Chapter 4

Membrane Application in Soy Sauce Processing

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4.1 INTRODUCTION

Soy sauce is a traditional condiment widely used in Chinese cuisine and in the cuisine of other oriental countries as it not only imparts a delicious flavor but also promotes digestion [1]. In China, the annual production of soy sauce is around 5 million tons, accounting for about 60% of the total annual production of around 8 million tons in the world. Applied for thousands of years, soy sauce fermentation is one of the oldest techniques in food industry. The natural brewed soy sauce is obtained in three distinct steps: koji-making, brine fermentation, and refining. After fermentation, the resulting broth contains large amounts of bacteria, enzyme, and undecomposed protein that need to be removed. A conventional refining process normally includes

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pasteurization at 70−85 °C for 30 min, and subsequent sedimentation or filter-aid filtration. However, the sediment formed in heat treatment is difficult to filter out using traditional methods. Moreover, due to the incomplete clarification, the remaining bacteria grow rapidly and secondary sedimentation usually takes place during the product shelf period, thus deteriorating the quality of soy sauce product. With the development of membrane technologies, cross-flow membrane filtration has become an attractive and economical alternative for fluid clarification/pasteurization/sterilization in the beverage, brewing, and dairy industries [2]. In the 1970s, membrane filtration as an alternative method was used for sterilization and clarification of raw soy sauce in Japan [3−9]. Microfiltration (MF) and ultrafiltration (UF) have been proved to be effective in refining soy sauce at high yield and ensuring quality products with a long shelf life [10]. Compared with conventional sedimentation and filter-aid filtration, membrane filtration can improve the recovery of soy sauce, eliminate the need for filter medium (thus eliminating additional solid waste), and require less downtime for cleaning. Since the 1990s, MF or UF has become a more attractive technology for sterilization and clarification of soy sauce in China and other Asian countries.

Traditionally, in order to avoid contamination by undesired microbes during soy sauce fermentation, brine fermentation is normally practiced, in which 18−20% NaCl is added. So the resulting broth contains a very high concentration of salt. However, according to recent medical studies, food with high sodium content has an adverse effect on health and high salt intake is linked to many diseases such as high blood pressure and kidney problems. Hence soy sauce with salt content not more than 130 g/L is currently preferred. Therefore, part of NaCl needs to be removed from the raw soy sauce to meet the growing demand for healthy foods. Moreover, for a good appearance of some dishes, light-colored soy sauce is preferred and the caramel coloring in soy sauce needs to be partly removed. The need for high-end products with low-salt content and light-colored soy sauce provides new opportunities for application of membrane technologies, such as reverse osmosis (RO) and nanofiltration (NF), to the production of these kinds of soy sauce [11−16].

As we know, membrane fouling remains the main obstacle to widespread applications of membrane separation. In soy sauce processing by membranes, membrane fouling can be very severe since the fermentation broth is a very complicated mixture, containing bacteria, bacteria debris, proteins, polysaccharides, amino acids, and inorganic salts; they all can be membrane foulants [17]. Therefore, fouling control and membrane regeneration or cleaning, which are the main factors determining the capital investment and operating cost, are critical to the practical use of membrane filtration in soy sauce processing.

This chapter deals with membrane application in soy sauce processing, with emphasis on the clarification and sterilization of soy sauce by MF and UF, and desalination of soy sauce by NF. Some important issues in soy sauce processing with membranes, such as membrane selection, optimization of process parameters, and membrane fouling and regeneration, are also included.

4.2 MICROFILTRATION AND ULTRAFILTRATION FOR STERILIZATION AND CLARIFICATION OF SOY SAUCE

Since the contents of amino nitrogen (AN), soluble solids excluding sodium chloride (SSESC), and viable count are three key parameters in determining the quality of soy sauce products, it is required to retain the AN and SSESC at a maximal level and to reduce the viable count as low as possible in soy sauce processing by membranes.

