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The chemical cleaning of ceramic membrane used in UF

Maria Tomaszewska, Lidia Białończyk

West Pomeranian University of Technology, Szczecin, Institute of Chemical and Environment Engineering, ul. Pułaskiego 10, 70-322 Szczecin, Poland, maria.tomaszewska@zut.edu.pl

Ultrafiltration (UF) is one of the membrane processes which is mostly used in the dairy industry for the separation and concentration of whey components or fermentation broth. Fouling of UF membranes in the food industry is primarily due to a deposition of microorganisms, proteins, fats and minerals on the membrane surface. Thus, cleaning of the membranes is an essential step of UF separation. The results from investigations of chemical cleaning of a ceramic UF membrane fouled by precipitation of whey components and yeast contained in the fermentation broth are presented. The effect of cleaning procedure on the degree of permeability restoration by the fouled membrane was studied. The results demonstrated that a combination of sodium hydroxide, phosphoric acid and sodium hypochlorite as a disinfectant could be successfully used to achieve an optimum recovery of the membrane properties.

Keywords: ultrafiltration, ceramic membrane, whey, broth, fouling, chemical cleaning.

INTRODUCTION

The development of membrane processes based on new advanced separation techniques allows for environmentally friendly waste disposal. Ultrafiltration (UF) is one of the processes of this technology which has the most applications in food industries such as milk dehydration, whey concentration and proteins separation to produce whey protein concentrates (WPC)[1–2]. The residual lactose can be fermented to useful products, such as ethanol or lactic acid. However, the whey proteins and yeast used in fermentation block the membrane surface, which may reduce its permeability[3].

The membrane fouling phenomenon is an important limitation of the membrane technology to be generally employed. Fouling is defined as existence and growth of microorganisms and a deposition of suspended or dissolved substances on the membrane surface and/or within its pores, which results in a flux decline[2,4]. Several types of fouling can occur in the membrane systems, e.g. inorganic fouling or scaling, particulate and colloidal fouling, organic fouling and biological fouling (biofouling). The organic fouling is mainly associated with adsorption/deposition of dissolved or colloidal organic material on the membrane surface. This can be adsorption at a molecular level or a gel layer formation of macromolecules on the membrane surface[4].

To overcome this problem, a cleaning process must be carried out. Cleaning is usually performed in the three forms: physical, chemical and biological[2]. Chemical methods are probably the most widely used. The first step of chemical cleaning is finding appropriate materials as cleaning agents. Choosing the best materials depends on the composition of the feed and precipitated layers on the membrane surface as well as a membrane material and in most cases is performed using a trial-and-error method[5]. The selected washing agents should be chemically stabile, safe, low cost and capable of water washing[6]. These agents must be also able to dissolve most of the precipitated and deposited materials and to remove them from the membrane surface. Simultaneously, they should not damage the membrane surface[7].

Some of these cleaning agents are acids, alkalis, surfactants, disinfectants and they can be used as a combination of these materials[2,8]. Using these materials as a cleaner, the effect of some parameters such as pH, concentration and washing time[7] and the operating conditions such as cross flow velocity, pressure and temperature[9–10] had to be considered. In order to clean the membranes fouled with milk and whey, a single-stage alkaline cleaning followed by an acid washing step has been suggested[9], and to get better results, one enzyme washing step could be used before chemical washing[5]. As an example, the ultrafiltration plants for milk and whey protein concentration are often cleaned as follows: rinsing with water at normal operating temperature, alkaline cleaning at 60–75°C for 30–60 minutes, rinsing with water, acid cleaning at 50–60°C for 20–60 minutes and the final rinsing with water. A commonly made mistake is trying to short the rinsing time between acid and alkaline cycles (and vice versa). In the first case, trapped acid solution lowers the pH of alkaline solution[10–11]. The last step of the procedure is disinfection, when all pathogenic microorganisms are destroyed. This step is often carried out at room temperature for 10–30 minutes. Thus, to reach the optimum conditions for cleaning processes, having enough information on the operating conditions and the effects of cleaning materials is necessary[2,6].

In order to obtain a good hydraulic cleaning effect, the circulation flow rate should be higher and the pressure lower than those used during normal operation. Under these conditions the compressible fouled layer is relaxed. Hydraulic cleaning can be affected by high shear rates at the membrane surface.

