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Fouling of the Nanofiltration Membrane NF270 Used for Separation of Fermentation Broths: Impact of Feed Pretreatment Process

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Abstract: Recent findings regarding nanofiltration (NF) have led to indications that it can be successfully used for separation of various biological solutions. As a novelty, this paper is the first to investigate the impact of the feed pretreatment process on the NF membrane performance used for separation of 1,3-propanediol (1,3-PD) fermentation broths. For this purpose, prior to the NF process, the feed was purified by microfiltration (MF) and ultrafiltration (UF) processes. Subsequently, the long-term NF process was carried out with the use of a commercial, flat-sheet, thin-film, polyamide NF270 nanofiltration membrane. Thereinto, to determine the dominant fouling mechanism, Hermia's model was used. With regards to the pretreatment processes performed, it has been determined that the MF membrane (0.14 μm) provided the reduction in the number of bacteria cells present in the permeate, while the UF membrane (450 Da) allowed obtaining the sterile permeate. Consequently, the NF permeate flux for the UF permeate was significantly higher. Analysis of the fouling mechanisms showed that during the separation of the MF permeate, formation of a cake layer on the NF membrane surface was dominant. In turn, with regards to the UF permeate, membrane blocking occurred in two separate phases involving standard blocking and then cake layer formation. Finally, a strategy of NF membrane cleaning with the use of sodium hydroxide (NaOH) solution has been proposed.

Keywords: fermentation broth; fouling; membrane cleaning; nanofiltration; pretreatment; purification; separation; sterility; turbidity

Citation: Tomczak, W. Fouling of the Nanofiltration Membrane NF270 Used for Separation of Fermentation Broths: Impact of Feed Pretreatment Process. *Processes* **2023**, *11*, 817. https://doi.org/10.3390/pr11030817

Academic Editor: Antonia Pérez de los Ríos

Received: 11 February 2023
Revised: 6 March 2023
Accepted: 8 March 2023
Published: 9 March 2023

1. Introduction

Presently, significant research focus is being placed on nanofiltration (NF), which is a pressure-driven membrane process characterized mainly by the high separation efficiency for polyvalent inorganic salts and small organic molecules. So far, NF is used in many fields of applications. Indeed, it has been successfully applied for desalination of seawater [1–3], as well as treatment of drinking water [4–6] and wastewaters [7–9]. Moreover, recently, various research has been oriented towards using NF membranes in biotechnology as one of the steps of fermentation broth separation [10–18]. A literature overview on the current advances in various applications of NF technology is given by Yadav et al. [19].

The major challenging operational issue in NF technology is membrane fouling. Indeed, NF membranes are subject to contamination by suspended matters and microorganisms present in a feed. Undoubtedly, it has a negative influence on the process performance and costs of plant operation, especially in the long term. As it has been indicated in [20], among the most important types of NF membrane fouling are scaling, particulate and organic fouling, as well as biofouling. Importantly, biofouling represents almost 45% of the total membrane fouling [21]. It is a very complicated process, which includes the following stages [22]: (i) conditioning of the membrane surface by organic and inorganic matter occurring in the feed, (ii) microorganisms adhesion and then attachment on the membrane surface, (iii) growth of deposited cells and (iv) formation of biofilm. So far, the biofouling phenomenon has been investigated in NF systems used for wastewater treatment [23–25].

Nevertheless, conducting a literature review allows for indicating that the biofouling of the NF membranes applied for the separation of fermentation broths has not yet been fully evaluated.

In the literature, there is general agreement that in order to maintain high NF processing performance and ensure the long-term stability of membrane systems, fouling controlling is required. For this purpose, the major employed strategies are manufacturing membranes with good antifouling abilities [26,27], as well as feed pretreatment [28], which can be achieved by pressure-driven membrane transport processes, namely, microfiltration (MF) and ultrafiltration (UF). The selectivity of the above-mentioned technologies is dominated by a sieving effect. They have the potential to replace conventional processes, such as centrifugation, which is high-power demanding and expensive. Generally, MF membranes are characterized by pore diameters of 0.1–5 μm. They would potentially remove suspended solids, macromolecular organics, colloidal particles and bacteria. In turn, UF membranes have pore sizes in the range between 0.01 and 0.04 μm. Comparing to MF, the UF process allows separating other molecules, such as carbohydrates, as well as large and small microorganisms. Moreover, the UF process requires higher operating pressures, and UF membranes are more expensive than those used for the MF process [29]. It has been documented that MF and UF membranes can be successfully used for the pretreatment of various media, for instance, raw seawater [30–32], as well as oily [33,34] and laundry [35,36] wastewaters. Moreover, in the recent decade, many researchers have made remarkable achievements in the application of MF processes, e.g., [29,37–42], and UF processes, e.g., [29,41,43–46], for purification of fermentation broths. This finding is confirmed by data presented in Figure 1, which clearly demonstrates the noticeable increase in the number of articles published on this issue during the last two decades. To sum up, it should be highlighted that the choice of the most suitable pretreatment process is a great challenge since it depends mainly on specific requirements for the removal of contaminants [47].

