Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Whey ultrafiltration in a tubular membrane: effect of selected operating parameters

D. Barba[a]; F. Beolchini[a]; D. Cifoni[b]; F. Veglio[c]
[a] Dipartimento di Chimica, Ingegneria Chimica e Materiali, Universita' degli Studi de L'Aquila, L'Aquila, Italy [b] Dipartimento di Ingegneria Chimica, Universita' degli Studi "La Sapienza" di Roma, Roma, Italy [c] Dipartimento di Ingegneria Chimica e di Processo "G.B. Bonino", Universita' degli Studi di Genova, Genova, Italy

Online publication date: 29 May 2002

To cite this Article Barba, D. , Beolchini, F. , Cifoni, D. and Veglio, F.(2002) 'Whey ultrafiltration in a tubular membrane: effect of selected operating parameters', Separation Science and Technology, 37: 8, 1771 — 1788
To link to this Article: DOI: 10.1081/SS-120003043
URL: http://dx.doi.org/10.1081/SS-120003043

SEPARATION SCIENCE AND TECHNOLOGY, 37(8), 1771–1788 (2002)

WHEY ULTRAFILTRATION IN A TUBULAR MEMBRANE: EFFECT OF SELECTED OPERATING PARAMETERS

D. Barba,[1] F. Beolchini,[1,*] D. Cifoni,[2] and F. Veglio'[3]

[1]Dipartimento di Chimica, Ingegneria Chimica e Materiali, Universita' degli Studi de L'Aquila, 67040 Monteluco di Roio, L'Aquila, Italy
[2]Dipartimento di Ingegneria Chimica, Universita' degli Studi "La Sapienza" di Roma, Roma, Italy
[3]Dipartimento di Ingegneria Chimica e di Processo "G.B. Bonino", Universita' degli Studi di Genova, via Opera Pia, 15, 16150 Genova, Italy

ABSTRACT

A study of whey ultrafiltration in a tubular membrane with a centrally inserted rod is reported in this work. Effects of the main operating conditions such as pH, temperature, and whey concentration on the ultrafiltration process have been investigated in a lab-scale tubular membrane. In particular, the mass-transfer resistance through the membrane (due to fouling and polarization), the flux decline vs. time, and the membrane-retention properties have been considered as representatives of the ultrafiltration process' performances. The study has been performed by using full factorial experiments, and results have been elaborated by the analysis of the variance (ANOVA). From

*Corresponding author. Fax: 39 862 434203; E-mail: beolfra@ing.univaq.it

permeability tests, the lowest value for the mass-transfer resistance (corresponding to the highest permeate flux) has been estimated at 5.8 ± 0.3 MPa hr m^{-1}, under the following operating conditions: pH 6, temperature 25°C, whey concentration factor (CF) 1. The ANOVA suggested that pH and whey concentration were significant factors, while temperature resulted not to influence the mass-transfer through the membrane in the investigated range (25–40°C). Flux declines have also been monitored during time and profiles have been fitted by an empirical model. In this case, the highest temperature (40°C) favored the decline kinetics and it determined the highest difference between initial and stationary fluxes. As concerns the membrane-retention properties, the highest proteins-rejection coefficient (which means the highest retention) was 0.90 (under pH 4, temperature 25°C, CF 5). Furthermore, pH was demonstrated to affect significantly the membrane-retention properties. In fact, the chromatogram of permeates showed that some native proteins pass through the membrane at pH 6, while just peptides pass at pH 4.

Key Words: Ultrafiltration; Whey; Inorganic membranes

INTRODUCTION

Ultrafiltration has become increasingly attractive to the processing of both food and biotechnological products (1). In particular, it has been applied extensively for cheese whey treatment, in order to recover valuable products such as whey protein concentrates (2–7). Considering the complexity of fluids to be treated, the study of ultrafiltration requires the investigation of a multiplicity of complex cases (8). In fact, factors involved in membrane fouling—such as gel, adsorption, and deposition of certain solutes—have been reported in the literature to be involved simultaneously, because of the complexity of the feed composition and the numerous interactions between the dietary components and the porous material of the membrane (9).

The aim of this work is to study the consequences of changes in the main operating conditions, such as pH, temperature, and whey concentration, on the ultrafiltration process in a lab-scale tubular membrane. In particular, the mass-transfer resistance through the membrane (due to fouling and polarization), the flux decline vs. time, and the membrane-retention properties have been considered as representatives of the ultrafiltration process' performances. The study has been performed by using full factorial experiments, and results have

been elaborated by the analysis of the variance (ANOVA). This approach that is relatively new in this field, should lead to a better evaluation of the main operating conditions influence on the ultrafiltration performances, in order to define the main parameters during the process design step.

