Separation of 1,3-Propanediol by Nanofiltration Method

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Abstract: The application potential of nanofiltration (NF) method on the separation of 1,3-propanediol (1,3-PDO) from synthetically prepared fermentation broth was investigated. The rejection tests at different pressures (10, 20, 30 bar) and pH values (7 and 10) were performed on laboratory scale using Desal DL-5 NF membrane. The rejection of succinic acid, having the molecular weight larger than or closer to the molecular weight cut-offs (MWCOs) of Desal-5 DL NF membrane was 100% independent of operating pressure and pH. The results of this study clearly showed that NF process is a very promising pretreatment step for the removal of volatile organic acids from the fermentation broth.

Keywords: Desal-5 DL, Fermentation broth, Nanofiltration, 1,3-Propanediol, Volatile organic acids.

INTRODUCTION

The 1,3-propanediol ($C_3H_8O_2$, 3G) is an economical source for the production of 3GT (a polymer of 3G and terephthalic acid), which is a novel polyester with good stretch, recovery, and dyeability [1,2]. The 1,3-propanediol (1,3-PDO) is used in a variety of applications, such as lubricants, medicines, cosmetics, food, and in the polymerization of polytrimethylene terephthalate [3,4]. It is produced through several reaction paths, involving different feed stocks, but a glycerol-based, bio-technological route promises to be the method preferred in the coming decades [5] as the chemical synthesis requires expensive catalyzers, high temperature, high pressure, and high level of safety measurement. The production of bio-based 1,3-PDO through the metabolism process occurs in substrates by microorganisms such as *Klebsiella pneumoniae, Clostridium pasteurianum, Citrobacter freundii, Enterobacter agglomerans* [6-8]. The biotechnological method is also characterized by the use of recombinant DNA technology for the preparation of the aforementioned microorganisms [9-10].

Considering the yield and recovery of product, environmental protection, and sustainable development of 1,3-propanediol, much attention has been paid to its microbial production, either based on glycerol or on glucose [11-23].

Increasingly, glycerol is produced as the by-product of the bio-diesel and soap industries, making it a low-cost renewable resource [24]. In the context of developing an economically competitive fermentation technology using renewable feedstock and industrial waste; glycerol which is a major byproduct of the biodiesel industries, promises to be a good substrate for 1,3-PDO production, which further changes the perception of glycerol as being an industrial waste [25]. The biotechnological method can also leap into the most appropriate method for 1,3-propanediol production if petroleum resources become exhausted [22].

However, the development of an efficient purification strategy is posing as a technical barrier against the successful commercialization of 1,3-propane diol from a biological source. A fermentation broth containing mixture of multiple components, such as, water, residual glycerol, glucose, by-products (acetate, lactate, succinate, ethanol and 2,3-butanediol), macromolecules (proteins, polysaccharides and nucleic acid), salts and residual medium makes the downstream processing of 1,3-propanediol a potentially difficult separation challenge. In addition, 1,3-propanediol is very hydrophilic and has a high boiling point. The boiling points of 1,3-propanediol and glycerol are 214 and 290°C, respectively at atmospheric pressure. These properties makes the purification of 1,3-propanediol from a complex fermentation broth a bottle neck for the development of a commercially viable process [26].

Several methods for the purification of 1,3-propanediol have been reported in many of previous studies. The major methods for the recovery of 1,3-propanediol studied are reactive extraction, liquid-liquid extraction, evaporation, distillation, membrane filtration, pervaporation and ion exchange chromatography. All

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E-ISSN: 2410-1869/15

these methods so far studied have some drawbacks or limitations [23, 26]. Nanofiltration (NF) is a membrane separation technology based on both charge (Donnan effect) and size (sieving effect). It was reported that NF technology could separate low molecular weight solutes (*e.g*. glucose, saccharides, amino acid, and peptide) from inorganic salt solutions [27-32], showing great potential in desalination and/or recovery of valuable organic substances [33]. To our knowledge, there has been no a detailed report yet regarding the separation of volatile organic acids using NF technology from the effluent of 1,3-PDO production.

The focus of this study was to identify the suitable operating conditions of Desal-5 DL membrane for the efficient removal of volatile organic acids; which will lead to a simplified effluent for post processing steps after NF application. In present study, the effect of pressure (10, 20 and 30 bar) and the effect of pH (7 and 10) were tested using synthetically prepared model fermentation solutions.

