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A pilot-plant test on desalination of soy sauce by nanofiltration

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1. Introduction

Soy sauce, a traditional Oriental food condiment, normally contains a high concentration of sodium chloride (NaCl, 18–20%, w/v). For the sake of health, part of NaCl needs to be removed from the raw soy sauce [1]. In previous studies [2–4], nanofiltration (NF) technology has been applied successfully to the desalination of soy sauce at laboratory-scale. With dead-end filtration at constant permeate flux, Luo et al. [4] found that, with NF270, the combination mode of dilution–concentration–dialfiltration could be the most suitable for desalination of soy sauce. However, when desalination of soy sauce by NF is applied in commercial production, it is likely to be operated in tangential flow at constant transmembrane pressure (TMP). Although the dead-end filtration at constant permeate flux has obvious advantages in the rapid evaluation of membranes performance and well understanding of separation mechanism [5,6], the results cannot be used directly in the design and operation of conventional tangential flow filtration process, the most commonly applied process in industry. Tansel et al. [7] found that ions rejections by NF in dead-end mode were always lower than that in cross flow mode because of the difference in shear force. And membrane fouling in constant TMP mode was also dissimilar to that in constant flux mode [8,9]. Thus many disparities will occur when membrane processes scale up from laboratory. Therefore, a pilot plant test on NF-filtration of soy sauce is required in order to industrialize this concept.

In industrial scale production, the cost resulted from membrane fouling and cleaning is significant in membrane process [10,11]. Since soy sauce is a concentrated mixture comprising protein, amino acid, peptide, saccharide, organic acid, NaCl, etc., a severe permeate flux decline during desalination process could be expected due to combined fouling [12], as found in membrane filtration of other complex effluents like fruit juice [13], dairy ultrafiltration (UF) permeate [14], and wastewater [15,16]. Li et al. [17] reported that concentration polarization and cake formation were the dominant fouling resistance for ceramic microfiltration of raw soy sauce. In NF of soy sauce, low molecular weight solutes such as amino acid and glucose could also block the membrane pores by adsorption, thus decreasing the membrane permeability. Although an alkali aqueous solution could effectively recover the flux in microfiltration of raw soy sauce [18], this cleaning procedure might not be efficient for cleaning the fouled NF membranes by soy sauce due to their different fouling mechanisms. Therefore, understanding the fouling tendency and finding an appropriate cleaning approach are essential to the application of low-salt soy sauce production by NF.

In this work, desalination of soy sauce by NF at pilot plant scale was investigated with spiral-wound membrane modules under constant TMP conditions. Based on our previous laboratory scale work [4], the objective of the present pilot scale study was to
develop an optimum operation mode for industrial production of low-salt soy sauce by NF, with focus on the effect of different operating parameters on permeate flux. The fouling tendency and cleaning method for desalination of soy sauce by NF were also examined. The outcome of the present work would serve as a valuable guide for process design and practical operation in subsequent industrial application.

2. Materials and methods

2.1. Soy sauce and chemicals

Soy sauce was directly taken from a local food plant in Foshan, Guangdong Province, China. Raw soy sauce was pretreated by sedimentation, centrifugation and ultrafiltration (UF) at industrial scale, and the soy sauce after UF was pumped into NF-system for further processing.

All chemicals used for cleaning and sterilizing were of food grade, provided by the local food plant. The proprietary liquid composite cleaning agent was composed of alkali, surfactant and enzyme, and 0.3% (w/v) concentration (pH ≈ 10) was used in the present work.

2.2. Equipment and membrane modules

A homemade NF pilot device was used in the experiments, equipped with a 100 L capacity feed tank, as shown in Fig. 1. Fig. 2 shows the schematic diagram of NF-system. Two multistage pumps (CRN3-36, Grundfos, Denmark) were furnished for feeding and cleaning, respectively. Pressure was measured by both digital and analogue manometers, and, as TMP reference value, the mean value between the inlet and outlet of membrane module was taken, and pressure drop never exceeded 0.9 bar. Experiments ran at a constant TMP of 24 bar except elsewhere stated. Operation temperature was controlled at 30 ± 1 °C by circulating water except for cleaning procedure. Crossflow rate and permeate flux were determined by rotameters.

