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REGENERATION OF POLYMER AND CERAMIC MODULES WITH THE USE OF RECOVERED SINGLE-PHASE DETERGENT. DAIRY INDUSTRY CASE STUDY

The effectiveness of recovered washing compositions containing single-phase detergents from cleaning-in-place (CIP) systems as solutions for the regeneration of membrane modules fouled during the filtration of wastewater from the prerinsing of the production line (white water) was assessed. The influence of process parameters (regeneration time, transmembrane pressure, cross-flow velocity, and solution temperature) on relative flux recovery was evaluated. A significantly higher regeneration efficiency of the ceramic and polymeric modules was obtained for the alkaline detergent compared to that of the acid formula. The key process parameters for the regeneration cycle were the contact time of the module with the cleaning detergent and its temperature. The influence of transmembrane pressure and cross-flow velocity on module permeability was negligible. Filtration experiments with white water confirmed that the membrane separation process is suitable for the recovery of milk compounds from dairy effluents.

1. INTRODUCTION

The dairy industry is one of the main agricultural production industries in Europe. It is estimated that total EU production is around 155 million tonnes per year. The main producers are Germany, France, Poland, the Netherlands, Italy, and Ireland, together processing almost 70% of the milk [1]. This sector processes raw milk, among others, for pasteurised milk, yoghurt, cream, butter, cheese, milk and whey powders, lactose, and different types of desserts. The amount of wastewater is estimated to be approximately 2.5 times the volume of milk processed, and its physicochemical characteristics depend largely on the size of the factory, the technology used and the cleaning-in-place (CIP) systems [2]. A typical dairy industry in the European Union produces approximately 180 000 m^3 of wastewater per year

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[3] and these effluents have high BOD (0.1–100 $g\cdot dm^{-3}$) [2], which makes them harmful to the environment if disposed of untreated.

One of the key processing tools in the dairy industry is membrane technology. This is mainly due to the high requirements regarding the quality of the product and the level of its hygiene, as well as strict legal regulations related to environmental protection. The largest share of the membrane market is for ultrafiltration (UF) systems (35%), followed by microfiltration (MF) processes (33%) and nanofiltration (NF)/reverse osmosis (RO) systems (30%) [4]. Microfiltration is mainly used to improve the microbiological quality of milk by separating fine impurities and bacteria. Ultrafiltration is used for milk standardisation processes in cheese production and its concentration. Ultrafiltration permeate can be further treated using nanofiltration or reverse osmosis membranes to obtain a concentrated stream to produce lactose. Ultrafiltration is also used to concentrate whey, while nanofiltration is used to partially desalinate salty whey with the simultaneous concentration of its components [4–7].

In the dairy industry, much attention is also paid to the management of water and wastewater to reduce both the consumption of water as raw material and the harmful effect of wastewater on the aquatic environment. This is done by reducing the volume of effluents and a load of pollutants, eliminating substances considered particularly harmful to the environment, using closed circuits and reusing water and highly effective treatment of wastewater before its discharge into the environment. Rational water and wastewater management are supported, among others, by CIP technology [8–10], which is used to clean and disinfect production lines and devices without disassembling the process.

The basic CIP process in dairy plant facilities consists of the following steps: pre-rinse, caustic wash, intermediate rinse, and final sanitising rinse [11]. Spent washing solutions that contain contaminants related to production technology are removed from the system. More often, dairy plants are changing, so far, the method used for production line cleaning in favour of single-phase detergents containing acids or bases, as well as surfactants, complexing agents, antifoaming and disinfecting compounds [12, 13]. The main advantage of single-phase cleaning is shortened cleaning procedures that create savings in water, chemicals, and energy [14].

The pre-rinsing of the production line with clean water makes it possible to recover valuable milk components from the white water and reuse them, which significantly reduces the load of organic matter of effluents [15, 16].

The research verified the usefulness of recovered washing compositions containing single-phase detergents from CIP systems as solutions for the regeneration of membrane modules fouled during white water filtering.

