Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22867

128 (2018) 236–242
October

Biofouling phenomena on the ceramic microfiltration membranes – an experimental research

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Received 30 March 2018; Accepted 5 July 2018

ABSTRACT

The research was focused on the study of biofouling on ceramic microfiltration membranes. The membranes differing in pores diameters (0.14, 0.20, and 0.45 μm) were examined. The influence of the driving force (transmembrane pressure) and the feed concentration on the amount of biomass deposited on membranes was tested. The low biomass concentration only caused the formation of a thin layer on the membrane surface (and pores filling) and a small decrease of the permeate flux (approximately 18% at 200 g m^{-3} cells concentration in the feed). In the case of the higher feed concentration a significant decline of the permeate flux – 46% and 55% (for 500 and 200 g m^{-3} feed concentration, respectively) was observed. It was associated with three types of phenomena: a pores filling, a formation of thin layer on the surface of the membrane and finally, the concentration polarization phenomenon. Despite significant differences of the initial permeate flux obtained for different Δp and different membranes, quasi-static (established) permeate fluxes were similar. The highest value of the final permeate flux was obtained during separation using 0.45 μm pores size membrane and it was almost the same in Δp ranged 0.2–1.0 bar. Finally, the selected membrane was modified by the phosphoric acid. Unfortunately, this modification did not bring the positive effects. The grafting of the ceramic membrane with phosphoric acid aggravated the biomass retention on its surface and it resulted in the permeate contamination by biomass.

Keywords: Permeate flux; Microfiltration; Biomass separation; Biofouling; Membrane modification

1. Introduction

Membrane processes are more and more often used in various industries, especially in food, pharmaceutical, or in environmental protection branches. Membranes are employed as a separation equipment and provide obtaining a pure product stream by retaining impurities in a retentate. Their ability to retain almost every kind and size of particles (by choosing an appropriate pores size of a membrane) is used especially in the wastewater treatment process [1,2].

To retain bigger size particles, for example, bacterial cells or high-molecular weight polymers, microfiltration membranes are usually employed. Microfiltration membranes are used in the dairy industry for cold sterilization [3] – during purification of milk or milk-derived products (e.g., whey) bacteria are retained and as a result, purified milk has no microbiological contamination, and thus its shelf-life is prolonged [4].

On the other hand, membranes can be used in any type of microbiological production for the separation of a product, primarily. A membrane bioreactor is worth to be mentioned [5,6]. A microbiological production in the membrane bioreactor is very common way to obtain valuable ingredients used in pharmaceutical, cosmetic, or food industry, like for example, lactic acid [7], xylitol [8], or ethanol [9]. A continuous system of production (a batch process is inefficient and unprofitable on an industrial scale) leads to a low concentration of

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Presented at the XII Scientific Conference "Membranes and Membrane Processes in Environmental Protection" – MEMPEP 2018 13–16 June 2018, Zakopane, Poland.

cells in a classical bioreactor, due to elution of proliferated cells. Thus, the membrane bioreactor brings a lot of benefits. Membranes application at the outlet stream from bioreactor leads to [10]:

- The biomass retention, so outlet stream (permeate) is free of bacterial cells
- The concentration of biomass (biocatalyst), which is eluted in the classical continuous bioreactor
- The retention (with an ultra- or a nanofiltration membrane) of unreacted substrates and their recycle to a bioreactor for further conversion.

However, one of the critical issues in the development of a stable working membrane bioreactor is a significant decrease of the permeate flux. At cross-flow separations, usually used for membrane filtrations [11], the deposition of the layer on the surface is accompanied with a phenomenon of concentration polarization (Fig. 1) [12].

According to Nigam's theory [12], there are three stages of a permeate flux decrease. Pores clogging is responsible for the initial decline of the permeate flux; a thin, irregular layer (a dirt cake) is formed on the membrane surface (Fig. 1). Above this layer, there forms a zone of much higher concentration of substances than in the solution (polarization phenomenon). Nigam's theory says that there is also a third stage, when the permeate flux becomes steady (quasi-static), but its value is very low (Fig. 2).

