

Membrane processes for the recovery of dairy cleaning-in-place solutions

Marlène Dresch^a, Georges Daufin^{a*}, Bernard Chaufer^b

^a Laboratoire de recherches de technologie laitière, Inra,
65, rue de Saint-Brieuc, 35042 Rennes cedex, France

^b Laboratoire des procédés de séparation, UA université de Rennes-I, Inra,
263, avenue du Général-Leclerc, 35042 Rennes cedex, France

(Received 30 June 1998; accepted 5 October 1998)

Abstract — The recovery of dairy cleaning-in-place (CIP) solutions contributes to saving chemicals, water and energy, maintaining cleaning efficiency, and reducing pH variation and volume of waste stream. The aim of this study was to compare different processes for this particular operation. Industrial cleaning solutions were ultrafiltered (300 kg·mol⁻¹): membrane performances were CIP-type dependent. One particular type (alkaline) of CIP solution was treated using decantation, centrifugation and cross-flow filtration (0.1 µm microfiltration [MF], 300 and 15 kg·mol⁻¹ ultrafiltration [UF], inorganic and organic nanofiltration [NF]). Centrifugation, decantation and 0.1 µm MF only removed particles; UF slightly reduced the soluble chemical oxygen demand (COD); and NF more largely. Increasing the volume reduction ratio (VRR) (up to 50 here) reduced the volume of sludge, but resulted in a higher fouling (although always moderate) and a higher organic content of the permeate. NF is a proper process: membrane performance stabilization when VRR increased, satisfactory flux (> 100 L·h⁻¹·m⁻² at 70 °C) and the best pollution reduction. A cascade with pretreatment of the CIP alkaline solution by 0.1 µm MF was detrimental to NF performances. © Inra/Elsevier, Paris

waste stream cleaning-in-place / microfiltration / ultrafiltration / nanofiltration

Résumé — Procédés à membranes pour la régénération des solutions de nettoyage en place de l'industrie laitière. Régénérer les solutions de nettoyage usées de l'industrie laitière permet d'économiser des produits chimiques, de l'eau et de l'énergie, de maintenir un meilleur niveau d'efficacité de nettoyage, et de réduire les variations de pH et le volume des effluents globaux. Le but de cette étude est de comparer différents procédés pour cette application. Des solutions de nettoyage industrielles provenant de centrales de nettoyage en place (NEP) différentes étaient ultrafiltrées (300 kg·mol⁻¹). Les performances de l'opération dépendaient de la NEP dont provenait la solution. Une solution industrielle provenant d'une même NEP était ensuite traitée par centrifugation, décantation et filtration tangentielle (microfiltration (MF) 0,1 µm, ultrafiltration (UF) 300 ou 15 kg·mol⁻¹, nanofiltration (NF)

* Correspondence and reprints. gdaufin@labtechno.roazhon.inra.fr

inorganique et organique). La centrifugation, la décantation et la MF retenant uniquement les particules, l'UF légèrement la demande chimique en oxygène (DCO) soluble, et la NF plus fortement. Augmenter le facteur de réduction volumique FRV (jusqu'à 50 dans ce travail) était nécessaire afin de réduire le volume des boues, mais cela entraînait une dégradation de la perméabilité (colmatage modéré) et de la qualité du perméat. La NF inorganique est le procédé le plus prometteur : stabilisation des performances quand le FRV augmentait, flux satisfaisant ($> 100 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ à 70°C) et épuration la plus poussée. Une cascade avec prétraitement de la solution par MF $0,1 \mu\text{m}$ altérerait les performances de la NF. © Inra/Elsevier, Paris

effluent nettoyage en place / microfiltration / ultrafiltration / nanofiltration

1. INTRODUCTION

Cleaning operations are crucial in the dairy industry to obtain microbiologically safe products. Hence, cleaning-in-place (CIP) systems were developed [16, 27]: the equipment is cleaned without taking it apart, using the circulation of chemicals and water. The cleaning solutions are discarded regularly either after one use (single-use system) or after re-use (multi-use and re-use systems) until the cleaning efficiency becomes too low. Consumption of chemicals ranges from 1.1 to 1.2 kg of alkaline products, and 0.6 to 1.1 kg of acid products per kg of processed milk [18]. The volume stemming from cleaning and disinfection operations represents 54 % of the total effluent volume in Germany [14] and can increase up to 98 % [17]. The global effluent volume varies from 0.5 to 5 L per L of processed milk [6], depending on the type and the age of the plant. Current regulations for waste water are becoming increasingly restrictive, and the costs of water and waste water treatment are increasing. Recovering cleaning

solutions would lead to maintaining cleaning efficiency, to minimizing pH fluctuations and volume of the total effluent, and to saving water, chemicals and energy [15, 23]. A process based on physicochemical treatment with a precipitation step followed by a conventional filtration has been proposed [19]. Membrane processes appear to be a promising alternative since they avoid additives, can withstand pH and temperature of cleaning solutions, and are able to reject particles, but also soluble molecules, depending on the membrane molecular weight cut-off (MWCO). These processes have already been investigated: Henck [14] tested process parameters using membranes ranging from $1.4 \mu\text{m}$ microfiltration (MF) to $15 \text{ kg}\cdot\text{mol}^{-1}$ ultrafiltration (UF); Condat-Ouillon [8] studied mainly $0.1 \mu\text{m}$ MF; some processes are commercially available, for example, Alkasave (nanofiltration, NF) from Koch International (Roissy, France), Chemsaver (NF) from Filtration Engineering Co., Inc. (New Hope, MN, USA) or Micro-Steel (MF) from Membrane System Specialists (Wisconsin Rapids, WI, USA).

Abbreviations: CIP: cleaning-in-place; COD: chemical oxygen demand; MF: microfiltration; MWCO: molecular weight cut-off; NF: nanofiltration; SM: suspended matter; UF: ultrafiltration.