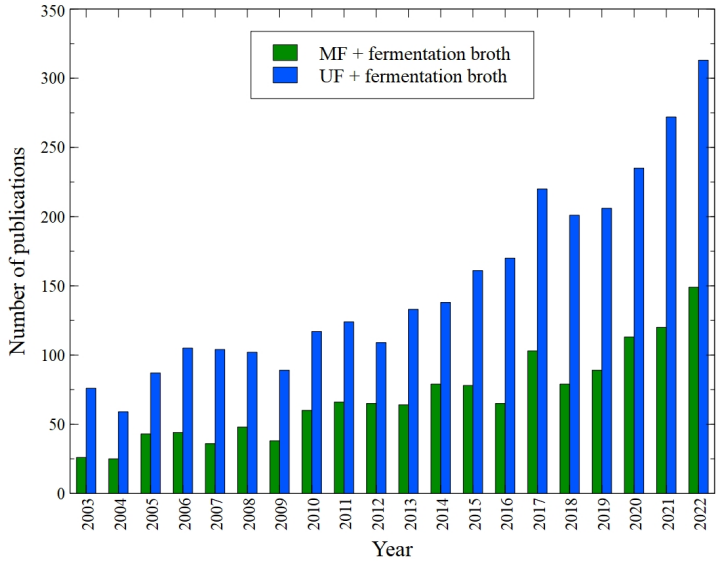


Figure 1. Number of research papers focused on the applications of MF and UF processes for pretreatment of fermentation broths according to ScienceDirect. Data retrieved: 6 February 2023.

The present work is a continuation of the previous study [17], wherein it was shown that commercial, flat-sheet, thin-film, polyamide NF270 membrane ensured the high separation of 1,3-propanediol (1,3-PD) fermentation broths. Indeed, the complete 1,3-PD permeability and significant rejection of several broth components was noted. Moreover, in the above-mentioned study, the NF separation mechanisms were investigated in terms of the properties of both the NF270 membrane and the broth components. In turn, this

paper, to the best of the author's knowledge, is the first one that examines the impact of the feed pretreatment process on the long-term NF membrane performance used for the separation of fermentation broths. For this purpose, the membrane NF270 was used for separation of broths purified by MF and UF membranes. Moreover, in order to determine the dominant fouling mechanism leading to flux decline, Hermia's model was applied. Finally, an effective cleaning method of the NF membrane is presented.

2. Materials and Methods

2.1. Fermentation Broths

The investigations have been focused on the separation of 1,3-PD fermentation broths obtained via glycerol fermentation with the use of *Citrobacter freundii* bacteria. The detailed information on the fermentation process conditions have been presented in several previous articles [39,45,48,49]. After the fermentation, the broths contained bacteria; 1,3-PD; glycerol; mono-carboxylic acids (lactic, acetic and formic acid) and dicarboxylic acid (succinic acid); and ethanol, as well as residual bacterial growth medium. The concentrations of the chemical species present in the fermentation broths used in the present study were shown in [17].

2.2. Pretreatment Processes

According to the research objectives, the impact of the pretreatment process on the NF270 membrane performance has been studied. Based on the literature data, for this purpose, 1,3-PD fermentation broths were pretreated by ceramic MF and UF membranes (TAMI Industries, Lyon, France), the specifications of which are presented in Table 1. The studies were conducted in a conventional cross-flow filtration unit (Figure 2). The methodology of the above-mentioned processes was described in detail in previous studies [39,45].

Table 1. Specifications of the MF and UF membranes used for pretreatment of fermentation broths.

Parameter	Membrane MF	Membrane UF
Number of channels [-]	1	1
Selective layer	ZrO_2	TiO_2
Support material	TiO_2	α-Al_2O_3
Nominal pore size µm/Cut-off [Da]	0.14	450
Internal diameter [mm]	5.6	7.0
Surface area [m^2]	0.0039	0.0047

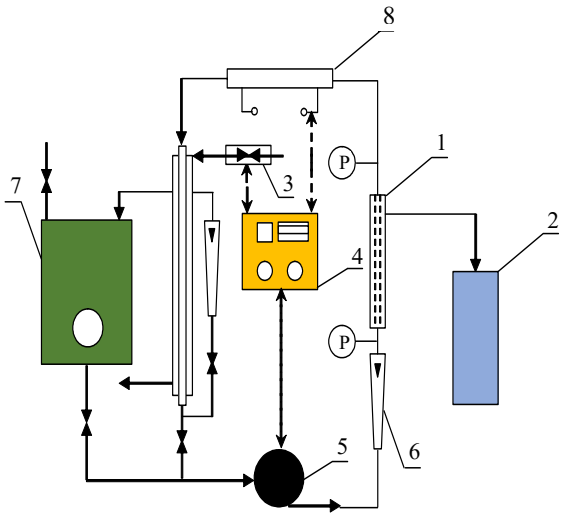


Figure 2. Experimental set-up of the cross-flow filtration unit. 1—MF module, 2—measuring cylinder, 3—heat exchanger, 4—controller of temperature and flow rate, 5—pump, 6—rotameter, 7—feed tank, 8—heater and P—manometer.

2.3. NF Process

For investigations of the NF used for the separation of purified fermentation broths, the Sepa-CFII flat membrane module manufactured by GE Osmonics (Minnetonka, MN, USA), with the commercial flat-sheet thin-film polyamide NF270 nanofiltration membrane (Table 2) from DOW-Filmtec (Minneapolis, USA), was used. A schematic diagram of the experimental apparatus is presented in Figure 3. The detailed information on the experimental set-up was described in a recently published paper [17].

