Desalination of Spent Brine from Prune Pickling Using a Nanofiltration Membrane System

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Desalination of the spent brine from prune pickling was investigated with a spiral-wound nanofiltration (NF) membrane system. This NF membrane showed only limited linear relationships between transmembrane pressure and permeate flux within the range of pressure tested for various feed concentrations and temperatures. Membrane fouling began significantly for all test conditions after 3−4 h of running. Desalinations were tried with diafiltration for various conditions of feed streams. At a concentration factor (CF) of 2 for the twice-diluted spent brine, retentions of salt and organic acids in the nanofiltered retentate were 54.5 and 80.2%, respectively. These values were 38.9 and 72.1%, respectively at CF of 3 for the three-times-diluted spent brine. These salt-reduced prune spent brine samples were then diluted and formulated with sugars to a prune-flavored drink. The drink was well accepted by a small taste test panel.

Keywords: *Nanofiltration; desalination; diafiltration; prune pickling; prune spent brine*

INTRODUCTION

Prune (Japanese apricot, or *mei* in Chinese, *Prunus mume Sieb*. et Zucc.) is an important hillside produce in Taiwan with an annual production of 80 000−90 000 metric tons (Anonymous, 1994). Most of the prunes are harvested when still green and immature, and are further processed to make dried or semi-dried, salted prunes right after the pickling process. Some prunes are processed to make prune preserves (Lin and Chang, 1987; Wen, 1990). When prunes are pickled, normally 20% (w/w, based on the prune weight) salt and 0.6% (w/w) citric acid are added without water into the tanks to facilitate the pickling process. After a period of four to eight weeks, the brine forms as osmotic pressure draws moisture from the prunes (Wen, 1990). This brine contains a very high concentration of salt and is not reusable for prune pickling. The brine normally contains 25−32% soluble solids, ∼80% of which is salt, and the balance is fruit organic acids and volatile flavor compounds, mainly benzaldehyde.

The flavor and taste of the prune spent brines are pleasant and unique, if saltiness is neglected. However, applications of spent brines have been limited because of the high salt content. Only a small portion of the spent brines have been used in food processing. An important and less well known application has been to aid in the development of a desired pink color of pickled young ginger by adding prune spent brine into ginger pickling tanks (Huang, 1988). Another application has been the use of a small amount as an ingredient in salt-pickled carambola juice to enhance the flavor. Nonetheless, most of the spent brines are discharged directly into drains or sewage without any treatment and thus contribute to pollution.

The literature show that distillation, ion exchange, and electrodialysis have been employed to remove salt from sea water (Spiegler, 1977). Pan et al. (1988) applied electrodialysis, with a current density of 20 mA/cm^2 and a feed superficial velocity of 10 cm/min, to desalinate prune spent brine. This method resulted in 90% removal of salt. About 80% of the organic acids and 50% of the flavor compounds were retained in the treated brine. Sensory testing of the salt-reduced brine reflected an acceptable level of typical prune flavor (Pan et al., 1988).

Demineralization by membrane filtration has become feasible because of the rapid development in membrane technology. Erikson (1988) first introduced the nanofiltration membrane and its applications in municipal water softening. Guu and Zall (1992, 1993) applied nanofiltration to remove minerals and salt from cheese whey and soy sauce, respectively. Results showed that the yield of lactose crystals from the nanofiltered cheese whey were increased (Guu and Zall, 1992), and taste and flavor of the nanofiltered soy sauce were mostly retained after 50% of the salt was removed (Guu and Zall, 1993). Applications of nanofiltration in the food industry are still few, and efforts are needed in developing new processes to desalinate and recover valuables from the salty waste streams. In this study, spiral-wound nanofiltration membranes were used to study their performance in partial removal of salt from spent prune pickling brine. If successful, this membrane process could be used for eliminating the salty waste problem in the prune pickling industry. Reduction in salt content of the brine could increase its applications in food processing. The kinetics of salt removal by nanofiltration was investigated to better understand the performances of the membrane.