A periodical backflushing involves reversal of the permeate flow by applying on the permeate side a higher pressure than that on the feed side of the membrane. During the backflush, the external cake (or a portion of it) may be lifted off the membrane and swept away by the crossflow. Internal flocculants may also be partially or completely removed. The efficiency of this type of cleaning depends strongly not only on the type of suspension to be treated and the type of fouling that it causes, but also on the frequency and amplitude of the pulse of reverse pressure. The term backflushing refers to low- frequency permeate flow reversal, otherwise, the process is similar to high-frequency backpulsing[12].

Two different types of a feed: a fermentation broth and deproteinized whey were chosen to elaborate the washing procedure after the ultrafiltration process using the ceramic membrane with cut-off value of 15 kDa. The future studies will be devoted to the fermentation process of the deproteinized acidic whey in a membrane bioreactor.

EXPERIMENTAL

The UF experiments were carried out using the system, presented in Fig.1. The installation was equipped with a tubular module with ceramic 7-channels membrane (TAMI INDUSTRIES, Germany) with the cut-off value of 15 kDa. The active layer of the ceramic membrane was made of TiO_2/ZrO_2. The module diameter was 10 mm and its length was 600 mm. The effective area for mass transfer amounted to 0.032 m^2.

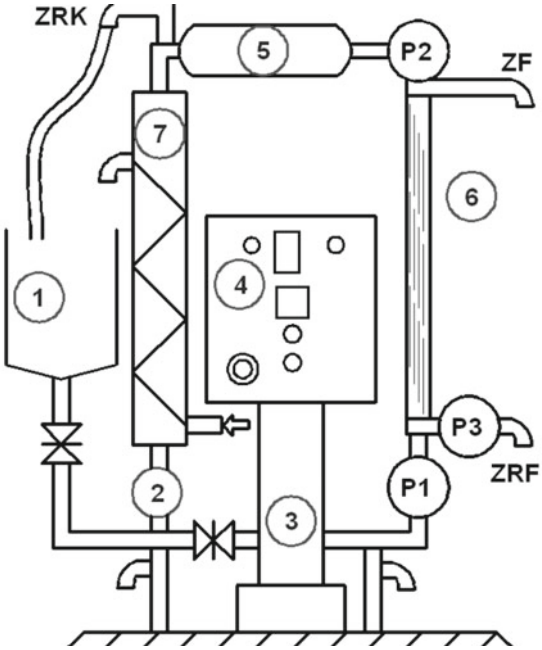

Figure 1. Scheme of the UF experimental set-up: 1 – feed tank, 2 – thermometer, 3 – pump, 4 – control panel, 5 – tube furnace, 6 – membrane module, 7 – cooling system, P1, P2, P3 – manometers

A fermentation solution for UF process was prepared by dissolution of 50 $g \cdot dm^{-3}$ of sucrose in tap water, boiled three times. A commercially available Gamma Hefe yeast (Saccharomyces cerevisiae, AB Enzymes, Germany) was used as the microorganism in the amount of 5 $g \cdot dm^{-3}$. The dry yeast was rehydrated for 30 min, while the broth was agitated periodically. The fermentation process was carried out for 24 hours and after that the broth was subjected to the UF separation[13].

The second process was carried out using a raw acidic whey collected from a local dairy which was characterized by the following parameters: proteins concentration range within 11–12 g/dm^3, the concentration of chlorides was 2–3 g/dm^3, whereas that of lactose 30–40 g/dm^3. The pH was in the range of 3.6–4.2. A preliminary treatment of whey was described earlier in[14]. The whey was deproteinized by thermal (92°C) and chemical coagulation (NaOH addition to adjust the pH at 6.2). The precipitated proteins were separated from the whey by centrifugation at 9000 rpm for 10 minutes at 20°C. The deproteinized whey was subjected to the separation of remained proteins from lactose by UF.

The determination of TOC both in the feed (the broth or deproteinized whey) and permeate was performed on the basis of an analysis of the total organic carbon (TOC-Analyzer multi N/C, Analytic Jena).