Table 2. Specification of the NF membrane used in the present study.

Parameter	Membrane NF
Skin-layer material	polyamide
Cut-off [Da]	200–300
Average pore radius [mm]	0.43
$MgSO_4$ rejection [%]	97
NaCl rejection [%]	50
Surface area [m^2]	0.0150

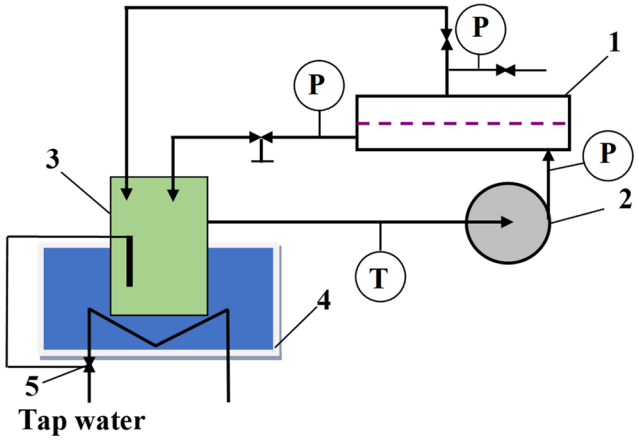


Figure 3. Experimental NF set-up. 1—SEPA-CFII module, 2—pump, 3—feed tank, 4–cooling bath, 5—thermostatic Grundfos valve, P—manometer and T—thermometer.

For comparative purposes, the NF process for both MF and UF permeates was carried out under the same, strictly controlled conditions. The feed temperature, transmembrane pressure (TMP) and feed flow rate were equal to 298 K, 1.4 MPa and 10 L/min, respectively. Each measurement series lasted 40 h.

The NF membrane cleaning was performed under the temperature 298 K and involved two stages. In the first one, the module was rinsing with distilled water for 15 min, and then with 0.1% NaOH solution for the same period of time.

2.4. Analytical Methods

The analytical methods used in the present study were presented in the previously published works [39,50]. The NF membrane morphology and the composition of the scale layer formed on its surface were studied using a Hitachi SU80 Scanning Electron Microscope (SEM) with Energy-dispersive X-ray Spectrometer (EDS). Samples were sputter coated with chromium.

2.5. Analysis of Fouling Mechanism

It has been widely established in the literature that in order to determine the dominant fouling mechanism during the NF process, Hermia's model can be used. Indeed, it is one of the most comprehensive fouling prediction models [51]. Several researchers investigated the possibility of applying this model to investigate the mechanism of the permeate flux

decline during the NF process of various feed solutions, such as fermentation broth [13], surface water [51,52], wastewater [53], juice [54], acid whey [55], red dye [56] and propolis extract [57].

The above-mentioned model is expressed by the following equation [58]:

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \quad (1)$$

where t is the filtration process time; V is the permeate volume; k is constant; and n is the characteristic exponent depending on the fouling mechanism, which includes: cake formation (n = 0), intermediate blocking (n = 1.0), standard blocking (n = 1.5) and complete blocking (n = 2.0). From the literature mentioned earlier, the characteristics of the above-mentioned mechanisms are as follows. (i) Cake formation (Figure 4a): the solutes' diameter is larger than the membrane pores' size, they deposit on the particles that already block the pores, and as a result, a cake layer is formed on the membrane surface. (ii) Intermediate blocking (Figure 4b): a single particle can precipitate on other particles to form multi-layers. (iii) Standard blocking (Figure 4c): particles are adsorbed and deposited on the internal pore wall, constricting the pore volume. (iv) Complete blocking (Figure 4d): the foulant's size is similar to the size of the membrane pores, and consequently, the number of open pores is reduced.

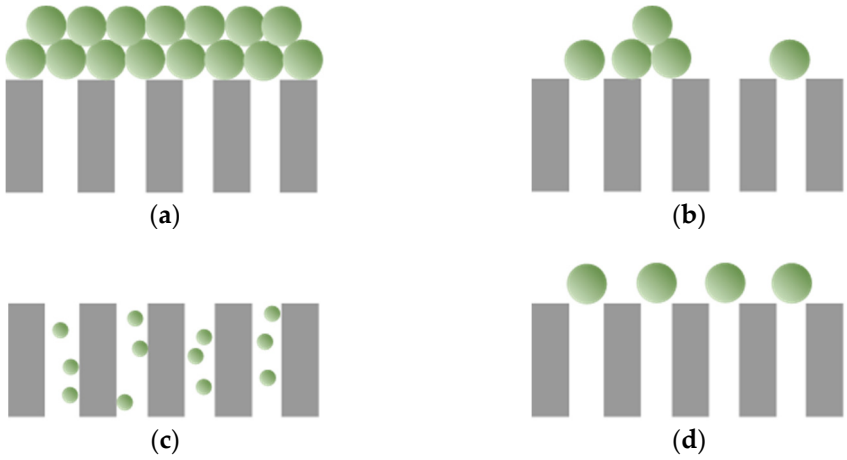


Figure 4. Schematic description of fouling mechanisms: (**a**) cake formation; (**b**) intermediate blocking; (**c**) standard blocking; (**d**) complete blocking.

