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The Application of Membrane Distillation for Broth Separation in Membrane Bioreactors

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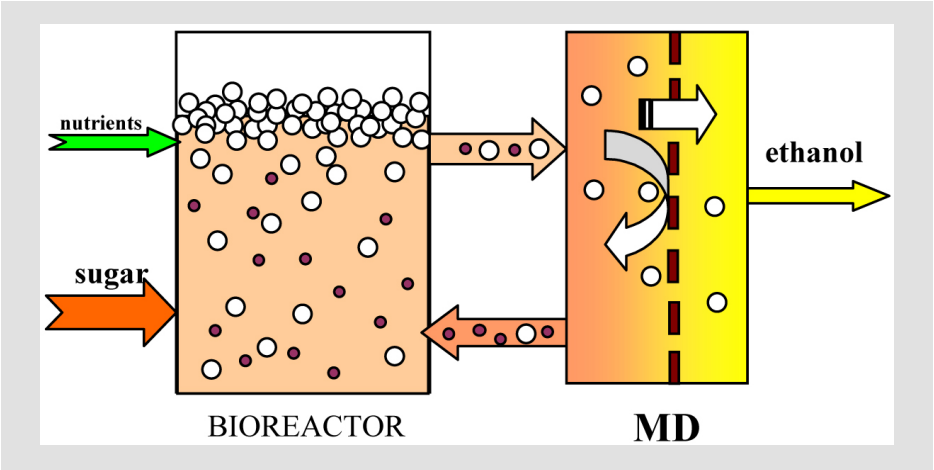
GRAPHICAL ABSTRACT



HIGHLIGHTS

- Separation of volatile compounds from the broths by membrane distillation.
- Studies of glycerol fermentation by *Citrobacter freundii* bacteria.
- Polypropylene membranes were not wetted by organic solutions and broth.

ABSTRACT

The possibility of applying membrane distillation to support the fermentation process was investigated. The capillary polypropylene membranes were assembled in the membrane modules. The studies were carried out using the standard solutions containing the compounds frequently occurring in the broths such as ethanol, citric, acetic and lactic acids, glycerol and 1,3-propanediol. The performance of membrane bioreactor, in which glycerol was fermented by the use of *Citrobacter freundii* bacteria was also examined. The separation of particular components of broths was investigated in a long-term application of membrane distillation and a good resistance to wetting of the used polypropylene membrane was demonstrated during the two year period.

1. Introduction

The solution in bioreactors (broth) contains different materials and chemicals including raw materials, products, microorganisms as well as the nutrients for their growth. Such a complex composition causes significant problems with the separation of pure products as well as with the achievement of good conditions for microorganisms' growth [1-3]. A part of these problems was solved by integration of bioreactor with the membrane separation (membrane bioreactor - MBR) [3, 4-7].

The application of the pressure-driven processes, such as micro- and ultrafiltration, is a means to obtain clear effluents and to retain biomass inside the bioreactor [4-7]. In this way, the cells concentration in the broth can be increased, which allows to limit the effect of products inhibition and to enhance the bioreactor productivity [3, 5]. Such process solutions are applied in the MBRs utilized for wastewater treatment [4, 7, 8]. The application of membrane separation allows the realization of water reuse technology in this case. A membrane in the bioreactors with a serial flow may also perform a role of barrier separating two different kinds of microorganisms that avoid the problems created by mixed cultures [4]. However, the membrane processes enable the separation and purification of biotechnology products. Several new membranes and modules have been developed specifically to meet the requirements of the biotechnology industry [4, 9].

The membrane processes allow the realization of a selective separation of solutions. The application of nanofiltration permits the bioreactor to retain not only microorganisms, but also nutrients, which prevents their losses in continuous fermentations [6, 10]. The selective separation is also possible in pervaporation (PV) [11, 12]. A coupling of fermentation with the PV process

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affords the removal of ethanol produced, thereby reducing the natural inhibition of cell growth caused by ethanol [13]. However, a significant deterioration in the membrane permeability and selectivity was observed when the pervaporation was carried out using the fermentation broth in comparison with that observed in the separation of ethanol–water solutions [14]. This deterioration is caused by the presence of high concentrations of yeast cells and residual by-products. In order to avoid a problem associated with fouling, the PV process should be carried out in the vapour/membrane/vacuum system or by the application of vapour permeation [15].

The volatile components can be separated from bioreactors using membrane distillation (MD), and such a system was termed a membrane distillation bioreactor (MDBR) [16-20]. In this case, both external and submerged MD membrane modules can be used [16, 20-22].

In the MD process, the volatile components of the solution evaporate through the pores of hydrophobic membranes (pores filled only by gas phase) [23, 24]. With regard to this, nonvolatile substances, such as salts, nutrients and cells are retained in the bioreactor [10, 16-21]. This allows only clean water to separate from treated wastewater, which is advantageous, where a long residence time is required for effective removal, e.g. organic solutes from the wastewater [20-22].

The effectiveness of the MD process increases along with the increase of feed temperature, however, the presence of microorganisms, as a rule, limits the feed temperature to 313-315 K. The application of higher feed temperature is possible when the thermophilic bacteria were utilized, which enables the achievement of a higher permeate flux [22, 25].

The fermentation products, such as alcohols or carboxylic acids, act adversely on the growth of microorganisms. The application of the MD process allowed for selective separation of alcohols from broth, and as a result, the process could be operated continuously and the efficiency of bioreactor operation was significantly enhanced [16-18]. MDBR was successfully applied for ethanol production from sugar [16, 17, 26] and pre-hydrolyzed lactose [27].