The UF process both for the broth and the whey was carried out at the feed temperature of 303 K, the transmembrane pressure of $\Delta P = 1$ bar and feed flow rate for 1 $m \cdot s^{-1}$ equal to 0.108 $m^3 \cdot h^{-1}$ for all the experiments. Mass of the permeate was measured every half hour. The permeate flux decreased after 2.5–3 hours of the process duration by about 30–40%. Then the UF separation was stopped and a cleaning procedure was performed after each experiment. In order to obtain a good hydraulic cleaning effect, the circulation flow rate and temperature were higher and the pressure was lower than those used during the normal operation. The UF installation was rinsed by distilled water to remove whey protein or yeast deposits from the membrane surface which caused a reduction in the permeate flux. Subsequently, the installation was rinsed with water at 30°C for 60 minutes followed by rinsing with alkaline bath at 70°C for 60 or 75 minutes (time depend on the NaOH concentration) The solution of NaClO with the maximum concentration of 0.3 $g \cdot dm^{-3}$ at 70°C for 5 minutes was used for completion cleaning. The module was then rinsed with water at 40°C for 30 minutes. The last step of cleaning was performed with 0.1% phosphoric acid at 50°C for 30 minutes and followed by rinsing with water at 30°C for 30 minutes. The content of total chlorine in sodium hypochlorite was 1.46 $g \cdot dm^{-3}$. The determination was performed by iodometry titration method[15]. After cleaning, it is advisable to determine the cleaning efficiency. Generally, the effectiveness of cleaning is evaluated by measuring the water flux after cleaning at defined pressure, temperature and circulation velocity. A low water flux is an indication that the cleaning is insufficient[11].

RESULTS AND DISCUSSION

The fermentation process and re-cleaning procedure of the membrane were repeated, to examine the effectiveness of recleaning of the membrane. As the fermentation progresses, usually after 24–48 hours, when the ethanol concentration decreases, yeast colonies disintegrate and falling to the bottom of the tank, creating a lees[16]. During the UF process of the broth separation, deposits of the yeast was retained on the membrane surface and blocked the membrane pores. On the other hand, the components with smaller molecular weight (water and dissolved salts, ethanol and gas components) were transferred through the membrane. Figure 2 shows the changes of permeate flux during ultrafiltration of the fermentation broth and the results of cleaning procedure performed at higher temperature then that of UF separation.

The permeate flux, amounted to 130.8 $dm^3 \cdot m^{-2} \cdot h^{-1}$ for the clean membrane when water was used as a feed. During the UF process of fermentation broth, the permeate flux was much lower and decreased after 3 hours of the process duration from 34.09 to 22.96 $dm^3 \cdot m^{-2} \cdot h^{-1}$ for fermentation broth I and II.

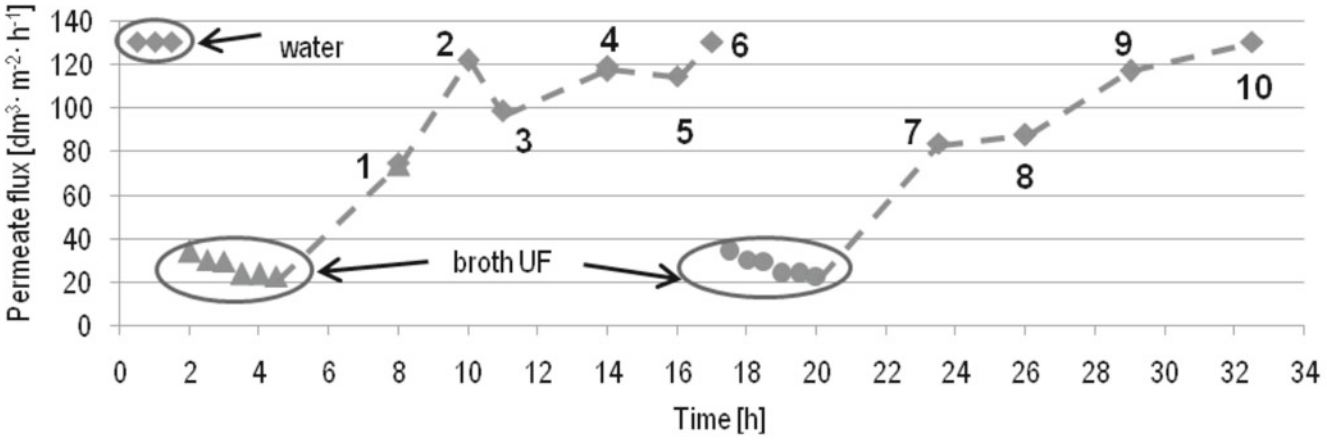

Figure 2. Changes of permeate flux versus UF time of the fermentation broth and during the cleaning procedure (membrane cut-off: 15kDa). A dotted line and points 1 to 10- cleaning operation, ▲ – broth I, ● – broth II

