Desalination and Water Treatment
www.deswater.com
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doi: 10.1080/19443994.2012.693581

51 (2013) 1366–1376
February

Taylor & Francis
Taylor & Francis Group

An assessment of the cleaning solutions' purification by membrane filtration

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Received 28 February 2012; Accepted 10 May 2012

ABSTRACT

The results of the purification of contaminated cleaning solutions (a single-phase detergent) emanating from a diary industry were reported. Flat-sheet ultrafiltration (UF) and nanofiltration (NF) membranes that differed in their molecular weight cut-offs were evaluated for their potential use in the recovery of cleaning solutions. The experiments were performed in a stirred cell operating in a dead-end filtration mode. The membranes were tested under different transmembrane pressures (0.5–4 bar), mainly for the purpose of: (i) a long-term evaluation of membrane hydraulic performance, (ii) an assessment of fouling tendency, (iii) an evaluation of the quality of the recovered solution in comparison with the fresh detergent, and (iv) an assessment of the chemical stability of a polymer material. Studies have demonstrated the usefulness of membrane filtration using polymeric membranes for the recovery of a single-phase detergent for the purpose of its reuse in cleaning systems. The recovered detergent maintained its basic cleaning properties, i.e. high pH, high concentration of NaOH and low value of surface tension. Moreover, the NF membranes and the tight UF membranes showed a high separation of specific milk components and organic matter expressed as TOC and COD.

Keywords: Pressure-driven process; Detergent; Cleaning solution; Recovery

1. Introduction

In several industries, an important component of the production process, which determines the quality of a finished product, is adherence to high standards of hygiene. It is possible to achieve proper sanitary conditions of production processes by adopting appropriate methods and bestowing proper attention to the cleaning frequency of the production equipment [1–3]. In the food industry, cleaning is usually performed by using cleaning-in-place (CIP) systems, which allow the processing equipment to be simultaneously cleaned and sterilized [4,5]. CIP is a method that is used for cleaning the process equipment without any need for dismantling them. The cleaning solutions are pumped from a storage tank, and then circulated in the process tanks, pipelines and finally returned to the storage tank [5].

To meet the requirements of high standards of hygiene, the dairy industry has been consuming a large quantity of chemicals. In the production plants connected to the diary industry, usually the cleaning

Presented at the International Conference on Desalination for the Environment, Clean Water and Energy, European Desalination Society, 23–26 April 2012, Barcelona, Spain

system is initially flushed with water. Later, chemical cleaning is carried out using alkalis, acids and disinfecting agents. Finally, the equipment is rinsed with water and dried. Cleaning solutions may be discharged into the sewage system after one use (single-use systems) or are used several times (multi-use systems) [6].

Sodium hydroxide solution, also known as caustic soda, is the most common used caustic cleaner. Its role is to remove the proteins and carbohydrates [7–9]. Whereas the role of an acid washing step is the removal of mineral deposits accumulated on the equipment surfaces. Moreover, at this stage the traces of an alkaline product formed are removed, thereby, enhancing draining and drying processes and providing bacteriostatic conditions that delay the growth of any remaining microorganisms [9].

The need for protecting the environment from the harmful effects of aggressive chemicals and the need for reducing water consumption during the washing process have brought about a change in the pattern of cleaning the production lines. Conventional methods for cleaning with the help of alkalis and acids are gradually being replaced by single-phase detergents. The composition of such a washing detergent includes alkalis or acids, surfactants, complexing and disinfecting agents, and defoamers.

The recovery and reuse of cleaning chemicals within the food industry is of utmost importance. The analysis of literature data indicates that the membrane processes can be used for the purification and recovery of the cleaning solutions. However, the published research has mainly focused on the recovery of sodium hydroxide and nitric acid. The processes used for the recovery of chemicals were mainly nanofiltration (NF) [10–13], as well as ultrafiltration (UF) [14,15] and microfiltration [16].

The research conducted by Fernández et al. [17] confirmed the usefulness of NF for the purification of a spent single-phase detergent used in the dairy industry. As it has been shown, the purified detergent was successfully reused for washing the production equipment, maintaining the high hygienic standards. Taking into account the literature reports, it is advisable to undertake a detailed research into the treatment of single-phase detergents and their recycling in the CIP systems.

In the present paper, the results of the purification of contaminated cleaning solutions (a single-phase detergent) were reported. Flat-sheet UF and NF membranes differing in MWCO were evaluated for their potential use in the recovery of cleaning solutions. The membranes have been operated mainly for the purpose of: (i) a long-term evaluation of membrane hydraulic performance, (ii) an assessment of the fouling tendency, (iii) an evaluation of the quality of the recovered solution in comparison with the fresh and (iv) an assessment of the chemical stability of a polymer material.

