

Original article

Whey crossflow microfiltration using an M14 Carbosep membrane: influence of initial hydraulic resistance

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Summary — Membrane hydraulic resistance (R_m) for the same nominal M14 Carbosep membrane (pore diameter $0.14 \mu\text{m}$) was found to vary significantly from 0.85 ± 0.05 to $1.22 \pm 0.09 \text{ } 10^{12} \text{ m}^{-1}$. Pre-treated whey microfiltration experiments carried out using these new membranes resulted in shorter operating time and lower protein transmission for the low R_m membranes. When the same membrane was used new, irreversibly fouled or cleaned ($R_m = 1.14, 2.48$ and $1.26 \text{ } 10^{12} \text{ m}^{-1}$ respectively) fouling evolution was positively correlated with R_m increase. It was assumed that a low R_m of a new membrane indicated a larger population of large pores which under constant permeation flux experiments filtered larger volumes and thus fouled faster. Residual fouling after cleaning was found to have a negative effect on performance presumably due to alteration of the membrane's morphological characteristics and to electrostatic and hydrophobic interactions of the feed stream with the residual fouling layer.

crossflow microfiltration / whey / hydraulic resistance / membrane fouling

Résumé — Microfiltration tangentielle de lactosérum avec une membrane M14 Carbosep : influence de la résistance hydraulique initiale. L'objectif de ce travail est de montrer les conséquences de la variation de la résistance hydraulique (R_m) de la membrane M14 Carbosep (diamètre de pores $0,14 \mu\text{m}$) à l'état neuf et nettoyé (avec colmatage résiduel) sur les performances de la microfiltration tangentielle de lactosérum doux prétraité. Deux lots de membranes (30 au total) montrent que la résistance R_m de cette membrane varie de $0,85 \pm 0,05$ à $1,22 \pm 0,09 \text{ } 10^{12} \text{ m}^{-1}$. En répétant une même

Abbreviations. A, membrane area (m^2); Cp, concentration of a component in the permeate ($\text{g} \cdot \text{l}^{-1}$); Cr, concentration of a component in the retentate ($\text{g} \cdot \text{l}^{-1}$); J, permeation flux ($\text{l} \cdot \text{h}^{-1} \cdot \text{m}^{-2}$); OD, optical density; Pr, mean pressure of the retentate compartment (10^5 Pa); Qr, retentate extraction flow rate ($\text{m}^3 \cdot \text{s}^{-1}$); T, temperature ($^\circ\text{C}$); TP, transmembrane pressure (10^5 Pa); Tr, transmission (%); v, flow velocity ($\text{m} \cdot \text{s}^{-1}$); VCR, volume concentration ratio; Rf, overall fouling hydraulic resistance (m^{-1}); Rif, irreversible fouling hydraulic resistance (m^{-1}); Rm, initial membrane hydraulic resistance (m^{-1}); RR, retention (%).

microfiltration avec différentes membranes M14, il s'avère qu'une membrane neuve de forte perméabilité initiale (Rm petit) réduit le colmatage aux temps courts, mais diminue la durée opératoire de la microfiltration. Quand une même membrane est utilisée neuve ou irréversiblement colmatée ou nettoyée ($Rm = 1,14; 2,48; 1,26 \text{ } 10^{12} \text{ m}^{-1}$ respectivement), un grand Rm réduit les performances de la microfiltration (durée opératoire plus faible, moins bonne récupération des protéines). De tels résultats peuvent être expliqués par l'existence d'une plus grande population de grands pores dans les membranes neuves de petit Rm : lors de microfiltrations menées à flux de perméation constant, un écoulement préférentiel se crée dans les zones de faible résistance, c'est-à-dire dans les grands pores, qui filtrent plus et se colmatent plus vite. Le colmatage résiduel après nettoyage affecte les performances de l'opération, ce qui peut être la conséquence d'une réduction de l'aire filtrante efficace et d'interactions électrostatiques et hydrophobes entre le produit à filtrer et le colmatage résiduel. Ces résultats mettent en évidence la nécessité de rechercher des procédures adéquates de nettoyage de membranes de microfiltration.

microfiltration tangentielle / lactosérum / résistance hydraulique / membrane / colmatage

INTRODUCTION

Characteristics of membranes are used as guidelines for research, to acquire better knowledge concerning the fouling and transmission properties of membranes, and for the use of membranes in filtration processes. Several techniques can be used to assess membrane pore size and distribution: scanning electron microscopy (Strathmann *et al*, 1975; Kim *et al*, 1990, 1991); transmission electron microscopy (Merin and Cheryan, 1981; Kim *et al*, 1991); tunnel and atomic force microscopy (Chahboun *et al*, 1992; Dietz *et al*, 1992); liquid displacement methods (Capannelli *et al*, 1983; McDonogh *et al*, 1992); and size exclusion techniques (De Balmann and Nobrega, 1989). However, those methods are almost impossible to be implemented by the industrial user. A disadvantage is the need to measure concentrations of transmitted and/or rejected solutes using analytical instruments or to break or cut the membrane for direct observation. Moreover, they are often irrelevant with respect to the membrane's actual permeability. In this regard, a preferable method is one which does not involve special instrumentation and can rely on hydraulic measurements which are always performed by the user.

