

Short communication

Comparative study of different nanofiltration and reverse osmosis membranes for dairy effluent treatment by dead-end filtration

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Abstract

The process waters of dairy industry issued from the starting, the equilibrating, the interrupting and the rinsing steps of the different plant units contribute, besides the cleaning in place, to the effluent production. Their treatment by membrane aimed to concentrate waste organic matter and to use permeate as disposable water for reuse, lowering both the load and volume effluent and the total water consumption of dairy plants.

The present work was focused on the concentration of 1/3 diluted skimmed milk (chemical oxygen demand, COD \approx 36 g O₂/L) to about 1/1 milk (volume reduction factor, VRF 3), with nine nanofiltration and reverse osmosis membranes by dead-end filtration. COD was the selected criterion for permeate quality, i.e. rejection of organic milk components assigned to lactose. High COD rejection (>99%) was achieved whatever the membrane and the feed concentration. Rejections of divalent cations >90% were too high for being in accordance with negative rejection of chloride at VRF 3 using NF membranes. The negatively charged proteins at pH 6.6 were likely entrapped in a soft gel which was observed at the end of the run of dead-end filtration. This gel was reversibly removed by a flush with tap water. Dead-end filtration appears as an useful tool to show the relative content of permeate and the occurrence of a limiting flux upon concentration involving a gel formation.

At the end of run (VRF 3) with an initial highly charged feed, COD of permeate was always far away the quality of water for human consumption (total organic carbon, TOC < 2 mg/L) but RO permeate can be released as waste. Water quality close to vapour condensates, issued from milk and whey drying steps, is needed for reuse in boiler feed; it should be likely reached with an RO + RO cascade and possibly with a single RO with a low charged feed.

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1. Introduction

The dairy industry generates a large amount of effluent ranging from 0.2 to 10 L per L of processed milk. The process waters used during the starting, equilibrating, interrupting and rinsing steps of the different units contribute to the effluent production and to the losses of dairy matter. In a global context of water resource availability and cost increasing, the treatment of the process water to produce purified water for reuse could lower the effluent volume and the total water consumption of the dairy factory. Several membrane operations have been proposed for the treatment of dairy effluents:

one-stage operations like ultrafiltration, UF [1], nanofiltration, NF [2], reverse osmosis, RO [3] or two-stage operations like UF + RO [4], NF + NF [5] and RO + RO [2]. It has been shown for low loaded process water (as vapour condensate) that membrane, namely NF and RO, is a convenient way for the production of water reusable in dairy plants [6]. Although the recycled water characteristics are very close to those for human consumption, the permeate cannot be used in direct contact with the dairy products according to French drinking water regulations mainly based on the origin of water. Possible remaining reuses are boiler feed water, cleaning in place water and cooling water. In the case of boiler feed water, requirements are more drastic with: Ca²⁺ < 0.4 mg/L, chemical oxygen demand, COD < 10 mg O₂/L and conductivity < 40 μ S/cm [6].

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The aim was to perform both a concentration step and a reusable permeate production by dead-end filtration for the choice of appropriated NF and RO membranes. Dead-end filtration runs, in spite of fouling conditions quite different from crossflow operations, are able to provide data about selectivity (retentate and permeate contents) close to those obtained by using of spiral wound-modules performed at a more high concentration ratio.

The feed selected was high loaded 1/3 diluted skimmed milk (COD \approx 36 g O₂/L) in order to avoid variability of industrial process water in this preliminary step and to concentrate to about 1/1 milk (volume reduction factor, VRF 3). COD was the selected criterion for permeate quality, i.e. rejection of organic milk components. Conductivity of the solution was measured as an indicator of the inorganic matter level. Finally cations and anions rejections were determined in order to provide a good characterisation of reusable water content after membrane operation for a high loaded effluent.

2. Materials and methods

2.1. Filtration batch cell

Filtration experiments were performed in a stainless steel cylindrical batch cell located on an anti-vibratory table in a temperature-controlled room at 25 °C. The 300 cm³ cell was manufactured by Reaktion (Le Rheu, France) according to our specifications. The working pressure in the cell, applied by a nitrogen tank, was 15 bar for NF membranes (including Koch TFC ULP) and 25 bar for RO membranes. The membrane sheet area was 44.2 cm². Stirring of the solution with a four blades stirrer, checked with an optical cell, was set at 100 rpm.