In the fermentation process, besides the major products, other metabolites, which are frequently the strong inhibitors are also formed. Acetic acid can be an example, which strongly limits the growth of microorganisms [2, 28]. The removal of volatile metabolites in MDBR allows an increase in the effectiveness of lactic acid production from glycerol [29].

The accumulation of cells and other impurities on the membrane surface can limit the membrane bioreactor yield [4, 21, 29, 30]. A permeate flux decline exceeding 50% was observed during the first few days of exploitation of MDBR used for the wastewater treatment by thermophilic bacteria [19, 25]. However, the MD process yield was stabilized in the successive days [20]. Only a slight fouling of the membranes was found after several months of studies on sugar fermentation by *Sacharomyces cerevisiae* yeast [26]. A definitely large decline of efficiency was observed during the fermentation of lactose due to the adsorption of protein [27]. The occurrence of membrane fouling in the bioreactors is required as a rule to perform a periodical chemical cleaning [31].

The membranes used in the MD process cannot be wetted by separated solutions [24]. However, the organic compounds present in the broth reduce the surface tension, which facilitates the wetting of hydrophobic membranes [32]. The membrane wettability is the second exploitation problem, besides fouling, in the MD process. In this work, a long-term study of MDBR was performed to determine the separation of organic compounds often occurring in the broths and the resistance to wetting of used polypropylene membranes.

2. Materials and methods

The studies were carried out in an experimental set-up schematically shown in Figure 1. Two submerged membrane modules with the external surface 0.0072 m^2 (MD1) and 0.0074 m^2 (MD2) were assembled in the feed tank. The tank was closed and air-tight. Polypropylene membranes Accurel PP (Membrana GmbH, Germany) were used for design of the used modules. The nominal and maximum diameters of the pores were 0.2 µm and 0.6 µm, respectively, and the open porosity was 73% (manufacturer's data). In the MD1 module, four membranes S6/2 (d_{in}/d_{out}=1.8/2.6 mm) were assembled with a length of 22 cm. The MD2 module was composed of a single membrane V8/2 HF (d_{in}/d_{out}=5.5/8.6 mm) with a length of 28 cm. The distillate flows inside the capillary membranes in each module. The peristaltic pumps were used to obtain the volume flow velocity of distillate equal to 6± 0.2 ml/s (0.59 m/s – MD1 module and 0.79 m/s – MD2 module).

The initial volume of liquid in the feed and distillate tanks amounted to 4 and 1.5 L, respectively. Long-term studies of MD process performance were performed in the first stage using as a feed the standard solutions containing about 5 g/L of ethanol, glycerol and 1,3-propanediol (1,3-PD), and 4 g/L of citric and lactic acids and 2 g/L of acetic acid (ChemPur, Poland). The MD installation was working continuously (day and night) throughout the several weeks. The permeate flux and the solute concentrations in the feed and distillate were measured usually once per day. Two kinds of experiments were carried-out, performing a continuous concentration of the feed or maintaining a relatively constant concentration of non-volatile solutes in the feed. In the latter case, the feed tank volume was refilled with distilled water up to a constant level.

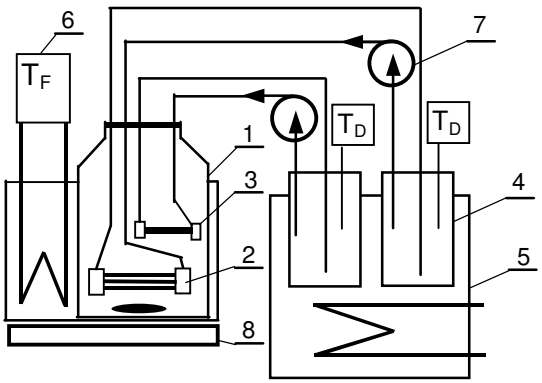

Fig. 1. Experimental set-up. 1– bioreactor (feed tank), 2– MD1 module, 3– MD2 module, 4– distillate tank, 5– cooling bath, 6– thermostat, 7– pump, 8– magnetic stirrer, T– thermometer.

The MDBR performance was studied with the use of broth containing glycerol and *Citrobacter freundii* bacteria. The feed-batch fermentations were carried out at a temperature of 304 K for the initial concentrations of glycerol at about 10 g/L. A prepared broth (culture medium) contained per liter: yeast extract 2 g, meat extract 1.5 g, peptone K 2.5 g, K_2HPO_4•$3H_2O$ 3.4 g, KH_2PO_4•1.3 g, $MgSO_4$•$7H_2O$ 0.4 g, $(NH_4)_2SO_4$•2 g, $CaCl_2$•$2H_2O$ 0.1 g and $CoCl_2$•$6H_2O$ 0.004 g. After sterilization, the medium was inoculated with bacteria in a lag phase (10% v/v). During a few series, a portion of pure glycerol (ChemPur, Poland) was also periodically added to the broth.

The determination of separated solution compositions was performed using a high-performance liquid chromatograph (HPLC) UlitiMate 3000 (Dionex, USA) with refractometer detector RI-101 (Shodex) and column Aminex HPX-87H 300x7.8 mm (BIORAD, USA), through which a H_2SO_4 solution (0.005M) was flowing (0.6 mL/min).

The anion and cation concentrations were measured using 850 Professional Ion Chromatograph with conductivity detector (Herisau Metrohm - Switherland). The separation of anions was performed on a 1.7x3.5mm Metrosep RP guard column in series with a 250x4.0 mm Metrohm A Supp5-250 analytical column. The eluent was in the form of solution comprising 3.2 mM/L Na_2CO_3 + 1.0 mM/L $NaHCO_3$ (flow rate 0.7 mL/min). A C2 guard column in series with a 150x4.0 mm Metrosep C2-150 analytical column was used for the cations separation. In this case, the eluent was a mixture of tartaric acid (4 mM/L) with 0.75 mM/L 2-picoline acid.