Initial membrane hydraulic resistance (Rm) according to water flux is an easy way to characterize water permeability of the membrane and consequently to roughly describe membrane cleanliness on-line. It is shown by Taddéi *et al* (1989) that the irreversible fouling hydraulic resistance can be calculated using the method of measuring water flux of the fouled membrane. The same technique is used for studying the cleaning efficiency of milk and whey ultrafiltration (UF) membranes (Daufin *et al*, 1991b, 1992).

In the analysis of the performance of an industrial microfiltration (MF) plant Rm is found to have a significant influence on operating time and thus on the overall MF operation (Gésan *et al*, 1993b). The role of Rm on membrane operating performance received some attention (Davis and Birdsell, 1987; Nilsson, 1988; Persson and Nilsson, 1991), but still many researchers neglect its effect on filtration modelling and schematic presentation of fouling which is used for comparison of filtration experiments.

The aim of this work was to study the influence of initial membrane hydraulic resistance on whey MF performance, which has emerged as a necessary step in producing high protein concentrates. It consists of

showing the consequences of variation in R_m values on fouling evolution in the course of time and on the schematic presentation of fouling. The work was performed by using membranes of the same nominal pore size in three different conditions (new clean; irreversibly fouled; fouled and cleaned) which gave different R_m values for testing. In addition, evaluation of the procedure of R_m measurement for MF membranes is also presented.

MATERIALS AND METHODS

Membranes

The membranes used were M14 Carbosep membranes (Tech-Sep, Miribel, France). The M14 membrane is a composite membrane with a 0.14 μm mean pore diameter and ZrO_2 and TiO_2 filtering layer on a carbon support (6 mm inner diameter, 1.2 m long; $2.26 \cdot 10^{-2} \text{ m}^2$). The membranes used were from two production batches. One membrane was used in three consecutive experiments: first as a clean membrane for an MF test, secondly after rinsing of the reversible fouling layer and finally after cleaning at the end of an MF run.

Feed

Whey was obtained at a local dairy plant (Préval, Montauban de Bretagne, France) from Emmental cheese production. The whey was prefiltered on a 20 μm industrial filter, defatted in the plant by centrifugation (9 000 g at 50°C) and cooled down at the laboratory (2–4°C in 5 min). MF was carried out with the pretreated whey: this operation results in a retentate composed of aggregates of lipids and calcium phosphates and a microfiltrate that contains proteins suitable for producing high purity whey protein concentrates. Aggregation of residual phospholipids was performed by a procedure adapted from Fauquant *et al.* (1985): whey at 2–4°C, plus CaCl_2 up to a calcium concentration of 1.2 $\text{g} \cdot \text{kg}^{-1}$ and 10 N NaOH, pH adjusted to 7.2, was heated to 50°C in 30 min with a holding time of 15 min. During the pretreatment, whey

pH decreased down to 6.4. NaN_3 at 0.2 $\text{g} \cdot \text{l}^{-1}$ was added to the whey to prevent bacterial growth. The chemical composition of the pretreated whey is presented in table I.

Chemical analyses

The whey and permeate and retentate samples withdrawn during MF were analysed for α -lactalbumin and β -lactoglobulin by reverse phase high performance liquid chromatography according to Jaubert and Martin (1992). Calcium was determined by atomic absorption (Varian AA 300, Les Ulis, France) as described by Brûlé *et al.* (1974), phosphorus by mineralization and colorimetric determination following the AFNOR standard NF V 04-284 (AFNOR-ITSV, 1986) turbidity by optical density (OD) at 600 nm (Beckman DU 62, Gagny, France). Density was determined using a densimeter (Haake DM 48, Karlsruhe, Germany), and the dynamic viscosity of fluids using a microdensimeter (Haake D8, Karlsruhe, Germany).

Microfiltration experiments

The MF rig, described in detail by Daufin *et al.* (1993), was equipped with a single membrane tube. MF, cleaning and water flux measurements were performed with permeate circulating co-current to the retentate in order to create a permeate pressure drop equal to the retentate pressure

Table I. Average composition of pretreated whey.
Composition moyenne du lactosérum prétraité.