2. EXPERIMENTAL

The spent detergent solutions (acidic – $D_{acid.}$ and alkaline – $D_{alk.}$) from the CIP systems of the dairy industry were regenerated by removing the basic milk components from them.

This procedure was carried out using a ceramic module (5 kDa) in batch concentration mode, with the assumed 75% recovery of the feed solutions according to the procedure described in the previous paper [17]. The composition of recovered single-phase detergents (and as a reference the composition of brand-new detergents) is given in Table 1.

Table 1

Average values of physicochemical parameters of the brand-new and the recovered single-phase detergents

Parameter	Brad-new detergent		Recovered detergent	
	acidic	alkaline	acidic ($D_{acid.}$)	alkaline ($D_{alk.}$)
pH	1.76	12.99	2.25	12.67
Acidity, mmol·dm^{-3}	33.6	–	23.4	–
NaOH, %	–	0.75		0.62
Conductivity, mS·cm^{-1}	13.48	42.9	9.68	32.4
Surfactant, %	0.029	<1 mg·dm^{-3}	4.9×10^{-4}	–
Surface tension, mN·m^{-1}	26.7	37.2	31.2	46.7
COD, mg O_2·dm^{-3}	2 814	408	843	706
Protein, mg·dm^{-3}	–		8.2	2.6
Lactose, mg·dm^{-3}	–		40.4	2.2
TDS, mg·dm^{-3}	1090	10 423	705	8961

The purpose of the research was to verify the suitability of recovered cleaning compositions for the regeneration of ultrafiltration and nanofiltration modules (Table 2) fouled during the filtration of white water (Table 3) coming from the first rinse in the CIP process. The influence of process parameters (transmembrane pressure (TMP), cross-flow velocity (CFV) and solution temperature) on relative flux (calculated as the ratio of the permeate flux to water flux of the clean module and expressed as a percentage) recovery was evaluated.

Table 2

Characteristics of the UF and NF modules

Module	Configuration	Material	MWCO [Da] Salt ret. [%]	Module area [m^2]	Flux of a clean module[a] [dm^3·m^{-2}·h^{-1}]
Ceramic UF modules					
C1	tubular	ZrO_2/TiO_2	1000	0.013	35
C5			5000		56
C10			10 000		219
Polymeric UF modules					
PM2	hollow fibre	polysulfone	2000	0.090	65
PM5			5000		238
Polymeric NF modules					
AFC30	tubular	polyamide film	$CaCl_2$, 75	0.024	12

[a] TMP = 3 bar.

Table 3

White water characteristics

Parameter	pH	Turbidity [NTU]	Conductivity [µS·cm^{-1}]	COD [mg O$_2$·dm^{-3}]	Protein [mg·dm^{-3}]	Lactose [mg·dm^{-3}]	Surface tension [mN·m^{-1}]	TDS [mg·dm^{-3}]
Average value	6.81	1980	1521	37 420	6 547	9 512	43.7	25 198