4.2.1 Membrane Selection

Both polymeric membranes and ceramic membranes can be used in soy sauce industry. The membranes of 0.2−0.5 μm pore size were chosen to filtrate raw soy sauce in most applications [7,10,18−20] because the size of bacteria in raw soy sauce was bigger than 0.5 μm. Table 4.1 summarizes the typical characteristics of different membranes used for the sterilization and clarification.

It is generally believed that ceramic membranes have an excellent tolerance for extreme operating conditions and higher permeate flux than polymeric membranes [25,26] while their cost could still be too high to be economical in practical applications. Tien and Chiang [10] reported the clarification of soy sauce by a 0.2-μm ceramic membrane and found that ceramic membrane filtration did not alter the general composition of soy sauce, but

TABLE 4.1 Characteristics of Membranes Used for Soy Sauce Refinement [18−24]

	Ceramic Membranes	Polymeric Membranes
Material	α-Al_2O_3, ZrO_2 [18]	Polyvinylidene fluoride (PVDF), regenerated cellulose (RC) [21], poly (phthalazinone ether sulfone ketone) (PPESK) [19], and polysulfone [23]
Thermal and chemical stability	High	Moderate
Permeate flux	~60 L/m^2 h [22,23]	~30 L/m^2 h [19,23]
Service life	4−5 years [22]	2−3 years [authors' work]
Cleaning	1.5% NaOH + 0.95% HNO_3, 40 °C [20]	0.0025% trypsinase + 0.3% NaOH, 40 °C [24]

significantly reduced turbidity and count of aerobic microorganisms in the product. In a laboratory-scale study [18], four ceramic tubular MF membranes with various nominal pore sizes and different materials were used to clarify raw soy sauce, and the α-Al_2O_3 membrane was found to be the suitable one, which gave the highest permeate flux and best permeate quality with more than 99% of bacteria removal (reduced to 30 cfu/mL from its initial 3200 cfu/mL). It was also found that the flux decline was much faster for membranes with large pore size due to more severe fouling, and the antifouling performance of α-Al_2O_3 ceramic membrane was better than that of the ZrO_2 membrane because the former had a higher charge at the membrane surface at the pH of raw soy sauce [18]. Wang et al. [22] studied clarification of soy sauce by ceramic UF membranes with 20-, 100-, and 200-kDa molecular weight cutoffs (MWCOs) and found that the membrane with 100-kDa MWCO was suitable for soy sauce filtration in terms of permeate flux and the quality of filtered soy sauce.

As compared with ceramic membrane, polymeric membranes are much cheaper and more widely used in practical applications. Tian et al. [19] investigated the removal of bacteria from soy sauce by a hollow fiber MF membrane made from polyphthalazinone ether sulfone ketone (PPESK). The pore size of the membrane was 0.2 μm. It was found that a complete removal of bacteria could be obtained with the membrane, and only a slight flux decline existed in the 30-h operation (i.e., the flux decreased to 24 L/m^2 h from the initial 27 L/m^2 h), suggesting the membrane had good antifouling performance. Liang et al. [23] examined the MF of soy sauce by polysulfone membranes with pore sizes of 0.1, 0.45, and 1.0 μm. The membrane with 0.1-μm pore size seemed to be suitable for soy sauce filtration in terms of its highest flux (41.77 L/m^2 h) and complete removal of microbes. Furukawa et al. [27] reported the application of cross-flow UF and MF in recovering refined soy sauce from soy sauce lees by polysulfone membranes. The membranes examined were 50- and 750-kDa UF membranes and 0.2-μm MF membrane. The experimental results showed that under the same operating conditions, with increasing pore size of the membrane, the initial permeate flux increased, but decreased quickly as filtration continued. After 3-h filtration, the highest permeate flux was observed for the 50-kDa UF membrane. However, the permeate quality of MF membrane filtration was found to be much better than that of UF [26]. Table 4.2 summarizes some typical results reported in literatures.