In the present study, Hermia's model was used in order to evaluate the fouling mechanism of the NF270 membrane during the separation of pretreated fermentation broths. For this purpose, the fitness of the obtained permeate flux values with the above-mentioned mechanisms was defined by determining the correlation coefficients, R^2, reported from linear regression analysis [59].

3. Results and Discussion

3.1. Quality of MF and UF Permeates

In the first strategy investigated, the 1,3-PD fermentation broths were purified with the use of the MF ceramic membrane with the nominal pore size equal to 0.14 µm (Table 1). The permeate quality was determined mainly in terms of the turbidity and sterility. It was confirmed that the MF membrane ensured the permeate characterized by turbidity at the level of 0.2 NTU. This finding is in line with the results demonstrated previously [39,60]. Figure 5 shows the changes in the log CFU (colony-forming units) in the feed and permeate samples analyzed during the MF process. It was determined that throughout the process run, the log CFU in the feed and permeate was in the ranges 16.6–18.1 and 4.4–5.4, respectively. Therefore, it can be concluded that the MF membrane

allowed reducing the number of bacteria cells present in the permeate. It should be pointed out that observations reported in the literature in terms of providing the sterile permeate by MF membranes are unequivocal, and in some cases, non-repetitive. The results obtained in the present study could not be unequivocally matched to the observations demonstrated in previous works [39,60], wherein it was pointed out that the membrane ensured sterile permeate. Of particular importance to the current study, the non-sterility of the permeate obtained during the MF processing of biological solutions has also been reported by Dahiya et al. [38]. The authors demonstrated that a ceramic tubular membrane with the average size of pores at 194 nm ensured the cell rejection of the bacteria *Kocuria rhizophila* BR-1 equal to 99.6%, with an average permeate flux of 3.6 L/m^{2}h at a pressure of 69 kPa and a cross-flow rate of 100 L/h. In turn, Persson et al. [42] found that a ceramic tubular membrane with an average size equal to 0.2 µm provided 100% cell retention of the bacteria *Lactococcus lactis* ssp. *lactis* under a wide range of operational parameters. The varying effectiveness of bacteria retention by MF membranes results from the fact that it depends on several factors, such as the size of membrane pores and microorganisms, as well as the process conditions. In addition, as indicated in [61], bacteria of the same size may behave differently during the filtration process, since the passage of bacterial cells through the membrane pores is determined by the mechanical properties of the bacterial cell wall.

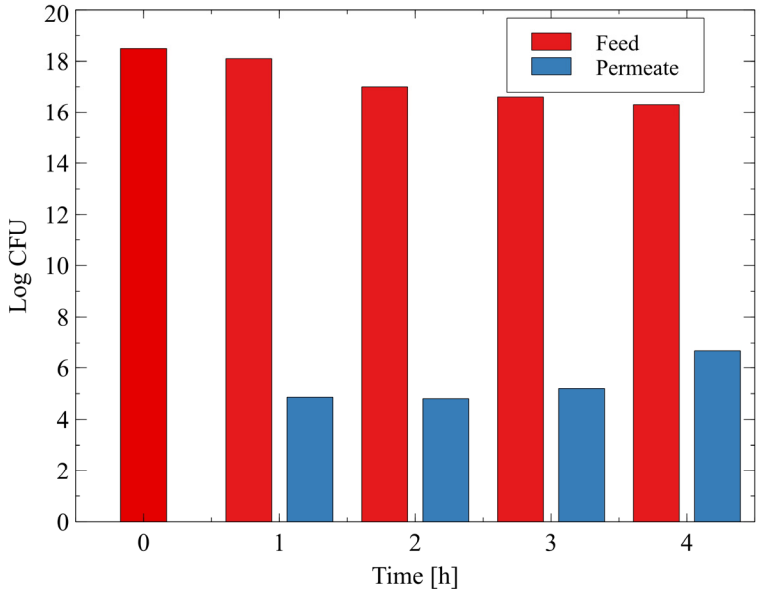


Figure 5. Changes in the log CFU during the MF process of 1,3-PD fermentation broth.

Clarification of the feed containing bacteria can cause their development in different parts of the membrane installation. Hence, to gain further insight, in the next stage of experimental research, the effectiveness of the bacteria removal with the use of sodium hydroxide (NaOH) solution was investigated. In the present study, NaOH solution was gradually added to the broth (pH = 7), and after 30 min of feed circulation, the number of bacteria was determined. As expected, the addition of NaOH solution led to a decrease in the number of bacteria present in the feed (Figure 6). Indeed, at feed pH equal to 7, 8.5 and 9.4, the log CFU was equal to 12.69, 11.90 and 10.50, respectively. Finally, after 30 min of feed (pH $\geq$ 10.3) recirculation, no bacteria were detected. Undoubtedly, the obtained results highlight the efficiency of NaOH in providing a sterile filtration system.

Similar to the MF process, the quality of the permeate obtained using the UF membrane was determined mainly in terms of the turbidity and sterility. It has been noted that the permeate turbidity was at the level of 0.1 NTU. Importantly, it has been determined that the obtained permeate was sterile. Hence, it should be pointed out that the results obtained in the present study are in line with those reported previously [45].