As can be seen in Fig. 1, this pilot device can simultaneously run three NF spiral-wound modules with two UF tubular modules as pretreatment, but in the present study, only one of pressure vessels loaded with a NF module was used for each test. The NF membrane modules of NF270-4040 and Desal-5 DK-4040 were supplied by DOW-Filmtec and GE-Osmonics, respectively. They consisted of a spiral-wound aromatic polyamide membrane with a total effective area of 7.6 m². The molecular weight cut-off of the membranes was about 150 Da [19].

2.3. Experimental procedure

First, new membrane modules were rinsed by pure water for 1 h at a TMP of around 0.3 bar, and the permeate was discharged. In order to compare with the results of laboratory scale tests, diluted soy sauce (soy sauce:pure water = 1:1) was added into feed tank and then concentrated to its original volume. Subsequently, the desalted soy sauce was further concentrated to meet the Super Class quality standards defined in China National Standards GB18186-2000, GB2717-2003 [20] (first stage); meanwhile, NF primary permeate was further concentrated to yield light-color soy sauce, which could meet the Class II quality standards [20] (second

Fig. 1. Photograph of the pilot equipment.

Fig. 2. Schematic diagram of the NF system.
stage), as described by the schematic diagram in Fig. 3. The original feed and desalted products at different stages were collected for general analysis.

When membrane fouling did not increase any more with operating time (almost steady), that is, suppose the effect of fouling on membrane process with operating time was negligible, a series of experiments on operation modes was carried out. Maybe this procedure was not very strict, but in pilot-plant study, frequent membrane cleaning would consume a mass of feed and pure water, and waste much time. Thus, these experiments were designed to exclude the influence of membrane fouling, and under the same conditions of membrane (stable fouling), the results could be available for comparison. Besides, in diafiltration step, the constant volume diafiltration mode (CVD) was employed and pure water was used as the diluent, as described elsewhere [21].

To evaluate the fouling or cleaning effect of each test, pure water permeability ($L_p$) of membrane module was measured before and after each series of experiments. The data of membrane fouling and cleaning was recorded all along in the above tests, but it was not systematical. After the membrane module was fully cleaned with an optimum cleaning strategy, flux decline tendency in total recirculation experiments and batch operations were examined systematically. Cleaning procedure was designed as follows: firstly, NF-system was flushed by pure water with zero TMP until the rinse water was clear; secondly, membrane module was washed by water with TMP of 2–3 bar then $L_p$ was measured; thirdly, alkali aqueous or cleaning agent solution was used to flush membrane at 30–35°C; fourthly, NF-system was rinsed by water again with TMP of 2–3 bar until pH of the permeate was neutral; Finally, membrane modules were soaked in water for 1 h to eliminate the effect of swelling by cleaning [22] then $L_p$ was measured again.

### 2.4. Analytic methods

Total acid, amino nitrogen, NaCl, total sugar, total nitrogen and soluble solids in feed, retentate, and permeate were analyzed by Product Inspection Centre of Haday Flavoring and Food Co., Ltd, according to the National Standard of the People’s Republic of China GB18186-2000, GB2717-2003 [20]. Primarily taste test was performed by the specialists of the company to identify products flavor. Amino acids in soy sauce were examined by an Amino Acid High Speed Analyzer (835-50, Hitachi, Japan), with an ion-exchange column of 2.6 × 150 mm, and a flow rate of pump was 0.225 ml min⁻¹ and injection sample volume was 50 μL.

### 2.5. Calculation methods

The loss of each component is expressed using removal rate (%), which is defined as the mass ratio of a solute in the permeate to its initial mass in the feed:

\[
\text{Removal rate} \ (%) = \frac{C_f - C_p}{C_0} \times 100
\]

where $C_f$ and $C_0$ are the solutes concentration in permeate and feed, $V_p$ and $V_0$ are the volume of permeate and feed, respectively.