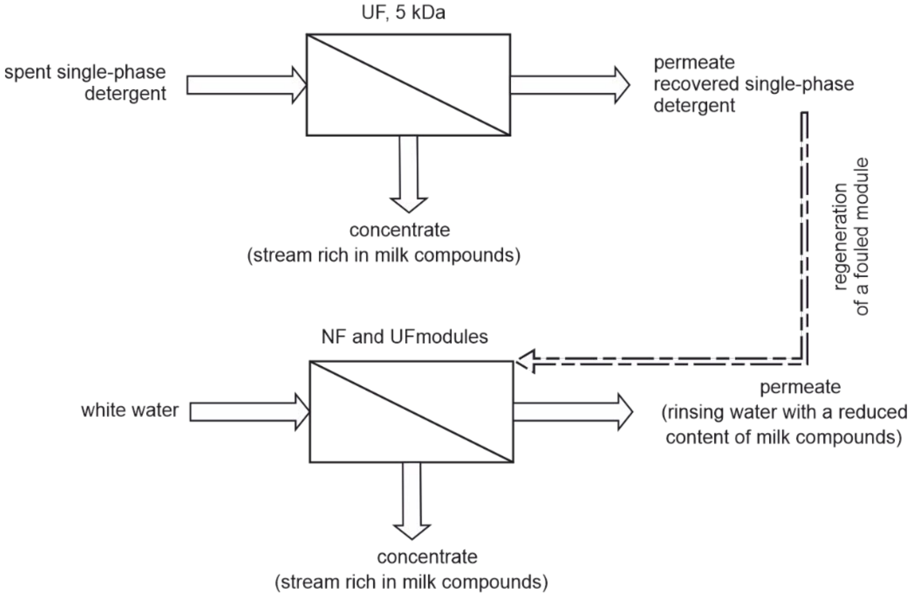

Fig. 1. The arrangement of the experiments

Filtration experiments with white water were also carried out in batch concentration mode, with the assumed 75% recovery of the feed solutions in two replicates. A secondary goal was to test the removal of milk components from white water by ultrafiltration and nanofiltration. The arrangement of the conducted experiments is shown in Fig. 1.

3. RESULTS AND DISCUSSION

In the first stage of experiments, white water was filtered using ultrafiltration and nanofiltration modules operating at specific process parameters (TPM and CVF) for 4 hours. Modules showed high separation of milk components from the clarified solution (Fig. 2). The protein concentration was reduced by more than 99%, ensuring that the concentration was lowered to 30–43 mg·dm^{-3}, depending on the type of module.