	Mean value	Standard deviation
T of pretreatment (°C)	50.3	± 0.5
Final pH of pretreatment (at 50°C)	6.40	± 0.05
α -lactalbumin ($\text{g} \cdot \text{kg}^{-1}$)	0.73	± 0.04
β -lactoglobulin ($\text{g} \cdot \text{kg}^{-1}$)	3.65	± 0.24
Optical density (600 nm)	1.7	± 0.4
Calcium ($\text{g} \cdot \text{kg}^{-1}$)	1.16	± 0.04
Phosphorus ($\text{g} \cdot \text{kg}^{-1}$)	0.38	± 0.02

drop, so as to get no transmembrane pressure (TP) difference along the membrane's hydraulic path (Sandblom, 1974; Plett, 1989).

Experimental procedure for conditioning and cleaning

The membrane was conditioned or cleaned before each MF experiment following the sequence: 1) acid wash: 55% technical HNO_3 at $3 \text{ ml}\cdot\text{l}^{-1}$ ($0.03 \text{ mol}\cdot\text{l}^{-1}$), $\text{pH} = 1.2$ at 50°C (45 min); 2) water rinse using $0.2 \mu\text{m}$ filtered tap water after 5 and $2 \mu\text{m}$ filters in series (10 min); 3) hypochlorite solution containing $1 \text{ g}\cdot\text{l}^{-1}$ active chlorine and pH adjusted to 11 using 10 N NaOH (30 min); and 4) filtered water rinse (10 min).

The acid and the alkaline solutions were prepared with the filtered water. The washes were performed at 50°C with flow velocity (v) $5.9 \text{ m}\cdot\text{s}^{-1}$, retentate compartment pressure (Pr) $2.1 \cdot 10^5 \text{ Pa}$ and $0.4 \cdot 10^5 \text{ Pa}$ constant TP.

Water flux measurement

After the cleaning and before the experiment, water flux was measured at the experimental conditions, *i.e.* filtered tap water (5, 2, and $0.2 \mu\text{m}$), $T = 50^\circ\text{C}$, $v = 4.5 \text{ m}\cdot\text{s}^{-1}$, $Pr = 2.1 \cdot 10^5 \text{ Pa}$, as described by Gésan (1993) after a comparative study using water of different quality. Fluxes were measured at four TP values between 0 and $0.5 \cdot 10^5 \text{ Pa}$. At each given TP value flux was left to stabilize for 5 min before data were acquired.

Microfiltration of whey

Microfiltration was performed at constant permeation flux (J). This mode is practised by the industry in order to ensure a continuous feed to the subsequent UF plant (Gésan et al., 1993b). Consequently TP increase meant that membrane fouling occurred, therefore TP will be used throughout the text to describe fouling along with the overall fouling hydraulic resistance (R_f).

When the rig was turned to operate from water to whey, flow velocity (v) was decreased to $3.0 \text{ m}\cdot\text{s}^{-1}$ and 2 l (≈ 2 the dead volume of the loop) of the pretreated whey were used to rinse the filtration loop from water before operation started.

Operating conditions

Operating parameters such as temperature, volume concentration ratio (VCR) and flow velocity (v) were chosen according to operating conditions practised by industrial plant (Gésan et al., 1993b). J was chosen in order to foul the membrane fast and this way to reduce the MF operating time (Gésan, 1993). The retentate pressure level was set in order to get a final TP that will cause high enough fouling to allow to model the evolution vs time but not too severe to ensure R_f recovery by cleaning.

Transient conditions to stationary operating conditions

When the feed tank was full with the whey, v was raised to its set value ($5.9 \text{ m}\cdot\text{s}^{-1}$) at a rate of $0.5 \text{ m}\cdot\text{s}^{-1}\cdot\text{min}^{-1}$ through the use of the automatic controller. In the meantime, permeate circulation was set to its automatic mode (a detailed description of the loop control was given by Daufin et al., 1993).

When the set v was attained, Pr was set to its automatic mode to get to the target value ($4.1 \cdot 10^5 \text{ Pa}$) in 5 min.

When the set Pr was reached, the permeation valve was turned on to increase J to its set value of $121 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ at the rate of $10 \text{ l}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ per min. The elapsed time from start to steady J was $\approx 30 \text{ min}$.

Stationary conditions

Filtration was performed in a concentration mode until VCR reached the set value (VCR=5.2) and VCR was maintained constant by extracting retentate at a flow of $Q_r (\text{m}^3\cdot\text{s}^{-1})$, working in a feed and bleed mode:

$$Q_r = J \cdot A / (\text{VCR}-1)$$

where A is the membrane area (m^2).

At the end of the run, retentate and permeate valves were closed, Pr was relieved and flow velocity of both retentate and permeate was decreased to the rinsing flow velocity manually.

Rinsing

After the completion of a run the membrane was rinsed with filtered tap water at 45°C for 30–35 min by increasing v to the test flow veloc-

ity ($5.9 \text{ m} \cdot \text{s}^{-1}$) in about three cycles, *i.e.* until no more proteins were released from the materials of the retentate compartment (stainless steel, rubber seals, etc) and from the membrane surface (no visible foam in the feed tank). Then, P_r was set to $2.1 \cdot 10^5 \text{ Pa}$ and J to $100 \text{ l} \cdot \text{h}^{-1} \cdot \text{m}^{-2}$ for 5 min. After the rinsing, water flux was measured as indicated.