The enrichment coefficient (β) was calculated taking into account the solute concentrations in the streams:

$$\beta = C_P/C_F \tag{1}$$

where C_F and C_P are the volatile compounds concentrations in the feed and permeate, respectively. The values of C_P were calculated from the equation:

$$C_P = \left(C_D^{t_2}V_D^{t_2} - C_D^{t_1}V_D^{t_1}\right)\Big/\left(V_D^{t_2} - V_D^{t_1}\right) \tag{2}$$

where C_D and V_D is the concentration (for each compound) and volume of the solution on the distillate side, respectively, and ($t_2 - t_1$) is a period of the MD process duration. In this study the period equal to 18-24 h was used.

The flux of volatile solutes (J_{Et} and J_{ACETIC}) was calculated using the equation:

$$J = \frac{C_D^{t2}V_D^{t2} - C_D^{t1}V_D^{t1}}{A\,(t_2 - t_1)} \tag{3}$$

where A is the membrane area.

Hydrophilicity/hydrophobicity of the membranes were determined by dynamic contact angle measurements based on the Wilhelmy plate method. The surface tension of test liquids was measured by the Du Noüy ring method

at 297-298 K. The measurements were carried out using a Sigma 701 microbalance (KSV Instrument, Ltd., Finland) integrated with a PC for automatic control and data acquisition.

3. Results and discussions

3.1. Module efficiency

In the first stage of studies, the standard solutions containing ethanol, glycerol, 1,3-PD, and citric, lactic and acetic acids were used as a feed. A higher permeate flux was obtained for membranes Accurel PP S6/2, because these membranes had thinner walls. Although the membranes Accurel PP V8/2 HF had almost four times thicker walls, the permeate flux obtained from these membranes was only two times smaller, and the permeate flux was 0.8 L/m^{2}h for feed temperature equal to 316 K (see Figure 2). An increase of wall thickness allows a limitation on the heat losses due to the conduction and as a result, the larger values of the driving force were achieved [33]. However, this advantage was diminished by the fact that the thick wall significantly increases the mass transfer resistance, which decreased the permeate flux.

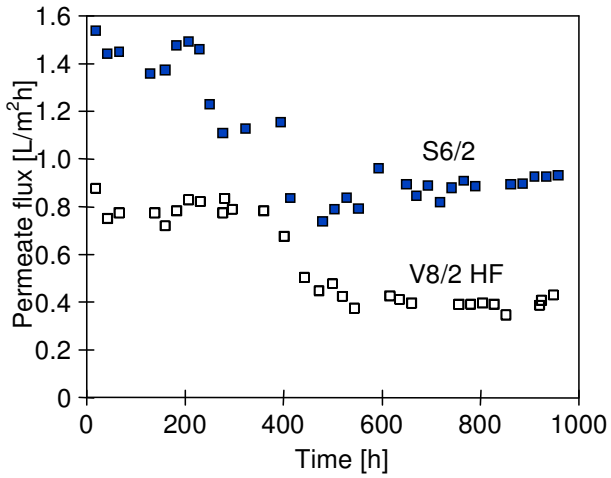

Fig. 2. Changes of the permeate flux (volume) during the concentration of standard organic solutions. S6/2 –MD1 module, V8/2 HF –MD2 module.

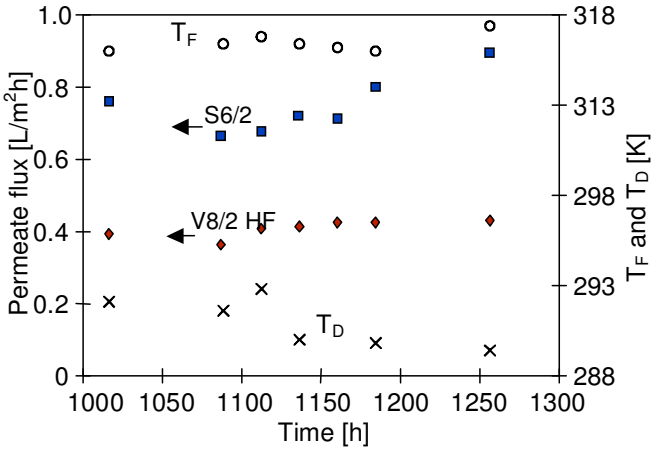

Fig. 3. Changes of feed (TF) and distillate (TD) temperatures during the MD and their influence on the permeate flux.

The MD installation was operated in a continuous mode and after several hundred hours of studies it was observed that the MD modules yield was decreased by almost two-fold (see Figure 2). A similar decrease of efficiency was observed for the membranes from PTFE, but this decline was found after 100 h of MDBR duration and was caused by membrane fouling [22,25]. However, such a reason could not exist in the case of tested clear standard solutions.

A magnitude of the permeate flux may be affected by fluctuation of the feed concentration. However, in the presented studies the feed was concentrated almost two-fold over a period from 700-1000 h of MD process operation and the module yield during this period did not undergo a large variation (see Figure 2). Thus, it can be concluded that the changes of feed concentration (in the studied range) were not able to cause almost a two-fold decline in the module yield. Surface wetting probably caused this decline. Previous work presented that wettability of the pores located on the membrane surface caused a significant decline of MD process yield [34]. Moreover, the results presented in Figure 3 indicated that a small fluctuation of the permeate flux resulted from a slight variation in the stream temperatures.

The organic compounds reduce the surface tension, thus, their presence in the feed will result in the membrane surface wetting [32]. The measurements of contact angle of Accurel PP S6/2 and V8/2 HF membranes demonstrated that a value of 103° to 106° was obtained for distilled water. In the case of used standard organic solutions (surface tension 56 mN/m), the contact angle was reduced to a value of 98° to 101° for the first immersion into solution.