It should be pointed out that the data reported in most literatures were based on short-time experiments (normally 2 or 3 h) and might not be used directly for scaling-up. In particular, a significant discrepancy existed for the data of permeate flux even with the same membranes. This could be attributed to the different soy sauce and different experimental conditions adopted by different researchers. Although the initial permeate flux normally increases with increasing membrane pore size, the steady flux could be

TABLE 4.2 Some Typical Results Reported in Literatures

		AN (g/L)	SSESC (g/L)	Absorbance	Viable Count (cfu/mL)	Permeate Flux (L/m^2 h)
0.2 μm ceramic membrane [9]	Feed	6.6	169.2	0.656 (at 700 nm)	2950	
	Permeate	6.3	155.7	0.001 (at 700 nm)	<25	15
0.2 μm α-Al_2O_3 membrane [22]	Feed	8.70		0.742 (at 650 nm)	3200	
	Permeate	8.53		0.587 (at 650 nm)	30	12
1.2 μm ceramic membrane [27]	Feed	8.32	342	0.163 (at 530 nm)	2800	
	Permeate	8.14	336	0.124 (at 530 nm)	100	150
0.1 μm polysulfone membrane [27]	Feed	8.40	374	0.256 (at 530 nm)	1165	
	Permeate	8.42	372	0.164 (at 530 nm)	0	41.77

nearly the same for some membranes with different pore sizes [22,23,27]. In some cases, the steady maintained flux of a membrane with larger pore size could be lower than that of a membrane with smaller pore size, as demonstrated by Furukawa et al. [27] in filtration of soy sauce lees with MF and UF membranes and by Li et al. [18] in soy sauce filtration with 0.2-, 0.5-, and 0.8-μm MF membranes. It was also reported that the permeate flux of an UF membrane could be higher than that of a MF membrane in the long term when membrane filtration was used for the treatment of cell suspensions [26]. Moreover, some cell debris and macromolecules present in raw soy sauce such as proteins may not be retained by MF membrane, and these substances may lead to the secondary sedimentation in the refined soy sauce after a long time of storage. Therefore, in practical applications, UF could be more suitable for refining soy sauce and an experiment conducted over an extended period of time was required for screening suitable membranes. In 2006, pilot-scale experiments on UF of soy sauce were performed in our laboratory and a soy sauce plant in South China with a pilot scale membrane system, in which a spiral-wound membrane module with 5.0-m^2 polymeric membrane can be housed. The membranes tested were 50-, 100-, and 150-kDa MWCOs polysulfone and PVDF membranes. Table 4.3 presents some typical results obtained in soy sauce UF with different membranes. Although

TABLE 4.3 Some Typical Results in Soy Sauce Ultrafiltration with Different Membranes

Items	Raw Soy Sauce	Permeate			
		50 kDa PS Membrane	100 kDa PS Membrane	100 kDa PVDF Membrane	150 kDa PVDF Membrane
AN (g/L)	9.3	9.2	9.3	9.3	9.3
NaCl (g/L)	188	189	187	186	18.9
Total acidity (g/L)	19.1	19.0	18.9	19.2	19.0
Reducing sugar (g/L)	51.6	51.3	52.0	51.8	52.6
Absorbance (at 760 nm)	0.545	0.062	0.090	0.088	0.100
Sediment (yes or no)	Yes	No	No	No	No
SSESC (g/L)	236	218	235	236	237
Viable count (cfu/mL)	6300	0	0	0	0
Permeate flux (L/m^2 h)	—	8.3	11.5	12.4	15.1

there were no changes in the general compositions of soy sauce after filtration with the three membrane and complete removal of bacteria could be obtained for all the three membranes (see Table 4.3), there existed changes in flavor and taste of the soy sauce treated with the 50- and 100-kDa MWCOs polysulfone (PS) membranes and 100-kDa MWCO polyvinylidene fluoride (PVDF) membranes, and the highest flux was found for the 150-kDa MWCO PVDF membrane. When the 50-kDa MWCO PS membrane was used, much clearer soy sauce with lighter color was obtained, but it gave poor flavor and salty taste. After 3 months of trial, it was concluded that the 150-kDa MWCO PVDF membrane was the most suitable one for sterilization and clarification of soy sauce.

