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NANOFILTRATION OF FERMENTATION SOLUTIONS – UNFAVOURABLE PHENOMENA AND MEMBRANE CLEANING

NANOFILTRACJA ROZTWORÓW FERMENTACYJNYCH – ZJAWISKA NIEKORZYSTNE ORAZ CZYSZCZENIE MEMBRAN

Abstract: The intensity of unfavourable phenomena occurring in the nanofiltration process of fermentation solutions, and the possibility of cleaning the membranes after this process were studied. The experiment was carried out using a tubular module equipped with the AFC-30 membrane. The filtration process was carried out at a transmembrane pressure of 2.0 MPa, linear velocity of the feed of 3.4 m/s and the temperature of the feed equal to 20 °C. Hydraulic performance of the membrane was tested both during the filtration of model and real solutions. The conditions for efficient cleaning of fouled surfaces of the membranes by using different chemical reagents were determined. It was also attempted to rinse the membrane with clean water. A preliminary study was performed to determine the transport and separation characteristics of the AFC-30 membrane for deionized water and salt solutions of NaCl and $MgSO_4$ representing mono- and divalent ions, respectively. In this case, the membrane was tested under varying transmembrane pressure in the range of 1.0 to 2.0 MPa.

Keywords: nanofiltration, fermentation solutions, decrease of hydraulic capacity of membrane, membrane surface cleaning

Membrane techniques are used, among others, as a separation tool in separation processes used for technological and waste streams occurring in the liquid or gas phase [1]. The use of pressure-driven membrane processes such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis, has become increasingly common in the case of liquid streams. Those processes have been applied in order to isolate the individual components present in the form of suspensions, colloids or true solution [1–2]. The characteristics of the pressure-driven membrane processes are presented in

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Table 1. The membranes are characterized by increasingly smaller pore size and smaller volumetric flux of permeate, depending on which process is concerned: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) or reverse osmosis (RO). Theoretically, the most dense membrane are only water-permeable and are used for the reverse osmosis process. Nanofiltration membranes, on the other hand, allow for the separation of ions of different valency and separation of organic substances, and ultrafiltration membranes retain fine suspensions, colloids, bacteria and viruses. Microfiltration membranes, which have the largest pores, permit separation of suspended microparticles. Due to the physical structure of membranes their hydraulic resistance increases hence correspondingly higher driving pressure is applied.

Table 1

Comparison of pressure-driven membrane processes [1]

Process	Transmembrane pressure [MPa]	Volumetric permeate flux [$m^3/m^2 \cdot s \cdot MPa$]
Microfiltration (MF)	0.01–0.2	$> 13.89 \cdot 10^{-5}$
Ultrafiltration (UF)	0.1–0.5	$2.78 \cdot 10^{-5}$–$13.89 \cdot 10^{-5}$
Nanofiltration (NF)	0.5–2.0	$0.39 \cdot 10^{-5}$–$3.33 \cdot 10^{-5}$
Reverse osmosis (RO)	1.0–10.0	$0.01 \cdot 10^{-5}$–$0.39 \cdot 10^{-5}$

The disadvantages associated with the membrane processes primarily concern the reduction of the hydraulic performance of membranes caused by adverse side effects of membrane filtration, this is, concentration polarization, formation of a gel layer on the membrane surface, the accumulation of impurities on the membrane surface or within the pores (fouling), and precipitation of sparingly soluble salts forming inorganic deposits (scaling) [3–8]. These phenomena occur simultaneously, and their negative effects are cumulative. As a result, a gradual decrease in the volumetric flux of permeate occurs during the operation of a membrane installation. The phenomenon of concentration polarization causes the formation of a boundary layer (termed as polarization layer) occurring in the immediate vicinity of the membrane and characterized by the solute concentration exceeding its mean concentration in the feed [1]. Concentration polarization effects are the most important in the processes of reverse osmosis and nanofiltration, and occur to a lesser extent in the process of microfiltration. The solid or thixotropic gels are formed when the solubility of a substance in the polarizing layer is exceeded [9]. The gel layer which exists between the membrane and the solution forms a secondary membrane. A phenomenon of precipitation of sparingly soluble salts (scaling), particularly calcium sulfate and calcium carbonate, may occur within the polarization layer or the concentrated solution on the membrane in the processes of reverse osmosis and nanofiltration [10]. Scaling of the membrane is therefore an adverse effect of the concentration polarization. The phenomenon of fouling occurs in the case of membrane processes, in which porous membranes are used (as in microfiltration and ultrafiltration), but also in the processes of reverse osmosis and nanofiltration, which require the pre-treatment of the feed [11]. Fouling can occur as a reversible or irreversible process. The former case is when the deposits retained on a membrane can be completely removed enabling full restoration of the initial performance of a membrane. The process in which membrane fouling is caused by microorganisms is referred to as biofouling.