When not only the surface pores, but also a part of the membrane wall is wetted, the salts present in the feed diffuse through the liquid filling the wetted pores. In this case, the electrical conductivity of distillate systematically increases during the MD process. However, such dependence was not observed when the NaCl solution was used as a feed. On the contrary, the electrical conductivity of distillate was decreased with process time (see Figure 4), which is characteristic of the MD process with non-wetted membranes. It is confirmed that in the MD1 and MD2 modules, only pores located on the membranes surface were wetted, and the permeate flux was significantly decreased (see Figure 2) due to the surface wettability.

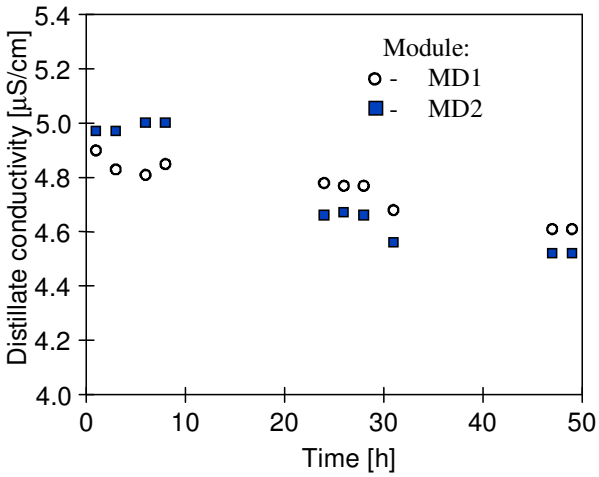

Fig. 4. Changes of the electrical conductivity of distillate during 50 h of MD process. Feed 1% NaCl. Modules MD1 and MD2 after 1000 h of exploitation.

Other studies have demonstrated that the Accurel PP membranes underwent the surface wetting after about 50-60 h of MD process when the distilled water was used as a feed [34]. Membranes Accurel PP have the dimension of pores located inside the wall significantly smaller than those on the walls surface. With regards to this, the surface wettability mainly proceeds at the initial period of the MD process and subsequently the permeate flux undergoes stabilization, which allows for a long-term exploitation of Accurel PP membranes in the MD process [26].

3.2. Retention of low-volatile compounds in the broth

In addition to salts, the fermentation broths also contained different organic compounds. Some of these compounds are characterized by a low volatility (see Figure 5). Data presented in this figure was obtained for pure compounds, and significantly lower values of the partial pressure are expected for their diluted solutions. For example, the vapor pressure of pure glycerol at 373 K is equal to 28.7 Pa (water 101313 Pa), and this value is additionally decreased in solutions as a result of the molecular association characteristic for alcohols [35]. Therefore, the compounds characterized by high boiling point (such as glycerol – 563 K, citric acid – 448 K, and 1,3- propanediol – 400 K) should be well retained by MD membranes, similar to the salts. This fact was confirmed by performed studies because citric and lactic acids, glycerol and 1,3-PD were not detected in the obtained distillate. However, the concentration of these compounds was systematically increased during the MD process (see Figure 6) due to their good retention. A local decrease of

concentration presented in this figure resulted from the periodical addition of distilled water into the feed.

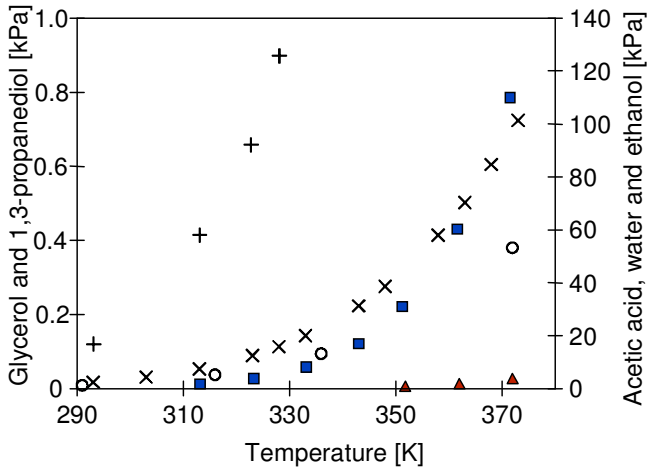

Fig. 5. The influence of temperature on vapour pressure. Data: glycerol (▲) and 1,3-propanediol (■) [35], ethanol (+) and water (x) [36], and acetic acid (○) [36,37].

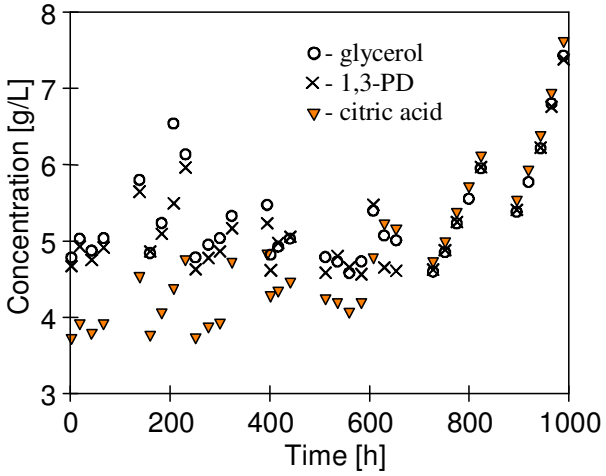

Fig. 6. Changes of concentration of low-volatile organic compounds in the feed during MD process.

The retention of nutrients and raw materials is an advantage for MDBR over the classical MBR, in which the pressure-driven processes such as micro- and ultrafiltration are used. However, the above-presented results indicated that in the case of MDBR, the low-volatile metabolites were also retained, which may cause inhibition by formed products in the case of continuous fermentation.