The knowledge about quasi-static fluxes is important for membrane bioreactors designing. The highest permeate flux leads to the highest bioprocess intensification [13]. The value of the permeate flux can be easily controlled by the selection of a membrane. The main problem is to keep the stable value of this flux. It is particularly important when the membrane bioreactor is additionally integrated with another process [14–18]. Therefore, the best way is to use membrane pores blocked by biomass, when a quasi-static flux is reached.

Membrane blocking discussed earlier is called in membrane science the fouling phenomenon [19,20]. Plenty of different strategies are undertaken to its limitation, for example, by modifying the membrane surface to make it less susceptible to adsorption or adhesion processes [21,22].

Ceramic membranes, in contrast to polymer ones, possess some important advantages such as mechanical resistance, chemical inactivity, thermal stability, and easy cleaning [23], but the same features make them resistant to modifications. The change of the surface properties is difficult in this case.

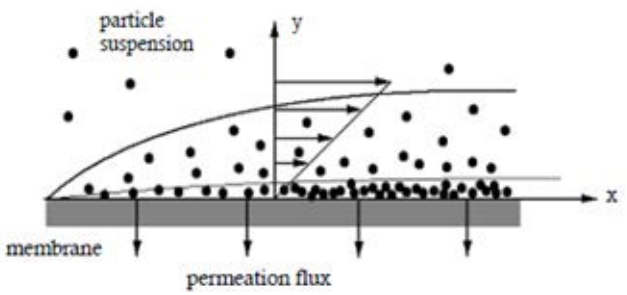

Fig. 1. Formation of thin dirt layer on membrane and concentration polarization zone along the membrane [12].

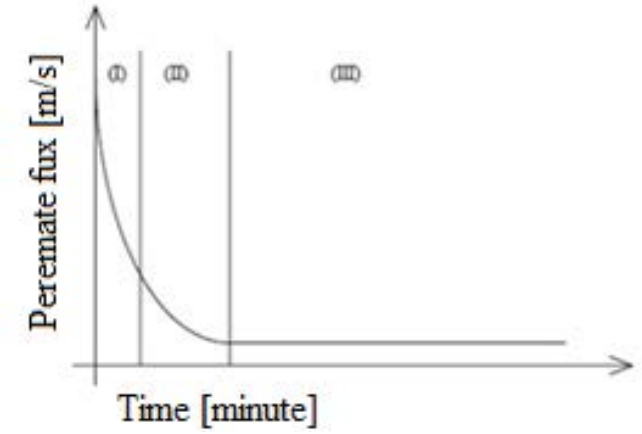

Fig. 2. The decrease of permeate flux. I – Initial, fast decrease, II – long-term, slow decrease, III – quasi-static, steady flux [12].

So far, grafting by different types of silanes [24] and using phosphoric acid and alkyl phosphoric acids [25] have been tested.

A presence of phosphate groups on a membrane surface (Fig. 3) can lead to better hydrophilic properties of the membrane and to the reduction of fouling sensitivity. So far ultra- and nanofiltration membranes have been grafted with phosphoric acid [25,26].

This paper is focused on the study of membrane fouling by *Lactobacillus rhamnosus* cells. The specific objective was to present the impact of the membrane pores size (0.14–0.45 μm), the transmembrane pressure (0.2–1.0 bar), and the biomass initial concentration in the feed (100–500 g m^{-3}) on the permeate flux decrease and its final value in a quasi-static stage and on the biomass quantity deposited on membranes. Finally, an attempt to modify the surface of ceramic membranes by using phosphoric acid was made.

2. Materials and methods

2.1. Membranes

Three ceramic microfiltration membranes (Tami Industries, France) were tested. Their main parameters are presented in Table 1.