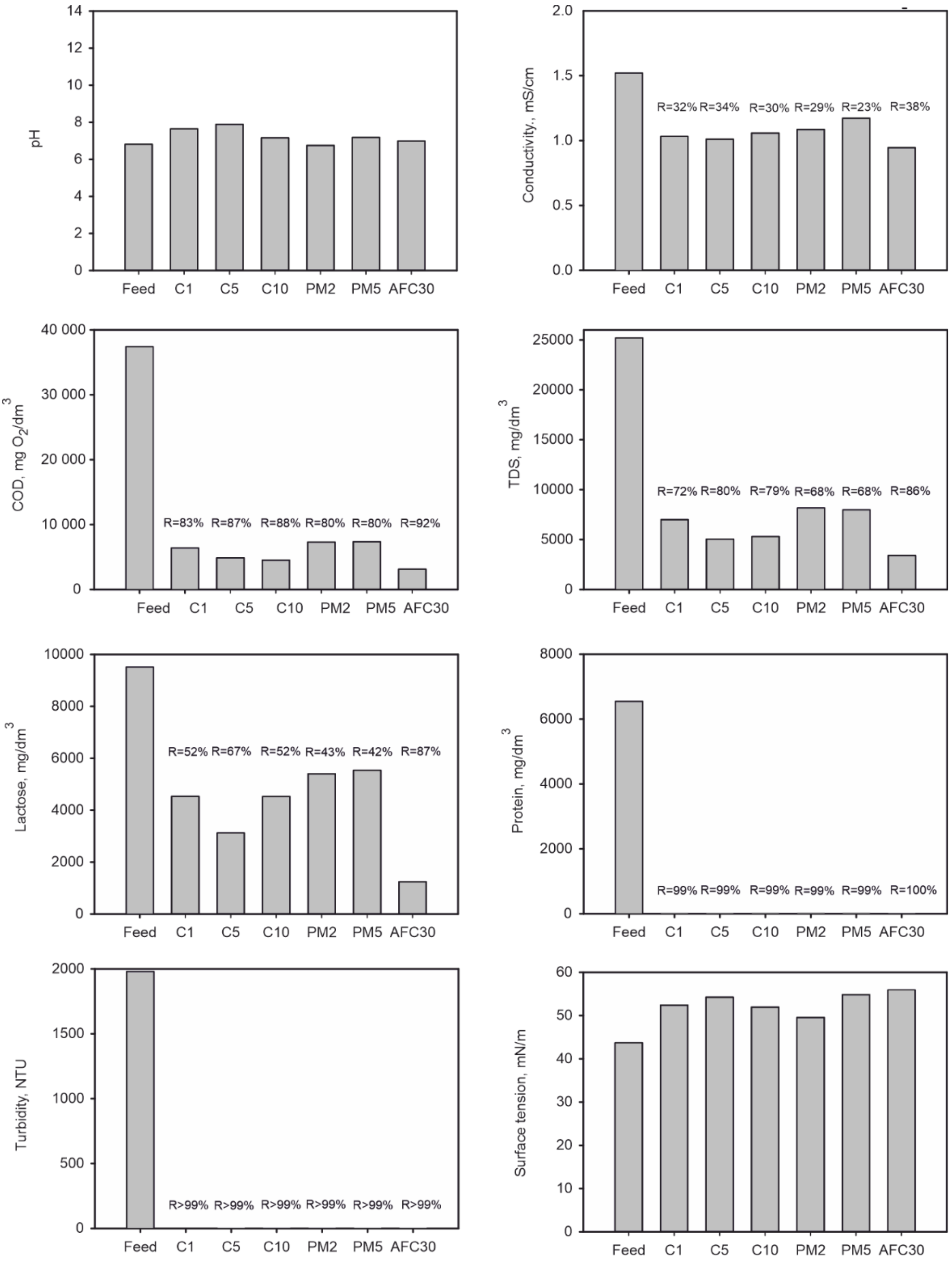

Fig. 2. Quality of the white water solution treated in the UF and NF modules

The highly effective separation of electrically charged proteins [18, 19] resulted in changes in the quality of the permeates such as a significant reduction in conductivity ($R = 23–38\%$), an increase in surface tension by approximately 6–12 $\mathrm{mN\cdot m^{-1}}$ and a reduction in turbidity of almost 100% (Fig. 3). However, the efficiency of lactose separation (due to low molecular weight) was more dependent on the cut-off value of the modules and ranged from 42% for PM2 to 67% for C5 and AFC30.

Fig. 3. Samples of feed solution (from left) and permeates from AFC30, C5, and PM5 modules

Membrane filtration significantly reduced the load of organic matter. The reduction in COD was in the range of 63–88% and 42–43% for ceramic and polymeric UF modules, respectively, and exceeded 90% for the NF module (AFC30).

The results confirmed that the membrane separation processes could be used to recover milk compounds and to produce high-quality water for reuse. Therefore, white water can be a potential source of profit for dairy plants. Ultrafiltration is an effective method for removing proteins and reducing the COD load from dairy wastewater, while nanofiltration additionally allows the separation of low-molecular-weight lactose; therefore, it has a greater potential in this area. Production of high-quality reused water for the dairy industry requires the use of reverse osmosis.

One limitation in the use of membrane processes for the recovery of milk components is the decrease in hydraulic efficiency (Fig. 4). In the initial phase of filtration, a sharp decrease in the permeate flux was noticed, which reached the pseudo-settled state after about 30–50 minutes. The tests carried out for the white water showed that the characteristics of the modules significantly affect their permeability and susceptibility to fouling. Because of the more intense blocking of the pores by the milk components, a greater drop in flux was observed for the less hydrophilic modules with a higher cut-off.

The modules most susceptible to fouling were polymeric UF modules (PM2 and PM5). The flux values at the end of the filtration cycle were approximately 12% and

15% pure water flux for PM2 and PM5, respectively. On the other hand, ceramic modules (C1, C5 and C10) with similar or even higher cut-offs, due to the hydrophilic nature of metal oxides [20–22], maintained much higher values of relative flux (49–57%) compared to polymeric modules.