2.2. Membranes

Nine membranes from different companies were used. Deionised water fluxes (at 25 °C) and other membrane characteristics are given in Table 1. Membranes are thin-film com-

posite (TFC) with polyamide rejecting surface on polysulfone support or polysulfone support and polyester matrix. Before first use, each membrane was wetted out by immersing in methanol for 30 s and by running at a pressure of 25 bar for 1 h in pure water.

2.3. Dairy process water composition

The industrial effluent (dairy process water) is a various composition mixture of water and milk without chemicals. The aim of the present study was to compare different membranes, so this comparison could be valid only if the feed composition remains constant. Therefore we chose a dairy effluent model solution which is assumed to be representative of the industrial process water: skimmed milk diluted with water (dilution 1/3). The skimmed milk solution, at 31 g/L dry matter content and pH 6.6, was prepared with “low heat” bovine skimmed milk powder (provided by LRTL-INRA, Rennes, France [7]).

2.4. Filtration experiments

The initial feed volume was 300 cm³. During filtration, permeate flow rate evolution as a function of time was monitored by weighting and permeate samples were taken at regular intervals for analysis. The filtration time was between 8 and 9 h.

The volume reduction factor (VRF) was calculated by

$$\text{VRF} = \frac{V_0}{V_R(t)} = \frac{V_0}{V_0 - V_P(t)} \quad (1)$$

where V_0 is the initial feed volume (300 cm³), $V_R(t)$ and $V_P(t)$ the retentate and permeate volumes at t time, respectively.

For ions, lactose and COD, the observed rejection of the membrane was obtained by the following equation:

$$R(\%) = \left(1 - \frac{C_P}{C_R}\right) \times 100 \quad (2)$$

where C_P and C_R are permeate and retentate concentration, respectively.

Table 1

Nanofiltration (NF) and reverse osmosis (RO) membrane characteristics (MWCO, material, maximum T (usually for spiral-wound elements) according to manufacturers data)

Supplier	Type	Reference	MWCO (g mol ⁻¹)	Material; maximum T (°C)	Pure water flux (L h ⁻¹ m ⁻² at 25 °C, 15 bar)
Osmonics (Le Mee sur Seine, France)	NF	Desal 5 DK	150–300	Polyamide/polysulfone; 50 °C	77
Osmonics (Le Mee sur Seine, France)	NF	Desal 5 DL	150–300	Polyamide/polysulfone; 50 °C	109
Filmtec (Dow, Boulogne, France)	NF	NF45	200	Polyamide/polysulfone/polyester; 45 °C	85
Filmtec (DSS, Silkeborg Denmark)	NF	NF	200	Polyamide/polysulfone/polyester; 45 °C	106
Koch-fluid systems (Villeurbanne, France)	NF	TFC S	–	Polyamide/polysulfone/polyester; 45 °C	96
Koch-fluid systems (Villeurbanne, France)	Ultra-low pressure RO	TFC ULP	–	Composite polyamide; 45 °C	92
Osmonics (Le Mee sur Seine, France)	RO	Desal 3 SF	–	Polyamide/polysulfone; 50 °C	25
Koch-fluid systems (Villeurbanne, France)	RO	TFC HR	–	Composite polyamide; 45 °C	43
Filmtec (DSS, Silkeborg Denmark)	RO	BW 30	–	Composite polyamide; 45 °C	40

2.5. Analysis

During experiments, feed, retentate and permeate were sampled and assessed for COD, lactose, conductivity, anions and cations.

COD was determined with rapid test tubes (oxidation with potassium dichromate/sulfuric acid/silver sulfate at 148 °C, accuracy $\pm 3\%$) and photometric measurement (Nanocolor 300D) provided by Macherey Nagel (Hoerd, France). Lactose concentration was determined spectrophotometrically at 488 nm by the phenol–sulfuric acid method with an accuracy of 3% [8]. Cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) concentrations were determined by atomic absorption (Varian Spectra 300) and anions (phosphate, citrate, Cl^-) concentrations by ion chromatography (DIONEX DX 500, Jouy-en-Josas, France) with an accuracy of 1% for all ions, according to the method previously described [9]. The conductivity was measured by a conductivitymeter (Tacussel Electronique CDM 210) from Radiometer Analytical (Villeurbanne, France) with an accuracy of 2%.