Symbols: C_F : feed solution concentration ($\text{g}\cdot\text{L}^{-1}$); C_P : permeate concentration ($\text{g}\cdot\text{L}^{-1}$); C_R : retentate concentration ($\text{g}\cdot\text{L}^{-1}$); J : permeate flux ($\text{L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$); R_f : total fouling resistance (m^{-1}); R_{if} : irreversible fouling resistance (m^{-1}); R_m : membrane resistance (m^{-1}); T : temperature ($^\circ\text{C}$); v : cross-flow velocity ($\text{m}\cdot\text{s}^{-1}$); VJP: volume of extracted permeate (L); VJR: volume of extracted retentate (L); VOR: retentate loop volume (L); VRR: volume reduction ratio; ΔP : transmembrane pressure (bar).

According to recent estimates, today there are at least 20 MF, 5 UF and 8 NF processes operating worldwide in the dairy industry to recover cleaning solutions [15].

The aim of this work is to study the recovery of cleaning solutions using pressure-driven membrane processes (ranging from MF to NF), to compare them with centrifugation and decantation, and to identify the problems which should be further considered. NF offers a proper compromise between flux and organic removal.

2. EXPERIMENTAL

2.1. Industrial cleaning-in-place solutions

The CIP solutions, either acid or alkaline, were supplied by Besnier-Bridel

(Retiers, France). They came from various CIP systems: concentration (evaporator solutions), milk tankers (milk tanker solutions), and skimming, standardization and pasteurization of milk (standardization solutions). Most of the runs were carried out with standardization NaOH (alkaline solution). The analytical characteristics (chemical oxygen demand, COD, suspended matter, SM) of the solutions (*table I*) varied greatly according to the type of chemicals used (NaOH, HNO₃), the type of equipment ('cold' or 'hot') that the solution cleaned as well as from day to day for the same CIP system. For standardization NaOH, NaOH concentration varied from 14 to 24 g·L⁻¹ (pH was about 13), COD from 3.4 to 5.0 g·L⁻¹ and SM from 613 to 1021 mg·L⁻¹. Soluble COD represented 60 to 83 % of the total COD.

Table I. Analytical characteristics of the industrial cleaning-in-place (CIP) solutions.

Tableau I. Caractéristiques analytiques des solutions de nettoyage industrielles.

CIP systems	Chemical	COD g·L ⁻¹	SM mg·kg ⁻¹
1 - Milk tanker	NaOH	2.1	580
2 - Standardization	NaOH	4.0	850
3 - Evaporator	NaOH	3.0	890
4 - Milk tanker	HNO ₃	0.1	5
5 - Standardization	HNO ₃	2.9	730
6 - Evaporator	HNO ₃	18.6	910
A - Standardization	NaOH	3.4	610
B - Standardization	NaOH	3.9	710
C - Standardization	NaOH	5.0	1 020
D - Standardization	NaOH	4.7	880
E - Standardization	NaOH	4.8	710
F - Standardization	NaOH	3.5	770
G - Standardization	NaOH	3.9	1 030
H - Standardization	NaOH	3.9	620
I - MF permeate	(obtained	NaOH	60
J - MF permeate	from A)	NaOH	50

COD: chemical oxygen demand; SM: suspended matter; MF: microfiltration.

COD : demande chimique en oxygène ; SM : matières en suspension ; MF : microfiltration.

2.2. Unit operations

2.2.1. Decantation

Decantation was carried out on a laboratory scale (100 mL, 13.2 cm²) at room temperature during 3.5 h. Supernatant was upwelled with a pipette.

2.2.2. Centrifugation

Samples were taken from a continuous centrifuge skimmer (6 000 g, 80 °C) operating on a industrial scale. Centrifugation was also carried out on a laboratory scale (50 mL tubes) with a SV 11 TH centrifuge (Firlabo, France) (3 000 g, 20 °C, 20 min). The process was discontinuous. It has to be considered as an ideal process with regard to industrial centrifugation because of the long residence time and low operating temperature.

2.2.3. Cross-flow filtration

2.2.3.1. Membranes

Membrane selection was limited by the chemical resistance to the feed solution. Materials must withstand pH ranging from 0 to 14, temperature (70–80 °C), and transmembrane pressure (ΔP) up to 15 bar for an NF operation.

Membranes were of two types:

– Multichannel tubular inorganic membrane (Kerasep, ORELIS, Miribel, France): 19 channels, 2.6 to 2.8 mm internal diameter, length 0.856 m, area 0.12 m²; 0.1 μm MF, 300 and 15 kg·mol⁻¹ UF and prototype Sol-gel NF (lactose [1 g·L⁻¹] retention: 0.35) membranes were used; these membranes are claimed to resist pH ranging from 0 to 14, 350 °C, $\Delta P \leq 50$ bar.

– Tubular organic MPT-34 NF membrane (Koch International, Roissy, France): (lactose [50 g·L⁻¹] retention: 0.98), internal diameter 12.7 mm, length 0.6 m, area 0.024 m²; this membrane is claimed to resist pH ranging from 1 to 14 at 80 °C and $\Delta P \leq 15$ bar.

Before each run, the membranes were cleaned with an alkaline detergent and nitric acid (0.3 % w, 55 °C). The alkaline detergents were supplied by Henkel-Ecolab (Issy-les-Moulineaux, France): Ultrasil 13 for Kerasep membrane (10 g·L⁻¹, 80 °C), and Ultrasil 91 (10 g·L⁻¹, 45 °C) for MPT-34 NF. Membranes were flushed out by 0.2 μm filtered water. Water flux was measured to determine membrane flow resistance before and after each experiment.

2.2.3.2. Filtration rigs

Two rigs were used, depending on the ΔP used. Both were used in a feed-and-bleed mode with the retentate not recycled in the feed tank, but circulating in a closed loop. For MF and UF ($\Delta P \leq 7$ bar), the rig was similar to that described by Daufin et al. [9], except that the regulations were controlled by a computer and the rig was fed by a system screw pump–regulation valve. The retentate loop volume was 2.49 L with a Kerasep membrane. The permeate side was assumed to be a plug-flow reactor, and no correction was made for permeate concentrations. Pressure was corrected from pressure gauge locations. The NF pilot (ORELIS, Miribel, France) ($\Delta P \leq 15$ bar) has been described elsewhere [13]. The retentate loop volume was 2.0 L with a Kerasep or MPT-34 membrane. Pressure was not corrected from the pressure gauge locations, but the error was negligible because of the high ΔP value (≥ 4 bar).