### 3. Results and discussion

#### 3.1. Separation performance at pilot-plant scale

**3.1.1. Membrane selection**

According to our previous study [4], NF270 module was chosen for pilot-plant study due to its high rejection of amino nitrogen as well as high flux. Table 1 shows the separation performance of spiral-wound membrane modules. As expected, for higher temperature (30°C), NF270 had lower rejection of amino nitrogen (59.47%) and higher flux (15.79 L m⁻² h⁻¹) compared with the results obtained in laboratory (66.33% and 6.64 L m⁻² h⁻¹ at 22°C), while Na⁺ and Cl⁻ ions could pass through the membrane freely as in laboratory. The slightly negative rejection of NaCl in Table 1 confirmed the results found in laboratory study [4], which was caused by Donnan effect, as the accumulation of amino acid ions (negatively charged) near the membrane surface would result in more Cl⁻ ions in the permeate side due to Gibbs–Donnan equilibrium, i.e. lower rejection of NaCl. Decreasing operation temperature could decrease the loss of nutritional components but it would increase the cost and decrease flux. Desal-5 DK was selected for the experiment because it showed higher rejection of salts than NF270 in previous report [23]. As shown in Table 1, Desal-5DK had the same NaCl removal rate (51%) and higher rejection of amino nitrogen while its flux was only one-ninth of that of NF270. This could be explained by the fact that, the pore size of Desal-5 DK was a little smaller than that of NF270 but the latter had a very high porosity [23]. Considering that NF membranes with high flux
were cost efficient when filtering the extremely large amounts of soy sauce in the food industry. NF270 was still thought to be the most suitable one. However, for countering the excessive loss of the nutritional components at higher temperature, low-salt soy sauce should be further concentrated to meet the Super Class quality standards [20]. In addition, because Desal-5 DK had higher amino nitrogen rejection and the organic contents in soy sauce permeate was much lower than those in soy sauce feed, Desal-5 DK could be suitable for concentrating the primary permeate to produce light-color soy sauce. Therefore, a two-stage NF process could be used for soy sauce processing: in the first stage of NF, low-salt soy sauce was obtained from the retentate by NF270, while in the second stage, light-color soy sauce could be produced by concentrating the primary permeate with Desal-5 DK (see Fig. 3).

3.1.2. Concentration of soy sauce permeate

As can be seen in Table 1, in soy sauce desalination, quite a lot of nutrient (e.g. amino acids) was lost along with NaCl in primary permeate. Under pilot-plant conditions examined, the primary permeate contained around 2.7 g L\(^{-1}\) amino nitrogen and 3.1 g L\(^{-1}\) total acid, being much more than that in laboratory tests. Desal-5 DK was used to concentrate the primary permeate from the first stage to produce light-color soy sauce. Besides, the secondary permeate could be reused as processing water in post-preparation of soy sauce, hence all the nutrients, NaCl and water could be utilized (see Fig. 3). Fig. 4 presents solutes concentration and flux profiles during concentration of soy sauce primary permeate. As shown in Fig. 4, amino nitrogen and total acid concentrations increased continuously with increasing VRR and permeate flux could be controlled at an acceptable level (average value ~4.8 L m\(^{-2}\) h\(^{-1}\)). When 125 L primary permeate was concentrated to 40 L (VRR = 3.125), the secondary retentate contained 5.7 g L\(^{-1}\) amino acid and 7.2 g L\(^{-1}\) total acid, which could meet the Class II quality standards [20]. As compared with NF270 used in previous study [4], Desal-5 DK had much higher recovery, indicating that Desal-5 DK was better for processing the NF primary permeate of soy sauce.

### Table 1

<table>
<thead>
<tr>
<th>Membranes</th>
<th>(R_{\text{num}}) (%)</th>
<th>Removal rate (%)</th>
<th>Average flux (L m(^{-2}) h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amino nitrogen</td>
<td>NaCl</td>
<td>Amino nitrogen</td>
</tr>
<tr>
<td>----------------</td>
<td>----------------</td>
<td>------------</td>
<td>---------------</td>
</tr>
<tr>
<td>NF270</td>
<td>59.47</td>
<td>-3.03</td>
<td>25.27</td>
</tr>
<tr>
<td>Desal-5 DK</td>
<td>67.52</td>
<td>-3.03</td>
<td>20.32</td>
</tr>
</tbody>
</table>

Diluted soy sauce (soy sauce:pure water = 1:1) was concentrated to its original volume; TMP: 24 bar; crossflow rate: 45 L min\(^{-1}\); temperature: 30 °C.