3. Results and discussion

3.1. Permeate flux

The dead-end filtration of the feed solution (one-third diluted skimmed milk) was performed with nine membranes in the continuous concentration mode from VRF 1 to about VRF 3 (experiments were duplicated for reproducibility). At the beginning of the filtration, permeate flux decreased sharply (Fig. 1). In spite of initial pure water fluxes in the ratio of 1–4

(Table 1), permeate flux of NF membranes ranged within $3.5\text{--}5\text{ L h}^{-1}\text{ m}^{-2}$ at transmembrane pressure, TMP = 15 bar and VRF about 3. For RO membranes, permeate flux was observed to decrease down to $3.5\text{--}4\text{ L h}^{-1}\text{ m}^{-2}$ at TMP = 25 bar and VRF about 3. Similar fluxes were previously observed using RO membranes with whole milk and skimmed milk [3]. For all membranes tested, a soft white gel deposit was observed on the membrane surface at the end of the run. Determination of the concentration gel was meaningless for this multicomponent solution since many components (caseins, whey proteins, lactose mainly) could be involved in the gel formation from our point of view. This dynamic membrane was the active layer leading to limiting flux conditions.

However, the gel deposit was successfully removed by a flush with tap water (after removal of the top of the cell, the membrane remaining in place at the bottom of the cell). Rinsing with deionised water usually at 25 °C (in a few cases up to 45 or 50 °C according to manufacturer data) was sufficient to restore the original water flux of the clean membrane. Accordingly, it can be concluded that fouling (in a dead-end filtration cell) is mainly reversible. This procedure is not yet applicable to plate and frame and spiral-wound membranes where a crossflow cleaning with acid and base cleaning solutions is the most common method to remove fouling compounds (i.e. gel deposit).

3.2. COD and lactose rejection

Performance of the different membranes, with the aim of specific reuse of water (permeate), was focused on permeate COD and its comparison to threshold COD of the target

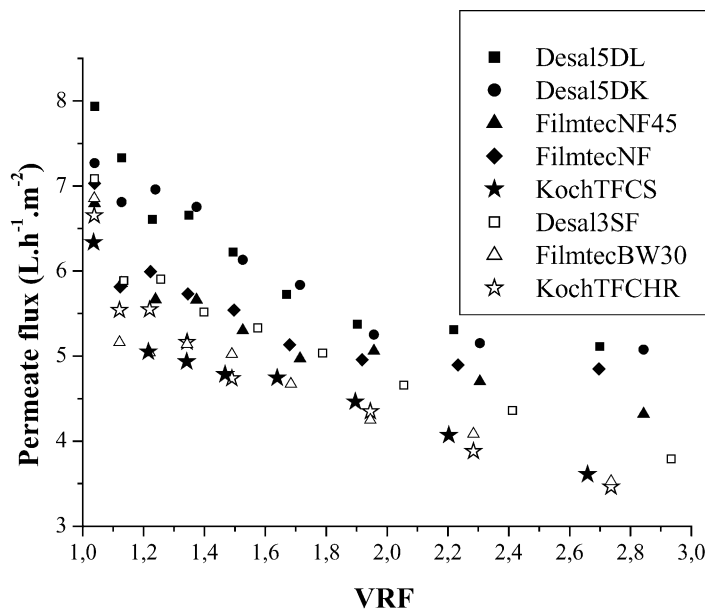


Fig. 1. Permeate flux vs. VRF during 1/3 diluted skimmed milk dead-end filtration with NF (solid symbols) and RO membranes (open symbols) (25 °C, 15 bar (NF) and 25 bar (RO), stirring velocity: 100 rpm).

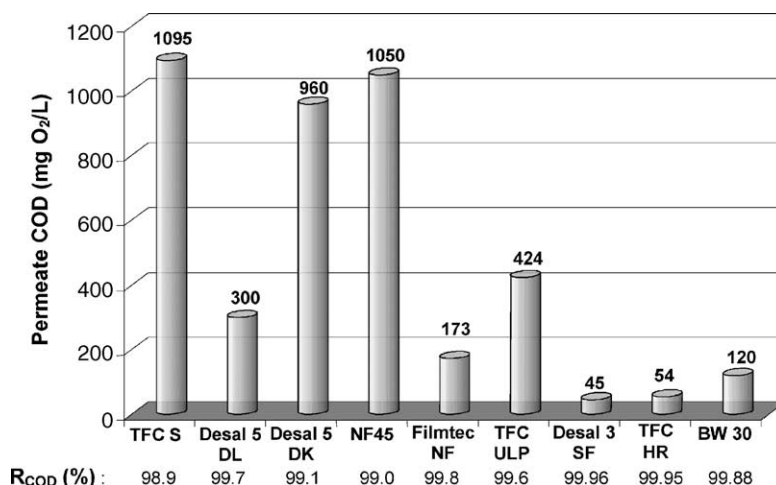


Fig. 2. Permeate COD and COD rejection at VRF about 3 for NF and RO membranes during 1/3 diluted skimmed milk dead-end filtration (25 °C, 15 bar (NF + TFC ULP) and 25 bar (RO), stirring velocity: 100 rpm).