2.2.3.3. Operating conditions

Operating conditions (*table II*) were selected from preliminary experiments [10] so that fouling could be kept under acceptable limits. For MF and UF, the CIP solutions were filtered up to a given volume reduction ratio (VRR) which was kept constant for 2 h. The process was carried out at constant permeate flux (J). For NF, the CIP solutions were continuously concentrated, until the end of the run. The process was performed at constant ΔP .

Table II. Operating conditions of cross-flow filtrations (only controlled parameters are given).**Tableau II.** Conditions opératoires des filtrations tangentielles (seuls les paramètres régulés sont répertoriés).

Filtered solution*	Process	v (m·s ⁻¹)	J (L·h ⁻¹ ·m ⁻²)	ΔP (bar)	Temperature (°C)
1-6	300 kg·mol ⁻¹ UF	4.0	200		70 ^a , 65 ^b
A	0.1 μm MF	7.0	300		70
B	0.1 μm MF	7.0	200		70
C	300 kg·mol ⁻¹ UF	7.0	200		70
D	15 kg·mol ⁻¹ UF	7.0	100		70
E	Sol-gel NF	2.7		10	70
F	Sol-gel NF	2.7		10	70
G	Sol-gel NF	2.7		4	70
I	Sol-gel NF	2.7		10	70
H	MPT-34 NF	2.7		10	70
J	MPT-34 NF	2.7		10	70

*: See table I; ^a: NaOH; ^b: HNO₃; v: cross-flow velocity; J: permeate flux; ΔP: transmembrane pressure; UF: ultrafiltration; NF: nanofiltration.

*: Voir tableau I; ^a: NaOH; ^b: HNO₃; v: vitesse tangentielle de circulation; J: densité de flux de perméation; ΔP: pression transmembranaire.

Cross-flow velocity (v) was the controlled hydrodynamic parameter, but the wall shear stress is the proper parameter to quantify erosion [4, 21]. This means that hydrodynamics was different between NF membranes, since nanofiltration was conducted at the same v, but the membrane diameter was different.

2.2.3.4. Cascade operation: MF + NF

MF permeate obtained at a VRR = 50 (operating conditions, see table II) from standardization NaOH (solution A, see table I) was collected and frozen, before being filtered by NF. This MF step (figure 1) was expected to increase NF performances by pretreating solutions. NF operating conditions are given in table II.

2.2.4. Analytical methods

Analyses were limited by the extreme pH values of the solutions.

2.2.4.1. Physicochemical parameters

The accuracy of the methods are given in parentheses.

Dynamic viscosity (< 1 %): D8 viscosimeter (Haake, Germany) for newtonian fluids. Conductivity (< 1 %): 660 conductimeter (Metrohm, Switzerland) at 20 °C. NaOH titration (2 %): by 1 N HCl, with phenolphthalein.

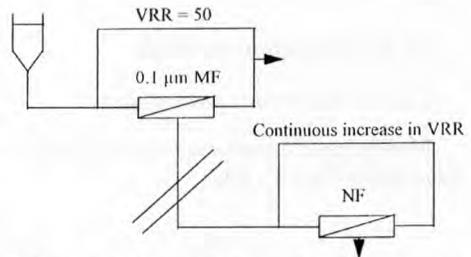


Figure 1. Scheme of the cascade microfiltration (MF) + nanofiltration (NF). VRR: volume reduction ratio.

Figure 1. Schéma de la cascade MF + NF.

Particle size: laser granulometer LS 230 (Coulter, FL, USA) for particle size ranging from 0.04 to 2 000 μm . Particle size distribution was measured for standardization NaOH. Most of the particles had a diameter of < 0.3 μm when determined in number percentage; the average number diameter was 0.088 μm . However, in volume percentage, a 2 peak distribution was observed with an average volume diameter equal to 0.14 μm and 9.0 μm respectively; the diameter of the second population ranged from 3 to 55 μm .

2.2.4.2. Pollution parameters

COD was measured by Nanocolor Test 29 cuvettes and a PF 10 pocket filter photometer (Macherey-Nagel, Hoerd, France). This method was correlated with the results given by Afnor French standard [3] (accuracy: 5 %). COD can either be total, when measured in the whole sample, or soluble, when measured in supernatant of centrifugation (3 000 g, 20 °C, 20 min). SM was determined according to AFNOR French standard [1]: filtration on a 1.2 μm glass-fiber filter and drying at 105 °C overnight (accuracy: 5 %). Total calcium concentration was measured by atomic absorption spectrometry on a AA 300 equipment (Varian SA, Les Ulis, France), after mineralization of the samples (accuracy: 5 %). Total phosphorus concentration was measured according to AFNOR French standard [2] after mineralization of the samples (accuracy: 5 %).

2.2.5. Calculation methods

2.2.5.1. Membrane parameters

Membrane flow resistances were calculated using Darcy's law:

$$J = \frac{\Delta P}{\mu \times R_{\text{TOT}}} \quad (1)$$

where J = permeate flux ($\text{m} \cdot \text{s}^{-1}$), ΔP = transmembrane pressure (Pa), μ = permeate vis-

cosity at the filtration temperature (Pa·s), R_{TOT} : resistance (m^{-1}), where $R_{\text{TOT}} = R_{\text{m}}$ (clean membrane resistance) after cleaning and before the run; $R_{\text{m}} + R_{\text{f}}$ (total fouling resistance) during the run, $R_{\text{m}} + R_{\text{if}}$ (irreversible fouling resistance) at the end of the run, after rinsing with 0.2 μm filtered water.

R_{m} and ($R_{\text{m}} + R_{\text{if}}$) were measured using water, whereas ($R_{\text{m}} + R_{\text{f}}$) was measured using the studied fluid, in particular caustic soda solutions. Thus, for comparison, membrane resistance should have been measured using the same solvent, that means caustic soda most of the time here. The problem was that the measurement of R_{if} became insignificant because caustic soda acted as a membrane cleaner.