MATERIALS AND METHODS

Solutions

Whey was provided by a dairy farm which produces *mozzarella* cheese near L'Aquila, Italy. After a pre-filtration for the removal of fines, it was lyophilized. In this way, the storage was easier and all tests were performed with a substance having the same physico-chemical characteristics. Before each trial, just the requested amount was dissolved in microfiltered (0.45 μm) deionized water and the pH was adjusted with H_2SO_4. Table 1 shows the whey composition before lyophilization.

Ultrafiltration Apparatus

The ultrafiltration tests were carried out in a laboratory experimental apparatus whose flowsheet is shown in Fig. 1. The membrane was a Carbosep type M5 (TECH-SEP, Miribel, France). It is made of ZrO_2 deposited inside a porous carbon tube (10,000 Da molecular weight cut off (MWCO); 6 mm in diameter; 60 cm in length). Before each trial, the membrane was cleaned according to a standard washing procedure reported in the literature (10). A stainless steel bar (4 mm in diameter) was introduced inside the tubular support in order to enhance the tangential velocity. In fact, permeate flux was very low without this modification (data not shown). The processed fluid was recirculated from an insulated tank using a peristaltic pump (Cellai s.r.l., Milan, Italy), with a maximum flowrate of 11 L min^{-1}. The tank temperature was kept constant by a jacket, connected to a Crioterm I.S.C.O. (Milan, Italy) (mod. 10-80) thermostat.

Table 1. Chemical Composition (g L^{-1}) of Whey

pH	6.3
Lactose	42.61
Proteins	7.69
Total dry matter	57.2
Ashes	5.4

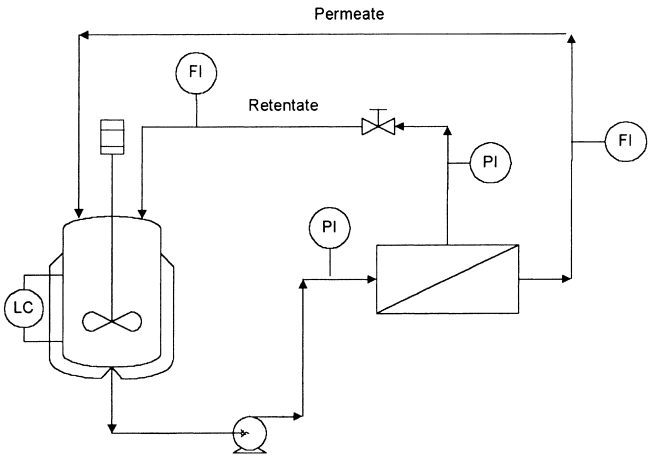

Figure 1. Flowsheet of the experimental apparatus for whey ultrafiltration.

Pressure gauges were used at the inlet and outlet of the membrane tube to measure pressures and pressure drop.

Ultrafiltration Tests

Two hundred milliliters of whey were put in the jacketed tank in batch conditions. After a period of recirculation in the experimental system, the permeate was collected for flux determination. This period was long enough to reach a stationary permeate flux. Then, the inlet pressure was increased and after a further period of time a subsequent permeate flux determination was performed. This procedure was applied until a transmembrane pressure (TMP) of 140 kPa was reached, the maximum value allowed for the apparatus (maximum inlet pressure of 180 kPa). Then the pressure was decreased, and further permeate fluxes were determined in order to verify the presence of hysteresis phenomena (11). For the flux-decline determination, just the retentate was recirculated during the ultrafiltration process, and the permeate was periodically collected for flux determination.

Periodically, aliquot amounts (1.5 mL) of permeate were sampled for lactose and proteins determination.

The factors and levels investigated in these tests are shown in Table 2: pH, whey concentration, and temperature. In particular, operating conditions of all the performed treatments are shown in Table 3.

Table 2. Factors and Levels Investigated in Whey Ultrafiltration (Full Factorial Design)

Code	Factor	Levels	
A	pH	4	6
B	Temperature (°C)	25	40
C	Whey concentration factor	1	2

Analytical Determinations

Lactose concentration was determined through lactose/galactose UV method, Boehringer Mannheim. Protein concentration was determined by the Kjeldahl's method for protein nitrogen (heating digester Velp Scientifica (Milan, Italy) mod. DK6; automatic steam distilling unit Velp Scientifica mod. UDK 130; automatic titrator Crison Maseli S.p.A. (Milan, Italy) mod. microTT 2050); the analyzed values of elemental N were multiplied by 6.38 in order to obtain protein concentration.