3.3. Separation of volatile organic compounds

The volatile solutes, similarly as water vapour, diffuse through the gas filled membrane pores during the MD process. The degree of distillate enrichment depends on solute volatilities in relation to water volatility. The values of vapour pressure for the used feed ingredients were presented in Figure 5.

The compounds with a higher volatility than water will be enriched in the permeate. Such an example is ethanol, which can be successfully separated from diluted solutions by using the MD process. In the case of examined standard solutions, the values of enrichment coefficient at a level 4-8 or higher were obtained (see Figure 7). Such a result creates the possibility of performing a continuous fermentation to produce bioethanol and allows significant reduction in the costs of ethanol production via a preliminary concentration [26].

Various rates of the molecular diffusion of vapor components through a gas layer allow an enrichment of distillate in the more volatile components (diffusive distillation) to be obtained [38]. However, for membrane V8/2 HF with the wall thickness 4-fold higher, the obtained values of enrichment coefficient (see Figure 8) were close to those obtained for the membrane S6/2 (see Figure 7). Most probably, the fact that both membranes have small pores (0.2 μm) caused a significant contribution of the Knudsen diffusion, which did not allow the diffusive distillation effect, which is based on the molecular diffusion [38]. Moreover, a significantly larger flux of ethanol was achieved using the membrane with a thinner wall (Accurel PP S6/2), similar to the case of volume flux (see Figure 2).

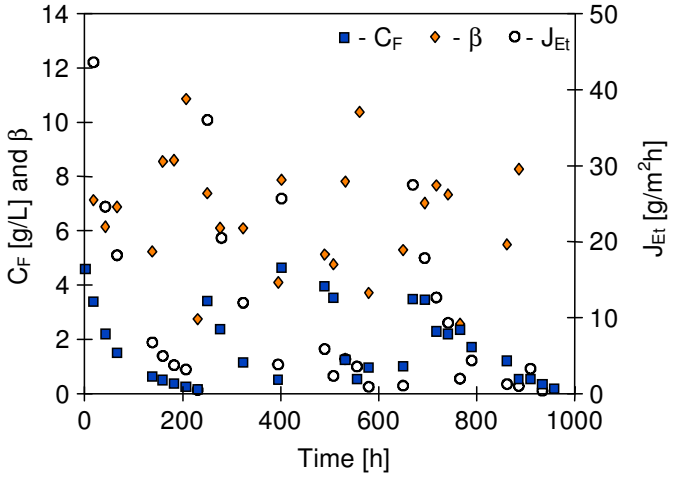

Fig. 7. Changes of the flux of ethanol, its concentration in the feed and the enrichment coefficient during separation of standard solutions. Module MD1 – Accurel PP S6/2.

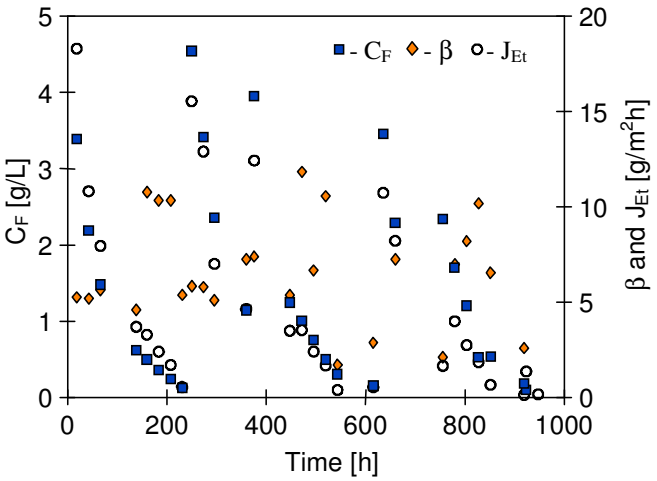

Fig. 8. Changes of the ethanol flux and its concentration in the feed and the enrichment coefficient during separation of standard solutions. Module MD2– Accurel PP V8/2 HF.

The boiling point of acetic acid (391.2 K) is higher than that of water (373.1 K), hence, its vapor pressure is also lower (see Figure 5), and the enrichment of permeate was not achieved for this acid. A value of the enrichment coefficient for examined solution was stabilized, in this case at a level of 0.5-0.6 (see Figures 9 and 10). It is worthy to notice that the distillate tank in MD installation was filled initially by pure water. This created an additional value of the driving force, which is utilized in the process of osmotic distillation. Distilled water was used as an osmotic solution for ethanol separation [39]. Therefore, the values of enrichment coefficient close to one were obtained for the initial period of experiments. In order to standardize the influence of osmotic effect, the distillate cycle was refilled every day with a new portion of distilled water after 300 h of the studies duration.

Moreover, the larger values of enrichment coefficient for acetic acid were achieved during the first 200 h of the process, which is in agreement with a period at which a higher permeate flux was obtained (see Figure 2). This results from fact that the degree of the surface wetting of a membrane has a significant impact on the separation of acetic acid. In the case of the surface wetted membrane, the acid evaporates from the interfacial surface that is created inside the membrane wall. There is no flow of liquid inside the wetted pores, and a lack of turbulence of the streams increases the polarization effects. Therefore, inside the pores the vapor pressure of acid is lower, which

results from the negative effects of temperature and concentration polarization phenomena.

