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UNIT AND INTEGRATED MEMBRANE OPERATIONS FOR PURIFICATION OF SPENT SINGLE-PHASE DETERGENT

Unit and integrated membrane operations were investigated for purification of a spent alkaline single-phase detergent from a CIP system in a milk production plant. The filtration experiments were performed in a concentration mode with the use of UF and NF modules differing in their configuration, MWCO, and polymer material. The performance of the modules was characterised in terms of their retention characteristics, hydraulic efficiency, and tendency to fouling. The results revealed that unit and integrated membrane processes were suitable for the recovery of spent cleaning baths containing single-phase detergents, and the permeates maintained their basic cleaning properties. Due to the greater selectivity of the NF module, integrated membrane operations resulted in a much greater modification of the composition of the single-phase detergent in comparison with unit UF processes.

LIST OF SYMBOLS

A – module surface area, m^2
AS – anionic surfactant, $mg\cdot dm^{-3}$
C_f – concentration of pollutant in the feed, $mg\cdot dm^{-3}$
CFV – cross-flow velocity, $m\cdot s^{-1}$
CIP – cleaning-in-place
COD – chemical oxygen demand, $mg\ O_2\cdot dm^{-3}$
C_p – concentration of pollutant in the permeate, $mg\cdot dm^{-3}$
J – permeate flux, $dm^3\cdot m^{-2}\cdot h^{-1}$
J_w – water flux of clean module, $dm^3\cdot m^{-2}\cdot h^{-1}$
MWCO – molecular weight cut-off, Da
NF – nanofiltration
R – retention coefficient, %
RF – relative flux, %
R_{ov} – permeate recovery rate, %
t – filtration time, s
TMP – transmembrane pressure, bar

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UF – ultrafiltration
V_0 – initial volume of the feed solution, dm^3
$V_p(t)$ – volume of the permeate at t time, dm^3

1. INTRODUCTION

The dairy industry is one of the most polluting industrial branches due to the volume of effluent generated per unit of production and its high organic load [1]. It is estimated that 1 dm^3 of processed milk generates approximately 6–10 dm^3 of effluents [2], and 54–98% of this volume comes from the cleaning and washing operations in milk processing plants [3].

In the food industry, effective cleaning of process equipment is essential for the production of high quality products that satisfy stringent microbiological requirements and guarantee consumer health and safety [4]. In industrial applications, the most common agents used for chemical cleaning are alkaline (sodium hydroxide to remove organic matter) and acidic aqueous solutions (nitric acid to remove mineral deposits) [3]. Cleaning-in-place (CIP) systems in dairy plants usually consist of the following stages: flushing with water, washing with the use of alkalis and acids followed by disinfection. In a further step, the equipment is rinsed with water and dried. The traditional cleaning processes consume a large amount of water and chemicals, and have significant economic and environmental impacts. The CIP systems, depending on the operating procedure, can be categorised as: (i) a single-use system where cleaning solutions are drained after a single CIP cycle, or (ii) a multi-use system where the rinsing water and the recovered cleaning solution of appropriate quality are subjected to reuse [5, 6].

The need to reduce water and aggressive chemicals has caused significant changes in procedures for washing and cleaning the production equipment. Conventional methods for cleaning with the help of alkalis and acids are gradually being replaced by single-phase detergents. The main advantages of single-phase cleaning include the removal of both organic and mineral deposits in one cleaning step and shortened cleaning procedures that create savings in water, chemicals and energy. To further reduce CIP operating costs, cleaning solutions based on single-phase detergents should be efficiently recovered for their reuse.

From among available purification techniques, the pressure-driven membrane processes should be regarded as particularly useful for the recovery of single-phase solutions. Until now, these methods have been successfully applied for the recovery of acids and alkalis used in conventional cleaning processes in the dairy industry [7–11]. Recovery of single-phase detergents of complex composition from spent cleaning solutions is a relatively new issue, and therefore, a very limited number of studies have been published. Research conducted by Fernández et al. [12] revealed the usefulness of the NF process for purification and successful reuse of spent alkaline single-phase detergent in a yogurt production plant. Also, Suarez et al. [13] obtained around 90% removal of

COD from spent cleaning solutions by means of an NF module. Reused permeate in CIP plants saved detergents in a yogurt plant at the level of 15–20%.