Single proteins in the collected samples have been determined by liquid chromatography [Waters S.p.A., Milan, Italy pump, model 510; Waters universal liquid chromatograph injector, model U6K; LC Spectrophotometer, Waters Lambda Max model 481, set at 280 nm; Biorad (Milan, Italy) Chromatographic Column, model Biosil Sec-250 (300 × 7.8 mm) and Biorad Biosil 250 Guard Column (80 × 7.8 mm)]. The mobile phase was a phosphate buffer, pH = 6.7,

Table 3. Operating Conditions Investigated in Whey Ultrafiltration

Treatment	pH	Temperature (°C)	Whey Concentration Factor	Estimated R'_F[a] (kPa hr m^2 L^{-1})
1	4	25	1	14.0
2	6	25	1	5.8
3	4	40	1	15.4
4	6	40	1	7.8
5	4	25	2	18.3
6	6	25	2	7.4
7	4	40	2	18.4
8	6	40	2	7.2
9	4	25	5	19.0
10	6	25	5	13.7

[a] Experimental error variance: 0.129 with 4 d.f.

containing urea 6 M (12). The eluent was kept at 50°C. All buffers were filtered and degassed prior to use. The system was run isocratically; injection volume was always 25 μL.

Data Analysis

(a) The resistance model (11) was applied for the fitting of permeability data:

$$J_p = \frac{\text{TMP}}{R_M + R_F + R_G} \tag{1}$$

Equation (1) has been fitted through linear regression to the experimental data of J_p vs. TMP, obtained during permeability tests. From the slope of the regression line, the total mass-transfer resistance can be estimated:

$$R_{TOT} = R_M + R_F + R_G \tag{2}$$

The mass-transfer resistance due to fouling and polarization, R'_F, has been estimated from Eq. (2), after the estimation of the membrane resistance through permeability tests with pure water, as follows:

$$R'_F = R_F + R_G = R_{TOT} - R_M \tag{3}$$

(b) The following empirical equation has been fitted to permeate flux vs. time declines (11):

$$J_p = J_\infty + De^{-t/\tau} \tag{4}$$

(c) The membrane-retention coefficient was calculated according to the following relation:

$$\sigma = 1 - \frac{C_P}{C_R} \tag{5}$$

The planning of some experimental runs was carried out using full factorial design. This methodology is very helpful, both in the experimental planning and in the statistical interpretation of the experimental results (by ANOVA analysis) (13,14). An orthogonal experimental plan is realized in which it is possible to evaluate independently both the main effect and the interaction, among the factors investigated for a given response. The response of the process under investigation was either the mass-transfer resistance, R'_F, estimated from permeability tests (Eq. (3)), or the Eq. (4) parameters, estimated during flux-decline determinations. The effect of a factor is the change in response produced

by a change in the level of the factor. When the effect of a factor depends on the level of another factor, the two factors are said to interact.

The experimental results have been elaborated using ANOVA, in which it is possible to evaluate whether the effect and the interaction among the investigated factors are significant with respect to the experimental error, estimated by replicated tests.

RESULTS

Flux Tests

The factors considered in these tests are (Table 2): pH, whey concentration, and temperature. These parameters have been found to be important by many researchers. In particular, the pH acts on the protein conformation and charge (15,16), according to the distance from the isoelectric point. As concerns temperature, there is not a unanimous theory in the literature (17). Considerations of the physico chemistry of the system indicate that it must be operated at as high a temperature as possible, since diffusivity increases (hence concentration polarization is reduced) and viscosity decreases (hence flux will increase). On the other hand, as the temperature increases, the stability of protein conformation decreases; denaturated proteins may have a tendency to either aggregate or adsorb to the membrane surface, increasing membrane fouling. The whey concentration factor (CF) was considered in this investigation, as a representative of whey components concentration. All treatments are shown in detail in Table 3. A full factorial plan (13) was implemented with factors and levels as in Table 2; this is composed of 8 treatments (2^3) that are treatments from 1 to 8 in Table 3. Further, two treatments have been performed with a concentration factor of 5 (treatments 9 and 10), in order to evidence the effect of whey concentration on the mass-transfer resistance through the membrane, R'_F.

The permeate flux vs. TMP [obtained in permeability tests, (11)] determined under pH 4, 25°C, and CF equal to 1 (treatment No. 1 of Table 3) is reported in Fig. 2, as an example. Other curves were similar, and they are not shown here. The permeability line obtained, processing water on the clean membrane (i.e., before the trial) is also shown in Fig. 2. The relation between the permeate flux, J_p, and the TMP, is linear in all cases, at any concentration factor in the investigated range. This is probably due to the relatively low pressure that is allowable for the experimental apparatus, which did not let the investigation of the process in the mass-transfer control region (11). The results obtained by increasing and decreasing the TMP, respectively, suggest that no hysteresis takes place with whey, in the investigated range of experimental conditions.