The VRR quantified the retentate concentration level of totally rejected species:

$$\text{VRR} = \frac{\text{VJP} + \text{VOR} + \text{VJR}}{\text{VOR} + \text{VJR}} \quad (2)$$

where VJP = volume of extracted permeate, VOR = retentate loop volume and VJR = volume of extracted retentate.

2.2.5.2. Pollution parameters

Pollution removal was quantified by the COD reduction, either total or soluble, defined by equation (3):

$$\text{Reduction} = 1 - \frac{C_{\text{p}}}{C_{\text{f}}} \quad (3)$$

where C_{p} = permeate concentration and C_{f} = feed solution concentration.

C_{p} was the concentration of the permeate at a given time, and not the average concentration of the whole permeate (from the beginning of the run). For the cascade operation MF + NF, the reduction was assessed for the whole process: C_{p} was the concentration of the nanofiltrate and C_{f} was the concentration of the MF feed solution.

Reduction was a better parameter than membrane rejection to estimate the process performances when VRR increased, because it compared directly the final product (permeate) to the feed.

The sludge rate for a single operation was equal to the ratio of the retentate volume to the initial volume:

$$\text{Sludge Rate} = \frac{1}{\text{VRR}} \quad (4)$$

Equation (5) [10] gives the sludge rate for the cascade operation MF + NF:

$$\text{Sludge Rate} = \frac{1}{\text{VRR}_{\text{MF}}} + \frac{1}{\text{VRR}_{\text{NF}}} \times \frac{\text{VRR}_{\text{MF}}^{-1}}{\text{VRR}_{\text{MF}}} \quad (5)$$

3. RESULTS

3.1. UF ($300 \text{ kg}\cdot\text{mol}^{-1}$) of different CIP solutions at VRR = 5

Using the procedure at constant $J = 200 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$, six cleaning solutions were filtered: VRR was increased up to 5, then

it was maintained constant during 2 h. Final ΔP (figure 2) depended on the solution and ranged from 0.2 to 2.0 bar. These ΔP were moderate and not dependent on the feed solution COD. Fouling was mostly irreversible: for NaOH solutions, it represented 60 to 100 % of total fouling, and 100 % for HNO_3 solutions. This irreversible fouling was responsible for the difficult cleaning of the membranes, especially after UF of acid solutions. For milk tanker HNO_3 , no irreversible fouling was observed since the CIP solution was nearly new and, in fact, needed no treatment.

As permeate and retentate conductivity values were equal, NaOH and HNO_3 were not rejected. The suspended matter was rejected at more than 99 %: The permeates were clear at the filtration temperature, but coloured. Permeate COD were in the range $0.10\text{--}20.2 \text{ mg}\cdot\text{L}^{-1}$ (table III) and greatly depended on the solution (table I). The total COD reduction was always < 0.5 (table III). It was low for low polluted milk tanker HNO_3 and for the evaporator and higher for the others.

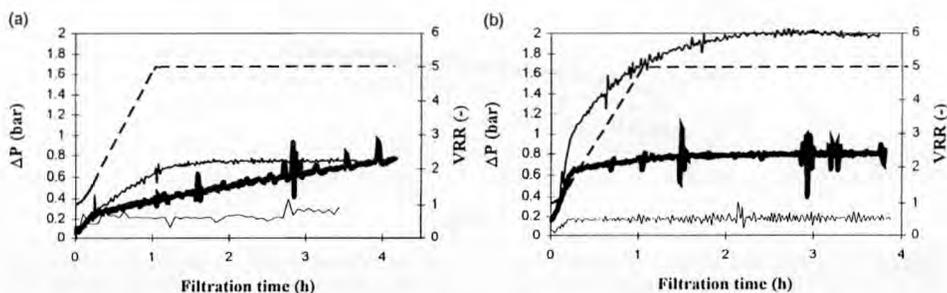


Figure 2. Transmembrane pressure (ΔP) and volume reduction ratio (VRR) versus ultrafiltration ($300 \text{ kg}\cdot\text{mol}^{-1}$) time of industrial cleaning-in-place solutions: [(a) alkaline, $T = 70 \text{ }^\circ\text{C}$; (b) acid, $T = 65 \text{ }^\circ\text{C}$]. For operating conditions, see table II.

VRR: — broken line; milk tanker: — thin line; standardization: — thicker line; evaporator: — thickest line.

Figure 2. Évolution de la pression transmembranaire ΔP , et du facteur de réduction volumique FRV en fonction de la durée de l'ultrafiltration ($300 \text{ kg}\cdot\text{mol}^{-1}$) de solutions industrielles de nettoyage [(a) alcaline, $T = 70 \text{ }^\circ\text{C}$ - (b) acide, $T = 65 \text{ }^\circ\text{C}$]. Conditions opératoires : voir tableau II.

FRV : — ; camions : — ; standardisation : — ; évaporateur : — .

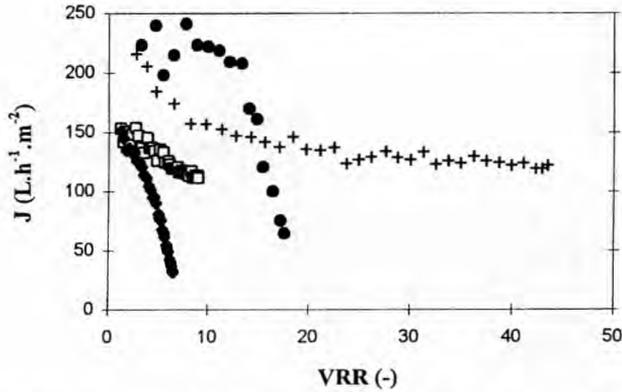


Figure 4. Permeate flux (J) versus volume reduction ratio (VRR) during nanofiltration (NF) (temperature = $70\text{ }^{\circ}\text{C}$, cross-flow velocity = $2.7\text{ m}\cdot\text{s}^{-1}$, ΔP permeate flux = 10 bar) of standardization NaOH: Sol-gel NF: + (solution E, see *table 1*); MPT-34 NF: \square (solution H). Microfiltration MF permeate (cascade): Sol-gel NF: \bullet (solution I); MPT-34 NF: \blacklozenge (solution J).