Calculations

Hydraulic resistances

Calculation of R_m , R_f and irreversible fouling hydraulic resistance (R_{if}) were done according to Darcy's law. The slope of a plot of J versus TP of the measured water flux of a clean membrane and after the experiment gave the values of R_m and R_{if} (Taddéi *et al.*, 1986). R_f was calculated from TP measurements during the experiments according to Daufin *et al.* (1991a).

Errors in measurements

Taking into account the error of each sensor (four pressure gauges ($0.02 \cdot 10^5 \text{ Pa}$ each), temperature (0.4%), viscosity (1%) and permeation flux (3%)) and the relative standard deviation that characterizes the dispersion of results obtained from a series of measurements of the same variable, the calculated error amounted to $\approx 27\%$ of the resistance. Nevertheless, consecutive measurements made on the same type M14 Carbosep membrane and on different days showed $<5\%$ error in hydraulic resistance measurements, either for a clean or for an irreversibly fouled membrane. It was therefore concluded that this measured error is a better estimate of the actual error in R_m and R_{if} and was therefore used in the evaluation of cleaning, fouling and comparison of results.

Transmission

Transmission (Tr) and retention (RR) were calculated as follows:

$$RR = 1 - Tr = 1 - Cp/Cr$$

with C_p the concentration of the component in the permeate and C_r its concentration in the reten-

tate withdrawn at the same MF time. This calculation was assessed assuming that the permeate compartment was a perfectly stirred reactor (Gésan, 1993). Accounting for the dilution of analysed components in the permeate compartment, relative errors of calcium and phosphorus retentions varied with operating time from 20 to 10%, and for α -lactalbumin and β -lactoglobulin transmissions from 40 to 10%. As can be seen, the experimental errors are much larger at short time of operation, when the dilution is higher.

RESULTS

R_m variability of new membranes

The calculated R_m of 30 new membranes of two different production batches ($n_1=20$; $n_2=10$) showed R_m to vary from 0.85 ± 0.05 to $1.22 \pm 0.09 \cdot 10^{12} \text{ m}^{-1}$. The mean R_m value of those 30 membranes was $1.04 \cdot 10^{12} \text{ m}^{-1}$ (standard deviation: $0.10 \cdot 10^{12} \text{ m}^{-1}$). The two batches significantly differed ($P<0.05$) in their average resistance (1.09 and $0.92 \cdot 10^{12} \text{ m}^{-1}$).

There were visual differences between the membranes with respect to the color of the filtering layer which ranged from white to greyish black showing the heterogeneity from one batch to another and from one membrane or part of it to another (such a color heterogeneity was also noticed while dismantling an industrial S252 Carbosep module).

Influence of R_m on microfiltration performance

New membranes

The present detailed reported results were obtained under the operating conditions described in *Materials and methods*. The influence of initial membrane hydraulic resistance, R_m on MF performance was con-

firmed using other operating conditions: static counter pressure mode (without recirculation of permeate); different whey pretreatment (temperature of whey -55°C , and pH maintained at 7.5 during the pretreatment (Gésan et al, 1994)).

Permeability

The measured TP when J reached its set value was positively correlated ($r^2 = 70\%$) to R_m (fig 1). The lower the R_m , the lower the TP. Two runs with similar R_m membranes resulted in almost identical fouling evolution (fig 2), underlining the quality of rig operation control and the reproducibility of the pretreatments. In comparison to membranes with this R_m ($1.17 - 1.18 \cdot 10^{12} \text{ m}^{-1}$) the low R_m membrane ($1.03 \cdot 10^{12} \text{ m}^{-1}$) (from the same production batch) resulted in less fouling in time $< 1 \text{ h}$. Thereafter, the low R_m membrane fouled fast and its oper-

ating time was 30 min shorter than that of the high R_m membranes (fig 2).

Selectivity

Calcium and phosphorus retentions were similar for the whole range of R_m values studied and increased with time and VCR (fig 3). Calcium retention increased from 65% to 80% during VCR increase from 1.0 to 5.2 and stabilized at 80% at VCR = 5.2. Phosphorus retention increased from 80% to 90% for the same conditions. The OD of the permeate along the experiment was 0.02–0.05, independent of R_m , indicating efficient clarification.