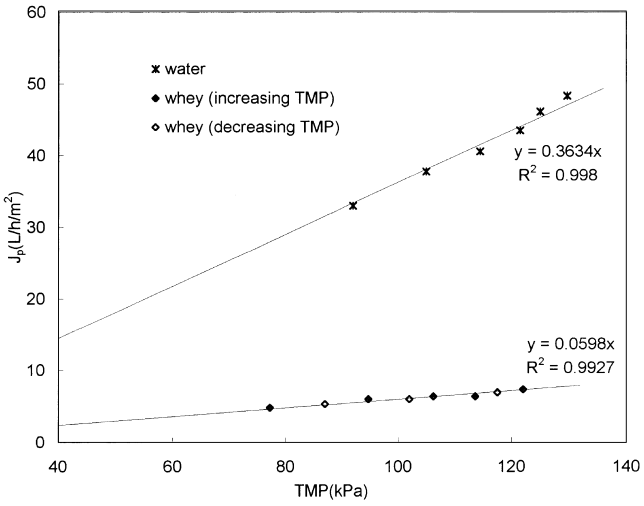

Figure 2. Permeability curve obtained in trial no. 1 of Table 3 (pH 4; temperature 25°C; CF 1). Stars represent permeability data obtained during processing of water with a clear membrane (i.e., before the trial into consideration).

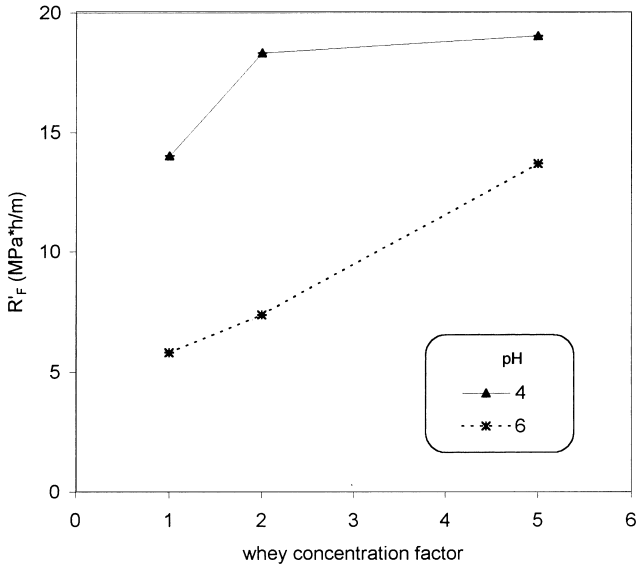

Figure 3. Effects pH and whey concentration on the mass-transfer resistance due to fouling and polarization.

The mass-transfer resistance through the membrane, R'_F, was calculated after linear regression, according to Eq. (3) for each treatment (Table 3). Figure 3 reports the estimated value for R'_F as a function of whey concentration, at two levels of pH. It is seen that the mass-transfer resistance at pH 4 is significantly higher than the one at pH 6, for any level of whey concentration. Furthermore, the positive effect on R'_F (and the consequent negative effect on permeate fluxes) of whey concentration is also remarkable, especially at pH 6, where mass-transfer resistances are lower.

The estimated values for R'_F obtained in the full factorial plan (treatments 1–8 of Table 3) were elaborated by an ANOVA, considering an experimental error variance equal to 0.129 $(\text{kPa hr m}^2\text{L}^{-1})^2$ with 4 d.f., as estimated from replicated trials, here not reported. The ANOVA results are shown in detail in Fig. 4. It is seen that the most significant factor is the solution pH (factor A, negative effect with 100% significance). A further positive effect (99% significance) has been found for the whey concentration (factor C); as the CF increases from 1 to 2, the mass-transfer resistance increases significantly (and permeate flux decreases). Last but not least, the double interaction AC (pH–whey concentration) has a 98% significant effect; this means that as the pH increases from 4 to 6, the effect of whey concentration on the mass-transfer resistance changes. All these results give a quantified confirmation of what has been previously qualitatively observed in Fig. 3. In that case, a further CF (equal to 5) has been considered in addition

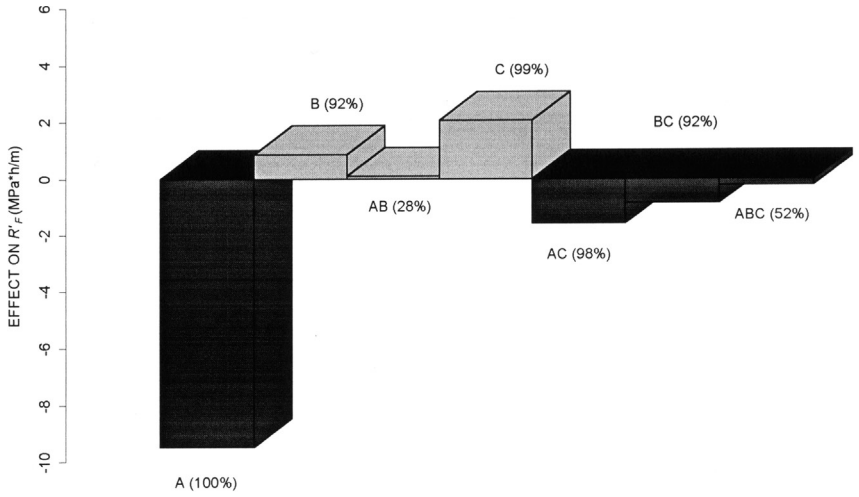

Figure 4. Principal effects' and interactions' significance on the mass-transfer resistance as resulted by the ANOVA (A: pH; B: temperature; C: CF).