2.2. Culture

MRS medium comprised of (in g dm^{-3}) peptone (10), eggs extract (8), yeast extract (4), glucose (20), CH_3COONa (5), Tween (1), K_2HPO_4 (2), triammonium citrate (2), $MgSO_4 \cdot 7H_2O$ (0.2),

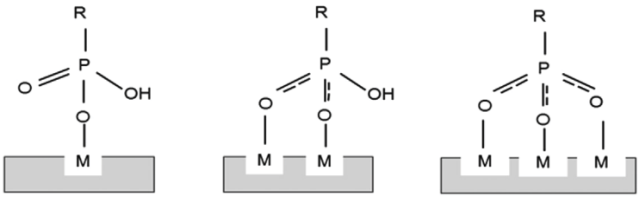

Fig. 3. Possible interactions of phosphoric acids with metal oxides on membranes surface [26].

Table 1
Characteristic of the tested ceramic membranes

Pores size (μm)	Length (mm)	Filtration area (m^2)	Number of channels	Support material	Membrane material
0.14 0.20 0.45	250	0.013	7	TiO_2	TiO_2

$MnSO_4 \cdot 4H_2O$ (0.05) [27] was prepared and sterilized in 121°C. Then 2 mL of the inoculum (*L. rhamnosus*, (PCM 489, Polish Academy of Science, Poland)) was transferred into 200 mL sterile medium in a conical flask and the flask was incubated for 24 h at 42°C.

The concentration of biomass was evaluated spectrophotometrically (Hitachi, USA). The content of biomass was measured at λ = 550 nm using the standard curves based on the dry mass method: X (g m^{-3}) = 1,010A_{550}. The analysis of cells size was performed using laser diffraction particle size analyzer (SALD – 2300, Shimadzu) with Wing – SALD II Software.

2.3. Membrane separation

The scheme of the measuring system is presented in Fig. 4. The membrane was placed in a steel module, which was connected to the peristaltic pump (Masterflex, four – head drive), which generated 300.06 × 10^{-8} m^3 s^{-1} retentate flow (velocity along membrane – 0.57 m s^{-1}). The transmembrane pressure was generated by closing valve V-1 and evaluated as an average value measured with two manometers (P-1 and P-2). It was in the range of 0.2–1.0 bar.

The membranes with and without modification were tested. The initial biomass concentration in the feed tank was approximately 500 g m^{-3}. The volume of feed for 0.2 bar separation was 2 × 10^{-3} m^3, for 0.5 bar – 3 × 10^{-3} m^3, and 1.0 bar – 4 × 10^{-3} m^3 (for each of tested membranes, respectively). During experiments, the permeate flux and the concentration of biomass in the permeate and the retentate were measured at certain intervals.

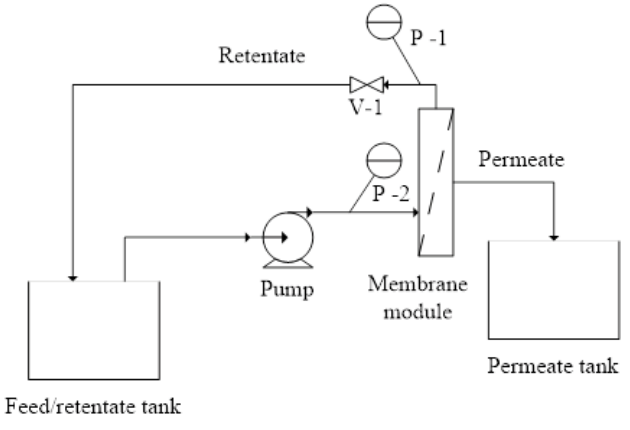

Fig. 4. The scheme of the used membrane system. P-1, P-2 – manometers, V-1 – throttle valve.

