial feed concentration (l/m^{2}h)
R_j	protein retention (%)
TMP	transmembrane pressure (bar)
V_f	feed volume (l)
V_p	permeate volume (l)
VCF	volume concentration factor
μ	bulk viscosity at given concentration or VCF (Pa.s)
μ_i	bulk viscosity at initial feed concentration (Pa.s)
μ_r	relative bulk viscosity
τ_w	wall shear stress at given concentration or VCF (Pa)
τ_{wi}	wall shear stress at given concentration or VCF (Pa)
τ_r	relative wall shear stress

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