to 1 and 2, as in the ANOVA analysis. Temperature (factor B) results not to be significant for the mass-transfer resistance through the membrane, in the investigated range (significance 92%). Figure 5 reports R'_F calculated values by the empirical mathematical model of the factorial experiments [Eq. 6 (14)] as a function of the experimental values:

$$R'_F = R'_{Faverage} + \frac{1}{2}\left[(X_1 - 5)A + \left(\frac{X_3 - 1.5}{0.5}\right)C + (X_1 - 5)\left(\frac{X_3 - 1.5}{0.5}\right)AC\right] \quad (6)$$

where $R'_{F\ average}$, is the average value obtained in all tests; X_1 is the pH value, and X_3 is the CF.

No patterns are evident in points distribution, as a confirmation of the ANOVA adequacy (14).

Flux Declines

The permeate flux vs. time profiles also have been monitored during whey ultrafiltration (treatments in Table 3), in order to evidence the main operating conditions' effects on flux declines. Figure 6 shows the flux vs. time profiles obtained in all tests reported in Table 3. Experimental data have been

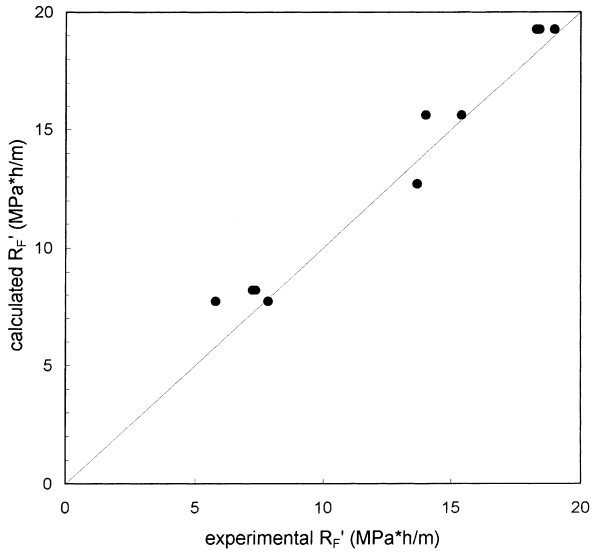

Figure 5. Calculated vs. experimental mass-transfer resistance R'_F (see text for details).

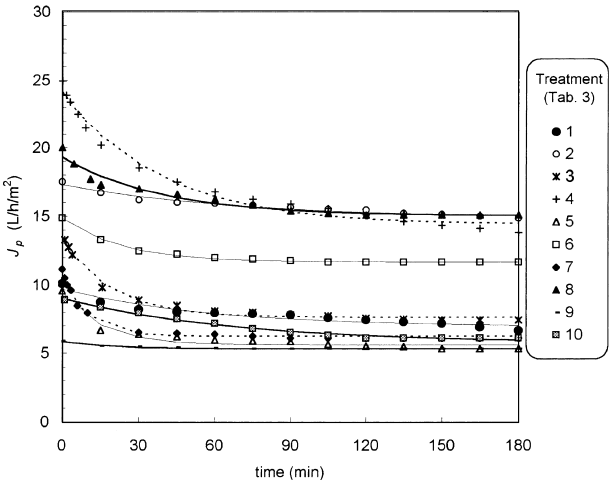

Figure 6. Flux declines during whey ultrafiltration (see Table 3 for tests' details; TMP 140 kPa). Lines have been calculated by Eq. (4), where parameters have been fixed according to Table 4.

represented by Eq. (4), where parameters J_∞, D, and τ have been estimated through a least square nonlinear regression technique (18). Table 4 shows the estimated values and 95% confidence limits of each parameter. A first analysis of data reported in Fig. 6 and in Table 4 suggest that higher fluxes are achieved in general at the highest pH, as expected considering the

Table 4. Estimated Values (and Confidences Limits) for Parameters J_∞, D, and τ (Eq. 4)

