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

Geneviève Gésan-Guiziou, G Daufin, U Merin

To cite this version:


HAL Id: hal-00929396
https://hal.science/hal-00929396
Submitted on 1 Jan 1994

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Original article

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

G Gésan¹, G Daufin¹, U Merin²

¹ Laboratoire de Recherche de Technologie Laitière, INRA, 65, rue de Saint-Brieuc, 35042 Rennes Cedex, France;
² Dairy Science Laboratory, ARO The Volcani Center, PO Box 6, Bet Dagan 50250, Israel

(Received 31 December 1993; accepted 6 April 1994)

Summary — Membrane hydraulic resistance (Rm) for the same nominal M14 Carbosep membrane (pore diameter 0.14 μm) was found to vary significantly from 0.85 ± 0.05 to 1.22 ± 0.09 10¹² m⁻¹. Pretreated whey microfiltration experiments carried out using these new membranes resulted in shorter operating time and lower protein transmission for the low Rm membranes. When the same membrane was used new, irreversibly fouled or cleaned (Rm = 1.14, 2.48 and 1.26 10¹² m⁻¹ respectively) fouling evolution was positively correlated with Rm increase. It was assumed that a low Rm 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 (Rm) de la membrane M14 Carbosep (diamètre de pores 0,14 μm) 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 Rm de cette membrane varie de 0,85 ± 0,05 à 1,22 ± 0,09 10¹² m⁻¹. En répétant une même

Abbreviations. A, membrane area (m²); Cp, concentration of a component in the permeate (g·l⁻¹); Cr, concentration of a component in the retentate (g·l⁻¹); J, permeation flux (l·h⁻¹·m⁻²); OD, optical density; Pr, mean pressure of the retentate compartment (10⁵ Pa); Qr, retentate extraction flow rate (m³·s⁻¹); T, temperature (°C); TP, transmembrane pressure (10⁵ Pa); Tr, transmission (%); v, flow velocity (m·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 10^{12} 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 préférant se crée dans les zones de faible résistance, c'est-à-dire dans les grands pores, qui filtre 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.

**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 Balman 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 \( \mu \)m mean pore diameter and \( \text{ZrO}_2 \) and \( \text{TiO}_2 \) filtering layer on a carbon support (6 mm inner diameter, 1.2 m long; 2.26 \( 10^{-2} \) 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 \( \mu \)m 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 \( \text{CaCl}_2 \) up to a calcium concentration of 1.2 \( \text{g kg}^{-1} \) 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 \( \text{pH} \) decreased down to 6.4. \( \text{Na}_2\text{SO}_4 \) at 0.2 \( \text{g}\text{L}^{-1} \) 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 \( \alpha \)-lactalbumin and \( \beta \)-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 Brulé *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.
<table>
<thead>
<tr>
<th>Composition moyenne du lactosérum prétraité.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Mean value} )</td>
</tr>
<tr>
<td>( T ) of pretreatment (°C)</td>
</tr>
<tr>
<td>Final pH of pretreatment (at 50°C)</td>
</tr>
<tr>
<td>( \alpha )-lactalbumin (g( \text{kg}^{-1} ))</td>
</tr>
<tr>
<td>( \beta )-lactoglobulin (g( \text{kg}^{-1} ))</td>
</tr>
<tr>
<td>Optical density (600 nm)</td>
</tr>
<tr>
<td>Calcium (g( \text{kg}^{-1} ))</td>
</tr>
<tr>
<td>Phosphorus (g( \text{kg}^{-1} ))</td>
</tr>
</tbody>
</table>
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 mol·L$^{-1}$ (0.03 mol·L$^{-1}$), pH = 1.2 at 50°C (45 min); 2) water rinse using 0.2 μm filtered tap water after 5 and 2 μm filters in series (10 min); 3) hypochlorite solution containing 1 g·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 m·s$^{-1}$, retentate compartment pressure (Pr) 2.1 × 10$^5$ Pa and 0.4 × 10$^5$ Pa constant TP.

**Water flux measurement**

After the cleaning and before the experiment, water flux was measured at the experimental conditions, ie filtered tap water (5, 2, and 0.2 μm), T = 50°C, v = 4.5 m·s$^{-1}$, Pr = 2.1 × 10$^5$ 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 × 10$^5$ 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 (Rf).

When the rig was turned to operate from water to whey, flow velocity (v) was decreased to 3.0 m·s$^{-1}$ and 2 l (= x 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 Rm 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 m·s$^{-1}$) at a rate of 0.5 m·s$^{-1}$·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 × 10$^5$ 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 l·h$^{-1}$·m$^{-2}$ at the rate of 10 l·h$^{-1}$·m$^{-2}$ per min. The elapsed time from start to steady J was ~30 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 Qr (m$^3$·s$^{-1}$), working in a feed and bleed mode:

\[
  Qr = J \cdot A / (VCR-1)
\]

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 m$^{-1}$) in about three cycles, ie 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, $Pr$ was set to 2.1 $10^5$ Pa and $J$ to 100 $1^{-1}m^{-2}$ for 5 min. After the rinsing, water flux was measured as indicated.