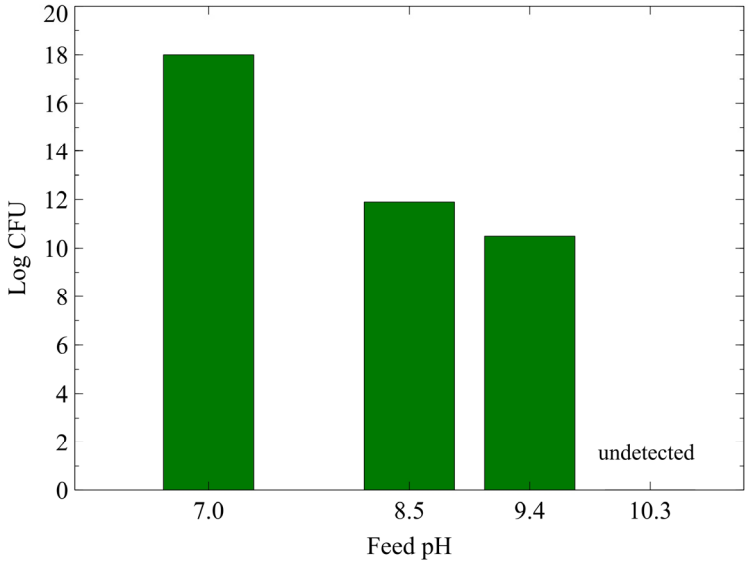


Figure 6. Impact of feed pH on the log CFU in the fermentation broth.

The above-discussed differences between the two pretreatment processes investigated in the present study can be attributed mainly to the significant difference in the size of the membranes' pores. To sum up, it should be indicated that both membranes used ensured the permeate was characterized by low turbidity (<0.2 NTU). Nonetheless, it must be noted that the MF membrane provided a reduction in the number of bacteria present in the permeate, while the UF process allowed obtaining sterile permeate.

3.2. NF Membrane Performance and Fouling Mechanism

The NF270 membrane ensured permeate characterized by a turbidity of 0.15 NTU for both type of solutions was used as a feed. Furthermore, it was determined that although the MF permeate contained the cell bacteria *Citrobacter freundii*, the obtained permeate was cell-free. This finding confirmed that NF technology is suitable for the treatment of fermentation broths. The retention degree of individual components was thoroughly discussed in the previously published study [17].

Figure 7 shows changes in the normalized permeate flux during the long-term NF processes performed for MF and UF permeates. Each of the NF processes was divided into five several-hour stages. After each, the membrane was rinsed with distilled water, and the process was restarted. It can be clearly seen that for both solutions, the permeate flux decreased significantly during the first hours of the process run. Indeed, after 60 min, the normalized flux of 0.30 and 0.37 was noted for the MF and UF permeates, respectively. Subsequently, the flux systematically decreased. After 6 h, the flux corresponded to 0.18 and 0.19 of its initial value for the MF and UF permeates, respectively. Undoubtedly, the obtained reduction in membrane performance was caused by the fouling phenomenon. This observation is in line with results reported in the literature. Indeed, the decrease in the NF membrane performance during the separation of fermentation broths was presented in several others studies [10,11,13]. Further investigations into the membrane performance (Figure 7, periods II-V) confirmed the low values of the normalized permeate flux. However, it should be pointed out that for each phase analyzed, the flux for the UF permeate was higher than that for the MF permeate. More specifically, the normalized flux for the UF permeate was higher by several percentage points. This observation clearly showed that the feed pretreatment process has a significant impact on the NF permeate flux. The reported difference may be attributed to different fouling mechanisms influencing the permeate decline.

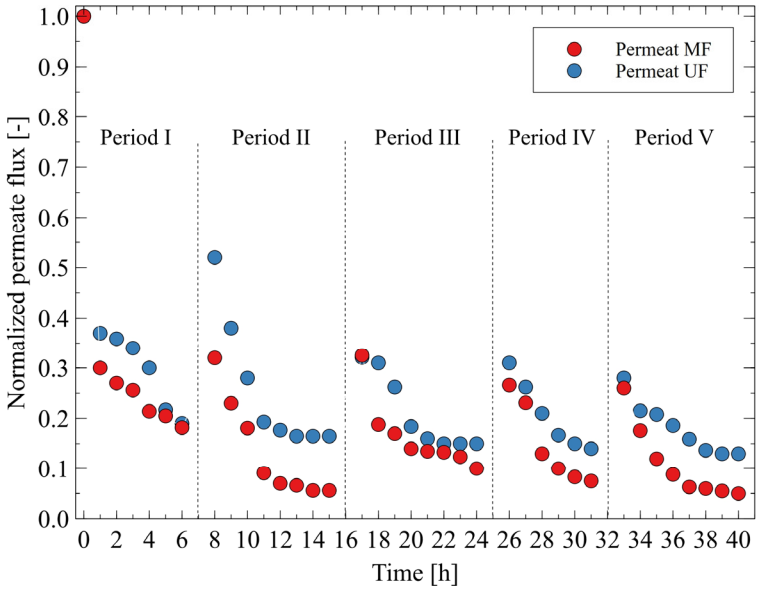


Figure 7. Changes in the normalized permeate flux during the long-term NF of MF and UF permeates. Dashed line—rinsing the membrane with distilled water.