2. Materials and methods

2.1. Solutions

In the present study, a single-phase detergent, which was mainly composed of sodium hydroxide with the addition of complexing agents and anionic surfactants, tailor-made for the CIP systems in the dairy industry was used. The filtration experiments were conducted for the following solutions: (i) 1–4% w/v aqueous solution of a single-phase detergent, (ii) 0.75% w/v aqueous solution of milk with a fat content of 3.2% w/v, and (iii) 2% w/v aqueous solution of a single-phase detergent to which was added 0.75% w/v of milk to simulate industrial conditions.

2.2. Filtration experiments

The filtration experiments were carried out using flat-sheet membranes, which are characterized in Table 1. Owing to the alkaline nature of the test solutions, polymers that showed high resistance to chemical agents were selected for the initial tests.

The UF and NF membranes with an area of $4.53 \times 10^{-3}\,m^2$ were tested in Amicon 8,400 filtration cells with a total capacity of $3.5 \times 10^{-4}\,m^2$. The transport and separation properties of the membranes were

Table 1
Membranes characteristics

Membrane	Polymer material	MWCO, kDa	Na_2SO_4 retention, %	pH range	Max. temperature, °C
NP030	PES		80–95	0–14	95
NP010	PES		25–55	0–14	95
PS1	PS	1		0–14	95
UP005	PES	5		0–14	95
UP010	PES	10		0–14	95

Table 2
Parameters for determination

Parameter	Equation	Unit
Permeate flux	$J = \frac{1}{A}\frac{dv}{dt}$	$m^3\,m^{-2}\,s^{-1}$
Relative flux	$RF = \frac{J}{J_w}$	–
Retention coefficient	$R = (1 - \frac{C_p}{C_f}) \times 100$	%

examined at the temperature of 20°C within the range of transmembrane pressures of 0.5–4 bar. To minimize the thickness of a polarization layer on the membrane surface, the solution was mixed at a speed of $300\,min^{-1}$.

The criteria for assessing the effectiveness of the filtration process are the following parameters listed in Table 2.

2.3. Analytical methods

The feed solutions and the permeates collected from the filtration runs were subjected to physicochemical analyses. The conductivity and the pH were measured with an Elmetron CC-411 conductometer (with an EC60 sensor designed for measuring the conductivity in the range of 10 μS/cm–100 mS/cm) and an Elmetron CP-315M pH-meter, respectively. The content of sodium hydroxide was analysed by an acid–base titration method with the use of 0.1 N HCl and phenolphthalein as an indicator. Surface tension measurements of the solutions were conducted with an automatic EasyDyne tensiometer (Küss) at the temperature of 20°C. The concentration of surfactants in aqueous solutions was determined on the apparatus 785 DMP Titrino using the potentiometric titration method. Total dissolved solids were determined according to Standard Methods [18]. The colour intensity was measured at the wavelength of 350 nm (Hitachi U-1900). The content of organic compounds was monitored by means of TOC (TOC 5050 Analyser, Shimadzu) and COD (DR/2000 spectrophotometer, Hach). The protein and lactose content was analysed by means of the Bradford reagent method [19] and the Miller method using dinitrosalicylic acid [20], respectively.

3. Results and discussion

3.1. Properties of feed solutions

In the first stage of the present study, the physicochemical properties of aqueous detergent solutions were studied. The mean values of several measurements are presented in Table 3. The results demonstrated a linear relationship depending on the detergent concentration in water solutions. Increasing concentration of the detergent resulted in a slight increase in the pH value from 12.6 to 13.2 for 1 and 4% w/v, respectively. The value of surface tension was reduced with increasing concentration of the single-phase detergent from 38.9 to 34.5 mN/m for 1 and 4% w/v, respectively.

