Recovery of Oligosaccharides from Steamed Soybean Waste Water in Tofu Processing by Reverse Osmosis and Nanofiltration Membranes

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The recovery of soybean oligosaccharides from the steamed soybean waste water in tofu (soybean protein curd) processing was carried out by using reverse osmosis and nanofiltration membranes. The feed solution was prepared by isoelectric and ultrafiltration treatments. Concentrations of the total oligosaccharides of 10% (w/v) and 22% (w/v) were obtained by using the RO and NF membranes in a batch operation. The chemical oxygen demand of the feed solution was simultaneously reduced from 8400–8700 ppm to 27–160 ppm. The permeate flux was mathematically analyzed by the osmotic pressure model with concentration polarization, the simulated results agreeing well with the experimental ones.

Key words: soybean oligosaccharides; reverse osmosis; nanofiltration; tofu processing; waste water

The reverse osmosis (RO) process is important technology with potential for saving energy and product quality by controlling the driving pressure without changing the phase. In the food industry, many investigations have been carried out on using RO to concentrate valuable components with high efficiency. The waste water from food processing contains various valuable components such as proteins and sugars, and their recovery is very important to fully utilize of valuable resources. The RO process may be adaptable for recovering the valuable components in waste water by controlling the permeation through the membrane. Nakao has recently summarized the membrane classification, in which nanofiltration (NF) uses a pressure between 1 and 4 MPa and rejects particles of molecular weight between 350 and 1000 Da. Although the distinction between RO and NF is not always clear, the NF process may also be useful like the RO process.

Soybeans are used for various raw materials of Japanese food such as miso (soybean paste), shoyu (soy sauce), natto (fermented soybeans), and tofu, which produce waste water during the manufacturing process. Watanabe et al. have successfully recovered valuable components from steamed soybean waste water in natto processing with an ultrafiltration (UF) membrane. Nakao et al. have shown that the protein and sugar from miso processing could be recovered by appropriate UF and RO/NF membranes. Kawashima has reported that protein, sugar, fat and ash could be obtained by concentrating the waste water from tofu processing by using UF and RO/NF membranes. The sugar from the soybean steaming or boiling process is generally named “soybean oligosaccharides,” which consist of stachyose, raffinose and sucrose. Soybean oligosaccharides are industrially produced by extraction and purification from soybean whey. When taken orally, soybean oligosaccharides have the function of promoting the growth of Bifidobacterium sp. in the large intestine, which leads to an improvement in intestinal microflora. The recovery of soybean oligosaccharides from steamed soybean waste water is of great value for the utilization of food materials. Few reports have been found concerning the recovery of soybean oligosaccharides by using RO/NF membranes.

In the present study, the recovery of soybean oligosaccharides from steamed soybean waste water in tofu processing was carried out by using UF and RO/NF membranes. The reduction of chemical oxygen demand (COD) was also examined. A mathematical analysis of the permeate flux was conducted by the osmotic pressure model, while taking account of the effect of concentration polarization, and the simulated results were compared with the experimental ones.

Materials and Methods

Apparatus: Figure 1 shows the schematic flow diagram of the experimental apparatus (RO UF test machine, RUW-5 Membrane Master, Nitto Denko Co., Ltd., Osaka) which was applied for both the RO/NF and UF experiments. A capillary-type UF membrane module (NTU-3250, Nitto Denko Co.) was used for preparing the feed solution, its character-

![Fig. 1. Schematic Flow Diagram of the Experimental Apparatus.](image-url)
istics being as follows: effective membrane area, 0.4 m²; molecular weight cut-off, 20,000; molecular weight permeate flux at 0.2 MPa transmembrane pressure, 1.94 × 10⁻⁷ m² s⁻¹ (made of polysulfone). A spiral-type RO membrane (NTR-7199, Nitto Denko Co.) with high rejection for sodium chloride (NaCl) and an NF membrane (NTR-7250, Nitto Denko Co.) with relatively low rejection for NaCl were used. The nominal rejection of each of these membranes for NaCl was 99.3% and 60%, respectively, and their characteristics are as follows: effective membrane area, 1.7 m²; equivalent hydraulic diameter, 1.4 × 10⁻⁷ m; effective membrane length, 0.80 m.

Materials. The steamed soybean waste water from oil processing was kindly supplied by Takamatsu Protein Cooperative Association (Kagawa Prefecture). A feed solution was prepared by adjusting its pH value to 4.0 ± 0.5 with a 1 N-HCl solution, this value being the isoelectric point of the soybean protein. After storing overnight at 4°C, the suspended solids (SS), high-molecular-weight proteins and polysaccharides were removed by the UF membrane. The resulting UF permeate was utilized for the RO/NF experiments.