The above-presented finding has been confirmed by the results obtained through the application of Hermia's model (Equation (1)). For the two types of feed solution used, some difference in the dominant fouling mechanism was found. Indeed, in terms of the MF permeate, the experimental data fit most closely with the cake formation mechanism (Figure 4a) throughout the NF process model run (Appendix A, Table 1). As indicated earlier, cake formation is caused by foulants present in the feed that deposit on the particles that already block the pores. Hence, it can be noted that microorganisms and high-molecular-weight uncharged solutes present in the MF permeate built the cake layer on the NF membrane surface, which led to a decline in the permeate flux. In turn, for the UF permeate used as a feed, it was found that membrane blocking occurred in two separate phases. During the first stage, the standard blocking (Figure 4c) was dominant, and then cake formation occurred (Appendix A, Table 1). An important point that should be noted is that the cut-off of the used ceramic membrane was equal to 450 Da, while the molar masses of the organic species presented in the fermentation broths were in the range from 46.05 to 118.08 Da [17]. Hence, it can be indicated that first, the organic compounds blocked the membrane pores, and then formation of a cake layer was dominant.

Finally, it should be pointed out that rinsing the NF membrane with distilled water was not effective. Indeed, it led to an increase of the permeate flux up to 30% of its maximum value. However, it has been found that 0.1% NaOH solution allowed recovering the membrane performance after the separation of the MF and UF performances. It can be explained by the fact that alkaline cleaning agents remove foulants through hydrolyzing proteins, electrostatically repelling charged solutes, as well as dissolving organic macromolecules [62]. Worthy of note, NaOH is one of the most commonly used cleaning agents in membrane technology. Performing a thorough literature review allows indicating that NaOH solutions have been successfully used in membranes fouled by various biological solutions during pressure-driven membrane techniques, e.g., MF [63], UF [50,64] and NF [65].

3.3. Deposit Composition

After completing the measurements series, the NF270 membrane was removed from the module. Figure 8 presents the photography of the membrane after the treatment process of fermentation broths purified by the MF membrane. It can be clearly seen that the membrane surface was covered by foulants. A mesh pattern was created on the

membrane surface. In places where its fibers touched the membrane, darker lines are visible, indicating places where a thicker layer of deposit occurred. The results of SEM studies of a new membrane (Figure 9a) and that used for the treatment process (Figure 9b) confirmed that the latter membrane was covered with a layer of deposit. Most of the deposit was amorphous, although agglomerates were also observed. With significant image magnification (35k), bacterial cells were observed (Figure 9c). To be complete, it should be noted that bacteria presence can cause the development of biofouling, which during industrial long-term operation, can lead to rapid damage of NF modules.

Figure 8. Photography of the NF membrane after treatment of MF permeate.