Treatment (Table 3)	Stationary Flux, J_∞ ($L\,hr^{-1}\,m^{-2}$)	Stationary Decline, D ($L\,hr^{-1}\,m^{-2}$)	Time Constant, τ (min)
1	6.9 ± 0.6	2.8 ± 0.6	59 ± 39
2	14.9 ± 0.4	2.4 ± 0.4	69 ± 31
3	7.6 ± 0.2	5.8 ± 0.4	19 ± 4
4	14.4 ± 0.6	9.7 ± 0.7	39 ± 9
5	5.6 ± 0.2	3.9 ± 0.7	16 ± 6
6	11.7 ± 0.1	3.1 ± 0.1	23 ± 14
7	6.2 ± 0.1	4.8 ± 0.2	9.0 ± 0.4
8	15.0 ± 0.4	4.3 ± 0.6	34 ± 15
9	5.31 ± 0.02	0.51 ± 0.05	19 ± 4
10	5.7 ± 0.3	3.3 ± 0.3	67 ± 17

previous results on the mass-transfer resistances obtained in the stationary phase flux. An ANOVA analysis also has been performed in order to quantify the effect of pH, temperature, and whey concentration on the three parameters J_∞, D/J_∞, and τ that are the steady-state flux, the dimensionless stationary flux decline (referred to the stationary flux), and the decline time constant, respectively (ANOVA here not reported). As concerns the first parameter—that is the stationary permeate flux, no new information has been achieved with respect to the one obtained from the mass-transfer resistance analysis (Fig. 4). On the other hand, the effects on the stationary flux decline and on the time constant, result to be interesting. In fact, not only the pH (factor A) results to have a significant effect on both parameters, as in the case of mass-transfer resistances, but also temperature (factor B), which previously have been shown not to influence mass-transfer resistances significantly. In particular, the flux decline increases (positive effect, 100% significance) and the time constant decreases (negative effect, 99% significance) with temperature. Probably a partial unfolding of proteins takes place during time, and such denaturated proteins may have a tendency to adsorb on the membrane surface (17). As a consequence of this, a significant flux decline is observed during time. As concerns the effect of temperature on the decline time constant, it could have been expected; in fact, an increase in temperature is supposed to be associated to an increase of the process kinetics.

Membrane-Retention Properties

A further investigation has been performed on the membrane-retention properties during whey ultrafiltration. In particular, the proteins-rejection coefficient has been determined according to Eq. (5) for each treatment in Table 3, after two different times of processing: 30 and 90 min, respectively. Table 5 reports the calculated data after 30 min, while data obtained after 90 min are not reported here since no significant difference has been observed with respect to values at 30 min. Results in Table 5 show that the operating pH is important even for the membrane-retention properties. This was also evidenced by an ANOVA analysis, not reported here. In particular, at pH 6, a lower rejection coefficient has been observed; this means that proteins pass through the membrane more easily at pH 6 than at pH 4. Figures 7 and 8 show the chromatogram of permeates obtained during two tests at different levels of pH (tests 5 and 6 of Table 3, respectively). These figures confirm that two native proteins (β-lactoglobuline and α-lactoalbumine) pass through the membrane at pH 6 (Fig. 8), while just peptides pass in the permeate at pH 4 (Fig. 7). This aspect has to be taken into account when the operating pH has to be set in the process design step. In fact, an optimization study should be

Table 5. Experimental Values (Calculated by Eq. (5)) for Proteins-Retention Coefficient, After 30 min of Permeation

Treatments (Table 3)	σ^a
1	0.80
2	0.74
3	0.74
4	0.73
5	0.79
6	0.72
7	0.78
8	0.78
9	0.90
10	0.66

[a] Experimental error variance 0.0017 with 13 d.f.

performed considering that a value of 4 is preferable taking into account retention properties and whey conservation, while a value of 6 might be preferred for the relatively low mass-transfer resistance (and the consequent high permeate flux).

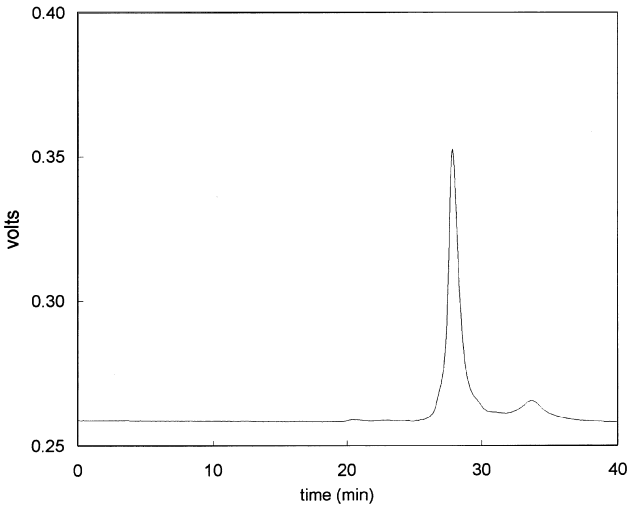

Figure 7. Chromatogram of permeate obtained in trial no. 5 of Table 3 (pH 4, temperature 25°C, CF 2, TMP 140 kPa), determined spectrophotometrically at 280 nm.