The transmission of the two major proteins of whey (α -lactalbumin and β -lactoglobulin) decreased with time as fouling increased (fig 4). α -Lactalbumin transmission was always higher than that of β -lactoglobulin. At short time, until $\approx 80 \text{ min}$ operation the evolution of both proteins' transmission had a similar behaviour regard-

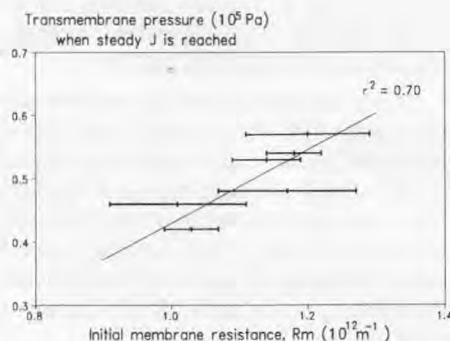


Fig 1. Transmembrane pressure when the steady permeation flux (J) is reached, vs the initial membrane hydraulic resistance, R_m . Operating conditions: Pretreated whey; M14 membrane; $v = 5.9 \text{ m s}^{-1}$; $P_r = 4.1 \cdot 10^5 \text{ Pa}$; $J = 121 \text{ l h}^{-1} \text{ m}^{-2}$; $VCR = 5.2$; $T = 50^{\circ}\text{C}$.

Pression transmembranaire quand le flux de perméation stationnaire (J) est atteint, en fonction de la résistance hydraulique initiale de la membrane, R_m . Conditions opératoires: Lactosérum prétraité; membrane M14; $v = 5,9 \text{ m s}^{-1}$; $P_r = 4,1 \cdot 10^5 \text{ Pa}$; $J = 121 \text{ l h}^{-1} \text{ m}^{-2}$; VCR (facteur de concentration volumique) = 5.2; $T = 50^{\circ}\text{C}$.

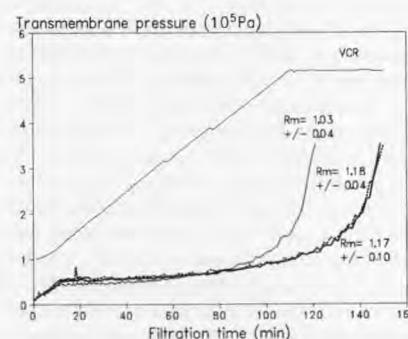


Fig 2. Volume concentration ratio (VCR) and transmembrane pressure vs filtration time for three new M14 membranes with different initial membrane hydraulic resistance R_m (expressed in 10^{12} m^{-1}). Operating conditions: see legend to figure 1.
Facteur de concentration volumique (VCR) et pression transmembranaire en fonction du temps de filtration pour 3 membranes M14 neuves de différentes résistances hydrauliques initiales R_m (exprimées en 10^{12} m^{-1}). Conditions opératoires: voir figure 1.

less of membrane R_m , and decreased thereafter faster with the low R_m membrane.

Membrane of different state of cleanliness

Permeability

A second set of experiments was performed using the same membrane after conditioning ($R_{m,use\ 1} = 1.14 \pm 0.05 \ 10^{12} \ m^{-1}$, for the clean membrane), after water rinse ($R_{m,use\ 2} = 2.48 \pm 0.16 \ 10^{12} \ m^{-1}$, for the irreversibly fouled membrane) and after cleaning ($R_{m,use\ 3} = 1.26 \pm 0.26 \ 10^{12} \ m^{-1}$). $R_{m,use\ 3}$ was about 10% higher than $R_{m,use\ 1}$ indicating that the membrane was not properly cleaned. Figure 5a shows the evolution of TP vs time during the experiment which lasted 60 min. The higher R_m membrane

resulted in higher TP during the experiment, indicating the higher pressure needed to maintain the set J (such results were confirmed by further experiments performed at other operating conditions and longer duration). When the results were plotted as resistance (R_f) evolution vs time (fig 5b) showed lower R_f value for the higher R_m membrane, but only for about 30 min when R_f started to increase at a faster rate compared to the other two membranes. It should be noted that R_f is the addition of fouling during the experiment to the already existing resistance, that of the membrane and of the uncleared residual fouling.

Selectivity

During the above experiments with the three membranes at different fouling state, cal-

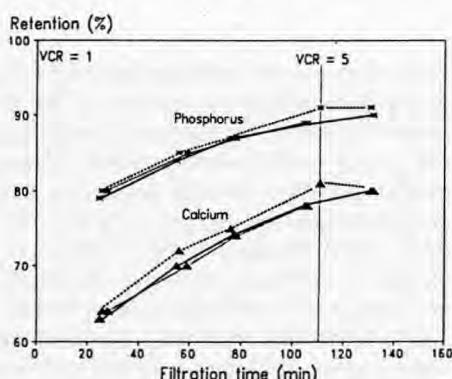


Fig. 3. Calcium and phosphorus retentions vs filtration time for three new M14 membranes with different initial membrane hydraulic resistance R_m : $R_m = 1.03 \pm 0.04 \ 10^{12} \ m^{-1}$ (.....); $R_m = 1.17 \pm 0.10 \ 10^{12} \ m^{-1}$ (—); $R_m = 1.18 \pm 0.04 \ 10^{12} \ m^{-1}$ (---). VCR: volume concentration ratio. Operating conditions: see figure 1. Error bars are similar for β -lactoglobulin.