The results of the purification of contaminated cleaning solutions by means of unit and integrated membrane operations have been reported in the present paper. The effect of the long-term filtration in a concentration mode on the tendency to fouling of the modules and quality of recovered solutions has been evaluated.

2. MATERIALS AND METHODS

The experiments were conducted in a semi-pilot plant in a concentration mode, where the retentate stream was recycled back to the feed tank, and the permeate stream was collected separately. The purification system was implemented as a single unit (UF) or integrated units (UF-NF), where the permeate collected from the ultrafiltration stage was transferred to the NF unit as the feed solution. The selection of the UF and NF modules was conditioned by two factors: (i) the alkaline character of the feed streams (pH slightly lower than 13), and (ii) the filtration results obtained for model solutions [14, 15]. The properties of the modules are shown in Table 1.

Table 1

Characteristics of the UF and NF modules

Module	Configuration	Material	MWCO [Da] Salt retention [%]	A [m^2]	$(J_w)^a$ [dm^3·m^{-2}·h^{-1}]
C5	tubular	zirconium dioxide /titanium dioxide	5 000	0.013	54
C10			10 000		225
PM5	hollow fibre	polysulfone	5 000	0.090	247
AFC30	tubular	polyamide film	75 $CaCl_2$	0.024	11.9

^{a}TMP = 3 bar.

For the tests, a spent alkaline single-phase detergent solutions from a CIP system in a milk production plant were used. A fresh cleaner was mainly composed of sodium hydroxide with the addition of anionic surfactants, complexing agents, polycarboxylates and enzymes.

The quality of feed solutions and permeates was evaluated based on the following physicochemical parameters: pH, conductivity, turbidity, surface tension, COD, and concentration of NaOH, anionic surfactants, lactose and protein. The details of the analytical methods have been presented elsewhere [14, 16].

The feed solutions varied in composition depending on the experimental series; the range of the physicochemical parameters is given in Table 2.

Table 2

Physicochemical properties of the feed solutions

Parameter	Range
pH	12.77–12.93
NaOH concentration, %	0.55–0.61
Conductivity, $mS\cdot cm^{-1}$	29,6–31,2
AS concentration, $mg\cdot dm^{-3}$	24.8–28.7
Surface tension, $mN\cdot m^{-1}$	36.2–39.7
COD, mg $O_2\cdot dm^{-3}$	3280–5990
Protein concentration, $mg\cdot dm^{-3}$	461–547
Lactose concentration, $mg\cdot dm^{-3}$	651–776
Turbidity, NTU	1084–1260

The efficiency of unit and integrated membrane operations during filtration experiments was evaluated based on the parameters listed in Table 3. Transport and separation properties of the modules were examined in selected operating conditions (transmembrane pressure and cross-flow velocity) at 20 °C in two to three replicates. Each filtration run consisted of the following stages: initial water rinsing, solution filtration and final water rinsing. In order to recover the original permeability of the modules, the cleaning step was implemented. Afterwards, rinsing steps with water were performed for 30 min.

Table 3

Parameters for evaluating
the efficiency of the membrane process

Parameter	Equation
Permeate recovery rate	$R_{ov} = \frac{V_p(t)}{V_0} \times 100$
Retention coefficient	$R = \left(1 - \frac{C_p}{C_f}\right) \times 100$
Permeate flux	$J = \frac{dV_p}{Adt}$
Relative flux	$RF = \frac{J}{J_w} \times 100$
Permeate flux decline	$100 - RF$

3. RESULTS AND DISCUSSION

3.1. TRANSPORT PROPERTIES

The concentration of heavily polluted feed solutions caused a systematic decline of permeate flux in comparison with water flux (Fig. 1). The estimated average values of flux decline for filtration cycles were 55%, 64% and 61% for C5, C10 and PM5, respectively (Table 4). The experimental results confirmed that factors that affected the permeate flux decline of the modules were MWCO of the skin layer and hydrophilicity of its material. The lowest susceptibility to fouling showed hydrophilic in nature C5 module with the lowest value of original permeability.