The concentration of anionic surfactants was below $1\,g/m^3$ for all applied detergent concentrations. This value confirms the manufacturer's declaration of a low foaming nature of the composition. The concentration of anionic surfactants is much lower than the critical micelle concentration (CMC) of typical alkyl sulphates and alkylbenzene sulphonates (CMC_{SLES} =

Table 3
Physicochemical properties of aqueous solution of the single-phase detergent

Parameter	Detergent concentration, % w/v				Linear approximation
	1	2	3	4	
C_{NaOH}, %	0.38	0.75	1.13	1.52	$C_{NaOH} = 0.38 \times Cdet.$ $R^2 = 0.99$
Conductivity, mS/cm	22.3	42.9	61.6	80.6	$Cond. = 20.5 \times Cdet.$ $R^2 = 0.99$
TOC, gC/m^3	68	116	160	202	$TOC = 52.9 \times Cdet.$ $R^2 = 0.96$
COD, gO_2/m^3	232	408	562	704	$COD = 185 \times Cdet.$ $R^2 = 0.98$
Colour, gPt/m^3	1.2	3.3	6.7	9.0	$Colour = 2.1 \times Cdet.$ $R^2 = 0.94$
TDS, g/m^3	5,379	10,423	15,501	21,294	$TDS = 5.3 \times Cdet.$ $R^2 = 0.99$

Table 4
Physicochemical properties of tested solutions

Parameter	Solution A	Solution B
pH	7.09	12.9
C_{NaOH}, %	–	0.75
Conductivity, mS/cm	73.9×10^{-3}	43.5
TOC, gC/m^3	216	327
COD, gO_2/m^3	1,256	1,688
Protein, g/m^3	237	237
Lactose, g/m^3	323	323
TDS, g/m^3	831	11,276

$300\,g/m^3$ [21]; $CMC_{SDS} = 2{,}257\,g/m^3$ [22]; $CMC_{SDBS} = 800\,g/m^3$ [23]), which indicates the presence of these compounds in monomeric form.

The aqueous solutions containing 0.75% w/v of milk (Solution A) and 2% w/v aqueous solution of the single-phase detergent to which was added 0.75% w/v of milk (Solution B) are characterized in Table 4.

3.2. Membrane resistance

For NF and UF membranes filtration of water was performed in the transmembrane pressure range of 0.5–4 bar. Based on a linear relationship between the water flux and pressure the membrane resistance R_m (Table 5) was calculated according to the equation:

$$R_m = \frac{\Delta P}{\eta_w J_w} \quad (1)$$

The results showed that the membrane resistance decreases with increasing membrane molecular weight cut-off.

3.3. Filtration experiments

3.3.1. Transport properties of membranes

The transport properties of flat-sheet membranes are presented in Figs. 1 and 2. During the filtration cycle of the tested solutions, a systematic decrease in the permeate flux in comparison with the flux of deionized water was noticed. With increasing concentration of the single-phase detergent in the feed solutions, a greater reduction in the permeate flux was noticed (Table 6), due to more intense formation of a polarization layer on the membrane surface. NF and UF membranes were also characterized by significant susceptibility to blocking by milk components (mainly proteins) during filtration of 0.75% w/v solution of milk. The highest values of relative permeability of the membranes were observed for Solution B (2% w/v aqueous solution of the single-phase detergent to which was added 0.75% w/v of milk). In a strongly alkaline environment (pH = 13.0) caused by the presence of NaOH, a modification of the protein system took place as a result of protein denaturation. According to the model proposed by Erdem and Yuksel [24], the denatured proteins form complexes with casein micelles causing an enlargement of the casein micelles. During membrane filtration, the large particles are retained on the membrane surface and help us to protect the membrane pores from fouling and congestion. Moreover, the accumulated macroparticles form an additional sieving layer and thus the flow of permeate accelerates. The interpretation is also supported by the presented findings (Table 6).

A greater decrease in hydraulic performance of the membranes was observed with an increasing MWCO value for most of the tests. For example, the relative permeability of the membranes during solution B filtration was equal to 76, 73, 60 and 20% for NP030, NP010, UP005 and UP010, respectively. However, the PS1 kDa membrane with the highest hydrophobicity from among others, was generally more susceptible to fouling in comparison with the UP005 membrane with a higher MWCO value.

Rinsing with deionized water of the membranes helped to significantly restore of their original permeability or cause even an increase of water flux in comparison with the brand-new membranes (Table 7). After the regeneration step with the use of 0.1 N HCl (after filtration of the detergent solutions as well as Solution B) and 0.1 N NaOH (after filtration of solution A), permeability of the membranes accounted for more than 95% permeability of the brand new membranes.