Conditions and procedures. A batch experiment by the UF membrane was carried out for preparing the UF permeate under a transmembrane pressure of 0.2 MPA and a flow velocity of 1.0 m s⁻¹ at pH 6.8 and 50°C. To determine the best operating conditions for RO/NF processing, 30 liters of the UF permeate was used with recirculation, this being done by returning the permeate to the feed tank to keep the volume and the concentration of the feed solution constant. The recirculation experiment with the RO membrane was done in the range of transmembrane pressure of 1.0 MPa and flow velocity of 0.049 0.262 m s⁻¹ (this being calculated from the membrane characteristics, i.e., the equivalent hydraulic diameter of the flow channel and effective length given by Nitto Denko Co.), and the recirculation experiment with the NF membrane was done in the range of transmembrane pressure of 0.5 MPa and flow velocity of 0.078 0.195 m s⁻¹ at 25°C. The permeate flux and the observed rejection of oligosaccharides and NaCl under stable flux were measured in each experiment the permeate flux attained a constant value after 3 min operation from the start). Before and after each experiment, the pure water permeate flux was measured to check the condition of the membrane. The RO/NF membranes were cleaned by batch operation with water for 30 min.

Analytical. The concentration of saccharides was measured by high-performance liquid chromatography (HPLC) with a finely packed styrene divinylbenzene sulfonic acid column (Shodex Ionpack KS-801, Showa Denko Co., Ltd., Tokyo), using a differential refractometer. Standard saccharide reagents were purchased from Wako Pure Chemical Industries Ltd. (Osaka). Total nitrogen was determined by the Kjeldahl method, and the protein concentration was calculated to be 6.25 times as much as the total nitrogen. Total saccharide was measured by the phenol-sulfuric acid method, a sample solution (1.0 ml), 80% (w/w) phenol (25 μl) and sulfuric acid (2.5 ml) were mixed, and the absorbance at 490 nm was measured. Total solids and NaCl were determined by drying the method, and the dry residue, respectively. COD was measured according to the Japanese Industrial Standard (JIS) K 0120.14 The distributions of molecular weight (MW) of protein and saccharide in the feed and permeate in the UF process were measured by gel filtration chromatography with Toyopearl HW-55S (Tosoh Co., Ltd., Tokyo), in which a phosphate buffer (pH 7.2) with 0.1 M NaCl was used as the eluting solution. The eluate was fractionated into 2 ml portions at a flow rate of 50 ml h⁻¹. The fraction characteristics of the protein were determined using bovine serum albumin (MW = 67 kDa), ovalbumin (MW = 43 kDa), chymotrypsinogen (MW = 25 kDa), and ribonuclease (MW = 13.7 kDa). The concentration of the protein was measured by the modified Lowry method with a calibration curve for bovine serum albumin (Sigma Chemical Co., Ltd., U.S.A.).

Results and Discussion
Characteristics of the feed solution and UF permeate
Tables I and II show the chemical components of the steamed soybean waste water and UF permeate for the RO and NF processes. The oligosaccharide components (sucrose, raffinose, and stachyose) in the feed solution were

| Table I. Chemical Components of the Steamed Soybean Waste Water with the RO Process |
|----------------------------------------|----------------|----------------|----------------|----------------|
| Component | Feed solution | I.E.* | UF permeate | RO concentrate | RO permeate |
| COD (ppm) | 8,400 | 6,700 | 6,400 | 100,200 | 27 |
| Treatment amount (liter) | 250 | 200 | 141 | 8.87 | 132 |
| Total solid (g liter) | 14.5 | 13.9 | 13.3 | 96 | ND* |
| NaCl (g liter) | 2.0 | 2.7 | 2.7 | 40.9 | 3.3 |
| Total protein (g liter) | 3.1 | 2.5 | 1.3 | 19.4 | ND |
| Total saccharide (g liter) | 11.5 | 10.4 | 9.9 | 157 | ND |
| Fructose (g liter) | 0.045 | 0.045 | 0.041 | 0.62 | ND |
| Sucrose (g liter) | 3.5 | 3.4 | 3.3 | 54.9 | ND |
| Raffinose (g liter) | 0.53 | 0.53 | 0.52 | 8.3 | ND |
| Stachyose (g liter) | 2.4 | 2.3 | 2.2 | 35.3 | ND |

* Solution after isoelectric treatment.  
* Not determined.