MATERIALS AND METHODS

Materials. Prune spent brine was obtained directly from the pickling tank at Wenshan Foods Company, Ltd. of Wanluan, Pingtung County, and was passed through a 400-mesh screen before membrane processing. The composition of the spent brine is shown in Table 1. To facilitate desalination, the prune spent brine was diluted with distilled water for diafiltration. Two dilutions, two- and threefold (2-D and 3-D, respectively), were used. In either case, the volume of the retentate after diafiltration was kept the same as that of the original undiluted spent brine.

Membrane System. The spiral-wound nanofiltration membrane (NF-40−2514-A; FilmTec Membranes Company, Minnetonka, MN) was equipped with a circulating positive displacement pump (CatPump, model 2810; CatPump Company, Minneapolis, MN) as shown in Figure 1. Batchwise operation was employed by circulating retentate until the designated

Table 1. Composition of the Original and the Nanofiltered Prune Spent Brines and Percent Retention of the Major Components

component	original spent brine	nanofiltered spent brine 2-D[a]	3-D[b]	retention (%) 2-D[a]	3-D[b]
total solids (%)	30.5	18.3	14.5	60.0	47.5
salt (%)	21.1	11.5	8.2	54.5	38.9
organic acids (%)	8.6	6.9	6.2	80.2	72.1
citric acid (%)	7.3	5.9	5.4	80.8	74.0
malic acid (%)	1.2	0.9	0.7	75.0	58.3
oxalic acid (%)	0.1	0.06	0.05	60.0	50.0
benzaldehyde (ppm)	21.3	11.4	8.5	48.8	39.9
pH	2.1	2.4	2.6	–	–

[a] Original spent brine was first diluted to twice of its volume, then nanofiltered back to its original volume. [b] Same treatment but with threefold dilution of the original brine.

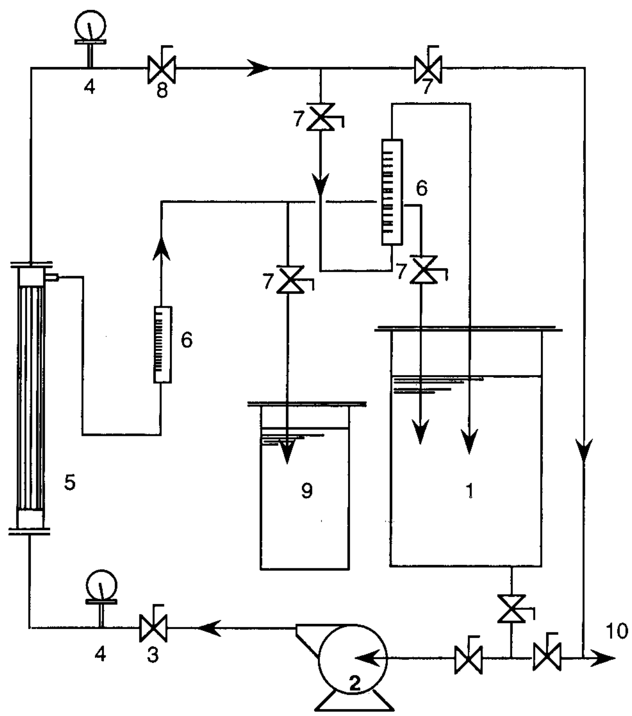

Figure 1. Schematic diagram of the nanofiltration desalination system.

concentration factor was reached. The temperature of the system was maintained by a thermostat. Inlet and outlet pressures were adjusted according to the experimental design. The back pressure of the permeate stream was maintained at 1 atm. Membrane performance was monitored by measuring its permeate flux (LMH: L/m^2/h) at certain time intervals.

Sample Analysis. Total solids and NaCl were determined by AOAC methods (AOAC, 1984). Fruit organic acids were analyzed by modifying the HPLC method of Gancedo and Luh (1986). The system consisted of a Hitachi intelligent pump (L-6200A), a UV–VIS detector (L-4200), a chromato-integrator (D-2500; Hitachi, Tokyo, Japan), and a sample injector (model 7251, Rheodyne, Cotati, CA). The separation column was a Lichrosorb RP-18 (E. Merck, Darmstadt, Germany) eluted with a potassium dihydrogen phosphate and phosphoric acid buffer at pH 2.4, a flow rate of 1.0 mL/min, and detection at 220 nm (Pan et al., 1988). Benzaldehyde was determined by a gas chromatographic (GC) method, which consisted of a HP-5980 system (Hewlett Packard, Palo Alto, CA) and a Chrompack fused silica capillary column (phase: CW-20 m; i.d.: 0.25 mm; length: 60 m). Temperature was ramped at 5 °C/min from 40 to 200 °C. Volatile compounds were extracted first from the samples by the Likens–Nickerson method (Yu et al., 1992). Each datum obtained was the average of at least three replicates.