3.1.3. Product analysis

As shown in Fig. 5, the primary retentate (low-salt soy sauce) had the same appearance as feed, and the secondary retentate was of a light brown or yellowish brown color, which was so-called “light-color soy sauce”, while the secondary permeate was nearly achromatous, indicating that the loss of soy sauce chromacontrol could be negligible. The analytical results shown in Table 2 indicate that the secondary permeate contained very little organic substances, therefore this two-stage NF process had a high recovery of organic nutrients, and the secondary permeate could be used as membrane cleaning water or processing water. A general analysis for all products was performed to ensure that the key indexes of components in processed soy sauce met the quality standard. From Table 2, it can be found that the nutrient contents in the primary retentate was higher than that in soy sauce feed except amino nitrogen, which also met the Super Class quality standards (amino nitrogen \(\geq 8.0\) g L\(^{-1}\)). Moreover, NaCl content decreased from 204.0 to 93.0 g L\(^{-1}\), and the flavor of low-salt soy sauce was improved in terms of the evaluation made by the local soy sauce plant. However, the content of total nitrogen in the light-color soy sauce failed to meet the Class II quality standards (total nitrogen \(\geq 10.0\) g L\(^{-1}\)) and improvement should be made to enhance its quality and flavor.

In order to better understand the variation of nutrients in NF of soy sauce, different amino acids in soy sauce were analyzed qualitatively and quantitatively. As shown in Table 3, glutamic acid (Glu) and aspartic acid (Asp) had the least removal rate. The reason might be that, the isoelectric points (pl) of Glu, Asp and NF270 membrane were 3.22, 2.97 and 3.30, [24] respectively, and for soy sauce at pH = 5.2, Glu, Asp and membrane would be negatively charged and the electrostatic repulsion between the membrane and amino acids resulted in high rejections of Glu and Asp. As for lysine (Lys) and arginine (Arg), they were alkaline amino acids and positively charged at pH = 5.2, but unexpectedly, their removal rates were relatively low. This could be partially attributed to the

![Fig. 4. Solute concentrations and flux profiles during concentration of soy sauce primary permeate by Desal-5 DK-4040. Feed: primary permeate from NF270; TMP: 24 bar; crossflow rate: 35 L min\(^{-1}\); temperature: 30 °C.](image1)

![Fig. 5. Comparison of different products (products order from left to right: feed, primary retentate, primary permeate, secondary retentate, secondary permeate).](image2)
charge screening effect by high salt concentration in soy sauce, which weakened the electric attraction between alkaline amino acids and membrane. On the other hand, most of Lys and Arg molecules dissociated into positive ions at pH 5.2, inducing a thicker hydration layer around amino acid molecules because the dynamic hydration numbers correlated well with charge density, with higher charge density being associated with higher dynamic hydration number [25]. Therefore, the effective size of Lys and Arg could become bigger and consequently they would be well rejected by the membrane due to steric exclusion. Since the pI of other amino acids was around 5–6, these amino acids were slightly charged, which weakened the electric attraction between alkaline amino acids and membrane. On the other hand, most of Lys and Arg molecules dissociated into positive ions at pH 5.2, inducing a thicker hydration layer around amino acid molecules because the dynamic hydration numbers correlated well with charge density, with higher charge density being associated with higher dynamic hydration number [25]. Therefore, the effective size of Lys and Arg could become bigger and consequently they would be well rejected by the membrane due to steric exclusion.

### 3.2. Optimization of operation modes at constant TMP

When NF was used for desalination of industrial fluid, concentration mode and diafiltration mode could be well combined to receive high desalination efficiency [29–32]. According to the previous study [4], it was found that dilution was a necessary step in desalination of soy sauce due to its high osmotic pressure resulting from the high salt concentration. After 50 L soy sauce was diluted with different volume of water, three operation modes, including concentration followed by diafiltration, concentration alone, and diafiltration followed by concentration were carried out respectively, as described in Table 4. For the modes (a), (b), and (c), the diluted soy sauce obtained by addition of water (15, 25 and 35 L, respectively) was first concentrated to it original volume, and then diafiltration step was employed with water as diluent, and water consumption was 21.5, 14.0 and 8.0 L, respectively. Finally, the desalted soy sauce was concentrated to 35 L. For the mode (d), 50 L soy sauce was diluted to 100 L and then concentrated to 35 L in one-step. For the modes (e), (f) and (g), the diluted soy sauce obtained by addition of water (15, 25 and 35 L, respectively) was first diafiltered with water (21.5, 14.0 and 8.0 L, respectively), and then the desalted soy sauce was directly concentrated to 35 L. The volume of water consumption in Table 4 was pre-calculated by the mathematical model proposed in the previous work [4], supposing that the salt concentration in soy sauce decreased to 90 g L\(^{-1}\). Additionally, no matter which operation mode was used, the desalted soy sauce should be concentrated to 35 L at last to ensure its amino nitrogen content equal or greater than 8.0 g L\(^{-1}\). Table 5 shows the comparison of water consumption and processing time under different operation modes.