Références du calcium et du phosphore en fonction du temps de filtration pour 3 membranes M14 neuves de différentes résistances hydrauliques initiales R_m : $R_m = 1,03 \pm 0,04 \ 10^{12} \ m^{-1}$ (.....); $R_m = 1,17 \pm 0,10 \ 10^{12} \ m^{-1}$ (—); $R_m = 1,18 \pm 0,04 \ 10^{12} \ m^{-1}$ (---). VCR: facteur de concentration volumique. Conditions opératoires: voir figure 1.

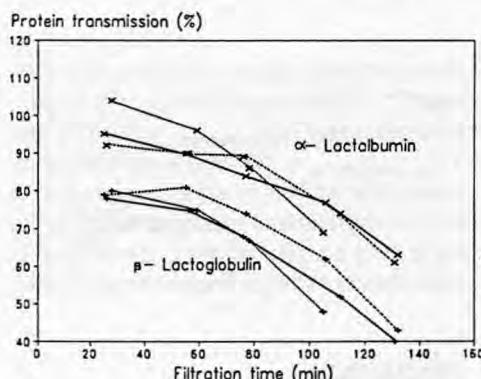


Fig. 4. Protein transmission vs filtration time for three new M14 membranes with different initial membrane hydraulic resistance R_m : $R_m = 1.03 \pm 0.04 \ 10^{12} \ m^{-1}$ (.....); $R_m = 1.17 \pm 0.10 \ 10^{12} \ m^{-1}$ (—); $R_m = 1.18 \pm 0.04 \ 10^{12} \ m^{-1}$ (---). VCR: volume concentration ratio. Operating conditions: see legend to figure 1. Error bars are similar for β -lactoglobulin.

Transmission des protéines en fonction du temps de filtration pour 3 membranes M14 de différentes résistances hydrauliques initiales R_m : $R_m = 1,03 \pm 0,04 \ 10^{12} \ m^{-1}$ (.....); $R_m = 1,17 \pm 0,10 \ 10^{12} \ m^{-1}$ (—); $R_m = 1,18 \pm 0,04 \ 10^{12} \ m^{-1}$ (---). VCR: facteur de concentration volumique. Conditions opératoires: voir figure 1. Les barres d'erreur sont similaires pour la β -lactoglobuline.

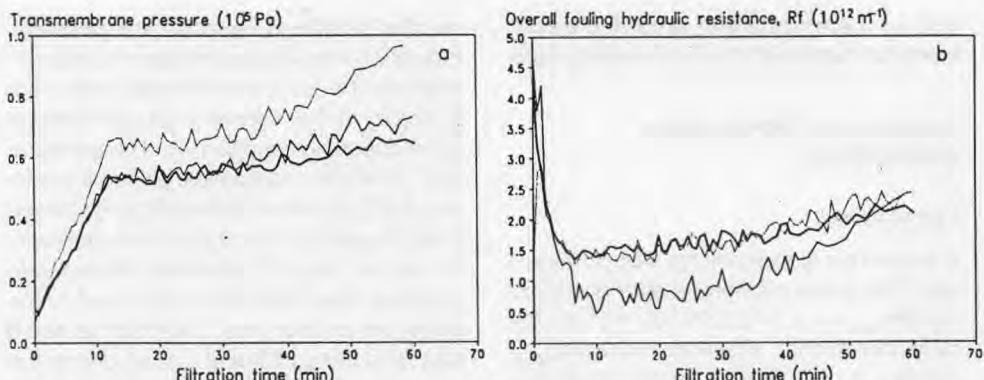


Fig 5. Evolution of transmembrane pressure (TP) (a); overall fouling hydraulic resistance (R_f) (b) vs filtration time for the same membrane after conditioning ($R_m = 1.14 \pm 0.05 \text{ } 10^{12} \text{ m}^{-1}$, clean membrane —) after water rinse ($R_m = 2.48 \pm 0.16 \text{ } 10^{12} \text{ m}^{-1}$ fouled membrane) and after cleaning ($R_m = 1.26 \pm 0.26 \text{ } 10^{12} \text{ m}^{-1}$, not properly cleaned membrane —). Operating conditions: see legend to figure 1.
Évolution de la pression transmembranaire (TP) (a) ; la résistance hydraulique de colmatage global (R_f) (b) en fonction du temps de filtration pour la même membrane après conditionnement ($R_m = 1,14 \pm 0,05 \text{ } 10^{12} \text{ m}^{-1}$, membrane propre —) après rinçage à l'eau ($R_m = 2,48 \pm 0,16 \text{ } 10^{12} \text{ m}^{-1}$; membrane colmatée.....) et après nettoyage ($R_m = 1,26 \pm 0,26 \text{ } 10^{12} \text{ m}^{-1}$, membrane nettoyée, non propre —). Conditions opératoires: voir figure 1.

cium and phosphorus retentions (68–69% and 81–82% respectively) and protein transmissions ($Tr_{\alpha\text{-Lactalbumin}} = 90\text{--}95\%$ and $Tr_{\beta\text{-Lactoglobulin}} = 73\text{--}80\%$) were not significantly different (this was the consequence of the too short time of experiment, and of the large error on calculations due to dilution of components in the permeate compartment).