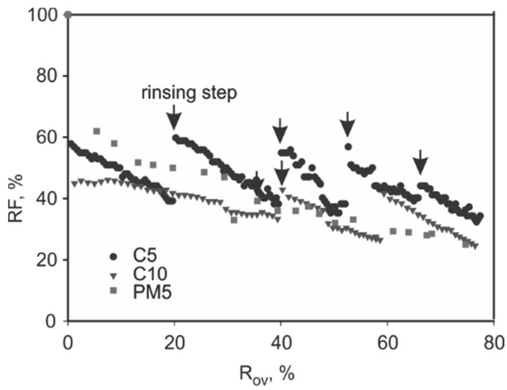

Fig. 1. Relative flux of UF modules during the concentration mode.
C5: TMP = 3.0 bar, CFV = 4.4 m/s;
C10: TMP = 3.0 bar, CFV = 3.8 m/s;
PM5: TMP = 1.0 bar, CFV = 2.2 m/s

In order to achieve a satisfactory hydraulic performance of UF modules during the concentration mode, intermediate rinsing steps were implemented. Concentration systems based on UF processes were able to achieve a very satisfactory permeate recovery rate at the level of around 75% (Table 4).

Table 4

Permeate recovery rate (R_{ov}) and average permeate flux decline (100 – *RF*) during UF concentration

Parameter	Module		
	C5	C10	PM5
R_{ov}, %	77	77	74
100 – *RF*, %	55	64	61

In the next stage of experiments, the permeate collected from the UF unit was transferred as the feed solution to the NF unit. Pretreatment of the spent detergent solutions contributed to reduce the susceptibility to fouling of the NF module by reducing the initial load of pollutants. It was shown that the use of modules having higher selectivity in the first purification step produced a smaller decrease in permeate flux of the NF module (Fig. 2). When C10 and PM5 modules were applied in the pretreatment stage, the estimated average values of flux decline of the AFC30 module were 12% and 11%, respectively (Table 5). However, the pretreatment of the feed solutions with the use of C5 module resulted in an increase of permeate flux of the AFC30 module in comparison with water flux.

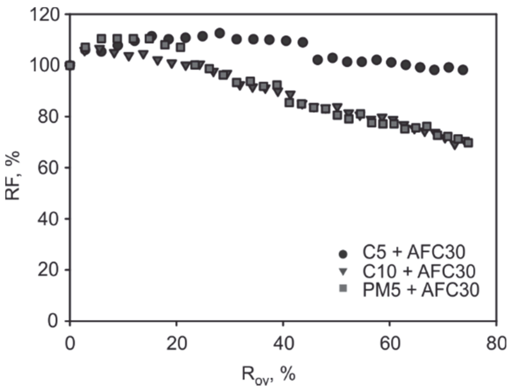

Fig. 2. Relative flux of NF module during the concentration mode. AFC30: TMP = 4.0 bar, CFV=0.6 m/s

Table 5

Permeate recovery rate (R_{ov}) and average value of permeate flux decline ($100 - RF$) during UF-NF concentration[a]

Parameter	Module		
	C5 + AFC30	C10 + AFC30	PM5 + AFC30
R_{ov}, %	74	74	75
$100 - RF$, %	–6[b]	12	11

[a]Values given for NF.
[b]Increase in permeate flux in comparison with the water flux of a clean module.

3.2. SEPARATION PROPERTIES

In the range of permeate recovery rates obtained during the concentration process (Tables 4 and 5), both UF and NF modules retained their stable separation properties. The parameters determined in the feed solutions and in the averaged samples of the permeate collected during concentration cycles are shown in Figs. 3 and 4. The calculated values of the retention coefficient are given in Table 6.

Ultrafiltration experiments have shown a higher selectivity of ceramic modules (C5 and C10) in comparison with the polymeric one (PM5). Through UF modules, a significant reduction of the concentration of organic compounds of both lactic and detergent origin was noticed. A decrease in the COD value amounted to 80%, 85% and 70% for C5, C10 and PM5, respectively. The cumulative effect of the reduction of the concentration of organic compounds depended primarily on the removal efficiency of lactose, protein and anionic surfactants at the level of 45–70%, 99% and 66–77%, respectively. As a consequence of lowering the concentration of proteins, anionic surfactants and complexing agents, an increase in the value of the surface tension of solutions at the level of approximately 6–10 mN/m was noticed. The UF modules, due to relatively high values of MWCO, removed sodium hydroxide from the feed solutions very slightly (13% for PM5; and 20% for C5 and C10), which correlated with the values of pH and conductivity of the permeates.