Figure 4. Densité de flux de perméation J en fonction du facteur de réduction volumique FRV lors de la nanofiltration ($T = 70\text{ }^{\circ}\text{C}$, $v = 2,7\text{ m}\cdot\text{s}^{-1}$, $\Delta P = 10\text{ bar}$) de NaOH standardisation : NF Sol-gel : + (solution E, voir *tableau 1*) ; NF MPT-34 : \square (solution H). Perméat de MF (cascade): NF Sol-gel : \bullet (solution I); NF MPT-34: \blacklozenge (solution J).

($\Delta P = 0.53\text{ bar}$, $R_f/R_m = 1.5$ at $\text{VRR} = 25$). For Sol-gel NF, the flux first decreased, then flattened out (*figure 4*); the same behaviour was expected with MPT-34 NF although high VRR was not reached because of the small membrane area. The Sol-gel NF flux was around $127\text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ at $\text{VRR} = 25$, whatever ΔP (10 and 4 bar) and the MPT-34 NF flux was $112\text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ at $\text{VRR} = 9$. NF fouling can be compared to MF and UF fouling through normalized fouling despite different operating modes (*figure 3*). Normalized fouling resistance increased more or less with VRR, depending on the operation.

Reversible fouling was dominant since irreversible fouling represented less than 9% of the total fouling, except for $0.1\text{ }\mu\text{m}$ MF conducted at $200\text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ (100%) and for Sol-gel NF (solution E, 39%).

From titrations, it was verified that NaOH was not rejected, even with MPT-34 NF membrane which had a low nominal cut-off ($0.2\text{ kg}\cdot\text{mol}^{-1}$). Permeates were clear at $70\text{ }^{\circ}\text{C}$, but only NF permeates were dis-

coloured presumably because of the retention of brown-yellow compounds due to lactose degradation [8].

As suspended matter was totally rejected by any membrane operations, soluble COD reduction was a more relevant parameter than total COD reduction to compare membrane processes (*figure 5a, b*), although total COD reduction is usually used [8, 14, 20]. Soluble COD reduction decreased with increasing VRR, before remaining steady for $300\text{ kg}\cdot\text{mol}^{-1}$ UF and Sol-gel NF for $\text{VRR} \geq 20$. The lower the nominal cut-off, the greater the reduction, except for $15\text{ kg}\cdot\text{mol}^{-1}$ UF, the reduction of which was lower than $300\text{ kg}\cdot\text{mol}^{-1}$ UF when VRR increased. Sol-gel NF yielded different COD reduction depending on the feed solution and the part of irreversible fouling (shown in parentheses): at $\text{VRR} = 30$, it was 0.36 for solution E (39%), and 0.11 and 0.07 only for solutions F and G (5 and 7%, respectively) (same results despite different ΔP). Sol-gel and MPT-34 NF membranes yielded

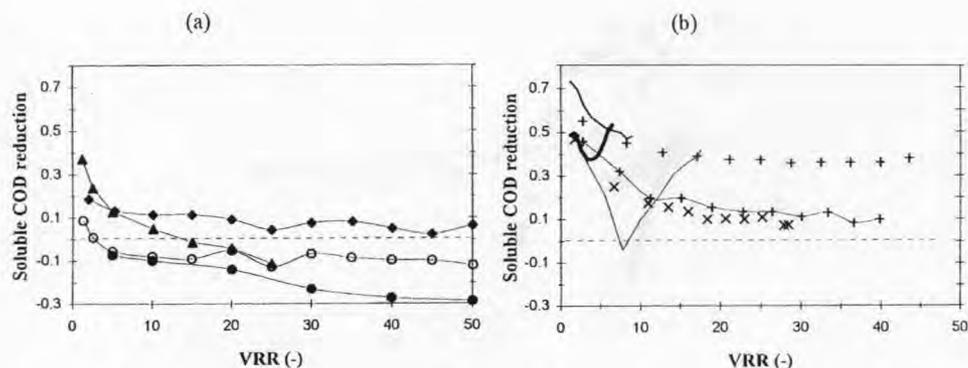


Figure 5. Soluble chemical oxygen demand (COD) reduction versus volume reduction ratio (VRR) during cross-flow filtration of standardization NaOH. For operating conditions, see *table II*. (a) 0.1 μm MF: ● (permeate flux $[J] = 300 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$); ○ ($J = 200 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$); 300 $\text{kg}\cdot\text{mol}^{-1}$ ultrafiltration (UF): ◆; 15 $\text{kg}\cdot\text{mol}^{-1}$ UF: ▲. (b) Sol-gel nanofiltration: transmembrane pressure (ΔP) = 10 bar: + (solution E); —+— (solution F); × ($\Delta P = 4$ bar). MPT-34 NF: —; Sol-gel cascade: —; MPT-34 cascade: —.

Figure 5. Abattement de demande chimique en oxygène (DCO) soluble en fonction du facteur de réduction volumique FRV lors de la filtration tangentielle de NaOH standardisation. Conditions opératoires, voir *tableau II*. (a) MF 0,1 μm : ● ($J = 300 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$); ○ ($J = 200 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$) UF 300 $\text{kg}\cdot\text{mol}^{-1}$: ◆ UF 15 $\text{kg}\cdot\text{mol}^{-1}$: ▲ (b) NF Sol-gel: $\Delta P = 10$ bar: + (solution E); —+— (solution F); × ($\Delta P = 4$ bar) NF MPT-34: — Cascade Sol-gel: — Cascade MPT-34: —.

similar reduction when VRR increased up to 9 (*figure 5b*): both membranes behaved as if they had similar MWCO while filtering alkaline solution. The negative reduction (significant for 0.1 μm MF and for 15 $\text{kg}\cdot\text{mol}^{-1}$ UF at VRR = 25) means that the permeate was enriched with soluble molecules compared to the feed solution. The trends were the same for total COD reduction, but within a higher range: 0.57 (Sol-gel NF) to 0.10 (0.1 μm MF) at VRR = 40.