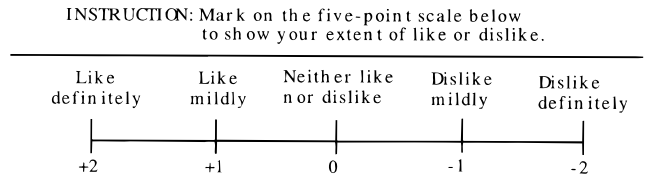

Figure 2. Score card for the consumer preference evaluation.

Preliminary Taste Tests. The recovered salt-reduced prune spent brine was mixed with sugar and water to formulate a prune-flavored beverage. Two local, similar, and popular juice drinks, salt-pickled carambola juice and *mei* juice from concentrate, were used as references (Ko and Lai, 1985; Wang et al., 1988; Wang and Fang, 1988; Tien and Fang, 1991; Wen and Fang, 1992). For preliminary evaluation purposes, a sensory panel consisting of six food science major students at NPPI was formed. A score card (Figure 2) with five degrees of acceptance levels was used for the consumer preference evaluation (Kramer and Twigg, 1974). Panelists were instructed to notice the specific prune flavor and sugar-acid ratio of prune juice before tests. The test samples were compared with the references that were assigned to be "like definitely".

RESULTS AND DISCUSSION

Performance of Nanofiltration Membranes. The effects of transmembrane pressure, temperature, and feed concentration on the permeate flux are shown in Figure 3. According to the data, the effects of transmembrane pressure did not consistently follow the Hagen–Poiseuille model, $J = \epsilon d_p^2 \Delta P_T / 32 \Delta x \eta$, where J is the permeate flux; ΔP_T is the transmembrane pressure; ϵ is the membrane porosity; d_p is the average pore diameter; Δx is the membrane thickness, and η is the viscosity of the solvent. This equation implies that permeate flux should vary directly with transmembrane pressure. However, a linear pressure-dependent relationship appeared only up to ~1500 kPa transmembrane pressure for original brine, up to ~2000 kPa for twice-diluted brine, and up to ~3000 kPa for three-times diluted brine. These results were satisfactory in explaining the ease of formation of a secondary membrane, or effect of concentration polarization for concentrated feed solutions (Cheryan, 1986). For predicting permeate flux under various transmembrane pressures, a power law model $J = A(\Delta P_T)^n$, where A and n were membrane coefficients, was employed in this study to acquire empirical equations for different feed conditions. Results of data fitting are tabulated in Table 2, which reveals a very high correlation coefficient (R^2) in each case.

Temperature definitely had a positive effect on the permeate flux according to data shown in Figure 3. However, differences in permeate flux between 20 and 40 °C within the pressure-dependent area were small. This study suggests that to conserve energy during feed preheating and to retain the specific flavor of prune spent brine, nanofiltration desalination should be conducted at normal ambient temperature (20 °C).

Concentration of the feed stream influenced permeate flux (Figure 3). The higher the feed concentration, the lower the permeate flux and the narrower the range of the linear pressure-dependent relationship. Dilution of

Table 2. Membrane Coefficients, *A* and *n* in the Empirical Equation $J = A(\Delta P_T)^n$, for Predicting Permeate Flux in the Nanofiltration Desalination Process, where *J* Is in LMH (Liters/m²/h) and ΔP_T Is in kPa

feed	temp, °C	*n*	*A*	R^{2c}
2-D[a] brine	20	0.0101	3.80×10^4	0.982
	40	0.0124	5.13×10^4	0.980
3-D[b] brine	20	0.0181	2.95×10^5	0.988
	40	0.0193	2.88×10^7	0.977
original brine	20	0.0051	7.8	0.994

[a] Original spent brine was first diluted to twice of its volume, then nanofiltered back to its original volume. [b] Same treatment but with threefold dilution of the original brine. [c] R^2 is the correlation coefficient.