| Table II. Chemical Components of the Steamed Soybean Waste Water with the NF Process |
|----------------------------------------|----------------|----------------|----------------|----------------|
| Component | Feed solution | I.E.* | UF permeate | NF concentrate | NF permeate |
| COD (ppm) | 8,700 | 7,100 | 6,300 | 189,600 | 160 |
| Treatment amount (liter) | 300 | 250 | 231 | 7.5 | 223 |
| Total solid (g liter) | 15.3 | 14.5 | 14.0 | 315 | 4.0 |
| NaCl (g liter) | 2.1 | 3.1 | 3.0 | 12.8 | 2.7 |
| Total protein (g liter) | 2.5 | 2.0 | 1.3 | 28.8 | ND* |
| Total saccharide (g liter) | 12.6 | 11.6 | 11.2 | 267 | ND |
| Fructose (g liter) | 0.056 | 0.050 | 0.044 | 1.3 | ND |
| Sucrose (g liter) | 4.0 | 3.9 | 3.9 | 121 | ND |
| Raffinose (g liter) | 0.57 | 0.55 | 0.54 | 16.9 | ND |
| Stachyose (g liter) | 2.6 | 2.6 | 2.5 | 77.8 | ND |

* Solution after isoelectric treatment.  
* Not determined.
scarcely rejected by the UF membrane. The concentration of total saccharide was reduced due to the rejection of polysaccharides as described later, the observed rejection \( R_{\text{obs}} \) being calculated to be 0.11-0.15 from Eq. (1).

\[
R_{\text{obs}} = 1 - C_p / C_b
\]  

(1)

where \( C_b \) and \( C_p \) are the concentrations of the bulk and permeate solution, respectively. The concentration of total protein was also reduced by the UF process due to the rejection of high-molecular-weight protein as described later. The \( R_{\text{obs}} \) value of total protein was calculated to be 0.35-0.48 from Eq. (1).

Figure 2 shows gel filtration chromatograms of the saccharides in the feed and UF permeate. The small peak near fraction number 6 indicates the presence of polysaccharides with a molecular weight of over 20 kDa, which caused the rejection of the total saccharides already mentioned. The large peaks near fraction numbers 70 and 80 are considered to correspond to the soybean oligosaccharides.

Figure 3 shows gel filtration chromatograms of the protein in the feed and UF permeate. The large peaks near fraction numbers 30 and 40 indicate the presence of protein. The former peak is considered to correspond to a high-molecular-weight of over 30 kDa which caused the rejection of total protein, and the latter to a low-molecular-weight of below 20 kDa.

**RO processing**

Figure 4 shows the permeate flux of the UF permeate solution and the \( R_{\text{obs}} \) values for the soybean oligosaccharides and NaCl against the transmembrane pressure, while Fig. 5 shows these values against the flow velocity in the RO process. The permeate flux increased linearly with increasing transmembrane pressure, while it slightly increased with increasing flow velocity. The \( R_{\text{obs}} \) values of oligosaccharides and NaCl in Figs. 4 and 5 were calculated to be approximately 1.0 and 0.995, respectively. This implies that the oligosaccharides and NaCl in the UF permeate can be almost completely recovered by the RO membrane. A batch experiment with the RO membrane, therefore, was carried out under conditions of a 5.0 MPa transmembrane pressure and 0.117 m s\(^{-1}\) flow velocity to obtain a high permeate flux.

Figure 6 shows the permeate flux of the UF permeate, and the rejection and concentration of fructose, sucrose, raffinose, stachyose, and NaCl against the concentration factor (CF) in the RO process. The CF value is the volume ratio of the feed solution to the concentrated one in the
batch RO operation. The permeate flux decreased rapidly with increasing CF value and reached 6% of its initial value at CF of 15.9. The $R_{obs}$ value for the oligosaccharides was calculated to be approximately 1.0, and that of NaCl varied from 0.967 to 0.995. The concentration of the oligosaccharides increased linearly with increasing CF value, the final CF value reaching about 16 times as much as the initial one. The obtained concentration of the soybean oligosaccharides was about 10% (w/v), which consisted of 5.49% sucrose, 0.83% raffinose, and 3.53% stachyose.

As shown in Table 1, a mean COD value of 27 ppm was obtained in the RO permeate. A COD value of 160 ppm is the maximum permissible for discharging to the environment according to the Japanese law for environmental pollution. The COD value reached about 15 times as much as the initial one, and the protein simultaneously became about the same as that of the UF permeate. The total amount of saccharide and COD value was found to be maintained during the RO process judging from the treatment volume and each concentration.