The amount of biomass deposited on the membrane was determined based on the mass balance:

$$m_m = m_f - m_p - m_r = V_f \cdot C_f - V_p \cdot C_p - V_r \cdot C_r \quad (1)$$

where m_m – biomass deposited on the membrane (g), m_f – biomass in feed (g), m_p – biomass in permeate (g), m_r – biomass in retentate (g), V_f – volume of feed (m^3), C_f – biomass concentration in feed (g m^{-3}), V_p – volume of permeate (m^3), C_p – biomass concentration in permeate (g m^{-3}), V_r – volume of retentate (m^3), and C_r – biomass concentration in retentate (g m^{-3}).

After each separation, the membranes were regenerated with 2% NaOH and 0.1% NaClO (POCH, Poland) solutions heated up to 60°C. 1 L of each cleaning solution was passed through the membranes, and next they were rinsed with distilled water as long as pH of permeate was neutral. The procedure was repeated until the permeate flux value was the same as before the separation process.

The membrane surface was modified with 1.0 M H_3PO_4 (POCH, Poland). The membrane modification was carried out in two steps:

- The ceramic membrane (0.45 μm pores size, Tami) was rinsed with 1.0 M H_3PO_4 for 2 h at the retentate flow rate along the membrane 3.33 × 10^{-7} m^3 s^{-1} and the transmembrane pressure 0.01 bar. Under these conditions, the permeate flux was approximately 6.41 × 10^{-6} m^3 s^{-1} m^{-2}.
- After rinsing, the membrane was immersed in 1.0 M H_3PO_4 for 24 h and then rinsed with deionized water until neutral pH was obtained and finally dried by compressed air.

3. Result and discussion

3.1. The decrease of permeate flux as a function of the transmembrane pressure and the membrane pores size

In all performed experiments, the measurements of biomass concentrations in the permeate and the retentate as well as the permeate flux during filtration were made. Retention coefficient (Eq. (2)) for biomass was 0.99 ± 0.01, so in further considerations, it was assumed that there were no bacteria cells in permeate.

$$R = 1 - \left(\frac{C_p}{C_r} \right) \quad (2)$$

where C_p – biomass concentration in permeate (g m^{-3}) and C_r – biomass concentration in retentate (g m^{-3}).

The analysis of the bacteria size distribution confirmed this assumption (Fig. 5). The culture contained bacteria cells ranged between 0.536 and 2.834 μm in diameter. The median was 0.864 μm, which was higher value than pores sizes of the used membranes (0.14, 0.2, and 0.45 μm).

The permeate flux changes in time are presented in Fig. 6.

Noticeable is the fact, that the most sharp drops in the permeate fluxes were observed at the highest transmembrane pressure. The smallest drop and therefore the most favorable result were obtained using the membrane with pores diameter 0.14 μm at the transmembrane pressure 0.2 bar (Fig. 7).

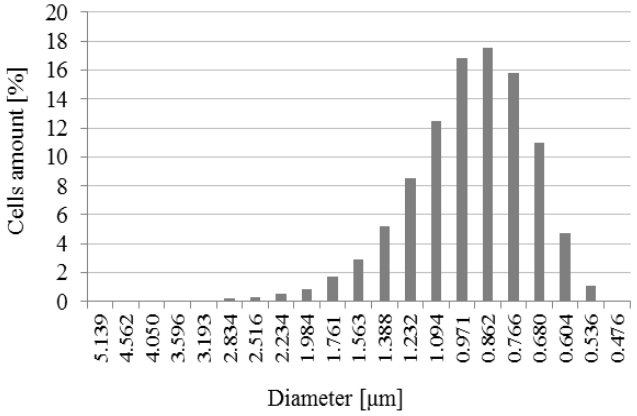

Fig. 5. The analysis of bacterial (*Lactobacillus rhamnosus*) size distribution (the initial cells concentration 500 g m^{-3}).

3.2. Deposition of biomass on the membrane

Fig. 8 presents the time relation between the mass of bacterial cells suspended in retentate and located on the membrane surface for an exemplary process (the membrane size pores 0.45 μm, Δp = 0.2 bar). Biomass was accumulated on the membrane surface mainly during the first 30 min.