A preliminary investigation demonstrated that a significant blocking of the membrane surface (when the permeate flux decreased more than 30–45% of the initial value for water) resulted in a prolongation of cleaning time and may even lead to the complete clogging of the membrane.

A cleaning procedure was performed after each separation process by ultrafiltration. The steps of the membrane cleaning, the agents, their concentration and time of subsequent steps duration with time which was required to heating and replacement the cleaning solutions were summarized in Table 1.

A dotted line and points 1–10 (Fig.2.) presents the changes of permeate flux (the membrane efficiency) during the cleaning operations.

Initially, the UF installation was rinsed by a mixture of distilled and tap water at 30°C for 60 minutes to remove the deposits from the membrane surface. Subsequently, the installation was subjected to cleaning by an alkaline bath (1% NaOH) at 70°C for 60 minutes. NaOH solution changes the pH to a higher value and thus provides better conditions to remove contaminations. As a cleaning agent, sodium hydroxide saponificates fat and hydrolyzes protein[11]. The next alkaline agent with free chlorine solution, e.g. sodium hypochlorite was used. Such a solution has a better cleaning effect than the alkali alone and also has a disinfectant and oxidizing properties. Sodium hypochlorite itself has some cleaning ability[11]. One reason for this is thought to be the cleaning of the membrane pores. The solution of NaClO with the maximum concentration of 0.3 g·dm^{-3} at 70°C for 5 minutes was used to complete cleaning. The module was then rinsed twice with water at 40°C. The last step of cleaning was performed with 0.1% phosphoric acid, used to dissolve the precipitate of inorganic salts[11], at 50°C for 60 minutes and followed by rinsing two times with water at 30°C for 30 minutes. After the whole cleaning cycle, the UF process was carried out with water as a feed (point 1, Fig.2.). The efficiency (for water) of the membrane was only restored in 57% of the initial value. Therefore, the cleaning cycle was repeated with the hydroxide solution at higher concentration equal to 3% during 75 minutes. The membrane performance was than tested twice: after the alkaline bath (point 2, Fig.2.) the efficiency increased to 94%, whereas after the acid bath (point 3, Fig.2.) decreased to76 %. The efficiency after acid bath was lower because of particles removed from the UF pilot plant (of dead spaces in pipes and the installation) was deposited on the membrane surface. The whole cleaning procedure was repeated again and the permeate flux amounted to 90% (point 4, Fig.2.). After the subsequent cleaning using the alkaline bath (3% NaOH), the membrane efficiency was 85% (point 5, Fig.2.). The initial (permeate flux) efficiency was restored in 100% after the acid bath (point 6, Fig.2.).

The ultrafiltration of fermentation broth was performed again using membrane subjected to chemical cleaning (Fig.2.). A preliminary investigation demonstrated that a significant blocking of the membrane surface (when the permeate flux decreased more than 30–45% of the initial value for water) resulted in a prolongation of cleaning time and may even lead to the complete clogging of the membrane. Therefore when the permeate flux decrease by about 45% (the last point in the 20h, Fig.2.), a similar cleaning procedure as before was carried out. After the first cycle of cleaning, the membrane efficiency amounted to 60% of initial value (point 7, Fig.2.), similarly as for process performed with the broth I. The cleaning cycle was carried out three times more and the efficiency amounted to: 69, 91 and 100%, respectively (points 8, 9 and

Table 1. A chemical cleaning procedure of ceramic membrane

Lp.	Operations	Time [minutes]	Temperature [^{0}C]
1	Water (3x 20 minutes)	60 +/- 5 minutes	30
2	Alkaline bath (1 or 3% NaOH solution) (Solution of NaOCl 0.3 g·dm^{-3}- used at last for 5 minutes of this operation)	60 (1% NaOH) or 75 (3% NaOH) +/- 20 minutes	70
3	Water (2x 15 minutes)	30 +/- 10 minutes	40
4	Acid bath (0.1% phosphoric acid)	30 +/- 20 minutes	50
5	Water (2x 15 minutes)	30 +/- 5 minutes	30

