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Separation of Succinate from Organic Acid Salts Using Nanofiltration Membranes

Jeng Yih Law[a,b], Abdul Wahab Mohammad*[,b]

[a]Section of Chemical Engineering Technology, Universiti Kuala Lumpur, Malaysian Institute of Chemical & Bioengineering Technology, 78000 Alor Gajah, Melaka, Malaysia.
[b]Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Malaysia.
drawm@ukm.edu.my

The fermentative production of bio-based succinic acid is often accompanied by organic acid byproducts. In this study, the separation of succinate from organic acid salts (acetate and formate) using pressure-driven nanofiltration (NF) was studied. The performances of three nanofiltration membranes were compared and discussed. The influence of feed ratio on the succinate recovery was not significant given that succinate rejections of greater than 81.9 % were obtained in all cases. A comparison between monovalent rejection and divalent rejection suggests that the separation of multi-salt solution was influenced by the Donnan-steric effects. Taking into account the permeation fluxes and organic acid salt retentions, the NFW membrane manufactured by Synder Filtration was considered the most appropriate membrane for the separation of divalent succinate from other organic acid salts. This study strongly supports the use of NF technology for the downstream recovery of high valuable products.

1. Introduction

Succinic acid ($C_4H_6O_4$) has been recognised as a valuable commodity that can be produced via biological pathway (fermentation). The applications of succinic acid and its potential as one of the future platform chemicals have been widely reported in a number of literatures (Brink and Nicol, 2014). Traditionally, succinic acid is produced by chemical process via hydrogenation of maleic anhydride on an industrial scale (Bechthold et al., 2008). The worldwide production of succinic acid is estimated to be 20,000 to 30,000 t/y (Cukalovic and Stevens, 2008). The annual growth rate for global succinic acid market is much smaller than other competing chemicals (i.e. maleic acid, maleic anhydride) due to the high conversion cost of maleic anhydride to succinic acid (Song and Lee, 2006).

In the last few years, a growing interest in the fermentative production of bio-based succinic acid was observed. The overall concern for the environment and the demand for 'greener' technology have been the driving forces toward the production of bio-based succinic acid. Table 1 shows a general comparison between the fermentative and chemical production routes (Cukalovic and Stevens, 2008). Unlike chemical production route which requires high operating temperature and pressure, fermentation operates at much milder conditions. Downstream recovery processes are cost intensive steps in the fermentation based processes (Song and Lee, 2006). Fermentation also generates a considerate amount of byproducts (i.e. acetic acid, formic acid). More efforts and studies are needed to improve the yield, concentration, purity and product recovery of the bio-based succinic acid (Song et al., 2007). Various separation techniques have been developed for the separation and purification of bio-based succinic acid including reactive extraction, crystallisation, acidification, electrodialysis, precipitation, ion-exchange chromatography, and pressure-driven filtration (Cheng et al., 2012). Typically, the downstream recovery process involves multiple separation and purification steps. Membrane based technologies, however, provide an alternative in replacing the complicated recovery steps (Sikder et al., 2012). The recoveries of carboxylic acids by nanofiltration (NF) have been reported in a number of literatures. Ecker et al. (2012) employed NF for the separation of lactic acid and amino acid. It was reported that a reduced retention of lactic acid (from 67 % to 42 %) was observed at lower

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pH value, thus, increasing the separation and recovery of lactic acid. Further purification steps are required to treat the remaining amino acid in the permeate, and vice versa.

Table 1: A general comparison between fermentative and chemical production routes for the production of succinic acid (Cukalovic and Stevens, 2008).