From these results, the recovery of the soybean oligosaccharides and the reduction of COD was found to be possible by using the UF and RO membranes. However, from a practical point of view, a higher oligosaccharide concentration would be desirable. A higher concentrated oligosaccharide solution may be obtainable when an NF membrane is used for the experiment, because of the lower osmotic pressure caused by the permeation of NaCl. In the subsequent experiment, the soybean oligosaccharides were recovered by using an NF membrane.

**Fig. 6.** Permeate Flux of a UF Permeate, and the Rejection and Concentration of Fructose, Sucrose, Raffinose, Stachyose, and NaCl against the Concentration Factor in the RO Process. Symbols are the same as those in Fig. 4. Operating conditions: pressure, 5.0 MPa; flow velocity, 0.117 m s$^{-1}$; pH 6.8; temperature, 25 C. (The solid line refers to the simulation.)

**Fig. 7.** Effect of Pressure on the Permeate Flux of a UF Permeate and the Rejection of Fructose, Sucrose, Raffinose, Stachyose, and NaCl in the NF Process. Symbols are the same as those in Fig. 4. Operating conditions: flow velocity, 0.117 m s$^{-1}$; pH 6.8; temperature, 25 C. (The solid line refers to the simulation.)

**Fig. 8.** Effect of Flow Velocity on the Permeate Flux of a UF Permeate and the Rejection of Fructose, Sucrose, Raffinose, Stachyose, and NaCl in the NF Process. Symbols are the same as those in Fig. 4. Operating conditions: pressure, 2.0 MPa; pH 6.8; temperature, 25 C. (The solid line refers to the simulation.)

**NF processing**

Figure 7 shows the permeate flux of the UF permeate solution and the $R_{obs}$ values for the soybean oligosaccharides and NaCl against the transmembrane pressure, while Fig. 8 shows these values against the flow velocity in the NF process. The permeate flux increased linearly with increasing transmembrane pressure, while it slightly increased with increasing flow velocity, similar to that in the RO process. An $R_{obs}$ value of about 1.0 was obtained for the oligosaccharides. $R_{obs}$ of 0.28–0.64 was obtained for NaCl under a transmembrane pressure of 0.5–3.0 MPa, which increased with increasing transmembrane pressure. $R_{obs}$ of 0.54–0.62 was also obtained for NaCl under a flow velocity of 0.078–0.195 m s$^{-1}$, which slightly increased with increasing flow velocity. A batch experiment with the NF membrane was, therefore, carried out under the conditions of 3.0 MPa transmembrane pressure and 0.117 m s$^{-1}$ flow...
velocity to obtain a high permeate flux.

Figure 9 shows the permeate flux of the UF permeate, and the rejection and concentration of fructose, sucrose, raffinose, stachyose, and NaCl against CF in the NF process. The permeate flux decreased rapidly with increasing CF value and reached 1.7% of its initial value at CF of 30.7. The $R_{obs}$ value for the oligosaccharides during NF processing was calculated to be about 1.0, and that of NaCl changed from 0.60 to 0.09 with increasing CF value. The concentration of the oligosaccharides increased linearly with increasing CF value, the final CF value being about 30. The obtained concentration of the soybean oligosaccharides was about 22% (w/v), consisting of 12.1% sucrose, 1.69% raffinose, and 7.78% stachyose.

As shown in Table II, a mean COD value of 160 ppm was obtained in the NF permeate, which is the same as the critical value for discharging to the environment according to the Japanese law for environmental pollution. The protein was found to be concentrated by about 22 times as much as the initial concentration, which is obviously lower than the CF value of 30.7. This is because part of the protein permeated through the membrane. The total amount of saccharide and COD was maintained during NF processing, judging from the treatment volume and each concentration. From these results, the UF permeate was found to be concentrated to about 30 times as much as the initial concentration by using the NF membrane.

Prediction of the permeate flux

In the present experiment, the time for the total treatment by RO/NF processing (120–150 min) was much higher than that for reaching a stable permeate flux (3–5 min). Thus, the system was assumed to operate in a stationary manner. The permeate flux ($J_p$) in the RO/NF process can be expressed by Eqs. (2)–(4) according to transport theory:\(^{10}\)

$$J_p = L_p(\Delta P - \sigma \cdot \Delta \pi) \quad (2)$$

$$R = 1 - C_p/C_m = \sigma(1 - F)/(1 - \sigma \cdot F) \quad (3)$$

$$F = \exp(-(1 - \sigma) \cdot J_p/P) \quad (4)$$

where $\sigma$ is the reflection coefficient, $\Delta \pi$ is the osmotic pressure difference across the membrane, $\Delta P$ is the transmembrane pressure, $R$ is the actual rejection, $C_p$ is the solute concentration in the permeate, $C_m$ is the solute concentration at the membrane surface, $F$ is a flow parameter defined in Eq. (3), and $P$ is the solute permeability. When the rejection is sufficiently high, $\sigma$ can be assumed to be unity, and $\Delta \pi$ can be determined by the concentration at the membrane surface as

$$\Delta \pi = \pi(C_m) - \pi(C_p) = \pi(C_m) \quad (5)$$

Equation (2) can then be rewritten as

$$J_p = L_p(\Delta P - \pi(C_m)) \quad (6)$$

The pure water permeability ($L_p$) can be obtained from the relationship between the pure water permeate flux ($J_p$) and the transmembrane pressure ($\Delta P$) as shown in Eq. (7).