2. EXPERIMENTAL METHOD

2.1. NF Membrane and Membrane Test Unit

A commercial flat-sheet NF membrane, Desal-5 DL from Osmonics (with four layers - polyester, polysulphone and two proprietary layers) is used in this study. Based on the manufacturer's data sheet and the info in the literature [33], the properties of the membrane are shown in Table **1**. The effective membrane surface area was 0.0266 m^2.

The membranes used for the tests were treated by soaking in deionized water overnight.

Then, the Desal-5 DL membranes were compacted before each experiment by filtering deionized water at 280 kPa for 2 h.

Table 1: Summary of Desal DL-5 NF Membranes

Manufacturer	Osmonics (GE)
Surface material	Polyamide
MWCO ($gmol^{-1}$)	150-300
Temperature, max. (^{o}C)	45
Pressure, max. (bar)	41
pH range	2-11
Isoelectric point (pH)	~4,2

To examine the effectiveness of the NF membrane for removing organic acids in model solution, a lab-scale cross-flow flat-sheet configuration membrane test unit (SEPA CF II, Osmonics) was used (Figure **1**). The meshed spacer was inserted in the cell in order to induce a turbulent flow for the prevention of

Figure 1: Lab-scale cross-flow flat-sheet configuration test unit (SEPA CF II, Osmonics) [34].

concentration polarization on the membrane surface. A new NF membrane coupon was used for each test.

2.2. Feed Composition

Model solution used in the experiments, containing 1,3-propanediol (13.5 gL^{-1}), glycerol (3.5 gL^{-1}), succinic acid (0.5 gL^{-1}), lactic acid (1 gL^{-1}) and acetic acid (2 gL^{-1}), was prepared by dissolving these chemical compounds in deionized water. The initial pH was set to 7 prior to pressure studies.

2.3. Filtration Tests and Analysis

The initial feed volume was 16 L. During experiments, feed, retentate and permeate were sampled and assessed for flow rates, pH, conductivity, temperature, salinity and total dissolved solid (TDS) concentration every 30 minutes.

The substrate glycerol, and the products 1,3-PDO, lactic acid, acetic acid and succinic acid were measured by HPLC (Agilent 1100) with a Phenomenex Rezex RHM Monosaccharide (H^+) 300 x 7.8 mm ion exchange column, using a Agilent 1100 Series G1362A Refractive Index Detector. The column temperature was set at 65°C and the detector temperature at 45°C. The injection volume was 15 μL. A solution of 5 mM H_2SO_4 was used as mobile phase with a flow rate of 0.8 mL/min [25].

3. RESULTS AND DISCUSSION

3.1. Effect of Pressure

In order to study the effect of operating pressure on the separation of by-products and glycerol from 1,3-PDO; three different pressure values were tested during 210 minutes of operation. Figure **2** gives the rejection percentages of all components in the model solution. Succinic acid was 100% rejected at the end of the test. The average rejections of acetic acid, lactic acid, 1,3-PDO and glycerol were 80%, 60%, 8% and 10%, respectively. For an efficient separation by NF technique; it is expected to get maximum rejection of substrate and by-products, and minimum rejection of 1,3-PDO or the opposite.

NF membranes, having a transition property between ultrafiltration (UF) and reverse osmosis (RO), tend to reject multivalent ions and organic compounds having molecular weight greater than 200 Da. Organic acids with lower molecular weight such as acetic acid, cannot be rejected efficiently by microfiltration and ultrafiltration. However, due to the electrostatic repulsion mechanism of NF membranes at neutral pH, organic acids can be removed from the aqueous solution as they are disassociated to give hydrogen ion and carboxylate group at neutral and alkali pH. As seen in Figure **3**, succinic acid rejection reached 100% at 20 bar of pressure and all other compounds' rejections increased by the increase in applied pressure.

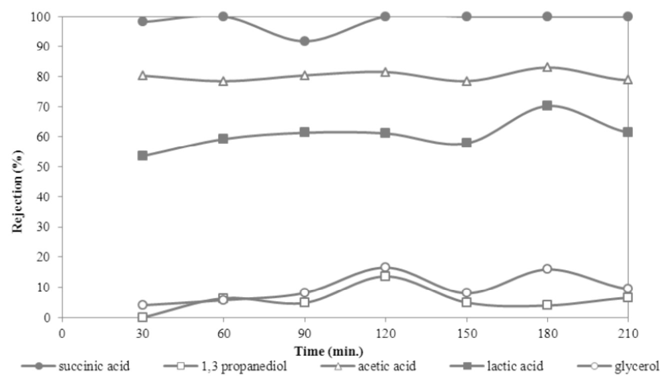

Figure 2: Percent rejections of fermentation broth products at 10 bar and pH 7.