	Chemical production route	Fermentative production route
Origin	Non-renewable feedstocks – petrochemicals	Renewable biomass feedstock – carbohydrates
Cost	Generally cheaper than the renewable sources	Downstream recovery processes accounts for more than 60% of the total production cost
Routes	Developed routes, established technologies	Routes under constant improvement, young technologies
Yields	Generally high	Accompanied by variety of byproducts, dilute broth solution, long reaction times
Disadvantages	High energy consumption (pressure and temperature), catalysts disposal issues	Sensitivity of microorganisms, nutrient requirements, complicated and expensive product recovery, large amounts of waste

Similar interest has been shown by Sikder et al. (2012) for the purification of lactic acid from fermentation broth. They found out that NF3 composite polyamide membrane could retain 94 % unconverted sugar while allowing 32 % lactic acid to permeate. Choi et al. (2008) explored the potential application of NF for the removal of organic acids at varying pH, pressures and concentrations. As anticipated, the rejection of organic acids was significantly influenced by the variation of pH. The dissociation of organic acids above their pKa values led to higher NF membrane rejection. Among the selected organic acids, succinic acid and citric acid had shown high rejection exceeding 90 % irrespective of the operating pressure and feed concentration. Since NF membrane is targeted to remove larger ions, succinic acid and citric acid which have molecular weight comparable to or larger than the molecular weight cut off (MWCO) of the employed NF membrane, were rejected. Kang and Chang (2005) investigated the recovery of succinate from simulated fermentation broth using five NF composite membranes. They reported that the succinate rejection in the multiple-salt solutions was much higher than that in its single salt solution. Among the tested membranes, NF45 and ESNA1 membranes demonstrated lower rejection to monovalent anion and higher rejection to divalent anion. Consequently, monovalent acid salts were separated from the multiple-salt solutions containing succinate.

At present, there is still lack of studies on the recovery of bio-based succinic acid via NF process. Generally, pH neutralisation is performed during fermentation and hence the organic acids are found in salt form. The objective of this work was to study the feasibility of using NF for the separation of succinate from byproduct salts. Two common types of organic acid byproducts are acetic acid and formic acid. The salt rejections were investigated in synthetic feed solutions containing ternary organic acid salts under varying feed ratios. The performances of three types of NF membranes were also compared and discussed.

2. Materials and methods

2.1 Chemicals and membranes

Succinic acid was purchased from Acros Organics (New Jersey, USA). Acetic acid (glacial) and formic acid (98 – 100 % purity) were supplied by R&M Chemicals (Malaysia) and Merck (Germany). Synthetic feed solutions were prepared by dissolving the organic acids in ultrapure (UP) water (arium® pro ultrapure water systems, Sartorius, Germany). The pH of the feed solution was adjusted by the addition of sodium hydroxide (R&M Chemicals) until pH 6.9 resembling the fermentation broth pH.

Three commercial NF flat sheet membranes, namely TS80, NF270, and NFW were used in this study. The area of the membrane used was 14.6 cm^2. The membranes were soaked in UP water overnight prior to each run. Detailed properties of the membranes are presented in Table 2.

Table 2: Properties of the NF membranes.

Membrane	Manufacturer	Material	MWCO (Da)
TS80	TriSep	Polyamide	~150
NF270	DOW FILMTEC	Polyamide	~200 - 400
NFW	Synder Filtration	Polyamide-TFC	~300 - 500

2.2 NF experimental set-up

The NF experimental setup (Figure 1) consisted of a dead-end filtration cell (SterlitechTM HP4750 Stirred Cell), nitrogen gas tank, permeate collector, and a weighing balance (GF-6100, A&D Company Limited, Japan). NF membrane was placed on the bottom of the stirred cell and supported by a circular plate. The stirred cell was filled with the feed solution and stirred with a removable PTFE stir bar rotating at 400 rpm. Prior to filtration, the membranes were compacted at a pressure of 3,300 kPa. Pure water permeability and organic acid salts removal were then performed at pressure ranging from 1,500 to 3,000 kPa. The permeate was collected and measured using a weighing balance for determining the flux.