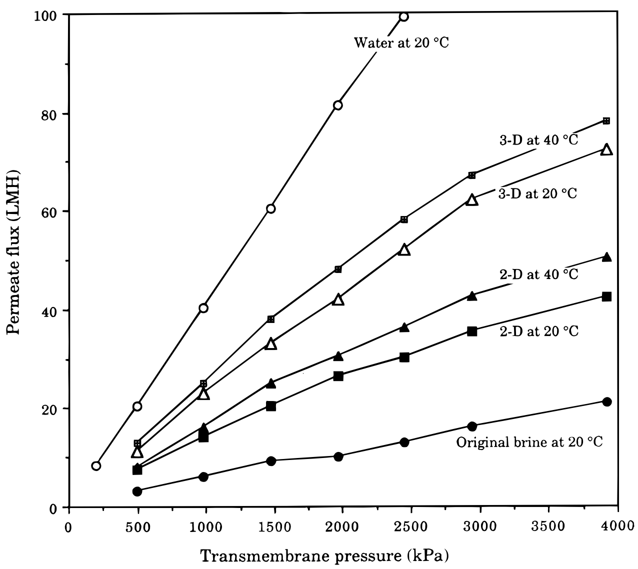

Figure 3. Effects of transmembrane pressure, temperature, and feed concentration on permeate flux (2-D, twofold dilution of the original brine; 3-D, threefold dilution).

the original spent brine before the nanofiltration process facilitated its desalination. Comparisons between the 2-D and 3-D dilutions were conducted to see which one was more efficient in retaining the specific flavor imparted by total organic acids and benzaldehyde if salt retention levels were acceptable in both cases. Results suggest that 2-D dilution was better in flavor retention, but producd less permeate for further treatment.

The decay of permeate flux during nanofiltration desalination at various conditions is shown in Figure 4. Membrane fouling was observed after 3–4 h. Higher temperature, lower pressure, and less concentrated feed stream prolonged the time for flux decline, though not substantially.

Retention of Major Components. Retention of each major component in the nanofiltered spent brine are tabulated in Table 1. The percentage retention of salt for 2-D and 3-D treatments were 54.5 and 38.9%, respectively; respective organic acid retentions were 80.2 and 72.1%. Citric acid was predominant. Retention of the different solutes differed between the two dilutions because of the effects of dilution and dialfiltration. In addition, the time to reach the same retentate volume differed between the two dilutions. However, when permeability of each species through the NF-40 membrane was calculated and plotted (Figure 5), there was not much difference between dilutions. This result was almost consistent with the technical data claimed by the membrane manufacturer (Maeda, 1993). Therefore, it is recommended that the 2-D dilution be

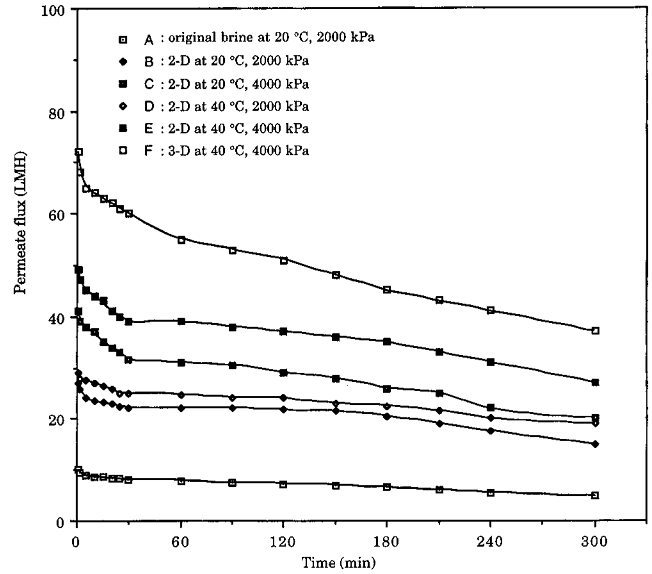

Figure 4. Decay of permeate flux under various conditions.

