Chemical Engineering Journal xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

The ultrafiltration ceramic membrane used for broth separation in membrane bioreactor

Marta Waszak, Marek Gryta *

West Pomeranian University of Technology, Szczecin, Institute of Inorganic Technology and Environment Engineering, ul. Pułaskiego 10, 70-322 Szczecin, Poland

HIGHLIGHTS

- The glycerol bioconversion to 1,3-propanediol was presented.
- The membrane bioreactor with ceramic ultrafiltration membrane was studied.
- The intensity of membrane fouling caused by broth during ultrafiltration was studied.
- The effect of process parameters on the intensity of membrane fouling was discussed.

ARTICLE INFO

Article history:
Available online xxxx

Keywords:
Membrane bioreactor
Ultrafiltration
Ceramic membrane
1,3-Propanediol

ABSTRACT

In this work the studies of glycerol fermentation in a bioreactor connected with separation of broth by ultrafiltration process were presented. The study was carried out with broths, which were prepared using *Citrobacter freundii* bacteria. A tubular tight ultrafiltration ceramic membrane (8 kD) was applied and the complete rejection of bacterial and other suspended solids was achieved. The produced permeate was clear, with a turbidity at a level of 0.1 NTU. Although a tight ultrafiltration membrane was used, the ions retention was at a low level – below 10%. In a comparison with a classical method of fermentation with broth bleeding, the yield of fermentation was increased by the application of ultrafiltration for treatment of broth from the bioreactor. However, a significant (over 70%) permeate flux decrease was observed due to a fouling, which is an essential limitation in the application of the membrane separation. A periodical module rinsing with 1% NaOH solutions was used for limitation of the fouling influence on a flux decline.

1. Introduction

A membrane bioreactor is an integrated device to carry out simultaneous biochemical reactions and the separation of broth components. In this system, the microfiltration or ultrafiltration is usually used for separation of bacteria, which are retained inside the bioreactor [1–4]. In this case, a membrane acts as a selective barrier that enables an immobilization of suspended cells in the reaction zone. A process intensification proceeds in a microbiological membrane bioreactor is due to a higher concentration of bacterial biomass in a comparison to the traditional reactors [3–8].

Microfiltration (MF) is used primarily to retain the microbial cells on a membrane, whereas ultrafiltration (UF) to retain also proteins, including enzymatic proteins [9,10]. It is assumed that the retention of components during MF and UF proceeds according to a sieve mechanism. The sieve mechanism is based on the difference of sizes of retained compounds in relation to the size of membrane pores. Moreover, the ceramic tight UF membranes can be negatively charged [11,12]. Due to the interaction of charges, the negatively charged ions should be rejected more effectively. Thus, the charged membrane can reject the negative ions, which are significantly smaller than the membrane pore size. A high retention of phosphate by TiO_2 UF membranes was observed [11]. A rejection based on the electrostatic interactions can be physically explained by the Donnan exclusion and the formation of electrical double layer in the membrane pores [12].

The effectiveness of the biotechnology is based mainly on the two parameters: yield of biosynthesis and the productivity of the bioreactor. The yield can be improved by screening for more efficient production strains [13]. Productivity depends on the biocatalysts concentration and the mode of the bioreactor operation being batch, fed-batch, continuous or high cell density cultures [3–10,13]. In the cell-recycle fermentation, the yield was greater

* Corresponding author. Fax: +48 (91) 449 46 86.
E-mail address: Marek.Gryta@zut.edu.pl (M. Gryta).

http://dx.doi.org/10.1016/j.cej.2015.11.058
1385-8947/

than that in batch fermentation because less substrate was needed to grow cells [5]. In the case of high cell density, the productivity increased due to the possibilities of higher dilution rate [4] and higher volumetric productivities [5–7].

A higher final concentration of products in the broth decrease the cost of production, however, the bioproducts created an inhibiting effect on the fermentation process [14–16]. Moreover, a fraction of substrate is converted to the different by-products. The separation of such mixtures is difficult to perform and is costly [17]. An integration of bioreactor with membrane processes enables the selective separation of products from the fermentation broth, and is sometimes associated with their preliminary treatment. The nanofiltration (NF) was used for selective separation of 1,3-propanediol (1,3-PD) from the fermenting solutions [18,19]. Due to a high turbidity of broth, the broth should be pre-filtered using the UF process if the spiral-wound NF modules will be applied [20].

A cost of membrane separation is the lower if the higher permeate flux is obtained. A hydraulic permeability of membranes determined for a pure solvent (water) has the highest value. Bacteria, suspended solids and solutes can form the deposits on the membrane surface (fouling), which result in an enhancement of mass transfer resistance through the membrane. The permeate flux decreases during the filtration process due to blocking of the membrane pores and the concentration polarization [2,18–20]. This is one of the main disadvantages of membrane processes. Several methods are used to reduce these undesirable phenomena, e.g. a selection of membrane material and applying a high feed flow velocity (shearing stress and high turbulence) [1,2,21]. The membranes can be made from inorganic materials (e.g. ceramics, metals) or organic compounds like in the case of polymer membranes [1–12]. A possibility of application of more harsh cleaning solutions, e.g. hot solutions of NaOH, that increases the effectiveness of membrane module cleaning, is an advantage of inorganic membranes [20,22].