Table 6

Retention coefficient of selected physicochemical indicators during unit and integrated membrane operations[a]

Process	COD	Lactose	Protein	AS	NaOH	Conductivity	Turbidity
C5	80	70	99	74	20	23	100
C5 + AFC30	88	99	100	90	28	29	100
C10	85	70	99	66	20	14	99
C10 + AFC30	92	99	100	76	24	22	100
PM5	70	45	99	77	13	13	100
PM5 + AFC30	85	99	100	89	25	21	100

[a]Retention coefficient is given in relation to the feed solutions.

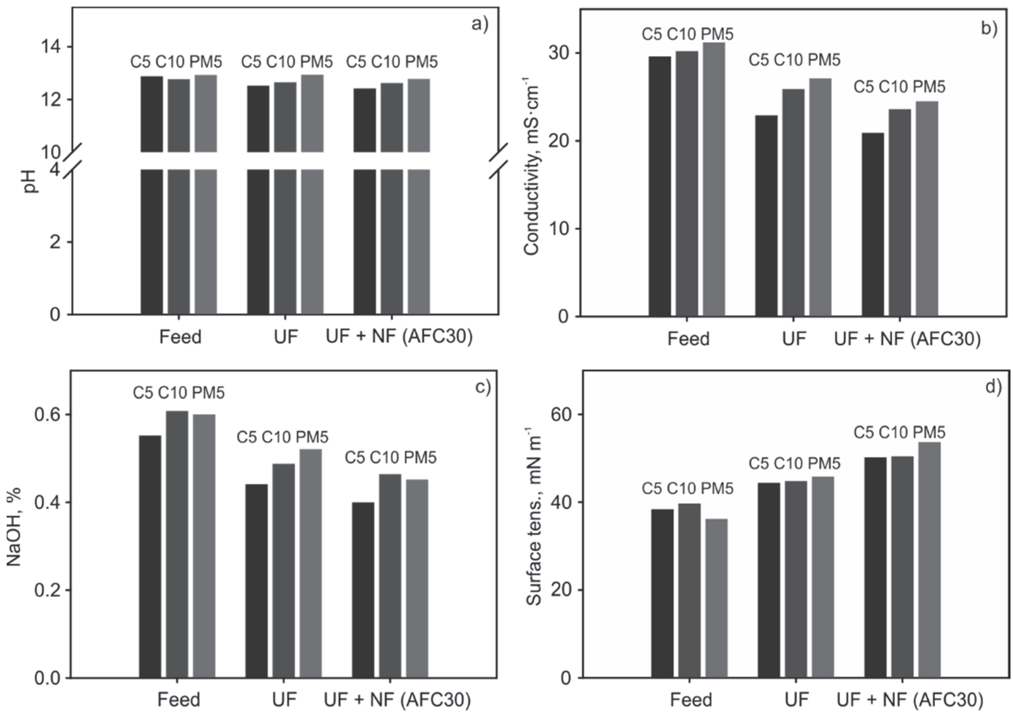

Fig. 3. Average values of physicochemical indicators determined during concentration cycle for unit and integrated membrane operations: a) pH, b) conductivity, c) NaOH concentration, d) conductivity. Process parameters: C5 – TMP = 3.0 bar, CFV = 4.4 m/s; C10 – TMP = 3.0 bar, CFV = 3.8 m/s; PM5 – TMP = 1.0 bar, CFV = 2.2 m/s; AFC30 – TMP = 4.0 bar, CFV = 0.6 m/s