The relations between biomass deposited on the membrane and the membranes pores sizes and the driving force values were similar (Fig. 9) to the previously presented dependence of the permeate flux drops on these parameters (Fig. 7). At the lowest value of the transmembrane pressure and the lowest pores size, the smallest amount of biomass was deposited on the membrane.

The permeate flux decrease was also a strong function of a biomass concentration in the feed (Fig. 10), because this concentration influenced on the amount of biomass deposited on the membrane (Fig. 11). The separation of low concentrated (100 g m^{-3}) feed only caused a thin layer formation; there was a slight drop of the permeate flux (Fig. 10). At such low biomass concentration, the feed solution passed through the membrane did not cause a complete pores clogging.

3.3. Permeate flux establishment

There were three stages of the permeate flux decline (Fig. 12). At the beginning of the process, the membrane was very porous, so bacteria cells could locate in any irregularities of the membrane (also in pores). Hence, a pronounced decrease of permeate flux was observed. A further decline of the parameter was caused by the accumulation of cells along the membrane. These stream declines were explained in the literature [28,29] by the concentration polarization phenomenon.

The last stage corresponded to a quasi-static decline [11], when permeate flux drops could be negligible. This stage occurred after almost the same time for all tested membranes and the final values of fluxes were also very similar in the range 3.00–5.00 × 10^{-5} m^3 s^{-1} m^{-2}, while the initial fluxes were different and increased with membrane pores size and transmembrane pressure increase (Fig. 13).

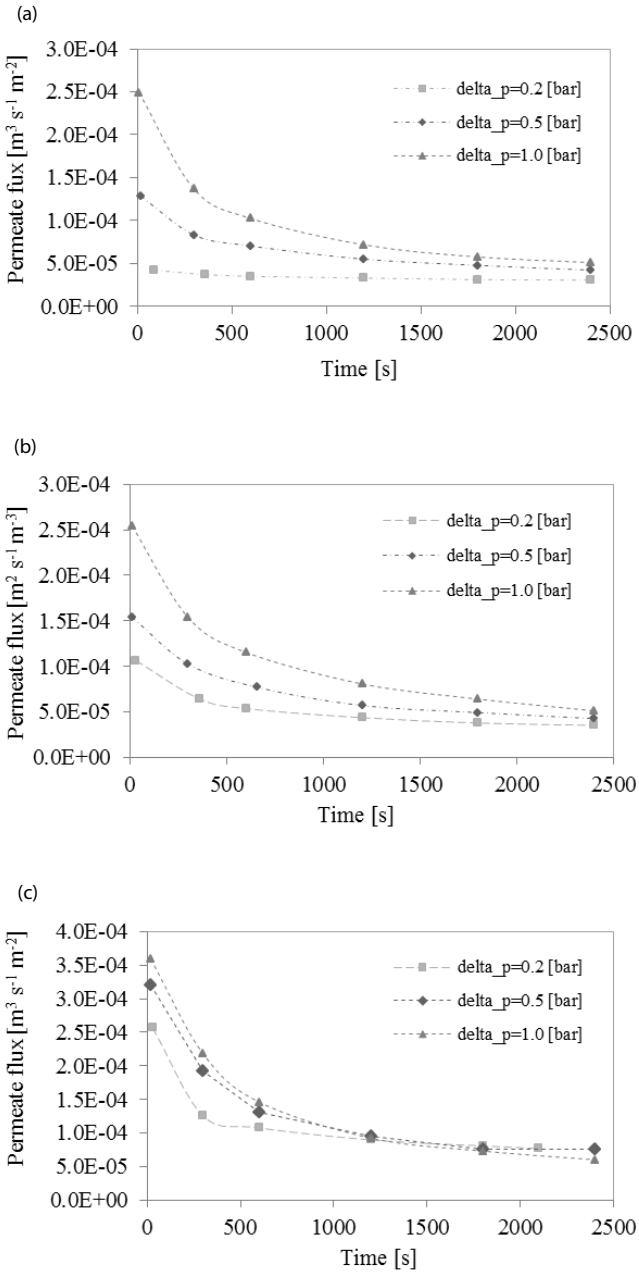

Fig. 6. The changes of the permeate flux during *Lactobacillus rhamnosus* separation. The membrane with pores size: (a) 0.14 μm, (b) 0.20 μm, (c) 0.45 μm (the initial cells concentration 500 g m^{-3}).