Since raw soy sauce contains various potential foulants, it is very important to choose the right membrane module and operational mode. The hollow fiber membrane module was widely used for refining soy sauce, and the outside-in mode was considered to be more suitable, though the inside-out mode was also adopted [19]. Tubular membranes were also intensively examined for soy sauce filtration; in this case, the inside-out mode was preferred [10,18,22]. To increase the recovery of soy sauce, the combination of different membrane modules was proposed [7], i.e., a flat sheet MF was used to refine soy sauce first and then a tubular UF membrane was employed to further recover soy sauce in the retentate obtained in MF. Furukawa et al. [28] used flat-sheet membrane (pore size, 0.2 μm) module to recover soy sauce products from the brewing soy sauce lees. Matsushitak et al. [29–31] adopted the agitated disk membrane module to clarify and recover soy sauce from its sediment, and the concentration ratio could be 1/20, much higher than that of conventional membrane modules with a much higher energy consumption [29].

4.2.2 Optimization of Process Parameters

In sterilization and clarification of soy sauce by MF or UF, the process efficiency and product quality are significantly affected by various process parameters, it is necessary to optimize these parameters. These include the property and composition of soy sauce, transmembrane pressure (TMP) or permeate flux, shear rate or cross-flow velocity, etc.

The efficiency of process was, as widely known, affected by feed composition. Li et al. [18] examined the effect of total solids concentration on permeate flux and concentration polarization in MF of soy sauce and found that increasing total solids concentration would enhance concentration polarization and decrease the flux. Matsushitak et al. [30] found a close correlation between the permeation flux and the total nitrogen (TN) concentration of the raw soy sauce for agitated disk membrane module, which could be used to predict the permeate flux from the TN concentration.

Generally, with the increase in TMP, permeate flux increases as long as the flux is below the limiting flux. An increase in flux could enhance the convective flow of colloid particles toward the membrane surface and consequently enhances concentration polarization and deposition of particles. In MF of proteins and cells, increasing TMP could result in a much higher fouling rate, and in some cases can actually reduce the flux [32]. Tan [33] showed that during the MF of soy sauce with 0.2 μm inorganic membranes, the initial flux decline became larger with an increase in TMP, and after a 30-min operation, the flux at 0.24 MPa was less than that at 0.22 MPa. Therefore, there is an optimum pressure at which the flux can be maximal, and this suitable TMP should be determined on the basis of the experimental results. Tian et al. [19] found a TMP at 0.07 MPa was optimal for soy sauce filtration using a hollow fiber MF membrane made from PPESK, while Yao et al. [23] found the suitable TMP was at 0.28 MPa when a ceramic tubular MF membrane was used for clarification of soy sauce. A TMP higher than the shredhold would not increase permeate flux, but would increase the deposition of particle, resulting in more pore blocking and compressing the cake, leading to a serious flux decline [18].

Increasing temperature normally leads to the increase in permeate flux [6,19,22,23]. However, with the increase in temperature solute solubility may increase, and precipitation may form when the temperature goes down. It was found that when the temperature was higher than 50 °C, the permeate soy sauce was to be cloudy after refrigeration [22,23]. In determining processing temperature for soy sauce filtration, in addition to permeate flux, energy consumption, heat resistance of the membrane, and product quality (e.g., possible decomposition of flavor molecules) should be taken into account.

Increasing the shear rate, e.g., the stirring speed for stirred cell and the cross-flow velocity (CFV) for cross-flow filtration, generally results in an enhancement of permeate flux and a reduction of fouling rate in both UF and MF of soy sauce [10,18,27,33]. Li et al. [18] investigated the effect of CFV on the overall filtration resistance and the concentration polarization layer resistance in cross-flow MF of soy sauce with a 0.2 μm α-Al_2O_3 membrane and found that both resistances decreased rapidly with an increase in CFV from 0.29 to 0.58 m/s and then decreased gradually with any further increase in CFV, indicating that increasing CFV would increase permeate flux and decrease concentration polarization. Furukawa et al. [27,34] examined the effect of CFV on permeate flux in MF and UF of soy sauce lees. The results showed that increasing CFV resulted in less rapid flux decline and a higher steady state flux. Similar results were also reported by Tan [33].