DISCUSSION

The hydraulic resistance of new M14 membranes used in this work highlighted the influence of their wide range ($\approx 40\%$ difference) of permeability on MF performance. The same trend was also observed with organic UF membrane pieces cut from a DDS GR 61P membrane (Nilsson, 1988), or Romicon PM50 hollow fiber polysulfone membranes with various R_m of $1.2\text{--}7.8 \text{ } 10^{12} \text{ m}^{-1}$ (Devereux and Hoare, 1986).

The variation in R_m of different production batches and within the same batch

might be due to the heterogeneity of the filtering layer (thickness, quality of the Zr and/or Ti oxides, production procedures, etc) and/or of the carbon support characteristics (porosity, pore size distribution, etc) of relative equal resistance of $0.69 \text{ } 10^{12} \text{ m}^{-1}$ (Nau, 1991). Variation in R_m could not be blamed on differences in hydrophobicity and charge since the filtering layer and the support of the two membranes were of the same nature. Therefore it seems that R_m depends on morphological characteristics of the filtering area, and consequently could mainly be the result of the membrane pore size distribution. Pore size distribution of MF organic membranes was very large compared to UF membranes (Dietz *et al.*, 1992; Persson *et al.*, 1993).

For the following discussion on pores and their influence on performance, the membrane pores will be assumed to be cylindrical in shape, of the same size and equal throughout their length (as was considered by Nilsson and Hallström (1991) for using R_m as a function of pore size distribution).

The determination of R_m of M14 membrane, new, fouled and cleaned after MF experiment, revealed the R_m variation due to residual fouling present on the surface and within the membrane after cleaning (Daufin *et al*, 1992). In the case of cleaned membranes, the R_m increase is assumed not to be solely due to the membrane's morphological characteristics but also, in comparison to new membrane's R_m , due to the differences in hydrophobicity and charge because of residual fouling. The cleaning procedure used was probably inefficient, which is in agreement with the observations made by Gésan *et al* (1993b) of an industrial plant and those of Heinemann *et al* (1988) and Warren *et al* (1991) who have observed water permeability reduction (33%) in hollow fiber MF of solutions of proteins and yeasts.

Microfiltration performance

The influence of initial R_m of new membranes was evidenced in a range of experimental conditions which corresponded to different localized filtration conditions resulting on different localized fouling layers' build-up. The major features were: fouling heterogeneity connected to counter-pressure modes, static and dynamic as reported by Gésan *et al* (1993a); aggregates size related to pretreatment and porosity of the fouling deposit thus created (Gésan *et al*, 1994).

Evolution of fouling and transmission versus time

Fouling increased in the course of time according to a 'complete blocking' filtration law accounting for a progressive decrease in the filtering area (Gésan *et al*, 1993a). According to previous and recent studies (Gésan *et al*, 1993a, 1994) the increase of fouling *versus* time could be the outcome of an increasing deposit layer thickness on the membrane surface. This deposit, composed

mainly of calcium and phosphate aggregates could entrap protein and consequently affect their transfer to the permeate.

Effect of R_m on microfiltration performance

During the first hour of MF and at whatever the state of the membrane (new, irreversibly fouled, cleaned), higher R_m coincide with higher TP and fouling (fig 1). MF performance appeared to be governed by R_m which characterized the membrane pore size distribution.

The overall quantity of material brought to the membrane by convection was independent of R_m since the experiments were performed at constant flux. For this reason the more pronounced decrease of protein transmission with low R_m membrane and increase in TP *vs* time (as presented in figs 4,5) could be explained by: i) an initial actual filtering layer characterized by a small number of pores (due to manufacturing) or an initial residually fouled membrane (bad cleaning); and ii) a large population of small pores, even if the global actual filtering area is the same. Using bi-liquid permiporometry method, Persson *et al* (1993) showed that large pores governed the major part of permeability. They observed that 10% of the larger pores were responsible for 90% of the permeability in the case of Nylon-66 MF membrane from Pall with a mean pore diameter of 0.2 μm . Similar observations were reported by Fane *et al* (1981) with Amicon UF membranes. Such a phenomenon was observed during filtration performed at constant TP. The phenomenon is the same during constant J experiments since permeation occurs preferentially in regions of low pressure drop, *i.e.* area of low resistance.

Consequently, it appears that the better hydraulic MF performance at short time is observed with the membranes which would have the larger population of large pores.