3.4. Ceramic membranes modification with phosphoric acid

Due to the highest quasi-static flux, the membrane with pores size 0.45 μm was selected for the modification with phosphoric acid. After the modification with 1.0 M of phosphoric acid, the separation of *L. rhamnosus* cells was performed under the same process conditions as previously (Δp = 0.2 bar, C_{feed} = 500 g m^{-3}, $\dot{V}_{ret}$ = 300.06 × 10^{-8} m^3 s^{-1}).

According to the literature [26], this modification led to decrease of biofouling; flow increased from 0.5 × 10^{-3} to 0.7 × 10^{-3} m^3 h^{-1} m^{-2} due to albumin deposition decrease from

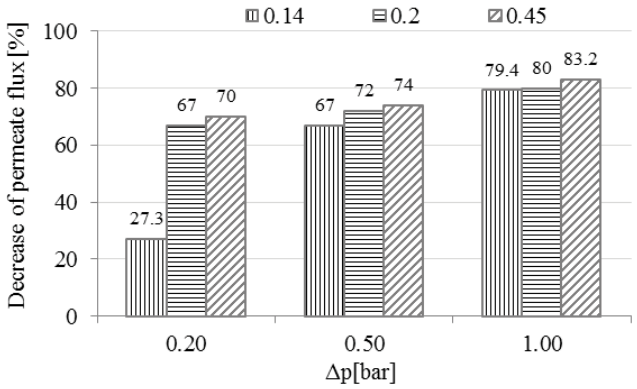

Fig. 7. Decrease of the permeate flux after 40 min process operation in relation to the transmembrane pressure and membrane pores sizes. The initial cell concentration is 500 g m^{-3}.

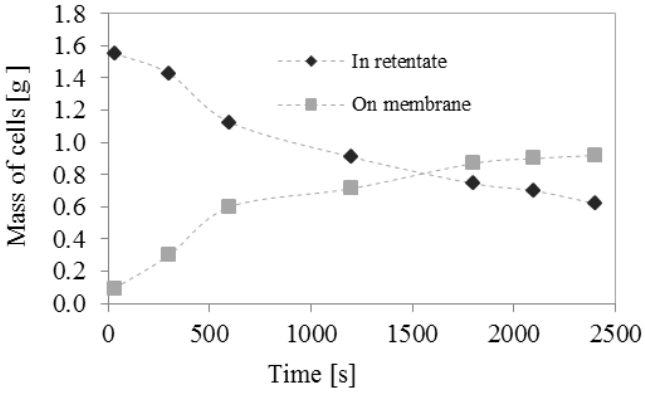

Fig. 8. The profile of bacteria cells distribution during separation (Δp = 0.2 bar, pores size – 0.45 μm, membrane area – 0.013 m^2). The initial cell concentration is 500 g m^{-3}.

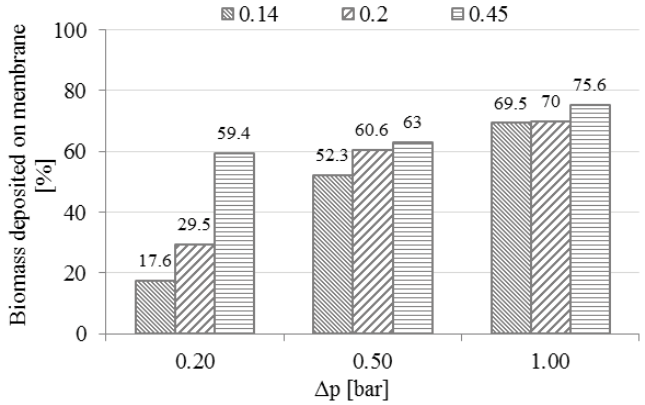

Fig. 9. The share of biomass deposited on the membranes (calculations based on the biomass balance, the initial cell concentration is 500 g m^{-3}).