Table 5
Membrane resistances

Membrane	NP030	NP010	PS1	UP005	UP010
R_m, $10^{12}\,m^{-1}$	170 ± 2.4	31.0 ± 0.4	66.6 ± 1.4	23.7 ± 3.2	6.9 ± 0.5

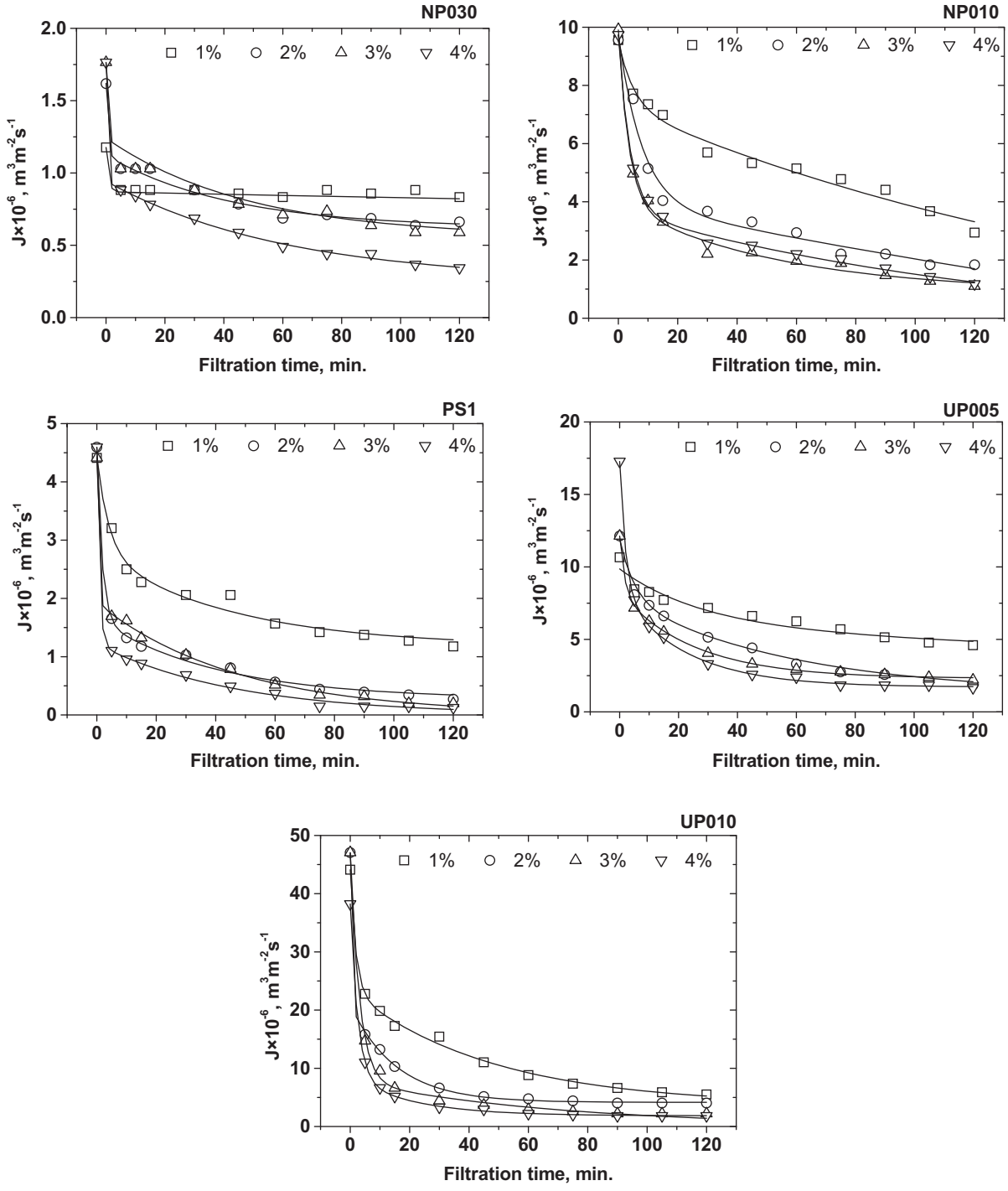

Fig. 1. Changes in the permeate flux during the filtration cycle of single-phase detergent solutions.

3.3.2. Separation properties of the membranes

The composition of the filtrates from each membrane was measured using the parameters described in Section 2.3. Analyses were conducted on the averaged samples that were collected within a filtration time of 120 min. The results obtained are presented in Fig. 3.