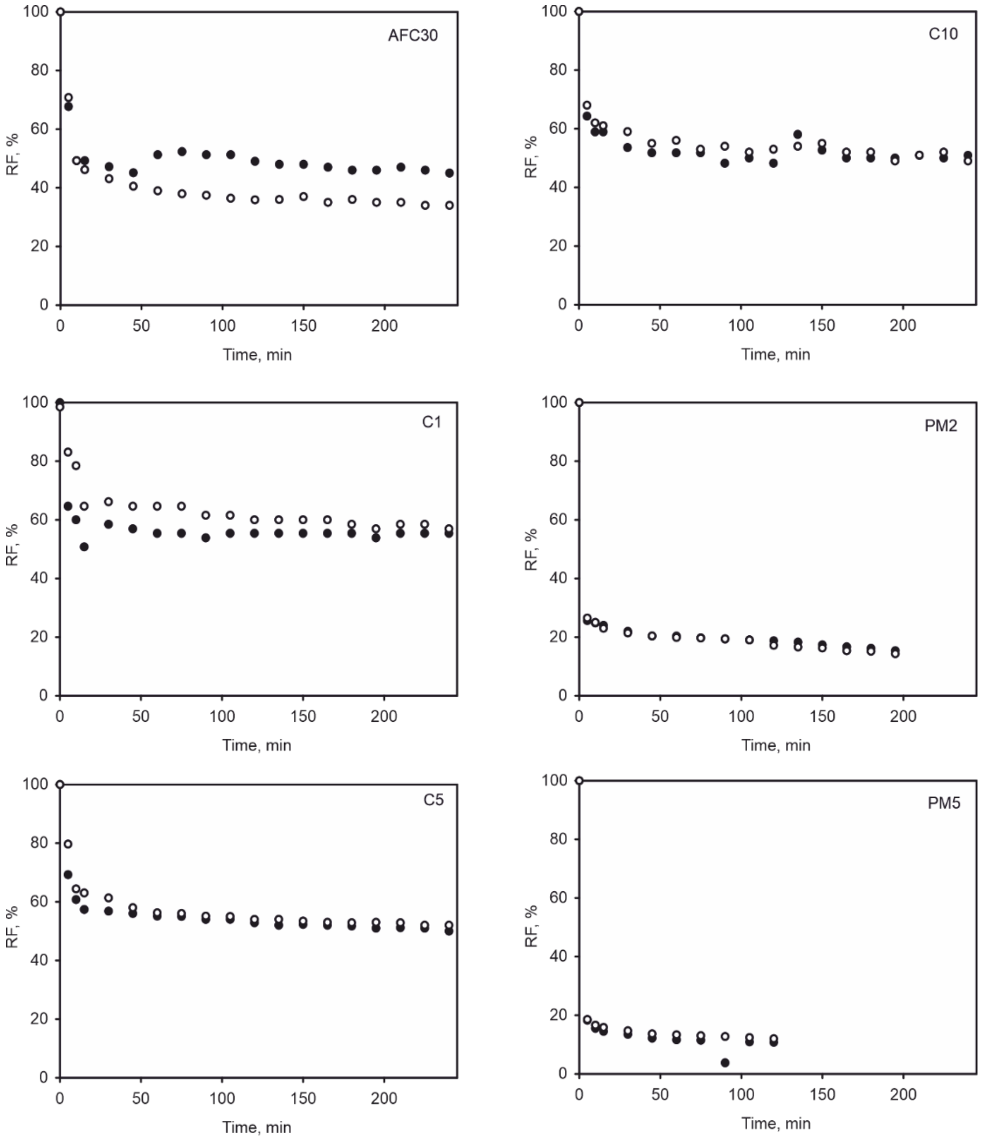

Fig. 4. Relative fluxes (RF) during white water filtration;
process parameters: C1 – TMP 3,0 bar, CFV 5.0 m/s; C5 – TMP 3.0 bar, CFV 5.0 m/s;
C10 – TMP 3.0 bar, CFV 6.7 m/s; PM2 – TMP 2.0 bar, CFV 3.1 m/s;
PM5 – TMP 2.0 bar, CFV 2.2 m/s; AFC30 – TMP 4.0 bar, CFV 0.7 m/s

Table 4

Relative flux (RF) of modules at different stages of regeneration [%]

Stage	C1	C5	C10	PM2	PM5	AFC30
After the filtration process of white water[a]	55–57	50–52	49–51	14–15	11–12	34–36
After rinsing with deionized water[a]	74–79	70–72	69–75	30–31	14–15	70–71
After regeneration with $D_{alk.}$ and rinsing with deionized water[b]	99–100	99–100	99–100	105–112	108–113	100–103
After regeneration with $D_{acid.}$ and rinsing with deionized water[b]	91–93	85–89	80–83	65–70	55–59	93–95

[a] Process parameters as for filtration of white water (Fig. 4).