10, Fig.2.). The results shown that the initial performance of the membrane in both processes was successfully restored after 12.5 hours for both of the ultrafiltration processes. In spite of using lower (1%) or higher (3%) NaOH concentration, the initial performance was not restored faster. The literature reports that the cleaning efficiency depends on the cleaner concentration. Using surfactant higher concentration causes higher resistance removal or flux recovery. However, the effect is insignificant at high concentration. This is due to the limited ability of cake removal by any agent. The adsorbed layers or irreversible fouling materials cannot be removed. For acid and alkali the cleaning efficiency increases with the cleaner concentration, passes a maximum and decreases afterwards. The concentration, which provides maximum efficiency, is the optimum concentration[17].

During the UF process of the deproteinized whey, a part of proteins was retained in the retentate, whereas the lactose and proteins with smaller molecular weight were transferred through the membrane. Figure 3 shows the changes of the permeate flux during the UF process carried out at 30°C. The permeate flux was 14 times smaller than that for the water and decreased after 2.5 h of the process duration. It was caused by a deposit of whey proteins on the membrane surface which blocked the membrane pores. The UF permeate flux for the module with a 15 kDa cut-off decreased and varied from 12.50 to 9.30 and from 9.30 to 8.09 $dm^3 \cdot m^{-2} h^{-1}$ for whey I and II, respectively. These results depend on the differences in the membrane performance after cleaning.

The cleaning procedure applied after UF of whey was the same as in the case of a fermentation broth (Tab.1). A dotted line and points 1 to 10 (Fig.3.) presents the changes of permeate flux (the membrane efficiency) after individual steps of the cleaning operations.

After the first cleaning cycle, the permeate flux (point 1, Fig.3.) achieved only 58% of the initial efficiency of the membrane (for water). Therefore, the cleaning cycle was repeated with the alkali bath of higher NaOH concentration equal to 3%. However, the efficiency decreased after the acid bath and amounted to 42% (point 2, Fig.3.). The same trend was observed when a fermentation broth was used as a feed (point 3, Fig.2.). The efficiency after acid bath was lower because of particles removed from the UF pilot plant (of dead spaces in pipes and the installation) was deposited on the membrane surface and blocked the membrane pores again. After that, the cleaning cycle with the alkali bath concentration equal to 3% was carried out additionally two times and the efficiency was still insufficient and equal to: 42 and 48%, respectively (points 3 and 4, Fig.3.). Therefore, the cleaning cycle was performed four times more. The performance increased after each cycle and amounted to 46, 58, 62 and 91% (points 5, 6, 7, 8, Fig.3.). Finally, after 8 cycles of cleaning (23 hours) the initial performance was not obtained and was only equal to 91%.

The ultrafiltration of whey was performed again using the washed membrane. In the first two cycles the membrane efficiency reached practically the same value equal to 79% (points 9 and 10, Fig.3.). After the subsequent third cycle of cleaning, the efficiency decreased rapidly to 44% of initial value (point 11, Fig.3.). The first three cycles of cleaning were performed using 1% alkaline bath. The cleaning cycle with higher concentration of the alkaline bath was carried out three times more and efficiency increased slowly to: 53, 58 and 70% (points 12 and 14, Fig.3., respectively). The point 13 corresponds only to the flux after the alkaline bath.

After the next cycle, the permeate flux decreased to 40% (point 15, Fig.3.) and the same cleaning procedure as before was performed twice again. The membrane performance was tested twice: after the first and the second alkaline bath (points 16 and 18, Fig.3.) and after acid bath (points 17 and 19 Fig.3.). The final efficiency after entire cleaning procedure and 30 minutes disinfection amounted to 90 % (point 20, Fig.3.). The results shown that the rinsing procedure takes much more time than in the case of a fermenting broth. The initial performance of the membrane in both operation for whey was restored only in 91 and 90 % after 23 and 29 hours for both ultrafiltration processes.

Based on TOC analysis, a retention coefficient for whey and fermentation broth was calculated. The results were presented in Table 2.

