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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 ≈ 36 g O_2/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.

Keywords: Effluent; Nanofiltration; Reverse osmosis; Milk; Dead-end

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: Ca^{2+} < 0.4 mg/L, chemical oxygen demand, COD < 10 mg O_2/L and conductivity <40 μS/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 ≈ 36 g O_2/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 cm^3 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 cm^2. 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 composite (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 cm^3. 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

$$\mathrm{VRF} = \frac{V_0}{V_R(t)} = \frac{V_0}{V_0 - V_P(t)} \qquad (1)$$

where V_0 is the initial feed volume (300 cm^3), $V_R(t)$ 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:

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

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