The adverse effects of all the above-discussed phenomena can be limited by several methods [1, 12]:

1) pre-treatment of the feed,
2) modification of the properties of the membrane,
3) ensuring optimal operational parameters of membrane installation,
4) cleaning the membranes.

The required treatment degree of the feed depends on the type of membrane process [1]. For example, in order to reduce fouling it is necessary to remove suspended solids, colloids, soluble macromolecules and microorganisms [11]. To this end, the following processes can be used: filtration, coagulation, disinfection, and adsorption on activated carbon. Modification of membranes allows for change of those properties that have major impact on fouling [1]. Those changes can be achieved by the use of small currents, the chemical adsorption of ionic substances, or by binding enzymes on the membrane surface. The optimization of operating parameters of a membrane process consists in, for example, selecting the appropriate hydrophobic of hydrophilic membrane, its pore size, and transmembrane pressure [10]. Since the application of the above-discussed solutions does not completely eliminate membrane blocking it is necessary to clean the membranes periodically. It can be carried out by chemical, hydraulic or mechanical methods [12]. Hydraulic cleaning involves rinsing the membrane with water and air or backwashing under reduced pressure. For chemical cleaning, depending on the composition of the deposited impurities, suitable chemical reagents are used, this is, phosphoric acid or citric acid, sodium hydroxide, anionic or nonionic detergents and complexing agents.

The aim of this study was to evaluate the intensity of adverse phenomena and the possibility of cleaning membranes used for nanofiltration of fermentation solution. Transport and separation properties of a nanofiltration membrane (AFC-30) were also determined. Separation properties of the membrane with respect to the components of the filtered fermentation solutions were not studied.

Materials and methods

Nanofiltration was carried out using a system with a cross-flow module equipped with a tubular membrane AFC-30 by company PCI Membrane System, Inc. (USA). The characteristics of the membrane are shown in Table 2.

Table 2

Characteristic of the AFC-30 membrane

Membrane	Material	Max pH range	Max pressure [MPa]	Max temp. [^oC]	Molecular weight cut-off [Da]	Removal of $CaCl_2$ [%]
AFC-30	composite (active layer-polyamide)	1.5–9.5	6.0	60	200	75

The transport and separation characteristics of the membrane were determined in the preliminary study using deionized water and salt solutions of sodium chloride NaCl and magnesium sulfate $MgSO_4$ (concentration 1 g/dm^3) representing mono- and divalent ions, respectively. These studies were performed under varying conditions of transmembrane pressure in the range of 1.0 to 2.0 MPa.

The effectiveness of filtration was assessed by determination the volumetric and relative permeate fluxes (J_w – for deionized water, J_v – for the model and real fermentation solutions (1) and α – relative permeability of membrane (2), Table 3). The concentration of the ions were assayed in the solutions (feed) and that purified with membrane techniques (permeate), which then formed the basis for calculating their retention coefficient R (3).

Table 3

Equations used to evaluate membrane properties and removal efficiencies

Parameter	Equation
Volumetric permeate flux, J_v (J_w) [m^3/m^2 · s]	$J_v(J_w) = \frac{V}{F \cdot t}$ (1)
Relative permeability of membrane, α	$\alpha = \frac{J_v}{J_w}$ (2)
Retention coefficient, R [%]	$R = \left(1 - \frac{C_p}{C_t}\right) \cdot 100$ (3)

V – volume [dm^3], F – membrane area [m^2], t – filtration time [s], C – concentrations [g/dm^3], f – feed, p – permeate.

Two types of solutions were used in the main part of the experiment. These solutions were: a model solution based on deionized water containing broth in a concentration of 1 g/dm^3 (MRS type, BTL Poland), and the real fermentation solution, which had previously been concentrated by ultrafiltration using a ceramic tubular membrane with a molecular weight cut-off 8000 Da. The main components of a fermentation solution were: glycerol, 1,3-propanediol, citric acid, lactic acid and acetic acid at a concentration of 13.49 g/dm^3, 2.44 g/dm^3, 2.40 g/dm^3, 0.74 g/dm^3 and 0.52 g/dm^3, respectively. Small amounts of mineral salts such as K_2HPO_4, KH_2PO_4, $(NH_4)_2SO_4$, $MgSO_4 \cdot 7\,H_2O$, $CaCl_2$ and $CoCl_2$ were also present in the test solution.