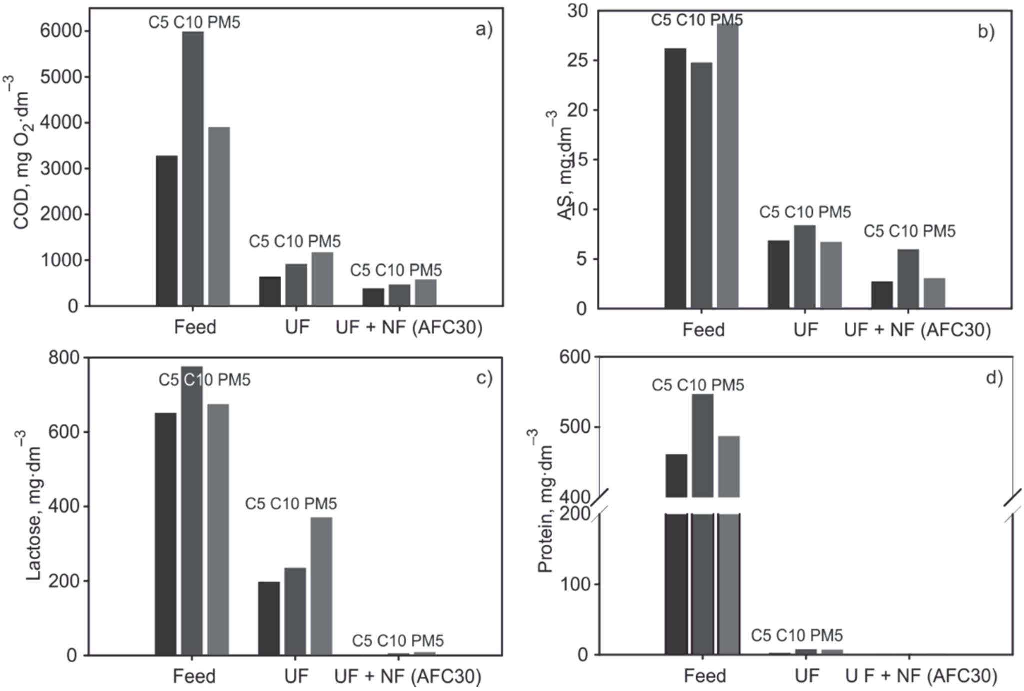

Fig. 4. Average values of the concentration of organic compounds determined during the concentration cycle for unit and integrated membrane operations: a) COD, b) anionic surfactants, c) lactose, d) protein. Process parameters: C5 – TMP = 3.0 bar, CFV = 4.4 m/s; C10 – TMP = 3.0 bar, CFV = 3.8 m/s; PM5 – TMP = 1.0 bar, CFV = 2.2 m/s; AFC30 – TMP = 4.0 bar, CFV = 0.6 m/s

Based on the experimental data, it can be stated that with the use of ceramic UF modules, a satisfactory reduction of the concentration of milk compounds (lactose and protein) from spent solutions was achieved. Furthermore, as a result of removal of the components present in the formula of the single-phase detergent, there was a lowering of detergency properties of the recovered solutions in comparison with fresh detergent. However, it should be stressed that the partial loss of the detergency properties of the recovered solutions still allows their reuse in the CIP systems.

The application of nanofiltration as a post-treatment process contributed to a further reduction of the concentration of organic and inorganic compounds. Integrated membrane processes were able to provide the separation of proteins and lactose on the level of 100% and 99%, respectively. This resulted in almost complete elimination of compounds of lactic origin. In relation to the feed solutions, the recovered solutions had only 10–24% of the original content of AS, and the value of surface tension increased by approximately 12–18 mN/m. The overall efficiency of integrated membrane processes in removal of organic matter expressed as COD was in the range of 85–92%.

Further separation of sodium hydroxide (24–28% and 5–13% in relation to the feed solutions and UF permeates, respectively) by means of the AFC30 module resulted in its concentration decrease in the permeate, and thus, with a consequent reduction in the pH value and the conductivity.

Use of the integrated membrane operations, due to the greater selectivity of NF module, contributed to a much greater modification of the detergent composition in comparison with the unit UF processes. The recovered solutions should be considered as pure solutions of sodium hydroxide of similar concentration (0.40–0.46% in the permeates; 0.55–0.61% in the feed solutions) with a small amount of anionic surfactants and complexing agents.

4. CONCLUSIONS

Unit and integrated membrane processes were suitable for the purification of spent cleaning baths containing single-phase detergents. The application of modules with a low value of MWCO (in order to effectively remove lactose from the treated solutions) contributed to the reduction of concentration of the basic components of single-phase detergents. Due to the higher selectivity of the NF module, integrated membrane operations resulted in a much greater modification of the composition of the single-phase detergent in comparison with unit UF processes. The recovered solutions should be considered as pure solutions of sodium hydroxide of similar concentration with a small amount of anionic surfactants and complexing agents. The treated solutions exhibited changes in the value of surface tension in comparison with feed solutions. However, it should be stressed that the partial loss of the detergency properties of the recovered solutions still allows their reuse in the CIP systems.

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