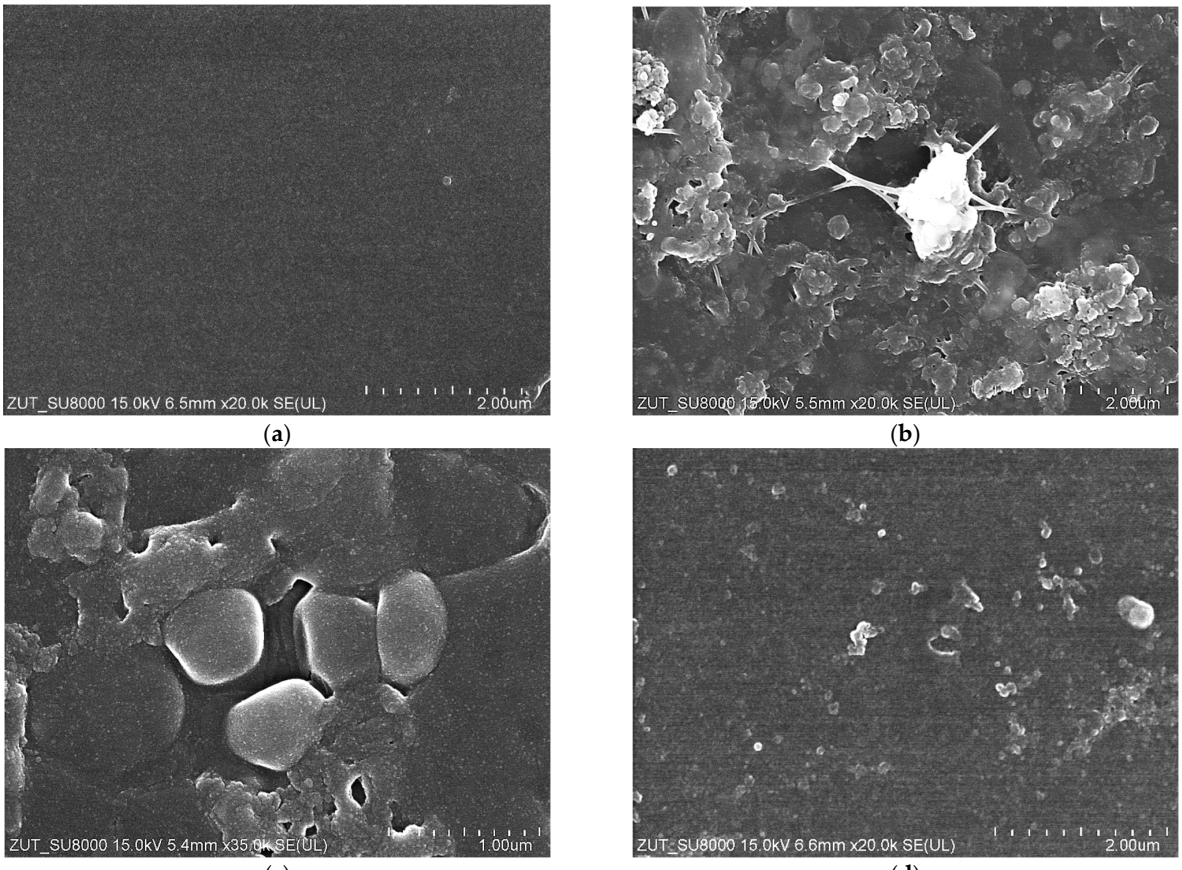


Figure 9. SEM images: (**a**) New (clean) NF270 membrane surface; (**b**) NF270 membrane surface covered by deposit after the separation of MF permeate; (**c**) Bacterial cells present in the deposit shown in Figure 9b; (**d**) NF270 membrane surface covered by deposit after the separation of UF permeate.

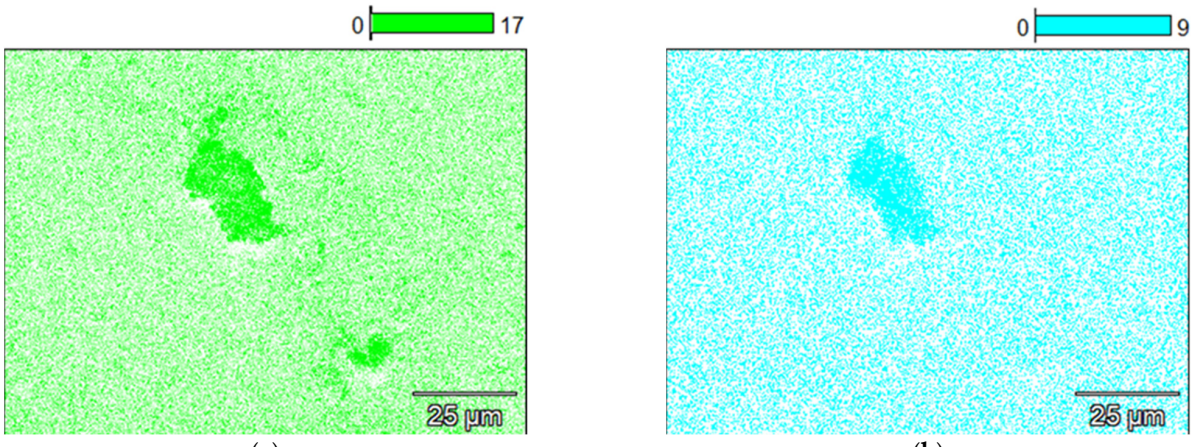
It is noteworthy that after the process using the broth pretreated by the UF process as a feed, the membrane color was much brighter than that shown in Figure 8, and no characteristic grid lines were visible. Indeed, the amount of deposit formed on the membrane surface was lower. Moreover, no bacteria were visible, and inorganic agglomerates were formed locally (Figure 9d). It is in agreement with findings presented earlier, which demonstrated that during the first stage of the NF process of the UF permeate, standard blocking was the dominant fouling mechanism.

Results of the SEM-EDX analysis are shown in Table 3. For both processes investigated, the greatest content was noted for such elements as C and O. It is attributed to the fact that in SEM-EDX analyses, the electron beam penetrates a few micrometers into the membrane; hence, in addition to the deposit composition, the analysis also included the elements forming the polyamide top layer of the NF270 membrane deposit [17]. It was found that the permeate MF used as a feed in the NF process formed deposits mainly containing such elements as Fe (4.678%), S (8.922%), Si (0.318%) and Ca (0.105%), as well as smaller amounts of P 50.074%) and Al (0.087%). With regards to the UF permeate, it has been noted that the deposit contained significantly less C (26.765%) compared to the results obtained for the MF permeate (41.862%). This finding indicated that during the NF process of the UF permeate, less protein was deposited on the membrane surface. It confirmed that the UF processes ensured high protein retention. Worthy of note, analysis of the inorganic agglomerates (Figure 10) composition showed the presence of Al, Si, Mg and O, indicating the formation of aluminosilicates.

Table 3. Results of the SEM-EDX analysis: membrane NF270 after the treatment of MF and UF permeate.

Element	Weight [%]	
	MF Permeate	UF Permeate
C	41.862	26.765
O	43.953	52.898
Na	nd	5.702
Al	0.087	0.124
Si	0.318	0.017
P	0.074	5.201
Cl	nd	0.671
K	nd	0.359
S	8.922	nd
Ca	0.105	0.551
Fe	4.678	7.712

nd—not detected.