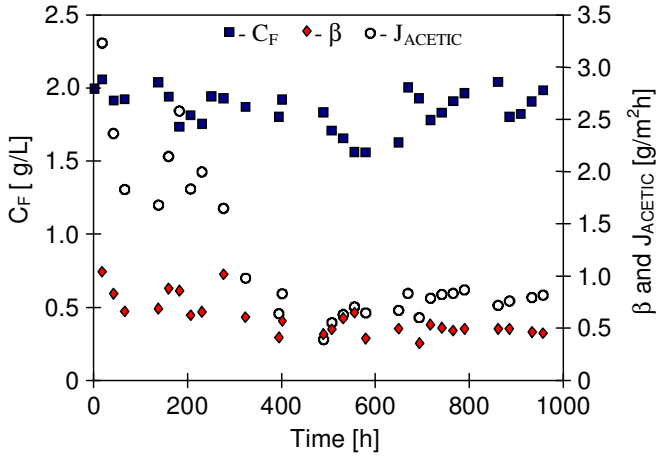

Fig. 9. Changes of the flux of acetic acid, its concentration in the feed and the enrichment coefficient during separation of standard solutions. Module MD1– Accurel PP S6/2.

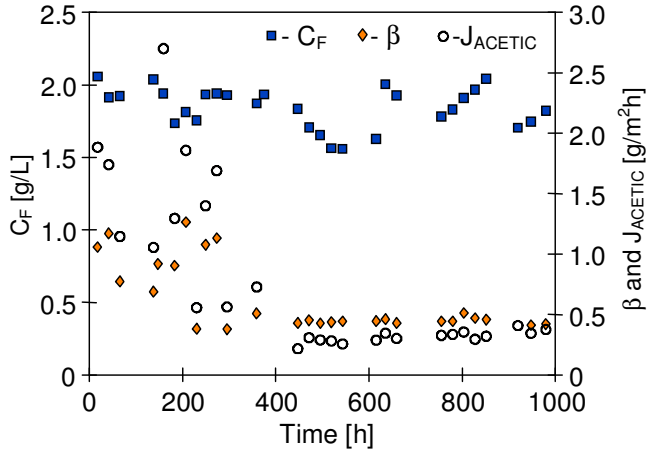

Fig. 10. Changes of the flux of acetic acid, its concentration in the feed and the enrichment coefficient during separation of standard solutions. Module MD2– Accurel PP V8/2 HF.

The above-mentioned relationships were not found in the case of ethanol, and the changes of enrichment coefficient values were similar at the beginning of studies as well as after 1000 h of their duration (see Figures 7 and 8). A stagnant liquid film exists inside the wetted pores. Ethanol is more hydrophobic than acetic acid, and as it was demonstrated in the previous work [40], a lack of turbulence promotes the enrichment of the evaporation surface in alcohol, which can recompense a negative effect of temperature polarization.

3.4. Glycerol fermentation in MDBR

In the consecutive stage of studies, the modules MD1 and MD2 were used for the separation of fermentation solutions. After completing the studies with the standard solutions (about 1500 h) the module yield was stabilized at a level of 0.8 and 0.4 L/m^{2}h for the membranes S6/2 and V8/2 HF, respectively, as was presented in Figure 3. However, when the MDBR was initiated, the magnitude of volume permeate flux was decreased to a level of 0.3 L/m^{2}h for both kinds of membranes (see Figure 11). In the case of the membranes Accurel PP S6/2, a similar permeate flux was obtained in the MDBR applied for the fermentation of glycerol with lactic bacteria [29]. In both cases, a reason for permeate flux reduction was the formation of biological deposit on the membranes surface. Moreover, declines of the MD module yield by over 50% were also observed in other studies of MDBR, due to the same reason [19-25].

After about 200 h of operation, the MDBR was rinsed several times with distilled water followed by a 3% solution of HCl, which allowed the majority of deposit from the membrane surface to be removed. As a result, the yield of the MD process was increased by more than 20% for membrane S6/2, whereas for V8/2 HF it was practically not changed (see Figure 11, from point MC). Most probably this results from a ratio of mass transfer resistance through the membrane (definitely larger for V8/2 HF) to resistance of the formed layer of deposit.

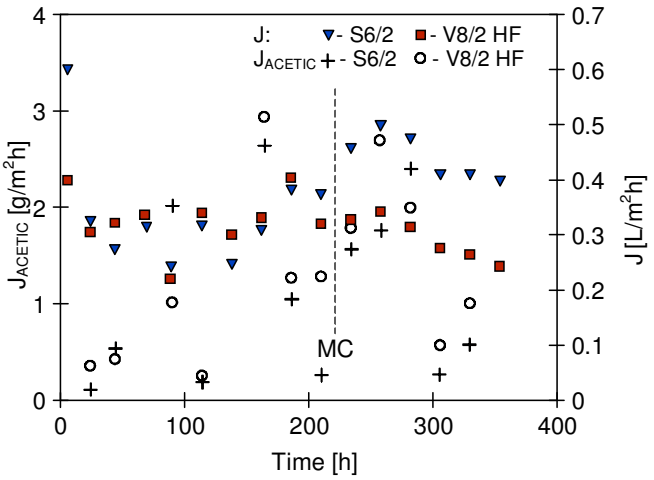

Fig. 11. Changes of acetic flux (J_{ACETIC}) and volume flux (J) obtained in the MD process of broth separation as a function of process time and kinds of used membranes. MC – bioreactor and modules rinsing.