$$J_p = L_p \cdot \Delta P \quad (7)$$

In the present study, the components in the UF permeate are assumed to have no fouling effect by adsorption to and/or deposition on the membrane, because the pure water permeability for RO/NF membranes was scarcely changed during the RO/NF treatments. To predict the permeate flux during the RO/NF treatments, the osmotic pressure model, which takes into account the effect of the concentration polarization, was adopted to the UF permeate from steamed soybean waste water which contained mainly NaCl, sucrose, and stachyose. According to the concentration polarization model, $C_m$ can be expressed by the following equation:\(^{10}\)

$$C_m - C_p = (C_b - C_p) \cdot \exp(J_p/k) \quad (8)$$

When the solute concentration in the permeate is zero ($C_p = 0$),

$$C_m = C_b \cdot \exp(J_p/k) \quad (9)$$

where $k$ is the mass transfer coefficient.

The $k$ value is generally represented as a function of the flow velocity, the equivalent hydraulic diameter of the flow channel, the diffusion coefficient of the solute, and the kinematic viscosity of the solution. When the solution in the membrane module flows in the laminar mode, the Lévêque equation, as shown by Eq. (10), can be used to calculate the $k$ value.\(^{21}\)

$$N_{kn} = 1.62(N_{kn} \cdot N_{kn} \cdot d_p/L)^{1.3} \quad (10)$$

When the permeate flux is very high ($J_p/k > 3$), the modified mass transfer correlation equation may be used to calculate the mass transfer coefficient, which has been proposed by Weiss et al.\(^{22}\) and Anazawa et al.\(^{32}\).

$$N_{kn} = 1.62(N_{kn}^{1.3} + 300 N_{kn}^{-0.1})(N_{kn} d_p/L)^{1.3} \quad (11)$$
where \( N_{Re} = \frac{d_w \cdot J_i \cdot v_w}{v_w} \) is the Reynolds number defined by the permeate flux \( (J_i) \), and Eq. (11) is equal to Eq. (10) at zero flux.

To calculate the \( k \) value by using Eqs. (10) or (11), the density, the viscosity of the solution and the diffusion coefficient of the solute have to be evaluated. These values at 25 C were obtained in the following way.

The density of an aqueous solution (\( \rho \)) can be expressed as a function of the solute concentration (\( C \)):

\[
\rho = 100 \cdot ((100 - C) \cdot \rho_w + \bar{\nu} C)
\]

(12)

where \( \rho_w \) and \( \bar{\nu} \) are the density of water \( (= 997 \text{ kg m}^{-3}) \) and the partial specific volume of the solute, respectively. The \( \bar{\nu} \) values for sucrose and NaCl are \( 0.626 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1} \) and \( 0.334 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1} \) respectively. The \( \bar{\nu} \) value for stachyose was obtained as \( 0.603 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1} \) by using a pycnometer in our experiment. This equation can be used in the concentration range of this experiment.

The viscosity of an aqueous solution (\( \mu \)) can be represented as a function of the solute concentration:

\[
\mu = \mu_w \exp (A \cdot C (100 - C))
\]

(13)

where \( \mu_w \) and \( A \) are the viscosity of water \( (= 8.94 \times 10^{-4} \text{ Pa s}) \) and the characteristic value for the solute, respectively. The \( A \) values for sucrose and NaCl are \( 2.6124^4 \) and \( 1.5225^5 \) respectively. The \( A \) value for stachyose was obtained as 3.14 by using an Ostwald viscometer in our experiment. This equation can be used in the concentration range of this experiment.