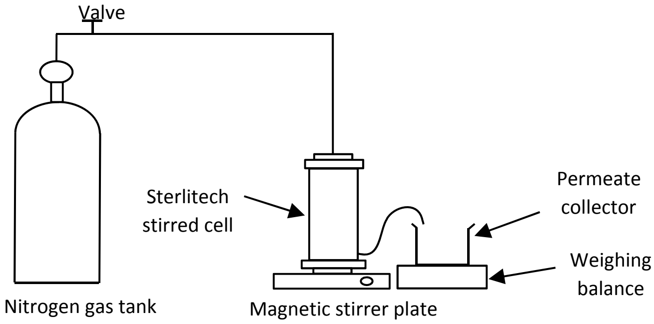

Figure 1: Schematic diagram of the dead-end NF system.

2.3 Measurements and analysis

The concentrations of organic acid salts were analysed by Thermo Scientific HPLC system (Dionex UltiMate 3000, Thermo Scientific, USA) equipped with a Refractive Index Detector (RefractoMax521). The operation and processing of the HPLC system was performed by Chromeleon Console software. Samples were analysed using 0.005 N H_2SO_4 mobile phase at a flow rate of 0.6 mL/min. Rezex ROA column (300 mm × 7.8 mm) was operated at 60 °C. The injection volume of each sample was 20 µL.
The observed rejection of solute is determined using Eq(1) (Li et al., 2003).

$$R\ (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100\ \% \quad (1)$$

where C_f is the solute concentration of the feed and C_p is the solute concentration of the permeate.

3. Results and discussion

3.1 Permeation fluxes

Figure 2 illustrates the permeate flux profiles of multi-salt solution containing 22.4 g/L succinate, 3.6 g/L acetate, and 3.4 g/L formate. As observed, the highest performing membrane was NF270 with permeate flux as high as 45.0 L/m^2h followed by the NFW membrane. By contrast, TS80 membrane had shown lower permeation fluxes due to the fact that it has a lower MWCO. The permeate collections for all three membranes were terminated at different operating time since longer duration was required for lower flux membrane. Membrane permeation flux is an important factor in selecting an appropriate NF membrane. The permeation flux performance was in consistent with the MWCO of the membranes as depicted in Table 2.

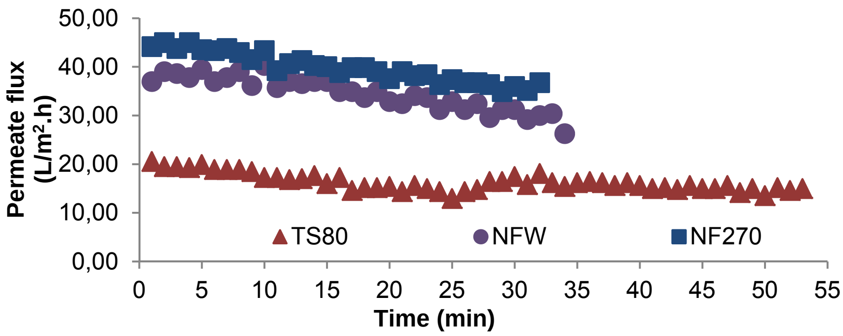

Figure 2: Permeate flux profiles as a function of time. Experimental conditions: pH 6.9; P = 3,000 kPa; T = 25 °C.

3.2 Rejection of organic acid salt in multi-salt solution

In this section, the rejection tests of organic acid salt at 5 selected feed concentration ratios (succinate:acetate:formate) were investigated (Figure 3). The initial feed concentration of succinate was ranged from 21.3 g/L to 22.4 g/L after the addition of sodium hydroxide. According to Figure 3, the variations of feed ratio seem to have little influence on the rejection of succinate ion. Of all the membranes, TS80 featured high succinate rejections exceeding 94 % in all the selected feed ratios. This can be explained by the molecular weight (MW) of succinic acid (118.09 Da), which is closer to the MWCO of the membrane. In the case of NF270 and NFW membranes, the MW of succinic acid is much smaller than the MWCO of these membranes, hence, the rejection of succinate cannot be explained by size exclusion phenomenon. It was found that succinate rejections as high as 93.4 % and 91.7 % were obtained for NF270 and NFW membranes (Table 3). The high rejections were mainly governed by Donnan effect.