The total calcium and phosphorus reductions for 0.1 μm MF to MPT-34 NF at high VRR were in the range 0.91–0.99 and 0.57–0.86, respectively. The permeate concentrations at high VRR were low, in the range 1–8 $\text{mg}\cdot\text{kg}^{-1}$ for total calcium and 5–12 $\text{mg}\cdot\text{kg}^{-1}$ for total phosphorus. Calcium and phosphorus were essentially insoluble in the retentate.

3.3. Centrifugation and decantation of standardization NaOH

The total COD reduction ranged from 0.22 to 0.35 for decantation, and 0.26 to 0.36 for centrifugation, on a laboratory scale. Besides, the reduction performed by an industrial centrifuge skimmer working at 80 °C did not exceed 0.04. Furthermore, centrifugation and decantation did not reduce soluble COD.

Membrane operations (UF, NF) had indeed a better performance than centrifugation and decantation. These results are in accordance with Condat-Ouillon [8], who has reported that turbidity reduction after treatment of a dairy alkaline cleaning solution is 0.93 for centrifugation (3 500 $\text{tr}\cdot\text{min}^{-1}$, 15 min, 80 °C), 0.57 for decantation (2 h, 80 °C), and 0.97 for dead-end filtration (polytetrafluoroethylene membrane,

pore size ranging from 0.2 to 0.05 μm , 80 °C). Thus, centrifugation and decantation are not suitable for CIP solution treatment, but they can be included as a pre-treatment that is less efficient than MF for particle removal.

3.4. Cascade MF + NF

The cascade flux and soluble COD reduction were compared to those of single NF (figures 4, 5b). At low VRR, the flux was higher for MF permeate (cascade operation), whatever the NF membrane (figure 4), but it decreased so sharply that the breakpoint could be named critical VRR (12 for Sol-gel NF and 5.2 for MPT-34 NF). Irreversible fouling for Sol-gel NF represented 5 to 39 % of the total fouling with standardization NaOH at VRR = 30–40, and 68 % with MF permeate at VRR = 18.

For the cascade operation, the soluble COD reduction variation was typically U-shaped with a sharp decrease and a minimum observed at VRR close to the critical VRR (VRR \approx 7–8 with Sol-gel NF, and 4 with MPT-34 NF) (figure 5b). Reduction was less for the cascade operation than for single NF, except at high VRR when the cascade could no longer be performed efficiently because of the vanishing flux.

The ratio of the cascade sludge rate to the single NF one was 1.3 for Sol-gel NF and 1.1 for MPT-34 NF (equations 4 and 5), so the cascade MF + NF produced more sludge than single NF.

4. DISCUSSION

The discussion focuses essentially on membrane processes since decantation and centrifugation have been shown to be far less efficient.

4.1. Heterogeneity of cleaning solutions and process performances

Three hundred $\text{kg}\cdot\text{mol}^{-1}$ UF performances were not correlated to global ana-

lytical characteristics of CIP solutions such as COD or SM. It is linked to the chemical nature of contaminants [14]. Performances obtained with 0.1 μm MF of different kinds of alkaline cleaning solutions varies from 0.10 to 0.75 for total COD reduction and from 200 to 1 200 $\text{L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ for J (VRR = 1, $\Delta P = 2$ bar, $T = 50$ °C, 6 h filtration) [14]. Cleaning solution from an evaporator CIP contains hydrolyzed nitrogen compounds, which are easily transmitted through the membrane (especially MF and UF) [14]. COD reduction is greater and J is lower when the cleaned equipment processed fat-containing dairy products [14]. The same trends were observed in our work with 300 $\text{kg}\cdot\text{mol}^{-1}$ UF. Thus, the recycling process is to be optimized for each type of cleaning solutions.

Besides, for the same CIP system (standardization NaOH) analytical characteristics vary from one day to another. Filtration performances (ΔP for 15 $\text{kg}\cdot\text{mol}^{-1}$ UF, COD reduction for Sol-gel NF) also depended on the feed solution. Condat-Ouillon [8] has shown the consequences of the cleaning solution 'aging': COD reduction performed with 0.1 μm MF (VRR = 1) decreases from 0.71 with a dairy alkaline cleaning solution collected after the first cleaning step to 0.40 only after a 2-day storage. This decrease of permeate quality is assumed to be due to the presence of new smaller molecules coming from fat saponification, protein hydrolysis and depolymerization. Condat-Ouillon [8] recommends that recovery should be done as soon as possible to avoid this hydrolysis of compounds. Thus, the recycling process has to cope with the feed solution variation.

In-depth knowledge of the CIP solutions is needed to select the convenient membrane operation and to understand mechanisms of membrane fouling and retention. This involves not only global pollution concentrations such as COD (useful to figure membrane performances) but also particle and soluble molecule sizes (size exclusion

chromatography [10]), nature of contaminants and so on.

4.2. Increasing VRR induces bottlenecks in the recovery process

One of the aims of the process is to recover as much efficient cleaning solution as possible, and thus as less sludge volume as possible. Thus, VRR must be high. In this work, the achieved VRR was 50 (98 % recovery, 2 % sludge). According to Henck [14], at least VRR = 50 should be aimed at for an industrial application, and according to Condat-Ouillon [8], VRR = 325 (0.31 % sludge) is more than enough. Thus, VRR around 100 (99 % recovery, 1 % sludge) would be presumably appropriate. As far as the whole CIP system is concerned, the recovery of solution is actually significantly lower than 90 % due to losses of solution during cleaning [23]. Assuming a regular fouling increase with VRR for our filtrations, VRR = 100 would be achieved with acceptable final conditions: $\Delta P \leq 1.6$ bar for 0.1 μm MF, $\Delta P \leq 6.3$ bar for both UFs, and $J > 100 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ for both NFs.

The increase in VRR had two consequences: an increase in fouling and a decrease in pollution reduction, except for Sol-gel NF where both parameters tended to stabilize for VRR ≥ 20 . These increases can be explained by the increasing concentration in the retentate side. Condat-Ouillon [8] also observes that COD reduction decreases from 0.71 to 0.46 during 0.1 μm MF of dairy alkaline cleaning solution for VRR ranging from 1 to 325. It is assumed that concentration polarization increases with the retentate concentration, and so does the permeate concentration. Hydrolysis of molecules due to the residence time and temperature is also reported [8, 14]. The problem is to assess the limit not to exceed: the measurement of permeate cleaning efficiency could be a proper criterion but the methodology remains an open question [14].