The diffusion coefficient of sucrose \( (D_s) \) can be expressed as a function of the solute concentration by Eq. (14) according to Nabatani et al.\(^{24}\):

\[
D_s = D_{0,s} \cdot \frac{\mu_w}{\mu_s (C_s)}
\]

(14)

where \( D_{0,s} \) is \( 5.24 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \) in a dilute solution. A similar equation to Eq. (14) can be derived to calculate the diffusion coefficients of stachyose \( (D_a) \) and NaCl \( (D_n) \) by a direct comparison with data from the literature: \(^{25}\)

\[
D_a = D_{0,a} \cdot \frac{\mu_w}{\mu_a (C_a)}
\]

\[
D_n = D_{0,n} \cdot \frac{\mu_w}{\mu_n (C_n)}
\]

(15)

(16)

where \( D_{0,a} \) and \( D_{0,n} \) are \( 4.08 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \) and \( 14.75 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \) in a dilute solution, respectively.

The osmotic pressure of a sucrose solution \( (\pi_s) \) can be expressed by Eq. (17) with the introduction of hydration number 4 according to Nabatani et al.\(^{24}\). The osmotic pressure of a stachyose solution \( (\pi_a) \) can be represented by Eq. (18), when the hydration number is assumed to be 8, because stachyose is regarded as being 2 times as large as sucrose. The osmotic pressure of NaCl \( (\pi_n) \) can be described by Eq. (19), when the osmotic coefficient is introduced.

\[
\pi_s (C_s) = \frac{RT}{V_w} \ln \left( \frac{100 - C_s}{100} \cdot \frac{M_s}{M} \right) - 4C_s \cdot M_s
\]

\[
\pi_a (C_a) = \frac{RT}{V_w} \ln \left( \frac{100 - C_a}{100} \cdot \frac{M_a}{M} \right) - 8C_s \cdot M_a
\]

\[
\pi_n (C_n) = \frac{RT}{V_w} \ln \left( \frac{100 - C_n}{100} \cdot \frac{M_n}{M} \right) + 2C_n \cdot M_a
\]

\[
\pi_s (C_s) = \frac{RT}{V_w} \ln \left( \frac{100 - C_s}{100} \cdot \frac{M_s}{M} \right) - 4C_s \cdot M_s
\]

\[
\pi_a (C_a) = \frac{RT}{V_w} \ln \left( \frac{100 - C_a}{100} \cdot \frac{M_a}{M} \right) - 8C_s \cdot M_a
\]

\[
\pi_n (C_n) = \frac{RT}{V_w} \ln \left( \frac{100 - C_n}{100} \cdot \frac{M_n}{M} \right) + 2C_n \cdot M_a
\]

In these three equations, \( R \) is the gas constant \( (= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \), \( T \) is the absolute temperature \( (K) \), \( M_s \) is the molar mass of water \( (= 18.016 \times 10^{-3} \text{ kg mol}^{-1}) \), \( V_w \) is the partial molar volume of water \( (= 18.07 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) \), and \( f_s \) is the osmotic coefficient of NaCl \( (= 0.9212^{29}) \).

The properties of a ternary solute solution containing sucrose, stachyose, and NaCl at 25 C were evaluated in the following way.

The density of a ternary solute solution \( (\rho_{mix}) \) can be expressed as

\[
\rho_{mix} = \frac{100}{(100 - C_s - C_a - C_n) \cdot \rho_w + \bar{\nu}_s C_s + \bar{\nu}_a C_a + \bar{\nu}_n C_n}
\]

(20)

The viscosity of a ternary solute solution \( (\mu_{mix}) \) can be represented as

\[
\mu_{mix} = \mu_w \exp \left[ \frac{2.614 C_s + 3.14 C_a + 1.52 C_n}{100 - C_s - C_a - C_n} \right]
\]

(21)

The diffusion coefficients of sucrose \( (D_{s, \text{in mix}}) \), stachyose \( (D_{a, \text{in mix}}) \), and NaCl \( (D_{n, \text{in mix}}) \) in a ternary solute solution can be described by

\[
D_{s, \text{in mix}} = D_{0,s} \cdot (\mu_w / \mu_{mix})^{0.45}
\]

(22)

\[
D_{a, \text{in mix}} = D_{0,a} \cdot (\mu_w / \mu_{mix})^{0.45}
\]

(23)

\[
D_{n, \text{in mix}} = D_{0,n} \cdot (\mu_w / \mu_{mix})^{0.45}
\]

(24)

The osmotic pressure of a ternary solute solution \( (\pi_{mix}) \) can be expressed by

\[
\pi_{mix} (C_s, C_a, C_n) = \frac{RT}{V_w} \ln \frac{100 - C_s - C_a - C_n}{M_w} - \frac{4C_s}{M_s} - \frac{8C_n}{M_n} + \frac{2f_s \cdot M_n}{M_s}
\]

(25)