[b] Process parameters for the regeneration stage

C1: TMP = 3.0 bar, CFV = 5.0 m/s,
C5: TMP = 3.0 bar, CFV = 5.0 m/s,
C10: TMP = 3.0 bar, CFV = 6.7 m/s,
PM2: TMP = 2.0 bar, CFV = 3.1 m/s,
PM5: TMP = 2.0 bar, CFV = 2.2 m/s,
AFC30: TMP = 4.0 bar, CFV = 0.7 m/s.

The AFC30 nanofiltration module was characterised by intermediate values of relative flux (34–45%). Due to the lowest cut-off value of the AFC30 module (200 Da), the permeate flux decrease is most probably caused by the surface adsorption of foulants (proteins, lactose, multivalent salt ions and their aggregates) and to a lesser extent because of pore narrowing. Moreover, for modules with a high cut-off value, the effect of irreversible fouling (defined as the part of fouling that is not removable by rinsing and backwashes but only by chemical cleaning) on the total flux decrease was particularly dominant (Table 4).

To restore the hydraulic performance of the fouled modules, the cleaning procedure using recovered single-phase detergents (Table 1) was applied. It successively included the following stages: rinsing with deionised water for 30 minutes, cleaning with recovered single-phase detergent for 60 minutes and re-rinsing with deionised water for 30 minutes.

Purified single-phase detergents were successfully used for the regeneration of polymeric and ceramic modules with different cut-off values (Table 4). A considerably higher cleaning efficiency of alkaline detergent was observed compared to that of the acidic formula. The alkaline detergent restored the original permeability of the modules; and in the case of PM2, PM5 and AFC30 modules, the original permeability was exceeded. This increase (for PM2, PM5 and AFC30 modules) is primarily related to the hydrophilisation of polymeric materials upon contact with the chemical. It should be noted that the change in hydrophilicity did not significantly affect the separation properties of the UF and NF modules. On this basis, damage to the polymer was excluded from contact with cleaning solutions. Studies in the literature support these findings. Oh et al. [23] observed that at lower NaOH concentrations, the morphological changes of polyacrylonitrile were negligible, and changes in hydrophilicity were dominant. Gul et al. [24] showed that the pore size of the polyamide membrane increased slightly under a low concentration of an alkaline cleaning agent (1% NaOH) concentration.

The use of acid detergent restored the original permeability of the UF and NF modules in the range of 55–95%. The obtained results are confirmed in the literature data. For cleaning membranes contaminated with proteins, it is recommended to use alkaline solutions of sodium hydroxide pH = 11–12 [25–27]. On the other hand, cleaning products containing inorganic acids are primarily aimed at dissolving mineral deposits [25].

In the next stage of the experiment, the influence of process parameters on the efficiency of the regeneration process using recovered single-phase detergents was determined. Representative results for the PM2 module are shown in Fig. 5.