4.3. Fouling mechanisms

Fouling increased differently with VRR according to the membrane operation. Fouling increased faster for MF ($J = 300 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$) than for MF ($J = 200 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$), UF and NF (figure 3). First, the solution to be filtered contained a group of particles with an average diameter (0.088 μm) close to the MF average pore diameter, which made it likely a mechanism of pore blocking. Then, the solution contained two populations of particles; the second population had a diameter far larger than the first one. This leads to a porous cake, quickly fouled by small particles, and to pore blocking; fouling is thus high [7]. MF conducted at $J = 200 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ did not show the same behaviour: since v (thus wall shear stress) was the same for both MF runs, the ratio of flux to wall shear stress (J/τ_w) was smaller. It is assumed to be below the critical value of the ratio for the system [5, 21]. Thus, a steady state was observed unlike the run at $J = 300 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$.

For UF and NF, all particles participated in the cake formation as particle size was larger than pore size. The deposit acted as a pre-filter which protected the membrane: fouling (in particular irreversible) of NF membrane was indeed moderate with solution containing particles, and increased sharply with the 0.1 μm MF permeate without particles. Furthermore, the dispersed phase (particles here) is detrimental to concentration polarization [25]. Thus, adsorption is less likely to occur with particles because adsorbent concentrations are lower at the membrane: irreversible fouling is reduced.

While increasing VRR, fouling did not increase much in NF, conducted at constant ΔP . Pritchard [26], while microfiltering baker yeast (far larger than pore size) with the same conducting mode, observed three steps when VRR increases: first the flux declines, then it remains steady, and finally, it drops to 0. Only the first two steps were observed during our NF of standardization

NaOH, presumably because VRR was too low to observe the last step. It is likely that a membrane process conducted at constant ΔP has to be operated below a critical value of VRR.

To summarize, fouling mechanisms depend on the VRR, the membrane cut-off, the feed solution and the conducting mode (constant $J/\Delta P$).

4.4. Selection of membrane operation

As expected, the lower the membrane cut-off, the higher the COD reduction, except for both 300 and 15 $\text{kg}\cdot\text{mol}^{-1}$ UF. MF only rejected particles, and even led to an enrichment of the permeate in soluble COD, likely due to concentration polarization and to the solubilization of some suspended matter. UF membranes are not able to reject short-chained peptides, amino acids, soaps, lactose by-products [14]. NF was the most efficient process to reduce soluble COD.

The hydraulic performances of membrane operations were difficult to compare since they were conducted at either different constant flux (MF, UF) or constant transmembrane pressure (NF). Fouling was moderate for all processes and tended to stabilize particularly for Sol-gel NF. The results of this work sometimes differed from the literature data because the feed solutions were different. For 0.1 μm MF, the transmembrane pressure is about 0.5 bar at $J = 1\ 000\ \text{L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ (VRR = 45) [8]. This is far better than our results, which can be explained mainly by the low pollution load of the solution (COD = 0.175 $\text{g}\cdot\text{L}^{-1}$ versus COD = 3.9 $\text{g}\cdot\text{L}^{-1}$ for our study). Alkasave system (MPT-34 NF) is a batch concentration process ($T = 65 - 70\ ^\circ\text{C}$, $\Delta P = 14\ \text{bar}$, VRR not given) treating alkaline solutions [20]. The flux is around $100\ \text{L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$, and decreases after 6 h of filtration. This system is cleaned by a single water flush, which confirms that there is no significant irreversible fouling for this NF membrane.

Thus, NF was a proper process to recycle standardization NaOH: it did not reject NaOH, it was the most efficient process to remove soluble COD (pollution load), total calcium and total phosphorus (minerals), and the flux remained satisfactory (over $100\ \text{L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ at $70\ ^\circ\text{C}$) even when operating at low transmembrane pressure (4 bar) for Sol-gel NF. A feed pretreatment by MF did not enhance NF performances. Although the advantages of a MF pretreatment step before NF or reverse osmosis are often reported in the literature [11, 22], Nuortila-Jokinen and Nyström [24] observed that pretreating a paper mill effluent by UF decreases the reductions performed by the spiral-wound NF step. In our work, a deterioration of the whole NF performances was observed when VRR increased.

It remains to assess the level of permeate quality that should be aimed at to obtain an efficient permeate for the cleaning of a stainless-steel dairy plant, even after numerous recycling runs. A threshold concerning global parameters (COD, suspended matter, etc.) or more likely specific concentrations (fatty acids, peptides, amino acids, etc.) has to be defined. Surface tension could be a well-adapted criterion to evaluate cleaning efficiency. Indeed, surfactants formed in situ by protein and fat hydrolysis during enzymatic cleaning are reported to participate in the cleaning process [12]. The permeate quality threshold will help to select a convenient recovery process.

Integration and sizing of the recycling process into the CIP system should be considered and the economic point of view must also be taken into account in the selection of the recovery process: investment and operating costs, induced savings (water, chemicals, energy, waste water treatment) [10].

5. CONCLUSION

Membrane performances, COD reduction and flux, depended on origin, history

and composition of the CIP solution. The recovery of different (acid, alkaline) CIP solutions was performed efficiently by using UF (MWCO = 300 kg·mol⁻¹). Besides, membrane processes are more efficient than centrifugation or decantation to recover one type of alkaline solution (standardization NaOH). To recover as much caustic soda and to yield as less sludge volume as possible, the VRR should be increased to at least 100, which means a sludge rate of 1 % (in this study, VRR was ≤ 50). A balance must be found between the increase in VRR and its consequences: an increase in fouling and in soluble organic content of the permeate. From the present work, a proper process was NF, even at low transmembrane pressure for inorganic NF: the flux was reasonable, soluble COD was significantly reduced, and flux and soluble COD reduction leveled off even when VRR increased. Adding a microfiltration pretreatment step deteriorated NF performances; the reason for this phenomenon has to be investigated. The recycling process must be optimized for each CIP solution, because membrane performances varied with the nature of contaminants.