The permeate flux in the RO process was then analyzed by the osmotic pressure model. The \( R_{obs} \) values for sucrose, stachyose, and NaCl were each assumed to be 1.0. Substituting the concentrations of sucrose, stachyose, and NaCl in a bulk solution \( (C_{b,s}, C_{b,a}, \text{ and } C_{b,n}) \) in Eqs. (20) and (21), the density and viscosity of a ternary solute solution were calculated, and the diffusion coefficient of each solute in the same solution was obtained by using Eqs. (22)-(24). The mass transfer coefficients of each solute in a ternary solute solution \( (k_{s, \text{in mix}}, k_{a, \text{in mix}}, \text{ and } k_{n, \text{in mix}}) \) were also calculated by substituting the above values, the flow velocities, the equivalent hydraulic diameter of the flow channel and the effective membrane length in Eq. (10). The permeate flux was then calculated by solving Eqs. (25)-(29) with a micro-computer.

\[
J_s = L_t (A P - \pi_{mix} (C_{s, \text{in}}, C_{a, \text{in}}, C_{n, \text{in}}))
\]

\[
C_{s, \text{in}} = C_{b,s} \times \exp (J_s / k_{s, \text{in mix}})
\]

\[
C_{a, \text{in}} = C_{b,a} \times \exp (J_s / k_{a, \text{in mix}})
\]

\[
C_{n, \text{in}} = C_{b,n} \times \exp (J_s / k_{n, \text{in mix}})
\]

The simulated results, as shown by the solid lines in Figs. 4, 5, and 6, agree well with the experimental ones. This means that the RO permeate flux of the UF permeate from steamed soybean waste water in tofu processing can be predicted by using the osmotic pressure model.
The permeate in the NF process was then analyzed by the osmotic pressure model and transport equations. The \( R_{\text{obs}} \) values for sucrose and stachyose were assumed to be 1.0, similar to those in the RO process. However, the \( R_{\text{obs}} \) value for NaCl changed considerably with transmembrane pressure as shown in Fig. 7, because NaCl partly passed through the NF membrane. Therefore, the reflection coefficient \( (\sigma_n) \) and solute permeability \( (P_n) \) for NaCl need to be taken into account for permeate calculations. To calculate the values for \( \sigma_n \) and \( P_n \), the actual rejection of NaCl \( (R_n) \) was evaluated from Eq. (3), where the NaCl concentration at the membrane surface \( (C_{m,n}) \) was derived from Eq. (8). Figure 10 shows the relationship between \( 1/J \) and \( R_n \). The value for \( \sigma_n \) was determined to be 0.94 from the intercept on the \( y \)-axis of a curve drawn by a curve-fitting method based on Eqs. (3) and (4),\(^{29,39}\) which means that the 94% of the osmotic pressure works effectively at the NF membrane surface. At the same time, \( P_n \) was calculated by substituting \( \sigma_n \) into Eq. (4), and the value was determined to be \( 5.32 \times 10^{-5} \text{ m s}^{-1} \). The physical properties of each solute in a ternary solute solution were obtained in a similar manner to that used in the RO process. By substituting those values, the flow velocities, the equivalent hydraulic diameters, the effective membrane length and \( J \), for the NF process into Eq. (11), the mass transfer coefficients for each solute in a ternary solute solution \( (k_{s,\text{inmix}}, k_{s,\text{inmix}}' \), and \( k_{n,\text{inmix}} \)) were also obtained. The permeate flux \( (J) \) and the observed rejection of NaCl \( (R_{\text{obs},n}) \) were calculated by solving Eqs. (17)-(19), (27), (28), and (30)-(33) by a microcomputer.

\[
J_s = L_p \Delta P - \pi(C_{m,s}) - \pi(C_{m,c}) - \sigma_n \times \pi(C_{m,n}) \quad (30)
\]

\[
R_n = \sigma_n(1 - F) / (1 - \sigma_n \times F) \quad (31)
\]

\[
F = \exp \left( -(1 - \sigma_n) \times J / P_n \right) \quad (32)
\]

\[
C_{m,n} = C_{p,n} = (C_{b,n} - C_{p,n}) \times \exp(J_s / k_{n,\text{inmix}}') \quad (33)
\]

The simulated results, as shown by the solid lines in Figs. 7, 8, and 9, agree well with the experimental ones. This means that the osmotic pressure model was also found to be applicable to predicting the permeate flux of a UF permeate and the observed rejection of NaCl in the NF experiment.