### Table 2
General components analysis for all products.\(^a\)

<table>
<thead>
<tr>
<th>Index</th>
<th>Feed (g L(^{-1}))</th>
<th>Primary retentate (g L(^{-1}))</th>
<th>Primary permeate (g L(^{-1}))</th>
<th>Secondary retentate (g L(^{-1}))</th>
<th>Secondary permeate (g L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total acid</td>
<td>16.6</td>
<td>17.3</td>
<td>3.1</td>
<td>7.2</td>
<td>1.1</td>
</tr>
<tr>
<td>Amino nitrogen</td>
<td>9.1</td>
<td>8.2</td>
<td>2.7</td>
<td>5.7</td>
<td>1.3</td>
</tr>
<tr>
<td>NaCl (g L(^{-1}))</td>
<td>204.0</td>
<td>93.0</td>
<td>105.0</td>
<td>108.0</td>
<td>103.0</td>
</tr>
<tr>
<td>Reductive sugar (g L(^{-1}))</td>
<td>52.0</td>
<td>38.0</td>
<td>10.9</td>
<td>29.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Total sugar (g L(^{-1}))</td>
<td>56.0</td>
<td>61.0</td>
<td>12.0</td>
<td>32.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Total nitrogen (g L(^{-1}))</td>
<td>16.1</td>
<td>16.3</td>
<td>3.7</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Soluble solids (g L(^{-1}))</td>
<td>186.0</td>
<td>191.0</td>
<td>42.0</td>
<td>104.0</td>
<td>12.0</td>
</tr>
<tr>
<td>Flavor</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| Description of operation modes.\(^a\)

<table>
<thead>
<tr>
<th>Operation mode</th>
<th>Water consumption (L)</th>
<th>Dilution</th>
<th>Diafiltration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilution-Concentration-Diafiltration</td>
<td>a</td>
<td>15.0</td>
<td>21.5</td>
</tr>
<tr>
<td>Dilution-Concentration-Diafiltration</td>
<td>b</td>
<td>25.0</td>
<td>14.0</td>
</tr>
<tr>
<td>Dilution-Concentration-Diafiltration</td>
<td>c</td>
<td>35.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Dilution-Diafiltration-Concentration</td>
<td>d</td>
<td>50.0</td>
<td>0</td>
</tr>
<tr>
<td>Dilution-Diafiltration-Concentration</td>
<td>e</td>
<td>15.0</td>
<td>28.0</td>
</tr>
<tr>
<td>Dilution-Diafiltration-Concentration</td>
<td>f</td>
<td>25.0</td>
<td>21.5</td>
</tr>
<tr>
<td>Dilution-Diafiltration-Concentration</td>
<td>g</td>
<td>35.0</td>
<td>14.0</td>
</tr>
</tbody>
</table>

* One hundred litres diluted soy sauce (soy sauce:pure water = 1:1) was concentrated to 35 L primary retentate; then 125 L primary permeate from two batches was concentrated to 40 L secondary retentate.
dilution–concentration–diafiltration mode (a) had the least water consumption but its processing time was the longest. Although water consumption in dilution–concentration mode (d) was the highest among all the operation modes examined, the processing time was the least. While in laboratory study under constant flux condition, the combination mode of dilution–concentration–diafiltration was found to be the most efficient one. The reason was that in constant flux mode, TMP was usually neglected when evaluating the desalination efficiency, and only water consumption and permeate flux governed the desalination efficiency. From Fig. 6 and Table 5, it can be seen that with increasing water consumption, permeate flux increased, and processing time decreased from the mode (a) to mode (c), but increased from the mode (e) to mode (g). Therefore, it could be concluded that, when dilution followed by concentration, more dilution water should be added to obtain higher flux, but when dilution followed by diafiltration, less dilution water should be added to increase salt removal for unit volume of diafiltration water and thus decrease total water consumption. Comparing the combination modes (c) and (e) with the single mode (d), the disparity of processing time between them was not statistically significant (less than 10%), and the combination modes might be attractive in terms of their less water consumption (more than 10%). However, the single mode (d) was much simpler in operation and preferred by the soy sauce manufacturer, and the permeate water could also be fully utilized in this process. Therefore, from practical application point of view, the dilution followed by concentration mode (d) was adopted.