The quality of the permeates obtained during UF of the pure single-phase detergent solutions indicates that the detergency properties of cleaning solutions

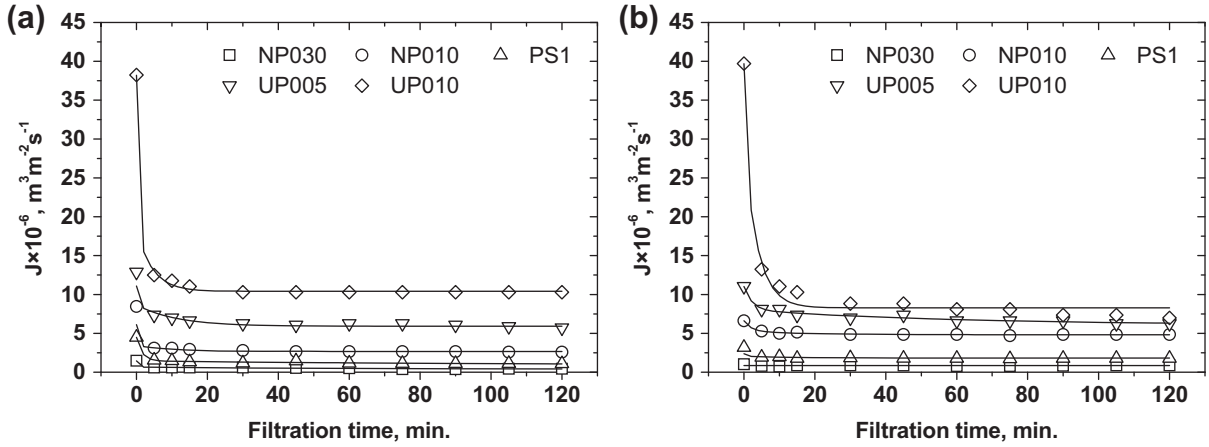

Fig. 2. Changes in the permeate flux during the filtration cycle of tested solutions (a: Solution A and b: Solution B).

Table 6
Relative flux of flat-sheet membranes for the filtration time $t = 60$ min

Membrane	Detergent concentration, % w/v				Solution A	Solution B
	1	2	3	4		
NP030	0.71	0.42	0.40	0.28	0.35	0.76
NP010	0.54	0.31	0.20	0.23	0.31	0.73
PS1	0.36	0.12	0.12	0.08	0.26	0.55
UP005	0.59	0.27	0.24	0.14	0.49	0.60
UP010	0.20	0.10	0.06	0.06	0.27	0.20

Table 7
Relative flux of flat-sheet membranes after the rinsing step with deionized water

Membrane	Detergent concentration, % w/v				Solution A	Solution B
	1	2	3	4		
NP030	1.38	1.36	0.89	0.80	0.75	2.00
NP010	0.81	0.96	0.61	0.68	0.79	0.89
PS1	0.92	0.86	0.78	0.75	0.49	1.08
UP005	0.90	0.92	0.82	0.83	0.75	0.90
UP010	0.90	0.89	1.25	1.38	0.70	0.81

were increased in comparison with the feed solutions (Fig. 3(d)). This phenomenon was caused probably due to the removal of organic additives from solutions, thus resulting in the reduction of colour intensity of filtrates. Whereas, the application of NF membranes resulted in a slight weakening of the detergency properties (Fig. 3(d)). One may have noticed that for NP010 and NP030 membranes, the surface tension in the permeate increased by about 12 mN/m in comparison with the feed solutions. This was mainly due to the separation of $EDTANa_4$ acting as a chelating agent, besides having the ability to reduce the surface tension of solutions [25]. As a result of the partial separation of $EDTANa_4$ (with a molecular weight of 416.21 Da) and other organic additives, the values of TOC and COD were reduced in the permeates (Fig. 3(e) and (f)). For example, the reduction of TOC amounted to 33, 25, 25, 20 and 10% for 3% w/v detergent solutions with the use of NP030, NP010, PS1, UP005 and UP010 membranes, respectively. Other parameters, such as pH, conductivity and concentration of NaOH, did not change and