In the case of broth, a retention coefficient amounted to above 91% at the beginning of the process and was higher than 90% after 3 hours of the UF process. The concentration of organic substances (determined as TOC) in the permeate during MD was stable and was in the range from 1.02 to 1.15 $g \cdot dm^{-3}$ for broth at the fermentation I and II. The yeasts was completely retained

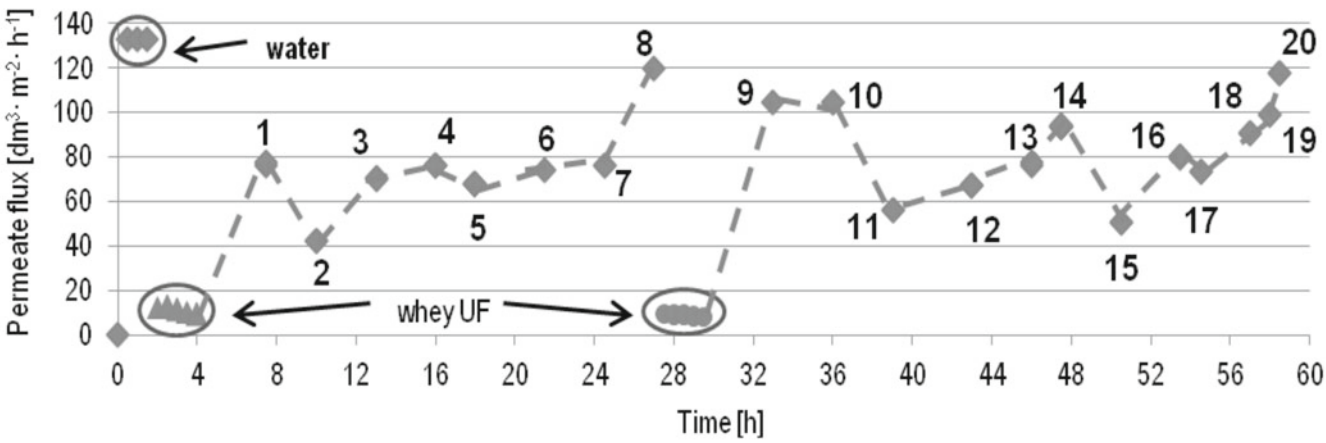

Figure 3. Changes of permeate flux versus UF time of the whey and during the cleaning procedure (membrane cut-off: 15kDa). A dotted line and points 1 to 10- cleaning operation, ▲ – UF I, ● – UF II

Table 2. A concentration of organic substances in the feed and permeate in both whey and fermentation broth

Feed		TOC Retentate [g·dm^{-3}]	TOC Permeate [g·dm^{-3}]	Retention coefficient [%]
Whey	0	18.90	7.65	59.52
	UF I	13.86	6.25	54.91
	UF II	11.37	4.95	56.46
Broth	0 (I)	11.66	1.02	91.25
	0 (II)	12.95	1.11	91.43
	Broth I	10.41	1.02	90.20
	Broth II	12.24	1.15	90.60

0 – initial value of the feed concentration

in the retentate, whereas only the volatile fermentation products such as ethanol were transferred through the membrane. The TOC value for whey was slightly higher in the retentate than that in the permeate due to the concentration process. A final retention coefficient for the whey amounted to 54.91 and 56.46% (process I and II, respectively) and an initial value was 59.52%. The low retention coefficient was result of transfer the lactose and proteins with smaller molecular weight through the membrane. The observed decrease of proteins concentration in the feed could be caused by its deposition on the membrane surface. The deposits were removed in the cleaning procedure. A significant prolongation of membrane cleaning time after whey ultrafiltration was observed. The proteins contained in the whey very quickly blocked the surface and pores of the membrane. A concentration of the solutes in the retentate and permeate of whey indicates that the membrane with cut- off 15 kDa was insufficient for the proteins separations[18].

CONCLUSIONS

The results shown that a fermentation broth can be effectively separated by means of ultrafiltration. However, a part of proteins and lactose was transferred through the membrane.

TOC values both in the retentate and permeate decreased during the UF process. The retention coefficient of organic substances during UF of deproteinized whey was above 55% and of the broth was above 90%.

The permeate flux decreased very fast during ultrafiltration of both whey and broth. The flux decline was caused by a deposit of the whey proteins or yeast on the membrane surface which blocked the membrane pores.