The chemical components of the steamed soybean waste water from tofu processing scarcely change, which hardly affects the operating conditions during the RO NF process. Therefore, the prediction of permeate flux by the method just described is considered to be useful. The soybean oligosaccharides solution obtained in this study was compared with a commercial one. The commercial soybean oligosaccharides solution contained 24% water, 18% stachyose, 6% raffinose, 34% sucrose, and 18% of other sugars,\(^{11}\) while the NF-concentrated solution contained 68.5% water, 7.78% stachyose, 1.69% raffinose, and 12.1% sucrose. The concentration ratios of stachyose, raffinose, and sucrose to the total saccharide in the commercial solution were given as 0.24, 0.08, and 0.45, respectively, while those in this experiment were 0.29, 0.06, and 0.45, which are similar to the commercial values. The NF-concentrated solution, therefore, may be utilized as a commercial product by further dehydration and purification. In addition, the NF process has the advantage of being able to discharge the permeate to the environment without the activated sludge treatment which is needed in many food processes. The NF membrane process was found to be useful in recovering the soybean oligosaccharides from steamed soybean waste water in tofu processing.

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**Nomenclature**

- \( A \) = constant
- \( C \) = concentration of solute
- \( D \) = diffusion coefficient
- \( d_h \) = equivalent hydraulic diameter
- \( f_t \) = flow parameter defined in Eq. (3)
- \( f_s \) = osmotic coefficient
- \( J_s \) = permeate flux in volume
- \( J_{ps} \) = pure water permeate flux
- \( K_m \) = mass transfer coefficient
- \( L \) = effective membrane length
- \( L_p \) = pure water permeability
- \( M \) = molar mass
- \( N_u \) = Reynolds number \( = \nu / d_h \)
- \( N_s\) = Schmidt number \( = \nu / D \)
- \( N_{bo} \) = Sherwood number \( = k \cdot d_h \)
- \( p \) = pressure
- \( R \) = actual reflection
- \( R_{n,\text{obs}} \) = observed rejection
- \( T \) = absolute temperature
- \( u \) = flow velocity
- \( v \) = partial molar volume
- \( \nu \) = partial specific volume
- \( \mu \) = viscosity
- \( \rho \) = density
- \( \sigma \) = reflection coefficient

**Subscripts**

- \( b \) = bulk
- \( \text{in mix} \) = in a ternary solute solution
- \( n \) = NaCl
- \( p \) = permeate
- \( s \) = sucrose
- \( st \) = stachyose
w = water
0 = dilute solution

Appendix

1. The viscosities of sucrose, stachyose, and NaCl were obtained from the following equations:

\[ \mu_s = \mu_s \exp(2.61 \times C_s (100 - C_s)) \]

\[ \mu_a = \mu_a \exp(3.14 \times C_a (100 - C_a)) \]

\[ \mu_n = \mu_n \exp(1.52 \times C_n (100 - C_n)) \]

In general, the viscosity of an aqueous solution (\(\mu_{aq}\)) can be represented by

\[ \mu_{aq} = \mu_s \exp(\sum (A_i \times C_i) (100 - \sum C_i)) \]

where \(A_i\) and \(C_i\) are the characteristic values for the solute and the solute concentration of each component in an aqueous solution. The viscosity of a ternary solution \(\mu_{aq}(s)\) containing sucrose, stachyose, and NaCl can then be calculated from Eq. (A1-5):

\[ \mu_{aq} = \mu_s \exp(2.61C_s + 3.14C_a + 1.52C_n (100 - C_s - C_a - C_n)) \]

2. The water activity \(a_w\) of a ternary solution composed of sucrose, stachyose, and NaCl can be represented by using the hydration numbers for sucrose (4) and stachyose (8), and the osmotic coefficient of NaCl \(f_s\) as follows:

\[ a_w = \frac{100 - C_a - C_n - C_s}{100} - \frac{4C_a}{M_a} - \frac{8C_n}{M_n} \]

\[ a_w = \frac{100 - C_a - C_n - C_s}{100} - \frac{8C_n}{M_n} + \frac{2f_s}{C_n} + \frac{2f_s}{C_n} \]

The osmotic pressure of a ternary solution \(\pi_{os}(C_s, C_a, C_n)\) can be calculated from the equation of state for water activity:

\[ \pi_{os}(C_s, C_a, C_n) = -\frac{RT}{V_a} \ln a_w \]

\[ -\frac{RT}{V_a} \ln \left( \frac{100 - C_a - C_n - C_s}{100} - \frac{8C_n}{M_n} \right) \]

\[ -\frac{RT}{V_a} \ln \left( \frac{100 - C_a - C_n - C_s}{100} - \frac{4C_a}{M_a} \right) \]

\[ -\frac{RT}{V_a} \ln \left( \frac{100 - C_a - C_n - C_s}{100} - \frac{8C_n}{M_n} + \frac{2f_s}{C_n} + \frac{2f_s}{C_n} \right) \]

References

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