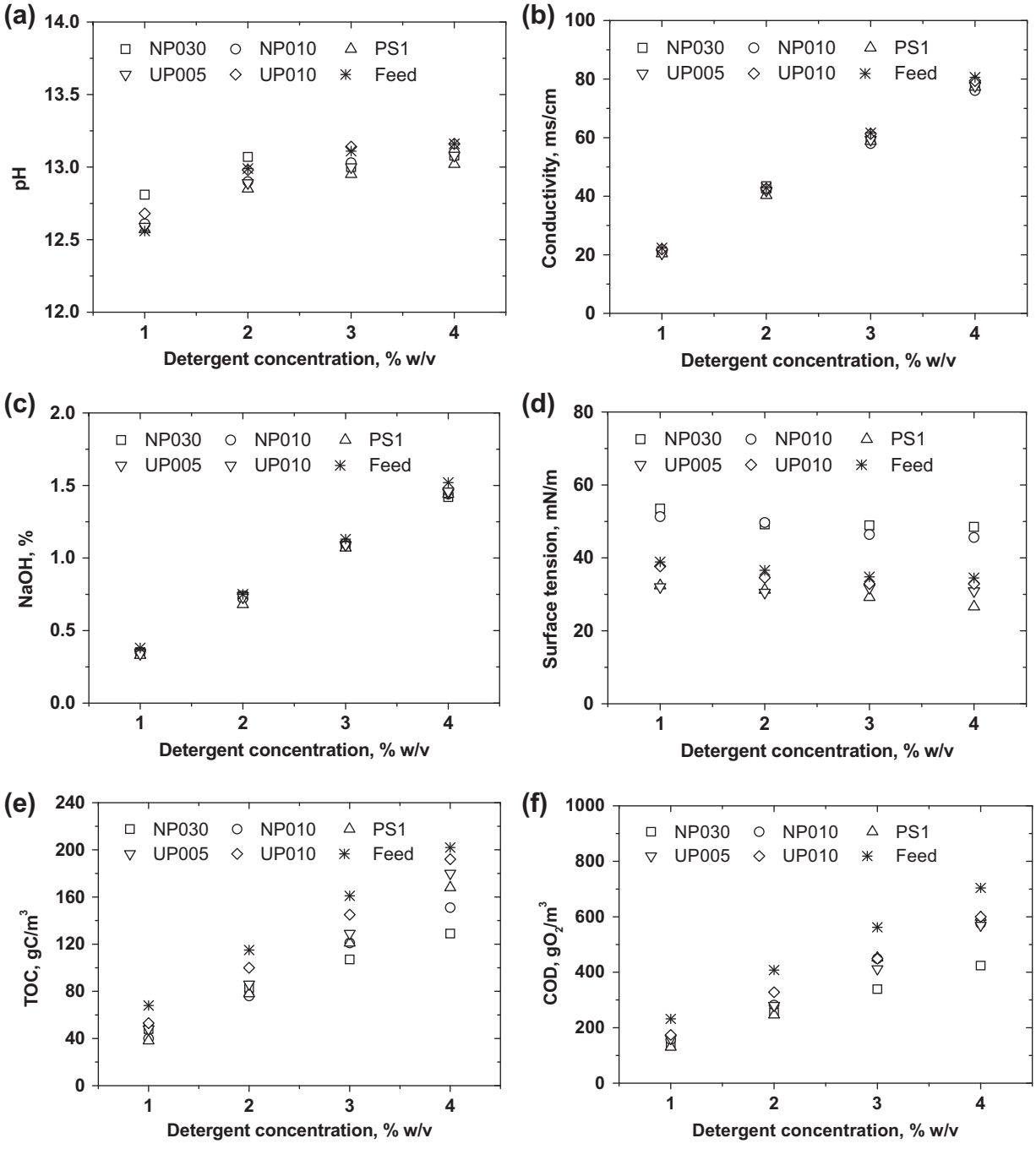

Fig. 3. Changes in the quality of the single-phase detergent solutions in membrane filtration.

remained at similar levels as in the feed solutions (Fig. 3(a)–(c)).

In the next stage of research, the effectiveness of NF and UF membranes for the separation of milk components from aqueous solutions and the single-phase detergent solutions was evaluated. The representative results are presented in Fig. 4.

The results showed that the pH of the filtrates remained constant and corresponded to the values for the feed solutions (Fig. 4(a)). The concentration of NaOH also did not change, confirming the lack of separation of this compound on NF and UF membranes (Fig. 4(c)). Whereas the conductivity of the filtrates decreased with decreasing MWCO value of the membranes (Fig. 4(b)). In the case of the tested solu-