The ternary-salt feed solution contained both divalent anion (succinate) and monovalent anions (acetate, formate). In all cases, the rejection of succinate was much higher than the acetate and formate rejections. It is interesting to note that negative rejection values were observed for the monovalent formate anion (Figure 3). For all the tested membranes, the lowest formate rejections were observed at feed ratio 3:1:0.2 indicating greater removal of formate anion. The separation mechanism of multi-salt solution may be explained by Donnan exclusion (Pontalier et al., 1997). In nanofiltration of ionic solution, the electrostatic repulsion between the anion and negatively charged NF membrane surface is observed. Comparing to monovalent anions, the divalent succinate anion contributed to the stronger electrostatic repulsion phenomenon and as a consequence, monovalent anions were pushed toward the membrane surface for electroneutrality with the counter ion in the membrane phase (Kang and Chang, 2005). Monovalent anions such as acetate and formate could pass through the membrane more easily.

The three selected polyamide NF membranes had responded to the variation in feed ratio in a similar manner. Based on the degrees of rejection as presented in Table 3, NFW membrane had demonstrated a promising performance in removing monovalent acetate and formate anions while rejecting the divalent succinate permeation considerably. TS80 was not a suitable membrane candidate for the removal of acetate anion despite its high rejection performance on the divalent succinate. For all experiments, the salt rejection decreased in the following order: succinate > acetate > formate.

Table 3: Monovalent and divalent anions rejection degrees in NF

Membrane	Succinate		Acetate		Formate	
	Highest R (%)	Lowest R (%)	Highest R (%)	Lowest R (%)	Highest R (%)	Lowest R (%)
TS80	98.0	94.0	57.0	34.7	-7.0	-29.1
NF270	93.4	87.7	52.5	27.6	-13.2	-36.8
NFW	91.7	81.9	23.7	4.5	-17.2	-42.4

3.3 Implications for NF recovery process

The downstream recovery of succinic acid remains one of the critical challenges in fermentative production of bio-based succinic acid. Succinic acid and other carboxylic acids (acetic acid and formic acid) are found in the salt forms rather than the free acid forms as a result of pH control requirement during fermentation. The results presented in the study highlighted the potential of NF which applies two separation mechanisms, Donnan exclusion and size exclusion. Sieving properties of NF membrane is dependent on their MWCO (Morão et al., 2006). High succinate rejection was achievable via stronger electrostatic repulsion while monovalent acetate and formate anions which are relatively smaller in terms of molecular size, were separated. It must be noted that the conversion of succinate into acid form is required so as to obtain the high value succinic acid. Bipolar electrodialysis which uses a bipolar membrane to split water into H^+ and OH^-, can be employed on the succinate retentate stream for generating succinic acid (Bouchoux et al., 2006).