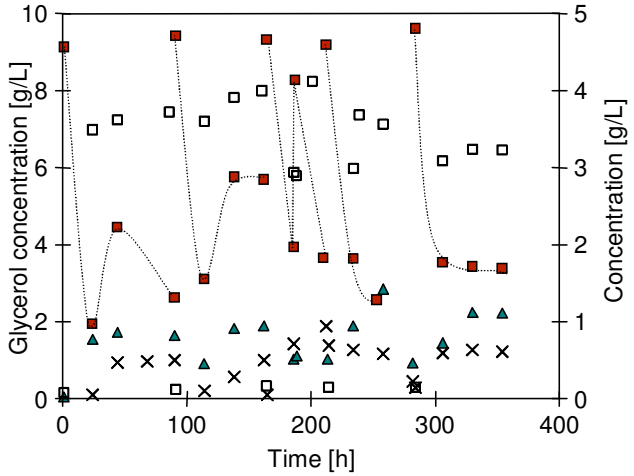

Fig. 12. Changes of concentration of broth components during glycerol fermentation in MDBR. Left axis: ■ glycerol; right axis: □ – 1,3-PD, ▲– acetic acid, x – lactic acid.

The fermentation studies were carried-out in a batch mode with a periodical dosage of new portions of glycerol or exchanging a solution from the bioreactor into a new portion of broth. The fermentation process was combined with the MD process over the entire period of the bioreactor operation. These processes were carried out at the same temperature (304 K). The major fermentation product was 1,3-PD for the used bacteria. The carboxylic acids, such as acetic, lactic, succinic and formic were also formed, but in smaller amounts. The concentration of adventitious metabolites was most often below 1 g/L. The concentration changes of the main components of broth were presented in Figure 12. The values of 1,3-PD concentration close to zero indicate a time when a new broth was used for the fermentation.

The degree of glycerol conversion at a level of 50-60% was obtained in the performed studies. The pH was not stabilized in the bioreactor, and pH values were naturally adjusted at a level of 4.9. As was already demonstrated, the pH=7 is advantageous for 1,3-PD production, whereas a lower degree of conversion and an incomplete fermentation of glycerol was obtained for lower pH values [41]. A high degree of conversion and stability of acetic acid concentration in the broth obtained in this work indicates that the removal of acetic acid by the MD process has a beneficial effect on the course of fermentation process carried out in the MDBR. A comparison of obtained values of acetic acid flux (see Figure 11 – J_{ACETIC}) with the values presented in Figure 12 indicates that temperature and feed concentration were not the only parameters determining the separation of acetic acid. Although the acid concentration was stabilized at a level of 1 g/L, the values of J_{ACETIC} were significantly varied during the fermentation. The largest values of J_{ACETIC} flux were achieved at the end of a given series of fermentation, when the

bioconversion of acetic acid was prevailing due to lowering the pH of broth [42].

3.5. Biofouling

The presented studies were carried out intermittently for almost two years. During break periods the organic solutions remained in the bioreactor, which caused their permanent interaction with the membrane material. Moreover, a lack of sterility caused an intensive growth of microorganisms in the feed that was observed over these periods. Therefore, a biofilm layer was formed on the membrane surfaces not only during a period of MDBR operation. Before each re-start of the MDBR studies, the bioreactor was intensively rinsed with distilled water followed by HCl solution. This procedure allowed the removal of the biofilm layer from the walls of the feed tank, as well as from the external surface of membranes assembled inside the tank.

After completing the MDBR studies and rinsing the bioreactor installation in the above-mentioned way, the membranes samples were collected for SEM observations. The performed SEM examinations confirmed that the majority of deposits formed on the membrane surface were removed after rinsing the modules, and only a thin layer of deposit covered a part of the membrane surface (see Figure 13). Such a result confirmed that a systematic application of periodical MDBR rinsing would create a limitation on the growth of biofilm on the membrane surfaces.

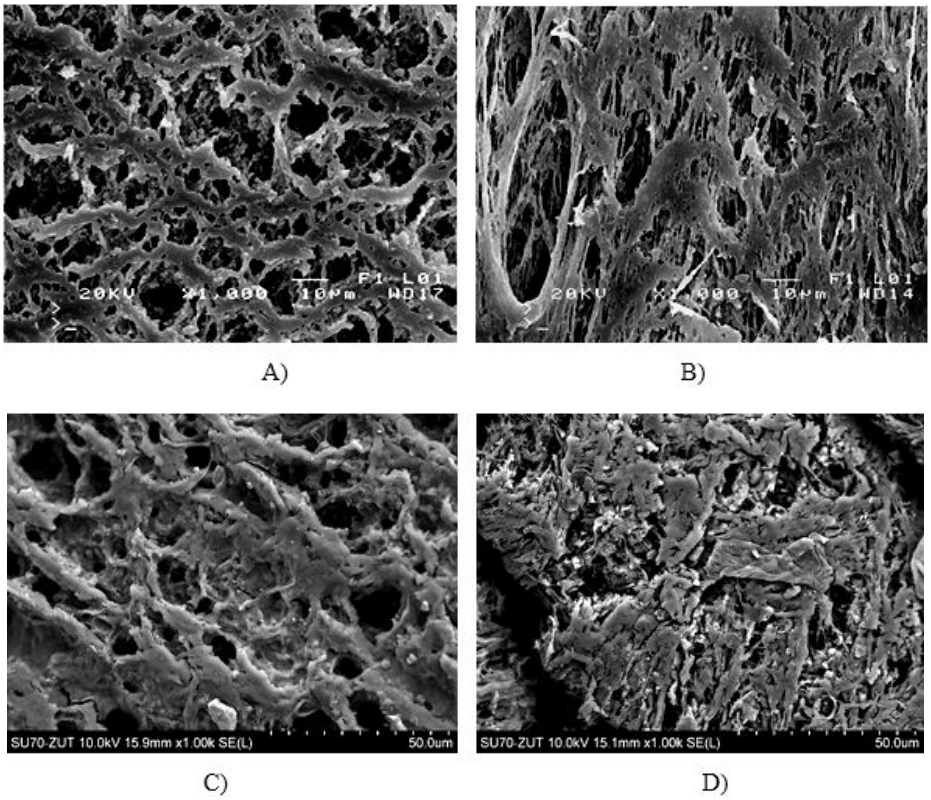

Fig. 13. SEM images of Accurel PP external surface. New membrane: A) S6/2, B) V8/2 HF. Membranes after MDBR studies: C) S6/2, D) V8/2 HF.