4.2.3 Industrial Application of Soy Sauce Ultrafiltration

China and Japan are two main soy sauce producing countries in the world. In China, commercial applications of membrane technologies for refining soy sauce were realized in the 1990s, whereas Japanese soy sauce manufacturers have employed cross-flow membrane filtration systems for soy sauce processing since the 1980s. Different membrane modules such as hollow fiber, tubular, spiral-wound, agitated disk, and plate-frame membrane modules have been used for sterilization and clarification of soy sauce. Unfortunately, no detailed information is available.

In 2007, a two-stage UF membrane system for refining soy sauce, designed by the authors, was built and put into operation in a soy sauce manufacturing plant in South China. In the membrane system, 12 spiral-wound UF elements, with total membrane area of 360 m^2, were employed and evenly distributed in 4 cylindrical membrane housings and a 150-kDa MWCO PVDF membrane was used. Prior to UF, raw soy sauce was prefiltered by a filter cloth (200 mesh). The prefiltered soy sauce was then subjected to a two-stage UF, each with two parallel membrane housings individually equipped with three spiral-wound UF elements. Figure 4.1 shows the picture of the membrane system.

Since its operation in 2007, the system has been working well, with an average permeate flux of around 14 L/m^2 h, the production capacity of refined soy sauce is around 5 m^3/h. The refined soy sauce is free from bacteria and has enriched flavor, and all the nutrient components in the product has remain unchanged after UF. Table 4.4 presents the comparison of the general composition of soy sauce before and after UF.

FIGURE 4.1 Picture of ultrafiltration membrane system for soy sauce processing.

TABLE 4.4 Comparison of the General Composition of Soy Sauce before and after UF

	AN (g/L)	NaCl (g/L)	Reducing Sugar (g/L)	SSESC (g/L)	Sediment	A_{760}[a]	Viable Count (cfu/mL)
Feed	8.8	188	200.3	185.0	Yes	0.355	5200
Permeate	8.9	189	201.8	179.5	No	0.034	0

[a]*Absorbance measured at 760 nm.*

4.3 REVERSE OSMOSIS AND NANOFILTRATION FOR DESALINATION AND DECOLORATION OF SOY SAUCE

A number of patents about RO and NF for desalination and decoloration of soy sauce were filed [11–16], while the research reports about these topics were very few [35–37]. With RO or NF membranes, salt and color can be partly removed from soy sauce and low-salt soy sauce with light color can be produced. Akiko et al. [11] filed a Japanese patent and proposed to produce soy sauce with light color and enriched flavor by subjecting soy sauce to permeating treatment with a low-pressure RO membrane. In another Japanese patent [15], a two-step NF process was employed to obtain light-colored, dense, and low-salt soy sauce. It involved processing with NF having 5−25% of salt rejection to obtain permeate liquid, and then concentrating the permeate liquid with NF having at least 60% salt rejection. In a Chinese patent [16], NF was used to produce low-salt and light-colored soy sauce. With an NF membrane having high amino acids rejection and around 50% rejection of NaCl, the low-salt soy sauce with around 8% NaCl was obtained by diafiltration or by concentrating a prediluted raw soy sauce. The light-colored soy sauce was produced by concentrating the permeate obtained in the first NF step with a NF membrane having high amino acid rejection and around 30% rejection of NaCl.

Recently, Luo et al. [36,37] developed a two-step NF process to produce low-salt soy sauce and light-colored soy sauce, respectively. In this process, the low-salt product was obtained by concentrating a prediluted raw soy sauce [36] or using a combination mode that concentrates the diluted soy sauce to its original volume, followed by diafiltration, while the light-colored product was obtained by concentrating the permeate produced in soy sauce desalination [37].