A chemical cleaning procedure of ceramic membranes was found to be effective. The results shown that the initial performance of the membrane was completely restored after ultrafiltration of the broth, whereas only in 90% after UF separation of whey.

LITERATURE CITED

1. Cancino, B., Espina & Orellana, C. (2006). Whey concentration using microfiltration and ultrafiltration. *Desalination*. 200, 557–558. DOI: 10.1016/j.desal.2006.03.463.

2. Kazemimoghadam, M. & Mohammadi, T. (2007). Chemical cleaning of ultrafiltration membranes in the milk industry. *Desalination*. 204, 213–218. DOI: 10.1016/j.desal.2006.04.030.

3. Guimarães, P.M.R., Teixeira, J.A. & Domingues, L. (2010). Fermentation of lactose to bio-ethanol by yeasts as part of integrated solutions for the valorization of cheese whey. *Biotechnology Advances*. 28, 375–384. DOI: 10.1016/j.biotechadv.2010.02.002.

4. Gryta, M. (2008). Fouling in direct contact membrane distillation process. *Journal of Membrane Science*. 325, 383–394. DOI: 10.1016/j.memsci.2008.08.001.

5. Munoz-Aguado, M.J., Wiley, D.E. & Fane, A.G. (1996). Enzymatic detergent cleaning of polysulphone membrane fouled with BSA and whey. *Journal of Membrane Science.* 117, (1–2), 175–187.

6. Kim, K.J., Sun, P., Chen, V., Wiley, D.E. & Fane, A.G. (1993). The cleaning of ultrafiltration membrane fouled by protein. *Journal of Membrane Science.* 80, 241–249.

7. Lindau, J. & Jonsson, A.S. (1994). Cleaning of ultrafiltration membrane after treatment of oily waste water. *Journal of Membrane Science*. 87, 71–78.

8. Moro, M., Yamaday, Y., Izumi, S. & Soeda, J. (1997). Chemical cleaning of membrane cartridges. *JP*. 0952,026.

9. Daufin, G., Merin, U. & Labbe, J.P. (1991). Cleaning of inorganic membranes after whey and milk ultrafiltration. *Biotechnol. Bioeng*. 38, (1), 82–89.

10. Bohner, H.F. & Bardley, R.L. (1992). Effective cleaning of polysulphone ultrafiltration system. *J. Dairy Sci*. 75, 3, 718–724. DOI:10.3168/jds.S0022-0302(92)77808-4.

11. Xing, C.H., Wen, X.H., Qian, Y., Wu, W.Z. & Klose, P.S. (2003). Fouling and Cleaning in an Ultrafiltration Membrane Bioreactor for Municipal Wastewater Treatment. *Separation Science and Technology* 38, 8, 1773–1789. DOI: 10.1081/SS-120019408.

12. Kuberkar, V.T. & Davis, R.H. (2001). Microfiltration of protein-cell mixtures with crossflushing or backflushing. *Journal of Membrane Science*. 183, 1–14. DOI: 10.1016/S0376-7388(00)00577-9.

13. Tomaszewska, M. & Białończyk, L. (2012). The separation of fermentation broth by ultrafiltration using ceramic membrane. *Membrany i Procesy Membranowe w Ochronie Środowiska. Monografie Komitetu Inżynierii Środowiska PAN*. (vol. 96, 73–80 (in Polish)).

14. Tomaszewska, M. & Białończyk, L. Influence of proteins content in the feed on the course of membrane distillation. (sent to Desalination and Water Treatment).

15. The norm PN-ISO-7393-3: 1994.

16. Grajek, W. & Szymanowska, D. (2008). Stresy środowiskowe działające na drożdże *Saccharomyces cerevisiae* w procesie fermentacji etanolowej. Biotechnologia. 3, 82, 46–63.

17. Madaeni, S.S. & Shahram Sharifnia (2000). Chemical Cleaning of Ultrafiltration Membranes Fouled by Whey. *Iranian Polymer Journal*. 9, 3, 143–151. DOI: 1026-1265/2000.

18. Tomaszewska, M. & Białończyk, L. (2011). The separation and concentration of whey using UF/MD process, International Workshop on Membrane Distillation and Related Technologies, Toruń, Poland.