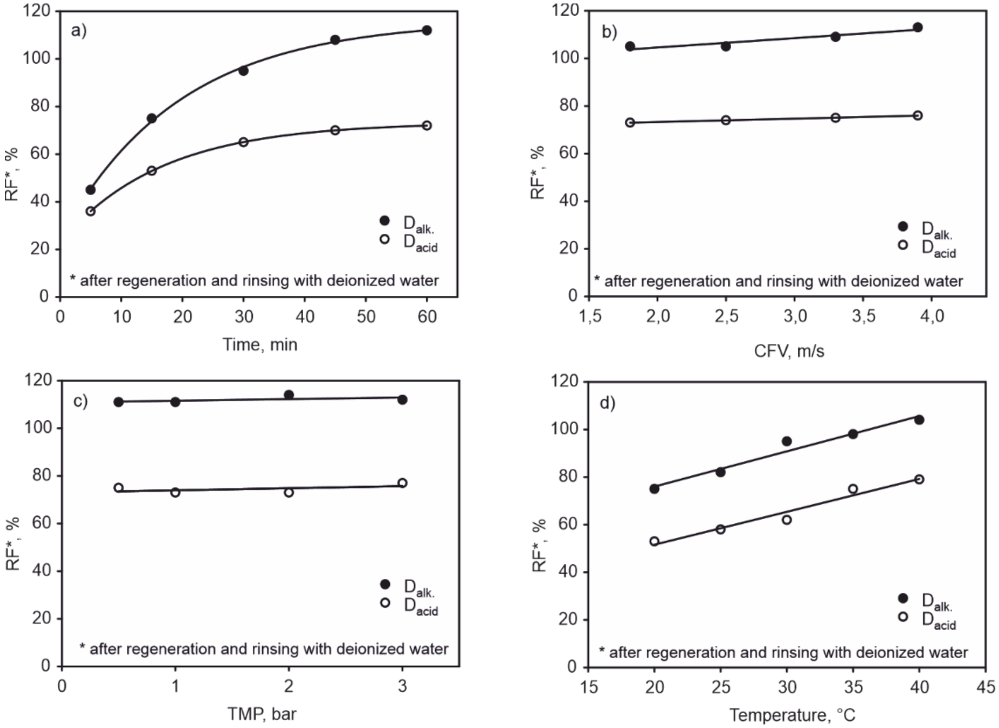

Fig. 5. Relative fluxes (RF) of the PM2 module depending on
a) regeneration time (temperate 20 °C, TMP 2.0 bar, CFV 3.1 m/s); b) cross-flow velocity
(regeneration time 60 min, temperature 20 °C, TMP 1.5 bar); c) transmembrane pressure
(regeneration time 60 min, temperature 20 °C, CFV = 3.1 m/s); d) temperature
of the cleaning solution (regeneration time 15 min, TMP 1.5, CFV 3.1 m/s)

The cleaning time of membranes in the regeneration process is a crucial parameter that determines the efficiency of the membrane process and, hence, its economics. It was shown that with the extension of the cleaning time using purified single-phase detergents, a better effect of regeneration was obtained. However, it should be noted that with time, its influence on the value of the relative permeability of membranes gradually decreases, which results mainly from the limited ability of the chemical agent to dissolve sediment deposited on the surface and in the membrane pores (Fig. 5a). The influence of process parameters (TMP and CFV) on regeneration efficiency was negligible (Figs. 5b and 5c). The relative flux did not differ by more than 6%.

The temperature tests (Fig. 5d) showed that the regeneration of modules contaminated with milk components was more effective with increasing the temperature of the cleaning solution. This is primarily related to the following: lowering the viscosity of the washing solution and its easier penetration into the layer of the filter cake, increasing the solubility of the deposited deposits on the membrane surface and inside its pores and the thermal expansion of the polymeric material.

4. CONCLUSIONS

Purified single-phase detergents from the CIP systems of the dairy industry were successfully applied for the regeneration of ultrafiltration and nanofiltration modules fouled during white water filtration. With the assumed parameters of the regeneration cycle, a significantly higher regeneration efficiency of modules was obtained for the alkaline detergent compared to that of the acid formula. The alkaline detergent restored the original permeability of the modules, and for the polymer modules, the original permeability was exceeded because of the hydrophilisation of the membrane material. The key process parameters for the regeneration cycle were the contact time of the module with the cleaning detergent and its temperature. The influence of transmembrane pressure and cross-flow velocity on module permeability was negligible. The relative flux for PM2 and the tested ranges (CFV = 1.8–3.9 m/s and TMP = 0.5–3.0 bar) did not differ by more than 6%.

Filtration experiments with white water confirmed that membrane separation processes are suitable for recovering milk compounds from dairy effluents. Ultrafiltration is an effective method of removing proteins and reducing the COD load from dairy wastewater, while nanofiltration additionally allows for the separation of low molecular weight lactose.

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