reuses:

- requirements for boiler feed water: COD < 10 mg O₂/L [6],
- water for human consumption with French regulations: KMnO₄ oxidability < 5 mg O₂/L, total organic carbon, TOC < 2 mg/L.

It must be outlined that the dairy effluent model feed was highly loaded with COD ranging from 36 g/L in feed solution at VRF 1 to about 110 g/L at VRF 3 at the end of the concentration run.

Fig. 2 shows that, for NF membranes, permeate COD at VRF 3 ranged from 1000 mg O₂/L to 173–300 mg O₂/L for the best ones (Filmtec NF, Desal5 DL). In this application, the criterion for NF membrane selection is the highest COD rejection. For RO membranes, permeate COD complied easily with authorised level of wastewater in natural medium (COD < 125 mg O₂/L), except with the TFC ULP membrane. Both Desal3 SF and TFC HR membranes seemed to be suitable for this application. For all membranes tested, COD levels in the permeate were always significantly higher than the threshold acceptable for human consumption water. However, RO membranes keep, in a single step, a water content with a COD level allowing its rejection in the natural medium.

Single-stage membrane process (NF or RO) is therefore insufficient to treat highly loaded dairy effluent and to pro-

duce low COD reusable water. Only a two-stage filtration treatment (very likely NF + RO or RO + RO) would be able to achieve this goal.

As lactose is involved in COD of milk, its concentration in permeates is shown in Table 2 for some experiments. Lactose rejection was ranging between 98.2 and 99.9%. The following linear correlation between concentration and COD of lactose diluted with water was experimentally established:

$$\text{COD}_{\text{lactose}} (\text{mg O}_2/\text{L}) = 1.1 C_{\text{lactose}} (\text{mg/L}) \quad (3)$$

Using Eq. (3), we calculated lactose contribution (COD_{lactose}) to the total COD of permeate (Table 2). The ratio COD_{lactose}/COD_{total} was higher for RO permeates (~97%) than those obtained for NF (≤94%).

This result agrees with feed solution content since lactose concentration in the feed solution is about two orders of magnitude higher than those of the other milk organic compounds (citrate, urea, organic acids) of molecular weight similar to the cut-off of the NF membranes. So it can be concluded that selection of membrane based on its permeate COD performance is in fact related to its lactose rejection.

Additional analysis showed that only traces of citrate were observed in the permeate. In fact, citrate is not in a free state in milk solution [8] but likely bound to Ca²⁺, Mg²⁺ or micellar casein. Its resulting size leads to the observed high rejection (>99.9%).

Table 2

COD and lactose concentration in permeate, COD due to lactose and COD_{lactose}/COD_{total} ratio calculated for different membranes at VRF close to 3

Membrane	Permeate COD (=COD _{total}) (mg/L)	Lactose concentration in the permeate (mg/L)	Calculated COD due to lactose (=COD _{lactose}) (mg/L)	COD _{lactose} /COD _{total} (%)
NF45	1050	900	990	94
TFC S	1095	888	977	89
TFC HR	54	48	53	97
BW30	120	106	117	98

Table 3
Permeate concentration in monovalent ion at VRF close to 3 for different NF and RO membranes

	Na ⁺ (mg/L)	K ⁺ (mg/L)	Cl ⁻ (mg/L)
Desal 5 DL	83	340	480
Desal 5 DK	92	410	460
NF45	105	440	430
Filmtec NF	100	350	440
TFC S	57	220	215
Desal 3 SF	16	55	79
TFC HR	10	31	28
BW30	14	66	54

3.3. Milk anions and cations rejection

Conductivity measurements of permeate and retentate samples allowed the estimation of ions rejection. For NF membranes, conductivity rejection was low (33–80%) and permeate conductivity at VRF close to 3 ranged from 1000 to 1900 $\mu\text{S}/\text{cm}$. RO membranes had better conductivity rejection (around 96%) as expected and permeate conductivity at VRF about 3 was between 130 and 300 $\mu\text{S}/\text{cm}$. For NF and RO, the conductivity obtained in the permeate solution do not comply with requirements for reuse as boiler feed water (<40 $\mu\text{S}/\text{cm}$ [6]).