(**a**) (**b**)

Figure 10. *Cont.*

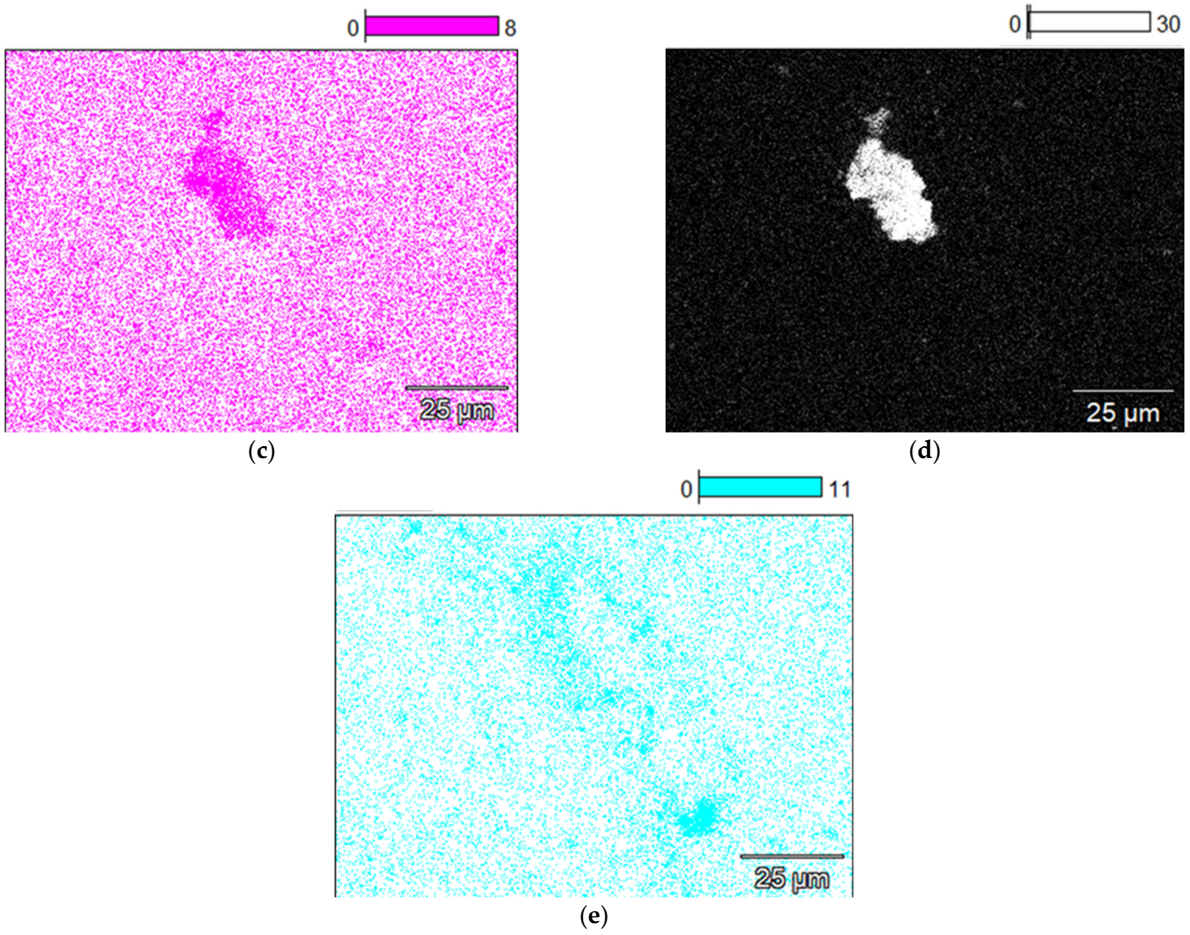


Figure 10. SEM-EDX analysis (elements mapping) of deposit formed on the NF membrane surface during the separation of UF permeate: (**a**) O; (**b**) Mg; (**c**) Al; (**d**) Si; (**e**) Fe.

4. Conclusions

The purpose of the current work was to investigate the impact of the feed pretreatment process on the performance of the long-term NF membrane used for the separation of 1,3-PD fermentation broths. A significant difference in the quality of the MF and UF permeates used as a feed in the NF process was observed. Indeed, it was found that the MF membrane (0.14 µm) endured the reduction in the number of bacteria cells present in the permeate, while the UF membrane (450 Da) allowed obtaining sterile permeate. Consequently, the NF process of the UF permeate showed several percentage points higher performance. The mechanism of the NF membrane fouling was investigated with the use of Hermia's model. It was noted that during the separation of the MF permeate, the formation of a cake layer played a major role in the permeate flux decline. In turn, with regards to the UF permeate, membrane blocking occurred in two separate phases involving standard blocking and then cake layer formation. Finally, the strategy of NF membrane cleaning with the use of a 0.1% NaOH solution for 15 min was proposed. Undoubtedly, the findings presented in this study provide insights into the role of the feed pretreatment process in the performance of the NF process applied for the separation of fermentation broths.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The author declares no conflict of interest.

Appendix A

Table 1. Coefficient of determination (R^2) of Hermia's model.

UF Period	UF Time [h]	Complete Blocking		Standard Blocking		Intermediate Blocking		Cake Formation	
		MF Permeate	UF Permeate	MF Permeate	UF Permeate	MF Permeate	UF Permeate	MF Permeate	UF Permeate
I	0–6	0.6689	0.8016	0.7647	0.8738 *	0.8525	0.9075	0.9546 *	0.8706
II	8–15	0.9048	0.8299	0.9315	0.8559	0.9475	0.8758	0.9519 *	0.9007 *
III	17–24	0.8258	0.8702	0.8762	0.8792	0.9082	0.8870	0.9105 *	0.8986 *
IV	26–31	0.9424	0.9707	0.9638	0.9758	0.9723	0.9711	0.9727 *	0.9766 *
V	33–40	0.9178	0.9475	0.9541	0.9587	0.9703	0.9640	0.9719 *	0.9642 *

* Indicates the best-fitting model.

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