Calculations

Hydraulic resistances

Calculation of $Rm$, $Rf$ and irreversible fouling hydraulic resistance ($Rif$) 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 $Rm$ and $Rif$ (Taddéi et al, 1986). $Rf$ 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 $10^5$ 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 $Rm$ and $Rif$ 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 $Cp$ the concentration of the component in the permeate and $Cr$ its concentration in the retentate 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 $\alpha$-lactalbumin and $\beta$-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

$Rm$ variability of new membranes

The calculated Rm of 30 new membranes of two different production batches ($n_1=20$; $n_2=10$) showed Rm to vary from $0.85 \pm 0.05$ to $1.22 \pm 0.09 \times 10^{12}$ m$^{-1}$. The mean Rm value of those 30 membranes was $1.04 \times 10^{12}$ m$^{-1}$ (standard deviation: $0.10 \times 10^{12}$ m$^{-1}$). The two batches significantly differed ($P<0.05$) in their average resistance ($1.09$ and $0.92 \times 10^{12}$ 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 Rm 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, Rm 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 Rm (fig 1). The lower the Rm, the lower the TP. Two runs with similar Rm 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 Rm ($1.17 - 1.18 \times 10^{12} \text{m}^{-1}$) the low Rm membrane ($1.03 \times 10^{12} \text{m}^{-1}$) (from the same production batch) resulted in less fouling in time < 1 h. Thereafter, the low Rm membrane fouled fast and its operating time was 30 min shorter than that of the high Rm membranes (fig 2).

**Selectivity**

Calcium and phosphorus retentions were similar for the whole range of Rm 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 Rm, indicating efficient clarification.

The transmission of the two major proteins of whey ($\alpha$-lactalbumin and $\beta$-lactoglobulin) decreased with time as fouling increased (fig 4). $\alpha$-Lactalbumin transmission was always higher than that of $\beta$-lactoglobulin. At short time, until ~80 min operation the evolution of both proteins' transmission had a similar behaviour regard-
less of membrane Rm, and decreased thereafter faster with the low Rm membrane.

**Membrane of different state of cleanliness**

**Permeability**

A second set of experiments was performed using the same membrane after conditioning (Rm\_use\_1 = 1.14 ± 0.05 10^{-12} m^{-1}, for the clean membrane), after water rinse (Rm\_use\_2 = 2.48 ± 0.16 10^{-12} m^{-1}, for the irreversibly fouled membrane) and after cleaning (Rm\_use\_3 = 1.26 ± 0.26 10^{-12} m^{-1}). Rm\_use\_3 was about 10% higher than Rm\_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 Rm 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 (Rf) evolution vs time (fig 5b) showed lower Rf value for the higher Rm membrane, but only for about 30 min when Rf started to increase at a faster rate compared to the other two membranes. It should be noted that Rf is the addition of fouling during the experiment to the already existing resistance, that of the membrane and of the uncleaned residual fouling.

**Selectivity**

During the above experiments with the three membranes at different fouling state, cal-
G Gésan et al

Fig 5. Evolution of transmembrane pressure (TP) (a); overall fouling hydraulic resistance (Rf) (b) vs filtration time for the same membrane after conditioning (Rm = 1.14 ± 0.05 \(10^{12}\) m\(^{-1}\), clean membrane ---) after water rinse (Rm = 2.48 ± 0.16 \(10^{12}\) m\(^{-1}\), fouled membrane .......) and after cleaning (Rm = 1.26 ± 0.26 \(10^{12}\) m\(^{-1}\), not properly cleaned membrane—). Operating conditions: see legend to figure 1.

Evolution de la pression transmembranaire (TP) (a); la résistance hydraulique de colmatage global (Rf) (b) en fonction du temps de filtration pour la même membrane après conditionnement (Rm = 1,14 ± 0,05 \(10^{12}\) m\(^{-1}\), membrane propre —) après rinçage à l’eau (Rm = 2,48 ± 0,16 \(10^{12}\) m\(^{-1}\); membrane colmatée.......) et après nettoyage (Rm = 1,26±0,26 \(10^{12}\) m\(^{-1}\), membrane nettoyée, non propre —). Conditions opératoires: voir figure 1.

cium and phosphorus retentions (68–69% and 81–82% respectively) and protein transmissions (\(T_{\alpha}\)-Lactalbumin = 90–95% and \(T_{\beta}\)-Lactoglobulin = 73–80%) 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 (= 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 Rm of 1.2–7.8 \(10^{12}\) m\(^{-1}\) (Devereux and Hoare, 1986).

The variation in Rm 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 \(10^{12}\) m\(^{-1}\) (Nau, 1991). Variation in Rm 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 Rm 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 Rm as a function of pore size distribution).
The determination of Rm of M14 membrane, new, fouled and cleaned after MF experiment, revealed the Rm 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 Rm increase is assumed not to be solely due to the membrane's morphological characteristics but also, in comparison to new membrane's Rm, 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 Rm of new membranes was evidenced in a range of experimental conditions which corresponded to different localized filtration conditions resulting in 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 Rm on microfiltration performance**

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

The overall quantity of material brought to the membrane by convection was independent of Rm since the experiments were performed at constant flux. For this reason the more pronounced decrease of protein transmission with low Rm 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 permeometry 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 Rm 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 Rm). 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 Rm 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 Rm 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 Rm 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 Rm 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 Rm determination.

Effect of Rm 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.

ACKNOWLEDGMENTS

This work was partially supported by a grant from the Etablissement Public Régional de Bretagne (Contract No 3051 B).

REFERENCES

Membrane resistance and MF performance