### 3.3. Membrane fouling and cleaning

#### 3.3.1. Fouling tendency

Membrane fouling was a key factor affecting productivity and cost in membrane applications especially for the concentrated and complex feed, and thus, investigation of fouling tendency in soy sauce desalination was a very important aspect in this pilot-plant study. Total recirculation experiments were first carried out for 8 h for each run, in which both permeate and retentate were recycled back to the feed tank. The results are displayed in Figs. 7 and 8, showing that when permeate flux was high in initial stage for the completely cleaned membrane, flux decline was fast especially in the first 2 hours, and when permeate flux became relatively low after a relatively long time operation (membrane was moderately fouled), the flux was almost constant. The reason could be that in high flux region, concentration polarization would be much severe and some relatively large pores of membrane would be plugged by foulants at first [15]; while flux fell to a certain point, the permeability was almost constant.

![Fig. 6. Permeate flux profiles in different operation modes. TMP: 24 bar; crossflow rate: 45 L min⁻¹; temperature: 30 °C.](image)

![Fig. 7. Flux profile in total recirculation experiment at high flux stage. Membrane: completely cleaned NF270; feed: diluted soy sauce (soy sauce:pure water = 1:1); TMP: 24 bar; crossflow rate: 45 L min⁻¹; temperature: 30 °C.](image)

![Fig. 8. Flux profile in total recirculation experiment at relatively low flux stage. Membrane: moderately fouled NF270; feed: diluted soy sauce (soy sauce:pure water = 1:1); TMP: 24 bar; crossflow rate: 45 L min⁻¹; temperature: 30 °C.](image)
value, probably below the critical flux [33,34], membrane fouling could be stable and no longer aggravated. As can be seen in Fig. 8, although the permeate flux was more or less constant, the pure water permeability slightly declined. This could be resulted from foulant adsorption, which did not block the pores but might change the hydrophobic performance of membrane. Fig. 9 shows the batch operations of desalination of soy sauce (100 L diluted soy sauce was concentrated to 35 L) at relatively low flux on the same day. In these experiments, no membrane cleaning was applied after each run. The processing time in these batches increased slightly for the first two batches and then was almost the same for the later four batches, which confirmed that NF270 membrane had a stable performance for desalination of soy sauce.

Based on the data from several batch operations of desalination (including the data from Fig. 9), the decline tendency of membrane productivity in low-salt sauce production using NF270 is shown in Fig. 10. In these experiments, no membrane cleaning was applied after each run and the experiments were repeatedly performed at different time. As shown in Fig. 10, productivity went down rapidly in the first 4 days and then kept steady over the next few days, indicating that this system could be always operated at a high productivity but frequent cleaning would be required. Moreover, it was also observed that the loss of amino nitrogen decreased when the fouled membrane was used (data not shown). Similar results were also reported by Nghiem and Hawkes [35] and Yangali-Quintanilla et al. [36], suggesting that the fouled membrane could be used to decrease the loss of amino nitrogen and may be of practical significance in low-salt soy sauce production.

3.3.2. Cleaning procedure

A series of cleaning tests was investigated to obtain an optimum cleaning strategy. As shown in Table 6, membrane fouling by soy sauce could not be eliminated completely by 0.1% (w/v) NaOH solution, even soaking overnight, while 0.3% (w/v) composite cleaning agent could rapidly recover the water permeability due to the effects of surfactant and enzyme in the solution. To examine the effect of different cleaning methods and prolonged operation on the efficiency of low-salt soy sauce production, processing time required for concentrating 100 L diluted soy sauce (soy sauce:pure water = 1:1) to 35 L was used for comparison. The operating conditions were the same as those in Fig. 10. Fig. 11 shows the processing time of batch operations after different operation cleaning stages. When membrane fouling got steady, the processing time required was 108 min for each batch, and after soaking with 0.1% (w/v) NaOH over two nights separately, the processing time decreased to 68 min, and when rinsing with 0.3% (w/v) cleaning agent for a short time (40 min), the processing time decreased from 81 to 35 min, indicating that composite cleaning agent could