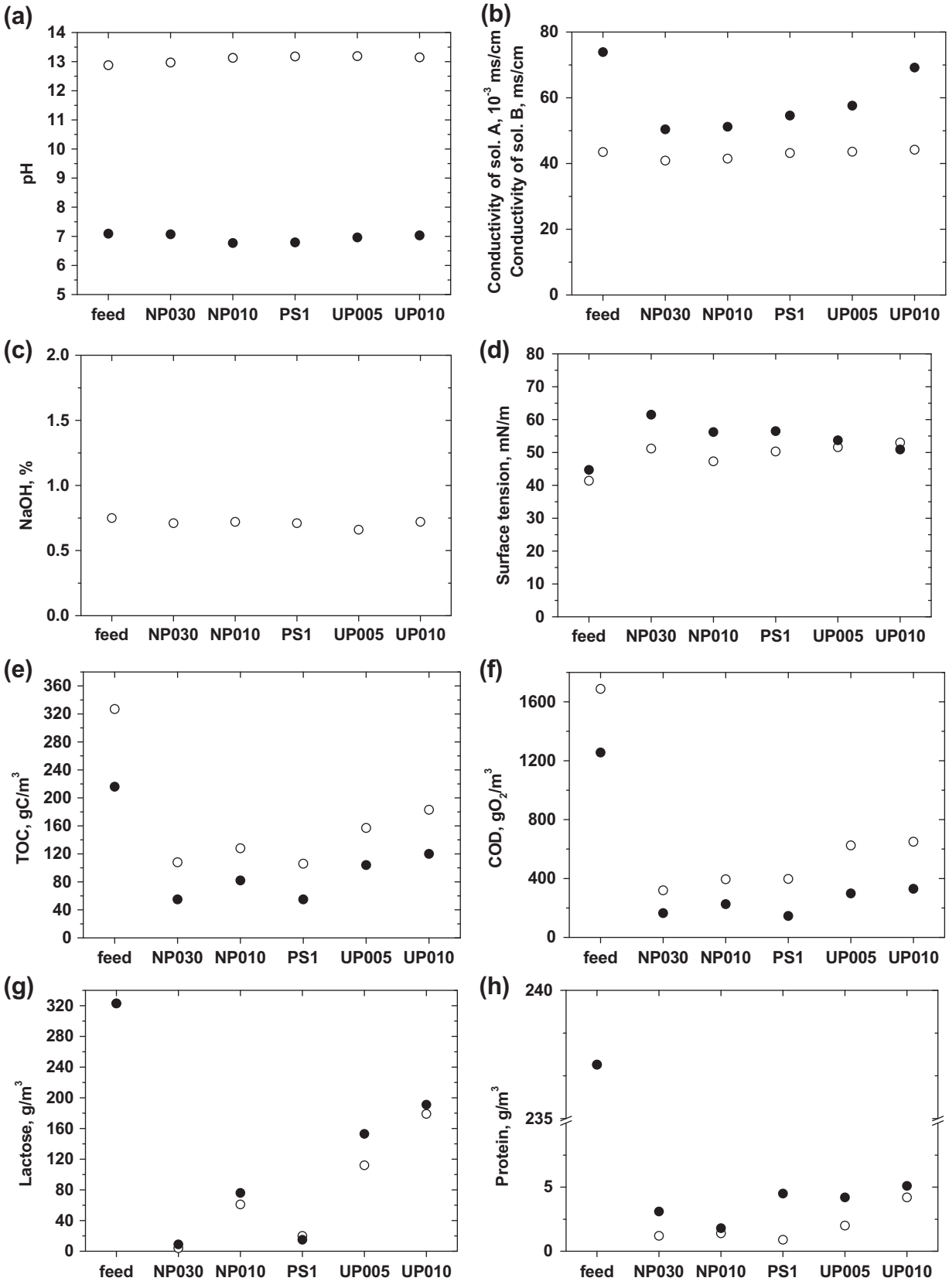

Fig. 4. Changes in the quality of the tested solutions in membrane filtration (solid symbols: Solution A and open symbols: Solution B).

tions, the decrease in conductivity was primarily related to the separation of multivalent ions (mainly $EDTA^{4-}$ and Ca^{2+}).

The permeates from filtration runs were characterized by a relatively high retention of organic matter expressed as TOC and COD (Fig. 4(e) and (f), Table 8). The retention of organic compounds for both solutions was similar. For example, the retention of COD amounted to 82 and 77% during filtration of Solutions A and B with the use of NP010 membrane, respectively. Räsänen et al. [26] reported a reduction in the COD content on a level of 90% and 87% with the use of Desal-5 DK (150–300 Da) and Desal-5 DL (150–300 Da), respectively. The Gésan-Guiziou [13] showed that NF helped in significant recovery of caustic solutions (>97%) with a reduction in the COD content of 14–71% depending on the NaOH life time. A very similar retention coefficient of COD was presented in the work of Fernandez et al. [17]. The retention of COD content from the detergent solutions ranged from 10 to 70%, and the higher the retention of COD content, the more detergent solutions were contaminated.