The UF membranes are defined as having a pore size in the range 0.001–0.02 μm and they retain fine particles, colloidal material, bacteria, viruses and some other pathogens and pyrogens such as endotoxins [3,9]. The broths have a fouling impact several times larger compared to the surface water and seawater, therefore, the effective membranes cleaning methods should be used in the case of UF integrated with bioreactor [20,21]. In UF process, a cross-flow is traditionally applied to prevent excessive build up of contaminants on the membrane surface. The cross-flow velocities normally create turbulent or transitional regime conditions in the feed channel, providing a highly effective method of restoration the surface from accumulated particulates [1].

In this work, a ceramic tight UF membrane was used for the separation of glycerol solutions fermented by *Citrobacter freundii* bacteria. The inhibitory effect of organic acids on the microorganisms is a well-known phenomenon and was demonstrated during the glycerol fermentation to produce 1,3-propanediol [13,15]. The results of other works confirmed that the fermentation conditions increasing the productivity of 1,3-PD are also accompanied by inhibition phenomena [14,16]. A periodic broth bleeding is usually used method for decreasing metabolites concentration [4–6]. Under favorable fermentation conditions (pH = 7), the obtained by-products (carboxylic acids) are practically always found in an anionic form as acetate and lactate [18,19]. However, the electrostatic repulsion between the surface of used tight ultrafiltration membrane and the anionic forms of organic acids may result in their enhanced retention [11,12]. In presented studies two methods: fed-batch fermentations with periodical broth bleeding and fermentation connected with UF process, were used for removal a part of broth from bioreactor.

2. Experimental

The fermentation of glycerol solutions was carried out in a pilot plant schematically shown in Fig. 1. The stainless-steel ASI 316 was used as a construction material. In this installation a single-channel (diameter 0.006 m, internal area $3.8 \cdot 10^{-3}$ m^2) UF tight ceramic membrane (8 kD) manufactured by TAMI (France) was used. Two kinds of fed-batch fermentation with periodical removal a part of broth were carried out. In the first method, a portion of broth was collected using a bleeding value (BV). In the second method of process operation, the BV value was closed and the UF valve was periodically opened (5 h per day). A volume of fermentation broth amounted to 2 L and the same volume of sterile culture medium was added in both cases in the place of collected solution. Additionally, a portion of pure glycerol (ChemPur, Poland) was also periodically added to the broth.

The UF process was carried out under the TMP pressure in the range of 0.1–0.25 MPa. The experiments were carried out using the feed flow equal to 350 L/h, which corresponds to the flow velocity tangential to the membrane surface of 3.64 m/s and the Reynolds number equal to 15,000. The rotameters (+/− 10 L/h) were used for the measurement of flow rate. The actual values of maximum permeate flux were determined using the distilled water as a reference solution. After completing each series of fermentation, the pilot plant was subjected to the chemical cleaning and the UF permeate flux was measured. The cleaning procedure was as follows: rinsing the installation with distilled water (10 min), washing with a 1 wt% solution of sodium hydroxide for 5 min, followed by rinsing with water over 5 min. If the initial UF flux was not restored, the cleaning procedure was repeated.

The glycerol fermentation was carried out using *C. freundii* bacteria at temperature 304 K. A prepared broth (culture medium) contained per liter: glycerol 20 g, yeast extract 2 g, meat extract 1.5 g, peptone K 2.5 g, $K_2HPO_4 \cdot 3H_2O$ 3.4 g, $KH_2PO_4 \cdot 1.3$ g, $MgSO_4 \cdot 7H_2O$ 0.4 g, $(NH_4)_2SO_4 \cdot 2$ g, $CaCl_2 \cdot 2H_2O$ 0.1 g and $CoCl_2 \cdot 6H_2O$ 0.004 g. After sterilization, the medium was inoculated with bacteria in a lag phase (10% v/v). During the preparation of culture media and fermentation, the acids produced were neutralized by the addition of sodium hydroxide (5 M).

A biomass concentration was estimated by a series of broths dilution prepared in a 0.9 wt% NaCl solution and the obtained samples were placed on the MRS agar (BTL, Poland). The plates were incubated for 24 h at 303 K and the colony-forming units (CFUs/mL) were then counted. This experiment was verified three

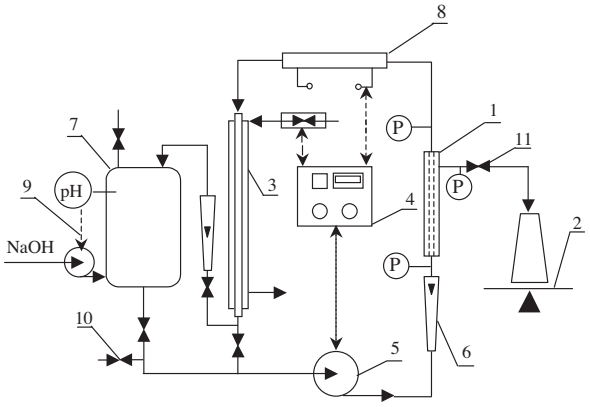

Fig. 1. A scheme of used membrane bioreactor. 1 – UF module, 2 – balance, 3 – heat exchanger, 4 – controller of temperature and flow rate, 5 – pump, 6 – rotameter, 7 – feed tank, 8 – heater, 9 – pH of broth controller, 10 – bleeding valve (BV), 11 – UF valve, P-manometer.

Please cite this article in press as: M. Waszak, M. Gryta, The ultrafiltration ceramic membrane used for broth separation in membrane bioreactor, Chem. Eng. J. (2015), http://dx.doi.org/10.1016/j.cej.2015.11.058