4.3.1 Performance of Different Membranes

A membrane with high rejection of organic solutes (e.g., amino acids, polysaccharides, etc.) and high flux but low rejection of monovalent ions is desirable for industrial application of soy sauce desalination. Luo et al. [36,37] examined the suitability of four commercial NF membranes, NF-, NF90, NF270, and Desal-5 DL for soy sauce desalination. NF90 was not suitable for desalination of soy sauce due to its high rejection of NaCl. For other NF membranes, the performance of desalination was almost the same, and the removal of AN and SSESC was in this order: NF-<NF270<Desal-5 DL [37]. Desal-5 DL was also excluded because of its high loss of AN and SSESC [36,37]. The loss of AN (18.57%) and SSESC (3.98%) by NF- was slightly lower than that by NF270, which were 18.81% and 4.87%, respectively. NF270 had an advantage of lower TMP at constant flux or higher flux at constant TMP when compared with NF- [37], it was then concluded that NF270 membrane was the most suitable one for this application in terms of its high nutritional component retention, high salt transmission, and relatively high permeate flux as compared with other commercially available NF polymeric membranes [37].

The permeate obtained in desalination of soy sauce was nearly colorless but had quite a lot of nutrient (e.g., amino acids), and it could be concentrated to produce light-colored soy sauce by NF. Again with NF270, a light-colored soy sauce with high quality was obtained [37]. Our recent results showed that Desal-5 DK (GE-Osmonics) could be more suitable for producing the light-colored soy sauce from the permeate due to its higher rejection of amino acids and relatively high NaCl transmission, though the permeate flux was lower than that of NF270.

4.3.2 Effect of Operating Conditions

Like MF and UF of soy sauce, desalination of soy sauce by NF is affected by a number of process parameters such as the property and composition of soy sauce, TMP or permeate flux, shear rate or crossflow velocity, etc.

Since high-quality soy sauce is normally produced by high-salt and diluted-state fermentation technology, the raw soy sauce contains high concentration of salt and other soluble solids. It is necessary to dilute the raw soy sauce when commercial NF membranes are used for soy sauce desalination [37]. In desalination of soy sauce with NF270, with increasing dilution factor (DF) salt removal and AN loss increased, while SSESC remains more or less constant [36]. Sensitivity study indicates that low DF favors soy sauce desalination with less water consumption, less processing time, and higher nutrient (e.g., AN) retention [37].

When desalination of soy sauce was performed at constant flux using concentration mode, with increasing permeate flux, TMP increased, the loss of SSESC and AN decreased, while salt removal was more or less constant [36]. Temperature can also affect desalination of soy sauce. It was found that with increasing temperature, the loss of SSESC and AN increased, the removal of NaCl slightly decreased, and the TMP also decreased [36]. This is because increasing temperature would decrease the viscosity and increase solute diffusivity, thus lessening concentration polarization. It was also found that increasing temperature would result in severer membrane fouling. This could be attributed to the denaturation of some biologically active substances present in soy sauce such as proteins and polypeptides [36].

Considering the high osmotic pressure and very low permeate flux applied in the undiluted soy sauce desalination, Luo et al. [37] examined the effect of different operation modes on the performance of soy sauce desalination. Four operation modes were examined including (1) diafiltration, (2) dilution followed by concentration, (3) dilution followed by concentration and then diafiltration, and (4) dilution followed by diafiltration and then concentration. The parameters for comparison included processing time, water consumption, AN loss, and average TMP when almost the same NaCl removal was obtained. The operation mode (4) that is, diafiltration was carried out after diluting raw soy sauce, which was followed by concentration to its original volume, was thought to be the most suitable for desalination of soy sauce by NF [37].

4.3.3 A Pilot-Plant Test

Recently, we performed a pilot-scale experiment on desalination of soy sauce at a soy sauce plant in South China. Figure 4.2 shows the pilot-plant membrane system used for the experiments. The membrane system could be equipped with three 4-inch spiral-wound membrane modules (4040), each having a membrane area of around 5.0 m^2. Based on previous bench experimental results, membrane modules NF270-4040 (DOW-Filmtec) and Desal-5 DK-4040 (GE-Osmonics) were tested. Table 4.5 presents some typical results obtained in desalination of soy sauce. Although higher rejection of AN was obtained for Desal-5 DK-4040, its permeate flux was only one-ninth of NF270-4040. Therefore, NF270-4040 was chosen for the pilot-scale experiments.