NF membranes, except TFC S, had similar permeate concentration in monovalent ions (Na, K, Cl) (Table 3). The monovalent ionic content of permeate with TFC S membrane was intermediate between NF and RO membranes in agreement with data for the filtration of paper mill effluent [10]. As expected, RO membranes showed the best permeate rejection of monovalent ions (Table 4). Rejection of cations whatever the valence was between 96 and 99.9%, that of Cl⁻ was higher than 94% and those of phosphate and citrate higher than 99.8%.

In NF, Na⁺ and K⁺ rejections were between 50 and 84% and Cl⁻ rejection was negative in three cases (–26 to –80%) in order to ensure the electroneutrality of the permeate in accordance with co-ion exclusion [11]. Citrate was totally rejected (>99.9%) and phosphate rejection was around 93%. Multivalent cations rejection was high: 99.0–99.9% for Ca²⁺ and 97.4–99.4% for Mg²⁺, although their transmission could be theoretically lowered through dynamic NF membranes

Table 4
Skimmed milk ion rejections at VRF close to 3 for different NF and RO membranes

Membrane	Rejection (%)						
	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Phosphate	Citrate	Cl ⁻
Desal 5 DL	69	68	99.9	99.4	92.4	>99.9	–80
Desal 5 DK	68	62	99.0	97.4	–	–	–
NF45	52	58	99.3	99.1	–	–	–28.7
Filmtec NF	49	65	99.3	97.7	93.0	–	–26.0
TFC S	84	80	99.5	98.9	–	–	77.8
Desal 3 SF	96.4	96.8	99.8	99.6	99.6	100	93.8
TFC HR	97.5	98.2	99.9	99.9	100	–	97.6
BW30	96.4	96.1	99.9	99.7	99.8	–	94.9

(accounting for negative charge of proteins involved in fouling).

In fact, only a minor part of Ca²⁺ and Mg²⁺ cations are in a free state in the feed solution as they are mainly entrapped in micellar caseins or bound to citrate and phosphate ions. Micellar casein is totally retained and compounds with citrate and phosphate of higher molecular weight than free Ca²⁺ and Mg²⁺ are more rejected by these membranes. Only free Ca²⁺ and Mg²⁺ are expected to be in the permeate stream and the rejection of divalent cations, using the expected free ions in the retentate side of NF membrane, was about 90% only.

Comparison with water reused in boiler feed [6,12] showed that concentrations of some monovalent ions (K⁺, Cl⁻) were higher as well as those of divalent Ca²⁺ and phosphate despite their high observed rejections with NF and RO membranes.

4. Conclusion

Recovery of milk components (reuse outside the scope of this study) and production of water of quality high enough to be reused in the dairy plants were the targets of the process water treatment. This study was focused on selection of NF and RO membranes during a concentration mode by dead-end filtration.

For a high loaded skimmed milk used as process water, both rejections of lactose, COD and multivalent ions with most NF and RO membranes were >94% during a concentration step by dead-end filtration. COD, involving lactose, was a valuable criterion for selection of NF and RO membranes. Rejections of divalent cations using NF membranes were unexpectedly high (>90%) for counter-ions in accordance with negative rejection of chloride (co-ion) only observed at VRF 3, balanced with monovalent cations. The negatively charged proteins at pH 6.6, acting as a dynamic membrane, were likely entrapped in a soft gel which was observed at the end of the run of dead-end filtrations. This gel was reversibly removed by a flush with tap water under pressure. Dead-end filtration appears as a useful tool to show the relative content of permeate and the occurrence of a limiting flux upon concentration involving a gel formation.

However, at end of run (VRF 3), COD concentrations in permeate (mainly due to lactose) were many times higher than the limiting value for human consumption water because of the high initial load of the effluent (COD \approx 36 g/L). Water quality, close to vapour condensates issued from milk and whey drying steps, is needed for reuse in boiler feed; it should be likely reached with an RO + RO cascade or possibly with a single RO with a low charged feed.

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