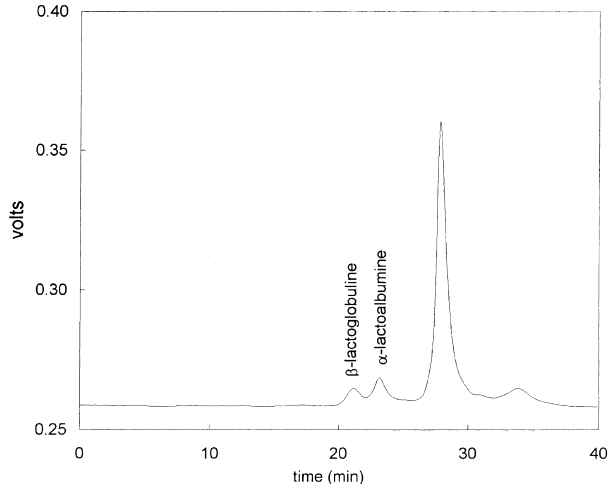

Figure 8. Chromatogram of permeate obtained in trial no. 6 of Table 3 (pH 4, temperature 25°C, CF 2, TMP 140 kPa), determined spectrophotometrically at 280 nm.

DISCUSSION

The pH and whey concentration have been demonstrated to be the most important factors for the process. This is probably due to different interactions between active groups of proteins, H^+ ions, salts, and other molecules in solution, which are responsible for membrane fouling. Mass-transfer resistance due to fouling and polarization at pH 4 was found to be significantly higher than the one at pH 6, for any level of whey concentration. Furthermore, the positive effect on this resistance (and the consequent negative effect on permeate fluxes) of whey concentration was particularly remarkable at pH 6, where mass-transfer resistances were lower. Probably the interactions between proteins (which are positively charged (18)) and ionic species in solution—which lead to precipitation on the membrane surface—are so high at pH 4 that they do not depend on whey concentration. On the other hand, these interactions are less significant at pH 6 (where proteins are negatively charged, considering that the whey proteins' isoelectric point ranges from 4.6 to 5.3 (18)), so that they depend on the whey components' concentration. Table 6 shows a comparison of the lowest estimated value for the mass-transfer resistance due to fouling and polarization with published data. A true comparison cannot be made, considering that operating conditions were different, but it appears that the employed system (with a centrally inserted rod) succeeded in producing relatively low mass-transfer resistance.

Table 6. Comparison Between the Mass-Transfer Resistance Due to Fouling and Polarization Estimated in This Work and Published Data

Membrane					
Material	MWCO (Da)	Configuration	pH	R'_F (10^{-9} Pa s m^{-1})	References
ZrO_2	10,000	Modified tabular	6	5.8	This work
Cellulose acetate	5,000	Flat channel	5	10.3	Pouliot et al. (1999) (19)
Polysulfone	5,000	Spacer filled flat channel	2.5–12	10–20	Da Costa et al. (1993) (20)
Polyethersulfone	10,000	Hollow fibre	Not available	20.5	Cheryan (1998) (11)
ZrO_2	20,000	Tubular	5.9	21.1	Taddei et al. (1989) (9)
ZrO_2	10,000	Tubular	6.5	10.1	Daufin et al. (1991) (10)

As concerns proteins retention, a bad protein retention was observed under pH 6; in fact some native proteins were found in the permeate, even if the molecular weights of these proteins are higher than the nominal membrane cut-off. This aspect is a little disconcerting in view of the fact that most whey is processed close to pH 6 rather than pH 4. A further investigation would be necessary in order to have a better understanding of membrane-retention properties' change with pH. As concerns temperature, it did influence neither the mass-transfer resistance through the membrane nor the membrane-retention properties, in the investigated range (25–40°C). On the other hand, it was shown to be effective on the flux decline, which was found to increase with temperature. The influence of temperature can be attributed to a partial unfolding of proteins that might take place during time; such denatured proteins may have a tendency to adsorb on the membrane surface and a significant flux decline is observed during time as a consequence.

CONCLUSIONS

A study on whey ultrafiltration has been performed in a lab-scale tubular membrane and the effect of operating conditions such as pH, whey concentration, and temperature have been investigated. Considering that dairy manufacturers are always interested in the process optimization, the performed work might be very useful for the application of the described membrane technology in a larger scale. Further work is still in progress, aimed principally at a better understanding of the change of membrane-retention properties with pH.