The membrane cleaning was carried out as a multi-stage process. For this purpose, the membranes were rinsed with deionized water (stage I) and were also cleaned chemically using 1 % basic solution of NaOH (stage II and IV) as well as 0.5 % aqueous solution of H_3PO_4 (stage III). The efficiency of membrane cleaning was determined based on the relative permeability of membrane α, which is the ratio of specific streams of deionized water before and after the regeneration process (mean value determined for the tested filtration cycles).

Results and discussion

The main parameter, which describes the transport properties of the membrane is the hydraulic performance determined by the volumetric flow of permeate (J_w). Figure 1 shows the dependence of the volumetric flow of deionized water on the process transmembrane pressure for the tested AFC-30 nanofiltration membrane. The deionized water flux increases with increasing transmembrane pressure, but is dependent to a small extent on the duration of the process (Fig. 2). The values of the tested parameter were in the classic range specified for nanofiltration membranes (Table 1).

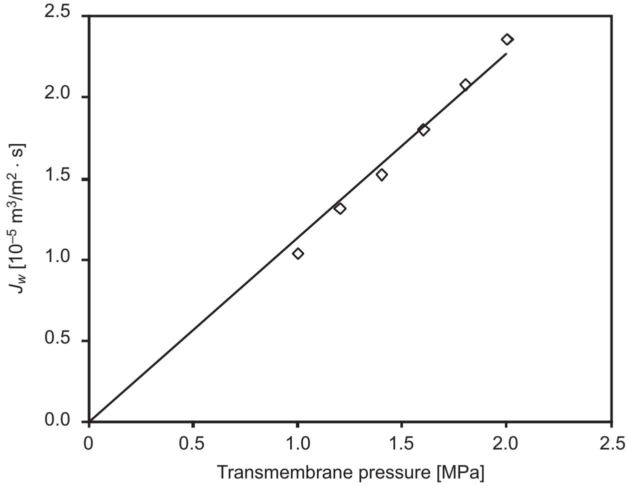

Fig. 1. Relationship between volume flux of deionized water and transmembrane pressure

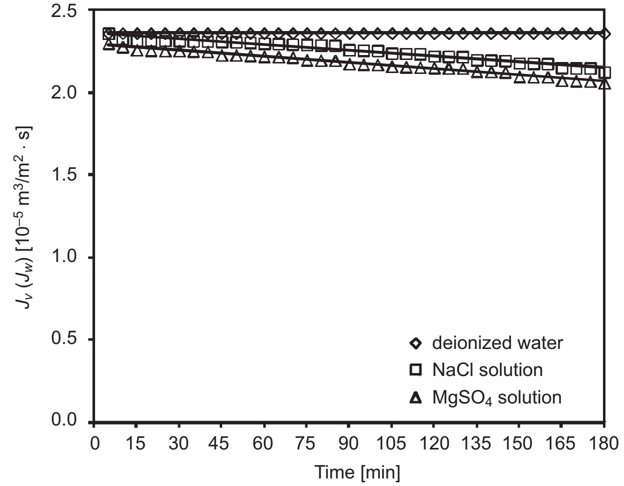

Fig. 2. Volumetric permeate flux on time during filtrations of deionized water and salt solutions (transmembrane pressure 2.0 MPa)

The retention factor for sodium chloride and magnesium sulfate (representing mono- and divalent ions, respectively) determines the separation properties of the nanofiltration membranes. For the AFC-30 membrane the retention coefficient of sodium chloride and magnesium sulfate was medium and high (approx. 58 and 83 %), respectively (Table 4).

Table 4

Volumetric permeate flux, relative permeability of the membrane and retention coefficient of NaCl and $MgSO_4$

Salt	Volumetric flux of deionized water $J_w \cdot 10^{-5}$ m^3/m$^2 \cdot$ s	Relative permeability of the membrane α [-]	Salt retention [%]
NaCl	2.36	0.95	58.4
$MgSO_4$		0.92	83.1

The obtained value of the salt retention coefficients, especially of sodium chloride, is not typical for nanofiltration membranes. The effect of the divalent ion separation is usually approx. three-fold higher than the effect observed for monovalent ions [13]. On this basis, it can be assumed that the tested nanofiltration membrane has separation properties similar to the membranes used in reverse osmosis. The salt retention depends on the process transmembrane pressure (Fig. 3). The retention of sodium chloride and magnesium sulfate is increasing with the increase in transmembrane pressure. The reason for this phenomenon is complex and results, among others, from the reduced concentration of salt at the membrane surface due to the increased feed flux [14].