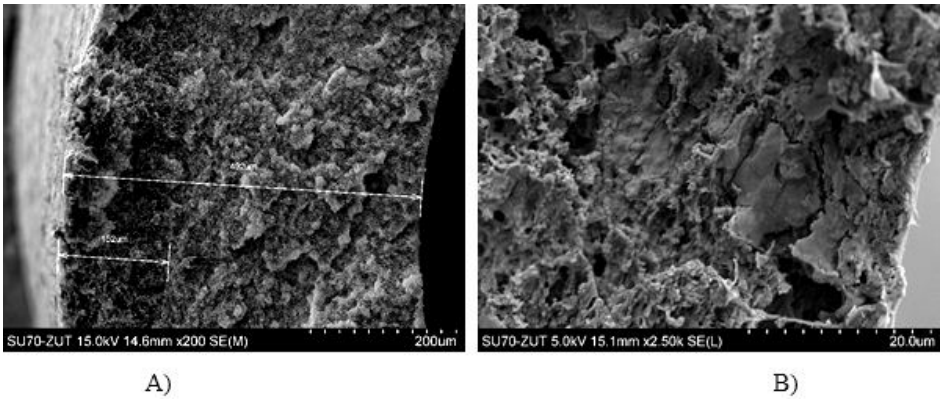

Fig. 14. SEM images of Accurel PP S6/2 membrane cross-section. A) close to external surface "dark ring" created by deposit layer formed inside the pores, B) deposit inside the pores.

The observation of membrane cross-sections revealed that small amounts of deposits were also found at a distance of up to 140-160 μm from the membrane surface (see Figures 14 and 15). The presence of deposit indicates that some parts of the membrane wall were wetted. In the case of membrane Accurell PP S6/2, a dark ring was well visible on a cross-section. This ring indicates that examined solutions uniformly wetted a membrane wall to the depth of about 150 μm. Inside the ring layer, significant amounts of deposits were observed (see Figure 14 B). A similar ring, but slightly lighter, was also observed inside the wall of the Accurel PP V8/2 HF membrane (see Figure 15A).

The SEM studies revealed that the evaporation surface was moved into the membrane wall up to 160 μm, due to the membrane wetting. A displacement of the evaporation surface into the wall decreases the driving force (temperature polarization effects), hence, the obtained results explain over a 50% decline of yield of tested modules (see Figure 2). These results confirm a conclusion from previous works [25,34], that it is advantageous applying the membranes with thicker walls in the industrial modules. Owing to this, the maintenance of a layer of the pores fulfilled by gas in the MD membranes over a long period is still possible, although the liquid or biofilm penetration into the pore interior will proceed.

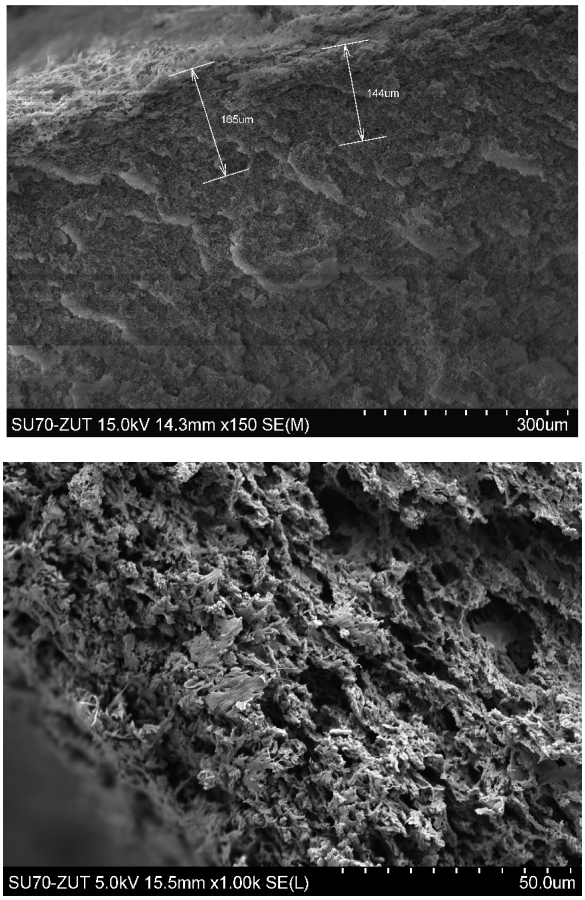

Fig. 15. SEM images of Accurel PP V8/2 HF membrane cross-section. A) image of membrane wall close to external surface, B) deposit inside the membrane pores.

4. Conclusions

The performed studies confirmed that the MD process could be used for the separation of volatile compounds from the broths formed in the bioreactors. The retention of nutrients and raw materials in the bioreactor and the separation of volatile metabolites creates favorable conditions for the operation of the fermentation process.

The application of MDBR for the glycerol fermentation by *Citrobacter freundii* bacteria allowed the separation of a fraction of acetic acid formed in the process from the broth. As a result, an enhancement of the degree of glycerol conversion into 1,3-propanediol, in comparison to the classical fermentation without pH adjustment of broth was observed.

The organic compounds and microorganisms present in the fermentation broth cause the surface wetting of the membranes, which leads to biofilm growth. The majority of deposit can be removed using an intensive rinsing with distilled water followed by HCl solution.

After about two years of MD modules exploitation, the membranes assembled were wetted to a depth of about 140-160 micrometers. A partial wetting of the membrane wall caused the module productivity to be reduced by about two-fold.

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