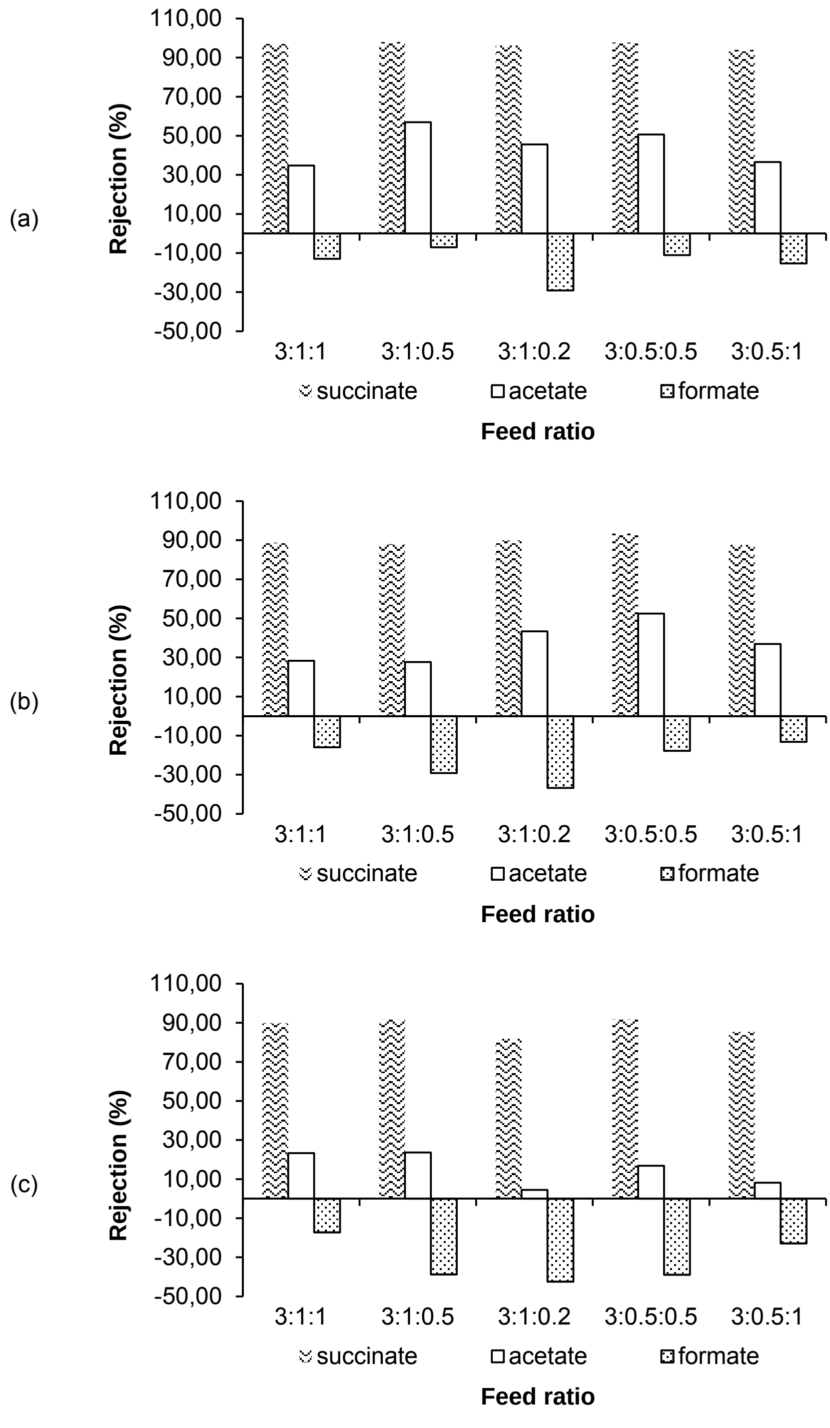

Figure 3: Effect of feed ratio on the rejection of organic acid salts using membrane (a) TS80, (b) NF270, and (c) NFW. Experimental conditions: pH 6.9; P = 3,000 kPa; T = 25 °C.

4. Conclusions

Separations of succinate from byproduct salts using three commercial nanofiltration membranes (TS80, NFW, and NF270) were investigated. The permeation fluxes study revealed that NF270 membrane was capable of achieving higher permeate flux as compared to the NFW and TS80 membranes. All selected membranes had responded to the variation of feed ratio in a similar manner. In all cases, negative rejection values were observed for the monovalent formate anion, which is noteworthy. Of all the tested membranes, NFW could effectively retain divalent succinate while removing acetate and formate to a high degree. It was evident from this study that the selective properties of nanofiltration membranes are influenced by the dissociation degree of organic acids. An integration of these results with real fermentation broth in future work would be desired.

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