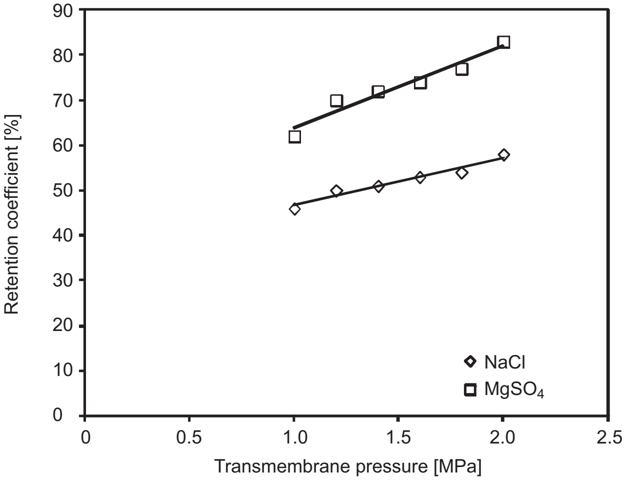

Fig. 3. Relationship between retention coefficient of NaCl or $MgSO_4$ and transmembrane pressure

During the filtration of salt solutions a decrease of volumetric permeate flux was observed (Fig. 2). The relative permeability of membrane α was respectively 0.95 for the filtration of NaCl solution and 0.92 for the filtration of $MgSO_4$ solution. This can be confirmed by the occurrence of adverse phenomena during the membrane filtration such as the concentration polarization.

Figure 4 shows the changes in hydraulic performance of the membrane during nanofiltration of the test solutions (a – model solution, b – real solution), and during the process of cleaning the membrane. In contrast, Figure 5 shows the average values of the relative permeability of membrane α, which characterize the respective filtrations.

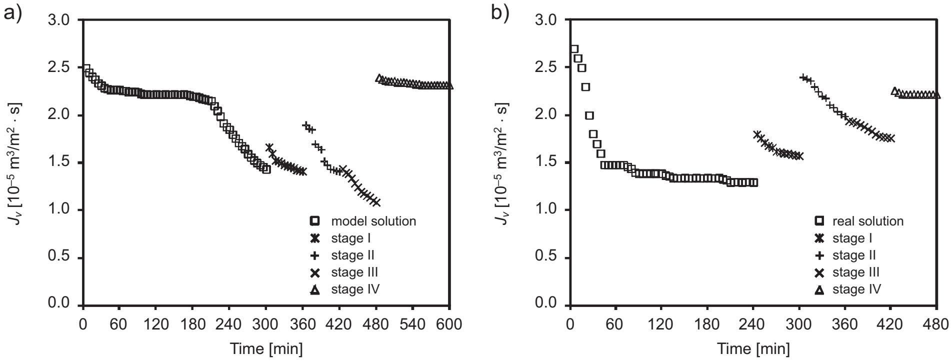

Fig. 4. Effect of type of solution (a – model; b – real) and cleaning process on hydraulic membrane capacity

The study indicated that nanofiltration of the real fermentation solution was characterized by rapid decrease of the hydraulic performance of the membrane in the first hour of filtration. In the case of filtration of the model solution similar phenomenon occurred in the fourth hour of the process. Based on these observations it appears that in the case of filtration of the real fermentation solution, fouling was found to be the predominant process among the adverse effects that accompany membrane filtration,

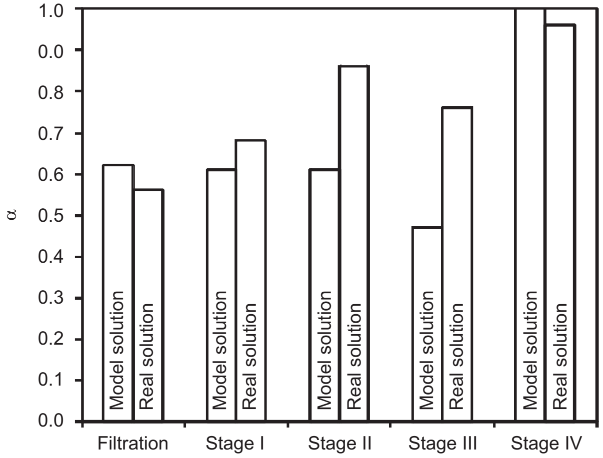

Fig. 5. Comparison of the relative volumetric permeate flux α in nanofiltration of investigated solutions and after cleaning process