NOTATIONS

ANOVA	analysis of the variance
CF	whey concentration factor
C_P [g L^{-1}]	concentration measured in the permeate
C_R [g L^{-1}]	concentration measured in the retentate
D [L hr^{-1} m^{-2}]	drop in flux from the start of the experiment to the development of steady state and it is indicated in the following as *stationary flux decline* (flux decline tests)
J_∞ [L hr^{-1} m^{-2}]	steady-state flux (flux decline tests)
J_p [L hr^{-1} m^{-2}]	permeate flux
R'_F [kPa hr m^2 L^{-1}]	mass-transfer resistance due to fouling and polarization
R_F [kPa hr m^2 L^{-1}]	resistance due to membrane fouling
R_G [kPa hr m^2 L^{-1}]	resistance due to concentration polarization and boundary layer

R_M [kPa hr m^2 L^{-1}]	membrane intrinsic resistance, determined using pure water as the feed
TMP [kPa]	transmembrane pressure
σ	membrane-retention coefficient
τ [min]	flux decline time constant, that is the time where the 63% of the stationary flux decline is achieved (flux decline tests)

ACKNOWLEDGMENTS

The authors are grateful to Mrs. Lia Mosca and to Dr. Simona Giuliano for their helpful collaboration in the experimental work. Furthermore they wish to thank Prof. Luigi Marrelli for his precious suggestions.

REFERENCES

1. Palecek, S.P.; Mochizuki, S.; Zydney, A.L. Effect of Ionic Environment on BSA Filtration and the Properties of BSA Deposits. Desalination **1993**, *90*, 147–159.
2. Tratnik, L.; Krsev, L. Production of Whey Protein Concentrates. Milchwissenschaft **1991**, *46* (2), 91–94.
3. Di Giacomo, G.; Del Re, G.; Spera, D. Milk Whey Treatment with Recovery of Valuable Products. Desalination **1996**, *108*, 273–276.
4. Morr, C.V. Composition Physicochemical and Functional Properties of Reference Whey Protein Concentrates. J. Food Sci. **1985**, *50* (5), 1406–1411.
5. Pompei, C.; Peri, C.; Ariatta Olivani, M. Whey Proteins Purification by Ultrafiltration and Diafiltration. Scienza e tecnologia degli alimenti **1973**, 209–215.
6. Barba, D.; Beolchini, F.; Veglio', F. Minimising Water Use in Diafiltration of Whey Protein Concentrates. Sep. Sci. Technol. **2000**, *35* (7), 951–966.
7. Barba, D.; Beolchini, F.; Veglio', F. Water Saving in a Two Stage Diafiltration for the Production of Whey Protein Concentrates. Desalination **1998**, *119*, 187–188.
8. Aimar, P.; Taddei, C.; Lafaille, J.P.; Sanchez, V. Mass Transfer Limitations During Ultrafiltration of Cheese Whey with Inorganic Membranes. J. Membr. Sci. **1988**, *16*, 203–221.
9. Taddei, C.; Daufin, G.; Aimar, P.; Sanchez, V. Role of Some Whey Components on Mass Transfer in Ultrafiltration. Biotechnol. Bioeng. **1989**, *34*, 171–179.

10. Daufin, G.; Merin, U.; Labbé, J.P.; Quémerais, A.; Kerhervé, F.L. Cleaning of Inorganic Membranes After Whey and Milk Ultrafiltration. Biotechnol. Bioeng. **1991**, *38*, 82–89.
11. Cheryan, M. *Ultrafiltration and Microfiltration Handbook*; Technomic Publishing Company: Lancaster, PA, 1998.
12. Zin El-Din, M.; Aoki, T. High Performance Gel and Ion-Exchange Chromatography of Buffalo Casein. Int. Dairy J. **1993**, *3*, 141–147.
13. Box, G.E.P.; Connor, L.R.; Cousins, W.R.; Davies, O.L.; Himsworth, F.R.; Sillitto, G.P. *The Design and Analysis of Industrial Experiments*; Longman, Davies, Eds.; 1979.
14. Montgomery, D.C. *Design and Analysis of Experiments*; John Wiley and Sons: New York, 1991.
15. Fane, A.G.; Fell, C.J.D.; Waters, A.G. Ultrafiltration of Protein Solutions Through Partially Permeable Membranes—the Effect of Adsorption and Solution Environment. J. Membr. Sci. **1983**, *16*, 195–210.
16. Kim, K.J.; Chen, V.; Fane, A.G. Some Factors Determining Protein Aggregation During Ultrafiltration. Biotechnol. Bioeng. **1993**, *42*, 260–265.
17. Campbell, M.B.; Walter, R.P.; McLoughlin, R.; Knowles, C.J. Effect of Temperature on Protein Conformation and Activity During Ultrafiltration. J. Membr. Sci. **1993**, *78*, 35–43.
18. Xiong, Y.L. Influence of pH and Ionic Environment on Thermal Aggregation of Whey Proteins. J. Agric. Food Chem. **1992**, *40*, 380–384.
19. Pouliot, Y.; Wijers, M.C.; Gauthier, S.F.; Nadeau, L. Fractionation of whey protein hydrolysates using charged UF/NF membranes. J. Membr. Sci. **1999**, *158*, 105–114.
20. Da Costa, A.R.; Fane, A.G.; Wiley, D.E. Ultrafiltration of whey protein solutions in spacer-filled flat channels. J. Membr. Sci. **1993**, *76*, 245–254.

Received November 2000
Revised June 2001