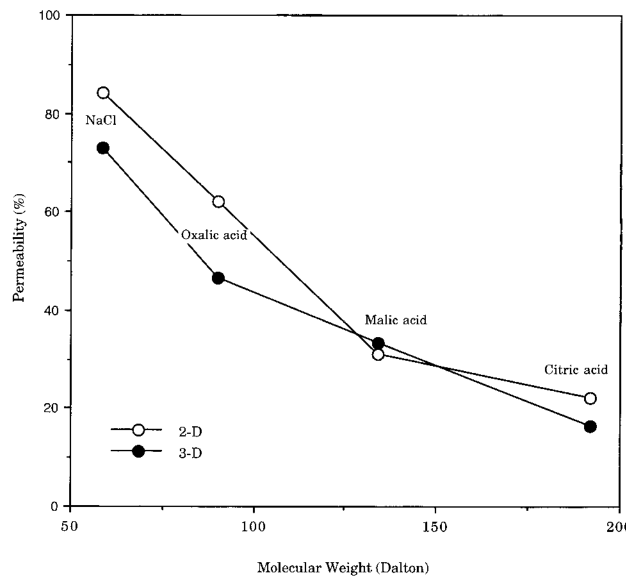

Figure 5. Permeability of each major component at different dilutions under transmembrane pressure of 2000 kPa and at 20 °C.

employed to maximize organic acid recovery, reduction in salt content, and energy conservation.

Nanofiltration Profiles of Major Components. Nanofiltration profiles of major components in the retentate were investigated by plotting concentrations of each major component versus the weight concentration ratio (WCR) during the nanofiltration desalination process, and are shown in Figure 6. Experimental data were also compared with the theoretical data calculated by the equation $C = C_0\ (WRC)^{\sigma}$ and the calculated rejection σ of each major component against nanofiltration membranes (C and C_0 are the concentration at a certain WCR and the initial concentration of the major component, respectively). Results suggest that the equation $C = C_0\ (WRC)^{\sigma}$ was sufficient to predict concentration of the retained species with few deviations.

Preliminary Taste Tests. The formulated prune juice drink was tested at least three times by each of the six panelists on different days, accumulating 20 replicates. The average score was ~1.73 based on the score card (Figure 2), indicating that the formulated

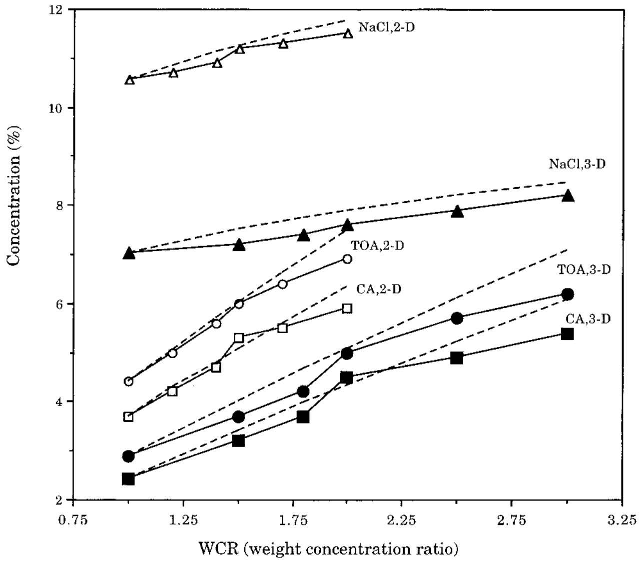

Figure 6. Nanofiltration profiles of the major retained components. TOA, total organic acids; CA, citric acid; NaCl, salt; —, experimental; - - -, theoretical. The transmembrane pressure was 2000 kPa, and the temperature was 20 °C.

prune juice drink was well accepted by the panel. This result also suggested that nanofiltration desalination might be useful for recovering valuable constituents from the salty waste stream to produce a byproduct that can be used as a food ingredient.

Conclusion. Diafiltration with nanofiltration membranes could be a feasible way to desalinate prune spent brine from the pickling industry. The salt-containing permeate from nanofiltration must be further desalinated before it can be recycled or discharged into the wastewater treatment plant. The recovered prune spent brine, which was much less salty but retained the typical prune flavor, could be used for a prune flavor enhanced drink. However, a lower operating temperature is suggested to prevent the volatile benzaldehyde from vaporizing off during the membrane process.

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