The protein and the lactose content determined in the treated solutions by means of NP030, NP010 and PS1 membranes was of very low concentration (Fig. 4 (g) and (h), Table 8). This indicates that the recovered permeates were almost the pure detergent, which were more dilute, the more dense membranes were used. The Erdem and Yuksel concept has also been confirmed at this stage of experiments. In the alkaline medium (Solution B), larger agglomerates were formed due to the denaturation of proteins. As a result of the increase in protein molecular weight, they were more efficiently separated on the membrane surface. The separation efficiency of lactose, because of its low molecular weight, was significantly dependent on the membrane type (Fig. 4(g), Table 8). A satisfactory separation was obtained on the NF membranes (NP030 and NP010) and the compact UF membrane (PS1). For these polymers, separation of lactose from Solutions A and B that took place was in the range of 77–97% and 80–99%, respectively.

The values of surface tension of Solution A (44.7 mN/m) and Solution B (41.4 mN/m) were slightly higher than the value of surface tension determined for a 2% w/v solution of the single-phase detergent. For Solution A, the surface tension of the permeates increased with decreasing the MWCO of the membranes (Fig. 4(d)). This phenomenon was most likely caused by the separation of peptides, which according to literature data have the ability to lower the surface tension of solutions. However, for Solution B, the surface tension determined in the permeates was the result of separation of the components that lowered the surface tension of liquids, such as peptides, anionic surfactants and $EDTANa_4$.

Literature reports corroborate the results of the present study obtained. According to Alvarez et al. [27] in successive cleaning cycles when using a 2% caustic solution, the surface tension of the solution got lowered from the value of 74–30 mN/m. The authors found that this phenomenon was due to chemical degradation of milk components by sodium hydroxide. Similar results have been published by Fernandez et al. [17]. The surface tension of a fresh detergent was 40 mN/m, and the spent detergent purified with the use of Koch MPS-34 module (200 Da) had a surface tension of 30–40 mN/m.

4. Conclusions

Studies have shown the usefulness of membrane filtration using polymeric membranes for the recovery of the single-phase detergent for the purpose of its reuse in cleaning systems. NF and UF membranes were susceptible to fouling mainly by the milk components during filtration experiments. However, rinsing and regeneration steps led to significant restoration of their original permeability. All the membranes tested were also characterized by chemical stability.

Table 8
Retention coefficients (R, %) of organic compounds on NF and UF membranes

Membrane	Solution A				Solution B			
	TOC	COD	Lactose	Protein	TOC	COD	Lactose	Protein
NP030	75	87	97	99	67	81	99	100
NP010	62	82	77	99	61	77	80	99
PS1	75	88	95	98	68	76	93	100
UP005	52	76	53	98	52	63	63	99
UP010	44	74	41	98	44	61	41	98

The recovered spent detergent maintained its basic cleaning properties, i.e. high pH, high concentration of NaOH and low value of surface tension. Moreover, the NF membranes (NP030 and NP010) and the tight UF membranes (PS1) showed high separation of specific milk components (protein and lactose) and organic matter expressed as TOC and COD. Other UF membranes were characterized by a significantly lower retention of these components.

Nomenclature

A	—	membrane area (m^2)
C_f	—	concentration of pollutants in the feed ($g\,m^{-3}$)
CIP	—	cleaning in place
CMC	—	critical micelle concentration
COD	—	chemical oxygen demand ($gO_2\,m^{-3}$)
C_p	—	concentration of pollutants in the permeate ($g\,m^{-3}$)
J	—	permeate flux ($m^3\,m^{-2}\,s^{-1}$)
J_w	—	flux of deionized water ($m^3\,m^{-2}\,s^{-1}$)
MWCO	—	molecular weight cut-off (Da)
PES	—	polyethersulphone
PS	—	polysulphone
R	—	retention coefficient (%)
R_m	—	membrane resistance (m^{-1})
RF	—	relative flux (–)
SDBS	—	sodium dodecylbenzenesulphonate
SDS	—	sodium dodecyl sulphate
SLEC	—	sodium lauryl ether sulphate
t	—	filtration time (s)
TDS	—	total dissolved solids ($g\,m^{-3}$)
TOC	—	total organic carbon ($gC\,m^{-3}$)
V	—	volume of the permeate (m^3)
Greek symbols		
ΔP	—	transmembrane pressure (bar)
η_w	—	viscosity of deionized water (Pa s)

Acknowledgement

The project was funded by the National Science Centre No. N N523 740 440.

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