since it usually occurs in the initial filtration step [3]. In the case of filtering the model solution a large amount of organic matter could have been rapidly retained on the membrane surface, probably due to the increase in the concentration of pollutants in the near-membrane layer (and concentration polarization phenomenon occurring simultaneously), which resulted in sharp reduction of the membrane hydraulic capacity. However, due to putrescibility of the broth, which is the basic component of the feed, the biofouling of the membrane cannot be ruled out [15, 16]. The value of the relative permeability of the membrane depended on the type of the feed solution and was slightly lower in the case of filtration of the real fermentation solution ($\alpha = 0.56$) than the value determined for filtration of the model solution ($\alpha = 0.62$).

In the final part of the study it was attempted to regenerate the membranes in the following sequence of the selected solutions: deionized water (stage I), an alkaline solution (stage II), acidic solution acid (stage III) and again alkaline solution (stage IV). The lowest efficiency within this sequence was observed in the first stage of the regeneration, this is washing the membrane with deionized water (Fig. 4). This was observed both in the case of the membrane used for filtration of the real fermentation, as well as for the membrane used for filtration of the model solution. It should be noted that in the case of the membrane used to filter the real fermentation solution it was found that filtration of deionized water resulted in approx. 12 % increase in its performance (Fig. 5). This confirms the initial assumptions regarding the occurrence of fouling, which was partially reversible. Chemical cleaning in the base-acid-base sequence, which was used afterwards, resulted in a significant increase in the performance of both tested membranes. In the case of the membrane used for filtration of the real solution regeneration was achieved in 96 %, and for the membrane for the filtration of the model solution the initial performance was restored in 100 %.

The obtained results confirm the high efficiency of chemical methods in the regeneration process of membranes fouled due to filtration of fermentation solutions. Rinsing the membrane with deionized water, in this specific case, was found to be virtually inefficient. In the case of chemical cleaning of the membranes it is crucial to use the reagents in a proper sequence, depending on the type of substances responsible for fouling (organic and/or inorganic). In this case the alkaline solution reacts with the organic substance and the acidic solution with the inorganic substance and to some extent with the organic substance [5]. The sequential use of these reagents markedly increases the efficiency of removing impurities from the surface of the membrane, which is particularly important when the retained precipitates have a multilayer structure.

Conclusion

1. The AFC-30 membrane possesses separation characteristics similar to the membranes used in reverse osmosis. The determined transport properties of the membrane allow, however, classifying it as a typical nanofiltration membrane.

2. The hydraulic efficiency of the membrane is lower in the case of filtering the real fermentation solution, than that observed for the model solution. This is due to the fact that the nature of the feed is essential for the occurrence and the mechanism of blocking the membrane pores.

3. Regeneration of the membrane surface fouled after filtration of the fermentation solutions requires the use of chemical methods, in the sequence of base-acid-base. In the studied case rinsing the membrane with deionized water only was virtually ineffective.

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NANOFILTRACJA ROZTWORÓW FERMENTACYJNYCH – ZJAWISKA NIEKORZYSTNE ORAZ CZYSZCZENIE MEMBRAN

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Abstrakt: Oceniono intensywność niekorzystnych zjawisk występujących podczas procesu nanofiltracji roztworów fermentacyjnych oraz zbadano możliwość czyszczenia membran po filtracji membranowej. Prace prowadzono z wykorzystaniem modułu rurowego wyposażonego w membranę AFC-30. Filtrację przeprowadzono pod ciśnieniem transmembranowym 2,0 MPa, przyjmując prędkość liniową nadawcy 3,4 m/s oraz temperaturę filtrowanego roztworu równą 20 °C. Wydajność hydrauliczną membrany badano zarówno podczas filtracji roztworów modelowych, jak i rzeczywistych. Określono warunki prowadzenia efektywnego czyszczenia zanieczyszczonej powierzchni membran metodą chemiczną z użyciem różnych reagentów. Membranę próbowano również płukać czystą wodą. W zakresie badań wstępnych wyznaczona została charakterystyka transportowa i separacyjna membrany AFC-30 dla wody zdejonizowanej oraz roztworów soli NaCl i $MgSO_4$ reprezentujących odpowiednio jony jedno- i dwuwartościowe. W tym przypadku właściwości membrany badano w zmiennych warunkach ciśnienia transmembranowego od 1,0 do 2,0 MPa.

Słowa kluczowe: nanofiltracja, roztwory fermentacyjne, obniżenie wydajności hydraulicznej membrany, czyszczenie powierzchni membran