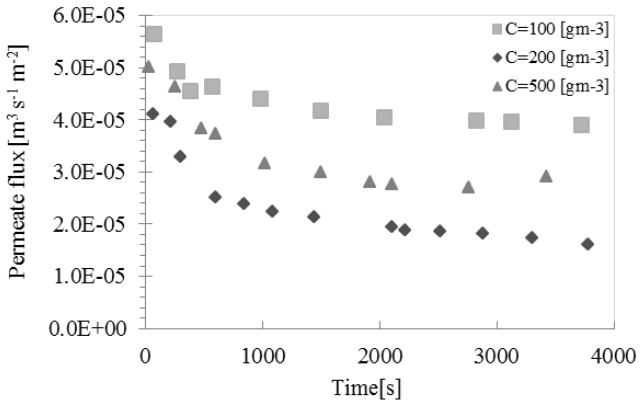

Fig. 10. The influence of the initial biomass concentration in the feed on the permeate flux decrease (membrane with pores size – 0.14 μm, Δp – 0.2 bar).

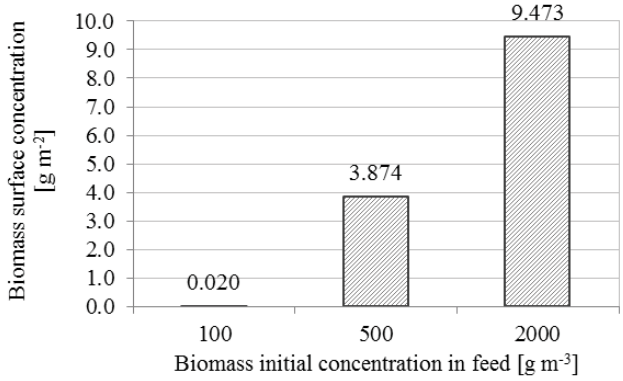

Fig. 11. The influence of the initial biomass concentration in the feed on the biomass surface concentration (membrane with pores size – 0.14 μm, Δp – 0.2 bar, membrane area – 0.013 m^2, initial feed volume – 2×10^{-3} m^3).

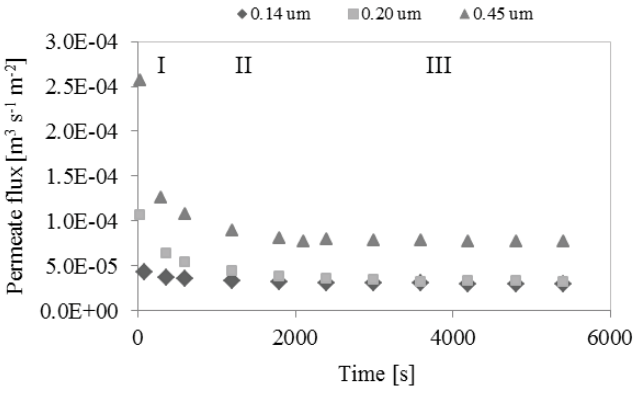

Fig. 12. The profiles of permeate flux decline for the membranes with different pores size. The initial cell concentration is 500 g m^{-3}, transmembrane pressure is 0.2 bar.

4.5 to 1.9 g m^{-2}. Unfortunately, in tested case these positive effects were not obtained. The permeate flux decrease was similar as during separation on the unmodified membrane and accounted for only 31.5% the initial flux using the modified membrane and 25.0% for the unmodified membrane (Fig. 14). It was followed by the deposition of biomass, similar for both membranes (deposited biomass accounted for 69.5% and 69.9% biomass from feed, respectively).