![Fig. 9. Batch operations of desalination of soy sauce at relatively low flux stage on the same day. One hundred litres diluted soy sauce {soy sauce:pure water = 1:1} was concentrated to 35 L; TMP: 24 bar; crossflow rate: 45 L min⁻¹; temperature: 30 °C.](image1)

![Fig. 10. Productivity decline with time (not the successive tests). One hundred litres diluted soy sauce {soy sauce:pure water = 1:1} was concentrated to 35 L; TMP: 24 bar; crossflow rate: 45 L min⁻¹; temperature: 30 °C.](image2)

![Fig. 11. Processing time for concentrating 100 L diluted soy sauce to 35 L after different operation. (1) After the membrane was fully fouled by soy sauce; (2) after soaking with 0.1% NaOH over night; (3) after concentration operation for 8 h followed by soaking with 0.1% NaOH over night; (4) after concentration operation for 17 h; (5) after concentration operation for 21 h; (6) after soaking with 0.1% NaOH over night; (7) after rinsing with 0.3% composite cleaning agent for 40 min.](image3)
effectively recover membrane performance but NaOH cleaning could not. However, in UF plant for soy sauce, NaOH cleaning was a routine method and was highly efficient. This diversity might be resulted from the difference fouling mechanism between UF and NF for soy sauce: for UF, foulants (e.g. protein) precipitating onto ultrafiltration membrane surface (cake formation) was the main reason for flux decline [17], but for NF, pore adsorption and blocking by low molecular weight solutes (e.g. amino acid, glucose) might be the dominating fouling cause [15,35]. Pore fouling was more adhesive and compact, and surfactant and enzyme were quite effective in reacting with organic foulants in the pores, while NaOH cleaning resulted in poor cleaning efficiency due to its limited reactivity with low molecular weight foulants [37]. Thus, this proprietary composite cleaning agent could substitute for alkali cleaning agent containing alkali, surfactant and enzyme could be utilized as processing water or membrane cleaning water so that this was an economical process. Systematic experiments showed that using spiral-wound membrane module, under constant TMP condition, dilution–concentration was thought to be the most efficient operation mode in practical application due to its simplicity in operation, though its water consumption was slightly higher than that in the dilution–concentration–diaphragm or dilution–diaphragm–concentration operation mode. Flux decline was severe in high flux stage and thus membrane productivity decreased rapidly in the first 4 days. However, a long-term stable operation could work under relatively low permeate flux without frequent membrane cleaning. Composite cleaning agent containing alkali, surfactant and enzyme could be used as an effective cleaning agent in NF process for soy sauce production. This NF-system could consistently produce high quality low-salt soy sauce with amino nitrogen > 8.0 g/L and NaCl < 100 g/L (primary retentate) and enhanced flavor, demonstrating that this two-stage NF process was very attractive for desalting soy sauce in industry.

4. Conclusions

Desalination of soy sauce by NF was carried out at pilot-plant scale in this study, NF270 was still thought to be most suitable for desalination of soy sauce because of its high permeate flux, and Desal-5 DK was appropriate to concentrate the primary permeate to produce light-color soy sauce. The secondary permeate could be utilized as processing water or membrane cleaning water so that this was an economical process. Systematic experiments showed that using spiral-wound membrane module, under constant TMP condition, dilution–concentration was thought to be the most efficient operation mode in practical application due to its simplicity in operation, though its water consumption was slightly higher than that in the dilution–concentration–diaphragm or dilution–diaphragm–concentration operation mode. Flux decline was severe in high flux stage and thus membrane productivity decreased rapidly in the first 4 days. However, a long-term stable operation could work under relatively low permeate flux without frequent membrane cleaning. Composite cleaning agent containing alkali, surfactant and enzyme could be used as an effective cleaning agent in NF process for soy sauce production. This NF-system could consistently produce high quality low-salt soy sauce with amino nitrogen > 8.0 g/L and NaCl < 100 g/L (primary retentate) and enhanced flavor, demonstrating that this two-stage NF process was very attractive for desalting soy sauce in industry.

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