After 1 h of MF using new membranes, fouling increased faster for low R_m membranes (fig 2). Such an evolution could be explained by the aforementioned assumptions about the presence of the large population of large pores in the membrane (compared to new membranes of higher R_m). Increase of MF membrane fouling with increased pore size was attributed to particles (Merin *et al.*, 1983; Gatenholm *et al.*, 1988; Ben Amar and Jaffrin, 1989; Attia *et al.*, 1991) or to proteins (Brink *et al.*, 1993). The larger pores filter more solvent and consequently a large amount of solutes and particles accumulates at their entrance or passes through them. This accelerates pore blocking and leads to a decrease in pore number resulting in a decrease of filtering area. Blocked pores observed by scanning electron microscopy were reported to be the cause of decreased permeability (Kelly *et al.*, 1992).

Consequently, taking into account the overall evolution of MF performance, a new M14 membrane with low R_m can be considered as a membrane with a large population of large pores, representing the major part of the actual filtering area.

In case of an used membrane the increase of R_m could correspond to a size reduction and/or disappearance of pores. Due to the reduction of filtering area, the quantity of material which must be filtered per unit area of residual filtering surface is higher (in an experiment performed at constant J) and therefore fouling increases faster. These conclusions emphasize the need for better knowledge of MF membrane cleaning, since MF performance appear to be related to the characteristics of the used membrane.

In the above discussion, we assumed that R_m depended mainly on the membrane's pore size distribution. Some experimental proofs of our assumptions could be obtained using specified methodology (mercury porosimetry, etc) to get quantitative information.

Reduction of the heterogeneity of filtration conditions

At the membrane's scale

According to these results obtained with an evenly distributed transmembrane pressure along the membrane, it appears that the heterogeneity of the pore size of the membrane (new or cleaned) governs the distribution of localized flux and in that way, the quality and quantity of global (irreversible and reversible) fouling. Therefore, in order to reduce the effect of large pores and to improve whey MF performance, it would be better to use a membrane of a more homogeneous pore size. This optimal mean pore size has to be determined taking into account the size distribution of solute and the system performance versus the ratio of solute size to pore size (Le and Atkinson, 1985; Matsumoto *et al.*, 1988) and operating parameters. Moreover, adequate procedures for assessment of proper cleaning have to be established since inadequate washes lead to residual fouling unevenly distributed throughout the membrane and to a poor performance as described in this work for three membranes.

At the industrial scale

It should be taken into account that mixing different R_m membranes in a module could result in uneven fouling layer distribution (as seen in our experiments) and thus lead to fast fouling and reduced protein transmission. The replacement of membranes in a module by new ones has to be done after R_m determination.

Effect of R_m on fouling schematic presentation

The initial membrane fouling resistance influences fouling kinetics. Consequently the

schematic presentation of fouling with TP or Rf vs time does not take into account the influence of Rm on MF performance. Different ways to compare filtration experiments' performance were proposed. Dejmek and Nilsson (1989) showed for example that when proteins were adsorbed to UF membranes $Rf/(Rm+Rf)$ was a better parameter compared to Rf alone for the schematic presentation of results since it reduced the effect contributed by Rm. Persson and Nilsson (1991) used the normalized resistance Rf/Rm considering Rf to be directly proportional to Rm. Such an assumption was not verified in our experiments except for a short time of MF when a low Rm induced a low Rf. Rf/Rm did not take into account the direct effect of Rm on operating duration and selectivity. In fact there is no single parameter that can schematically describe fouling evolution and compare performance of membranes of different Rm values. Moreover, if a membrane is not thoroughly cleaned, Rm corresponds to the Rm of the initial new and clean membrane plus the resistance of a residual fouling; the latter is not taken into account in Rf, which describes the fouling build-up during the MF. Consequently, Rf is an improper parameter to assess performance as could be wrongly deduced from its low value as seen in figure 5b.

CONCLUSION

MF performance (permeability and selectivity) during microfiltration of pretreated sweet whey using an M14 Carbosep membrane depended on the initial membrane hydraulic resistance (Rm). A new M14 membrane of low Rm resulted in a shorter operating time and lower protein transmission at the end of the operation. An improperly cleaned M14 membrane, with a high Rm resulted in a reduction of MF performance. Considering that Rm depends mainly on

morphological characteristics of the filtering area, this reduction of performance could be attributed to the preferential flow through low resistance area of large pores (for the new membrane of low Rm) and to the reduction of filtering area by residual fouling (for the used membrane). Therefore, in order to improve MF performance a membrane with a sharp pore size distribution and adequate cleaning procedures should be developed.

Rm is a major characteristic of a membrane as it is used at industrial plants in order to assess its initial state of cleanliness. One of the aims of this work is to draw the membrane user's attention to the potential consequence of initial Rm values on whey MF performance even though its contribution may be affected according to operating conditions.

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