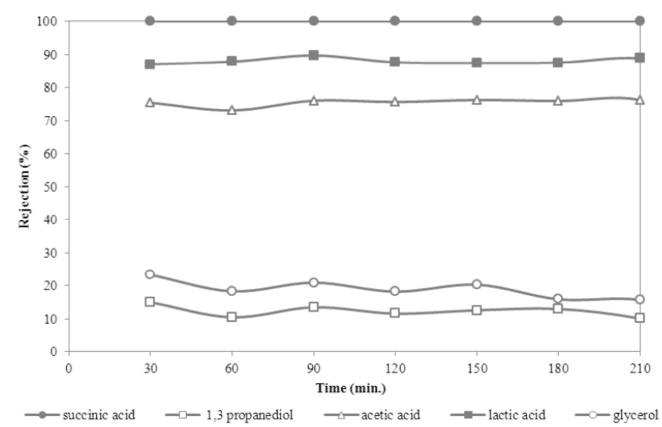

Figure 3: Percent rejection of fermentation broth products at 20 bar and pH 7.

It can be concluded that the separation of succinic acid from the fermentation broth by NF method, is totally dependent on the molecular weight of the compound and it is irrespective of the applied pressure. Contrarily, among the organic acids, lactic acid having a molecular weight smaller than MWCO of the Desal DL-5 membrane, is rejected gradually as the pressure increased. Although there is no a significant difference in 1,3-PDO rejection at 10 and 20 bar; the glycerol rejection is slightly increased at 20 bar. This difference would be a surplus for further separation and purification steps as glycerol and 1,3-PDO are the most complex compounds to be separated from each other.

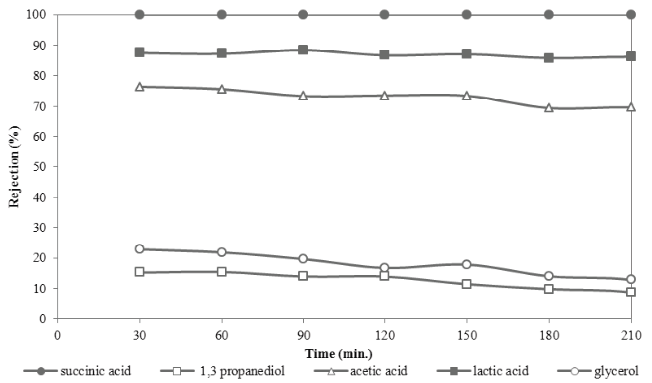

Figure 4: Percent rejection of fermentation broth products at 30 bar and pH 7.

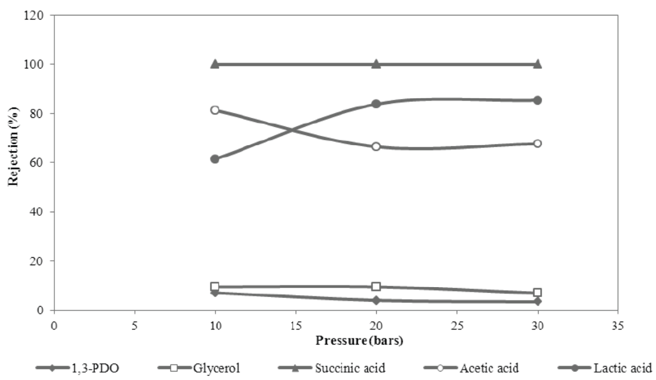

Figure 5: Rejection percentages of the compounds at different pressure values.

A final study on pressure effect was carried out at 30 bar (Figure **4**). Since the maximum operating pressure for Desal DL-5 NF membrane is 41 bar, it is not logical to try higher pressure values as higher pressures will cause membrane defects and decrease the rejection efficiencies. According to Figure **4**, it is clearly seen that the rejections for all of the compounds remained almost the same as in the case with 20 bar of applied pressure. Thus, it does not make any sense to increase the pressure furthermore and for such reason the optimum operating pressure for Desal DL-5 was considered as 20 bar for separation of 1,3-PDO.