ACKNOWLEDGEMENTS

This study was funded by ADEME (Agence de l'environnement et la maîtrise de l'énergie), BBA (Bretagne – biotechnologies – alimentaires), and the Brittany region. We thank BBA for scientific support, J.P. Ecalard, J.J. Maugas, J. Le Saouter, M. Pelleau and J.C. Desbois for valuable discussions, as well as Besnier-Bridel dairy (Retiers, France) for providing cleaning solutions and Tech-Sep (Miribel, France) for providing membranes. We also thank E. Boyaval for her contribution to analytical characterizations, and M. Chevrel and L. Burel (University of Rennes-I) for their collaboration in particle size characterization.

REFERENCES

[1] Afnor, Détermination des matières en suspension, French standard NF T 90-105, Paris, 1978.

- [2] Afnor, Détermination de la teneur en phosphore total – Méthode par spectrométrie d'absorption moléculaire, French standard NF V 04-284, Paris, 1985.
- [3] Afnor, Détermination de la demande chimique en oxygène, French standard NF T 90-101, Paris, 1988.
- [4] Barnier H., Lefebvre N., Contrôle d'un taux de rejet macromoléculaire en ultrafiltration tangentielle, Internal technical note n° 92-128, CEN Cadarache, DSD / SEP / SEATN, Saint-Paul-les-Durance, France, 1992.
- [5] Blake N.J., Cumming I.W., Streat M., Prediction of steady state cross-flow filtration using a force balance model, *J. Membrane Sci.* 68 (1992) 205-216.
- [6] Buson C., Impact sur les eaux : approche globale amont aval de l'impact des eaux résiduaires, journée d'étude association SESIL – IESIEL / Institut supérieur du lait : protection de l'environnement, nouveau défi de l'entreprise, 9 décembre 1993, 10 p.
- [7] Chang J.S., Tsai L.J., Vigneswaran S., Experimental investigation of the effect of particle size distribution of suspended particles in microfiltration, *Water Sci. Technol.* 34 (9) (1996) 133-140.
- [8] Condat-Ouillon C., Étude du comportement des constituants laitiers en milieu fortement sodique et leurs interactions en filtration sur membrane : application à la régénération par filtration tangentielle des solutions alcalines de NEP de l'industrie laitière, Ph.D. thesis, Institut national polytechnique de Toulouse, France, 1995.
- [9] Daufin G., Radenac J.F., Gésan G., Kervé F.L., Le Berre O., Michel F., Merin U., A novel rig design for ultrafiltration and microfiltration experiments, *Separ. Sci. Technol.* 28 (1993) 2365-2642.
- [10] Dresch M., Procédés à membrane de régénération des solutions de nettoyage de l'industrie laitière, Ph.D. thesis, ENSA, Rennes, France, 1998.
- [11] Ebrahim S., Bou-Hamed S., Abdel-Jawad M., Burney N., Microfiltration system as a pre-treatment for RO units: technical and economic assessment, *Desalination* 109 (1997) 165-175.
- [12] Friis A., Simon M., Emborg C., Olsen H.S., Enzyme cleaning of milk deposit in heat exchangers, in: *Proc. Fouling and Cleaning in Food Processing*, Cambridge, UK, 6-8 April 1998, 1998.
- [13] Garem A., Daufin G., Maubois J.L., Leonil J., Selective separation of amino-acids with a charged inorganic nanofiltration membrane: effect of physicochemical parameters on selectivity, *Biotechnol. Bioeng.* 54 (1997) 291-300.
- [14] Henck M.A., Recycling of caustic cleaning solutions using cross-flow filtration in the dairy industry, Ph.D. thesis, University of Zurich, Switzerland (English translation), 1993.

- [15] Horton B.S., Water, chemical and brine recycle or reuse – Applying membrane processes, *Aust. J. Dairy Technol.* 52 (1997) 68–70.
- [16] International Dairy Federation, Design and use of CIP systems in the dairy industry, *Bull. Int. Dairy Fed.* 117 (1979) 1–76.
- [17] International Dairy Federation, Nutrient sources in dairy effluents (phosphorus and nitrogen). Elimination & treatment, *Bull. Int. Dairy Fed.* 195 (1985) 1–8.
- [18] International Dairy Federation, Environmental influence of chemicals used in the dairy industry which can enter dairy waste water, *Bull. Int. Dairy Fed.* 288 (1993) 17–31.
- [19] Jung C., The recovery of washing caustic from CIP waste water, *Eur. Dairy Mag.* 5 (1996) 32–34.
- [20] Kviat H., Pasilac Alkasave – Recovery of CIP chemicals by membrane filtration, Application note n° TI.ALKA.UK.10.95, APV Anhydro AS membrane filtration, Silkeborg, Denmark, 1995.
- [21] Le Berre O., Daufin G., Skim milk crossflow filtration performance versus permeation flux to wall shear stress ratio, *J. Membrane Sci.* 117 (1996) 261–270.
- [22] Lee S.H., Kim J.Y., Lee C.H., Lee M.C., Chung K.J., Flux improvement in nanofiltration through a hybrid process with microfiltration, in: *Proceedings Euromembrane'95*, Bath, UK, 18–20 September, vol. 1, 1995, pp. 525–528.
- [23] Mawson A.J., Regeneration of cleaning and processing solutions, *Trends Food Sci. Technol.* 8 (1997) 7–13.
- [24] Nuortila-Jokinen J., Nyström M., Comparison of membrane separation processes in the internal purification of paper mill water, *J. Membrane Sci.* 119 (1996) 99–115.
- [25] Parvatiyar M.G., Govind R., Effect of dispersed phase on reducing concentration polarization, *J. Membrane Sci.* 105 (1995) 187–201.
- [26] Pritchard M., The influence of rheology upon mass transfer in crossflow membrane filtration, PhD thesis, University of Bath, UK, 1990.
- [27] Romney A.J.D., CIP: cleaning in place, 2nd edn., *The Society of Dairy Technology*, Cambridge, Shire, 1990.