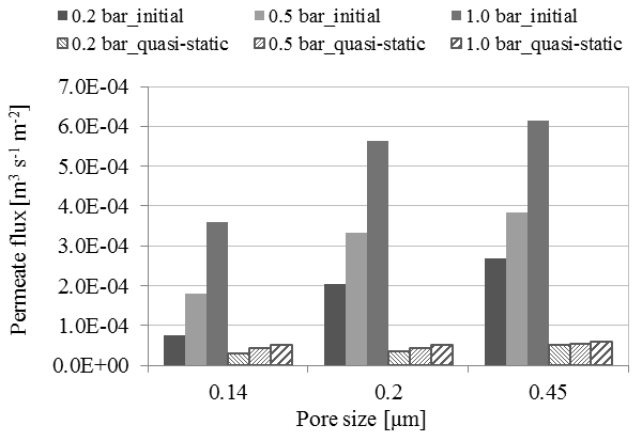

Fig. 13. The initial and quasi-static fluxes for ceramic membranes with different pores size and at the different transmembrane pressures. The initial cell concentration is 500 g m^{-3}.

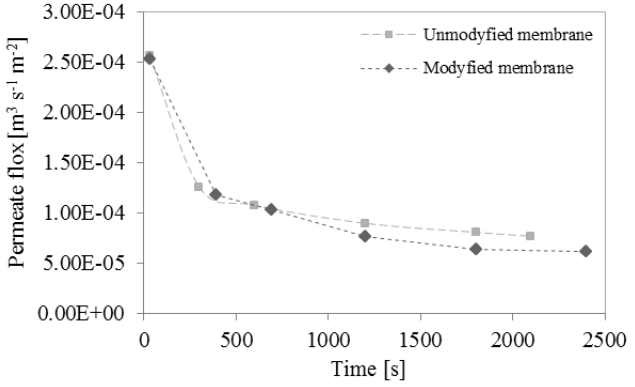

Fig. 14. The permeate flux decrease using the modified and the unmodified membrane (membrane with pores size 0.45 μm, Δp – 0.2 bar, the initial cell concentration – 500 g m^{-3}).

The value of retention coefficient for *L. rhamnosus* cells was close to 1.0 for all unmodified membranes differed in pores size. The grafting of the ceramic (titanium dioxide) membrane (0.45 μm) with phosphoric acid aggravated the biomass retention on its surface. The value of the retention coefficient decreased to 0.9, thus the permeate was contaminated by bacterial cells. The ceramic membranes are considered as the most chemical resistant [30–32], but Li [33] has shown that under extremely acidic or basic conditions ceramic membrane structure can be damaged. In consequence, after modification, for example, with phosphoric acid, the membrane selectivity can be deteriorated.

4. Conclusions

The performed study enabled to draw the following conclusions:

- The most intensive deposition of the bacterial cells occurs within the first minutes of microfiltration process and it leads to the most significant decrease of permeate flux. The concentration polarization is responsible for further decline of the permeate flux.
- The use of the high transmembrane pressure (e.g., 1 bar) is not necessary, because it leads to the most intensive decline of the permeate flux. After 40 min, regardless of the transmembrane pressure applied (in range of 0.2–1.0 bar), permeate fluxes are very low and have similar value.
- The use of the membrane with pores size 0.45 μm allows to obtain the highest quasi-static permeate flux (5.00×10^{-5} m^3 s^{-1} m^{-2} at 0.2 bar) and simultaneously this membrane is able to retain all bacteria cells in the retentate stream.
- The modification of the ceramic membrane with phosphoric acid provides undesirable results: the amount of biomass deposited on modified and unmodified membranes is almost the same and, in consequence, permeate flux declines are also similar. Simultaneously, the separation quality worsens (the value of retention coefficient for bacterial cells decreases from 1 to 0.9).

Acknowledgments

This project is supported by Wroclaw Centre of Biotechnology, The Leading National Research Centre (KNOW) program for years 2014–2018.

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