Figure **5**, resumes the rejection percentages for each compounds at three different pressure values. Succinic acid, independently from the pressure change, was rejected 100% by NF process. Acetic acid and lactic acid, both in 20 and 30 bar, were rejected around 70% and 85%, respectively. The situation in glycerol and 1,3-PDO is a little bit more complex and different than the case for organic acids. Both of them remained in the feed solution for all cases studied. However, at pH 7 and operating pressure of 20 bar; glycerol is a bit more rejected than those obtained at other conditions. This difference will ease further separation steps, especially for separation of 1,3-PDO from glycerol.

3.2. Effect of pH

Figure **6** shows the significant effect of pH in glycerol and 1,3-PDO rejections. While the results are compared for these two compounds at pH 7, the rejections decreased to less than 10% for both. Besides 1,3-PDO was almost not rejected. In contrast the rejections of acetic acid and lactic acid were reached their highest percentages in that condition. As the pH change affects the charges on the membrane; the ion passage is directly affected as well. The ion concentration of the solution will influence the property of the membrane pores and the passage of other molecules.

Organic acids are mainly weak acids and are dissociated according to the pH of the solution.

Table **2** gives the acidity constant of the organic acids used in this study.

The rejection of weak acids and bases are dependent on pH. For such reason they are highly rejected during NF process while they are in ionized forms. Thus, organic acid rejection is increasing while pH is above pK_a and decreasing when pH is below pKa. For the organic acids such as acetic acid, lactic acid having a pK_a value smaller than the pH range 3-5; the rejections are increased at pH 10.

Table 2: Acidity Constants of the Organic Acids Present in this Study

Organic Acid	Formula	M_W (Da)	pK_a
Acetic acid	$C_2H_4O_2$	60,05	4,75
Succinic acid	$C_4H_6O_4$	118,09	4,16
Lactic acid	$C_3H_6O_3$	90,1	3,88

In the case of succinic acid, the abundant mechanism is the “molecular sieving effect” as described previously. The reduced surface charges of NF membrane and neutral organic acids below pK_a value limit the electrostatic repulsion between membrane and organics. Thus the “sieve effect” according to molecular weight, plays a key role in the rejection.

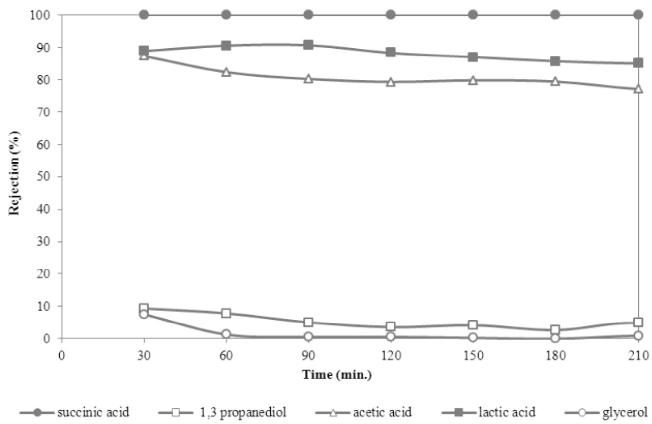

Figure 6: Percent rejection of fermentation broth products at 20 bar and pH 10.

4. CONCLUSIONS

Results of the NF method using Desal DL-5 membrane showed relatively good rejection performance for the separation of organic acids from the fermentation broth. According to the obtained results, the rejection of succinic acid did not change with an increase at operating pressure from 10 to 30 bar and its rejection was 100% irrespective of operating pressure employed. On the other hand, the rejection of lactic acid increased at 20 bar and remained constant with further increase in pressure. Contrarily, the rejection of acetic acid decreased somehow when pressure increased to 20 bar and then no change was observed at rejection with an increase in pressure up to 30 bar. The rejections of glycerol and 1,3-PDO were not affected much by the increase in applied pressure. The results of different pH levels showed that the degree of organic acids rejection by Desal DL-5 slightly changed when the pH is increased. In contrast, the rejection of glycerol and 1,3-PDO decreased by the increase in pH value. In conclusion, NF method revealed considerable applicability for removing organic acids in fermentation broth prior to further down-stream steps in purification of the final product.

ACKNOWLEDGEMENT

The authors wish to thank TUBITAK-CAYDAG for the financial support of this study under the grant No 109Y150. The data presented in this article was produced within the project above, however it is only the authors of this article who are responsible for the results and discussions made herein.

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Received on 06-08-2015 Accepted on 22-11-2015 Published on 27-11-2015

http://dx.doi.org/10.15379/2410-1869.2015.02.05