Our previous study [36,37] demonstrated that dilution was a necessary step in desalination of soy sauce due to its high osmotic pressure and the operation mode of dilution followed by concentration and diafiltration was preferential for desalination of soy sauce. Pilot-plant experimental results showed that the operation mode indeed gave higher recovery of AN and lower water consumption as compared with the operation mode of dilution-followed concentration. However, the latter was simple in operation and preferred by the soy sauce manufacturer. Therefore, from practical application point of view, the dilution followed by concentration mode was adopted. Soy sauce with around 200 g/L NaCl was tested for the experiments. The effects of operating parameters, including dilution ratio (volume ratio of water to raw soy sauce), TMP, CFV, and temperature, on AN recovery,

FIGURE 4.2 Picture of the nanofiltration equipment for pilot test.

TABLE 4.5 Separation Performance of NF270-4040 and Desal-5 DK-4040 for Soy Sauce

Membranes	R_{obs} (%)		Removal (%)			Average Flux (L/mh)
	Amino Nitrogen	NaCl	Amino Nitrogen	Total Acid	NaCl	
NF270	59.47	−3.03	25.27	18.51	51	15.79
Desal-5 DK	67.52	−3.03	20.32	12.96	51	1.75

Feed: diluted soy sauce (soy sauce: pure water = 1:1); TMP = 24 bar; CFD = 0.5 m/s; temperature = 30 °C.

TABLE 4.6 General Components Analysis for All Samples[a]

	Soy Sauce	Primary Retentate	Primary Permeate	Secondary Retentate	Secondary Permeate
Total acid (g/L)	16.6	17.3	3.1	7.2	1.1
AN (g/L)	9.1	8.2	2.7	5.7	1.3
SSESC (g/L)	186.0	191.0	42.0	104.0	12.0
NaCl (g/L)	204.0	93.0	105.0	108.0	103.0
Reducing sugar (g/L)	52.0	58.0	10.9	29.0	2.0
Total sugar (g/L)	56.0	61.0	12.0	32.0	2.0
Total nitrogen (g/L)	16.1	16.3	3.7	8.6	1.4
Flavor	Primary retentate > Feed > Secondary retentate				

[a]200 L diluted soy sauce (soy sauce: pure water = 1:1) was concentrated to 70 L (primary retentate), then 125 L primary permeate was concentrated to 40 L secondary retentate under the optimized operating conditions.

NaCl removal, and permeate flux were systematically examined. The most suitable operating conditions were obtained: dilution ratio 1, TMP 24 bar, CFV > 0.5 m/s, temperature 25−30 °C.

As can be seen in Table 4.5, in soy sauce desalination, quite a lot of nutrients (e.g., amino acids) were lost along with NaCl in permeate. Desal-5 DK was used to concentrate the permeate for producing light-colored soy sauce and secondary permeate was reused as processing water in postpreparation of soy sauce, hence all the nutrients, NaCl, and water could be utilized. Table 4.6 summarizes the general component analysis for all samples obtained in soy sauce processing. This NF system has been operated for 45 days with different kinds of soy sauce and has consistently produced high-quality low-salt soy sauce with AN $\geq$ 8.0 g/L and NaCl $\leq$ 100 g/L (primary retentate) with enhanced flavor, demonstrating that NF technology was very attractive for desalting soy sauce in industry.

4.4 MEMBRANE FOULING AND REGENERATION

A major limitation in applying MF and UF for soy sauce processing is the permeate flux decline due to the concentration polarization and membrane fouling (pore blocking and cake layer). A better understanding of the mechanisms of flux decline is critical for fouling control. Li et al. [18] studied the influence of membrane microstructure and operational conditions on fouling behavior of ceramic membranes during MF of raw soy sauce. Their results showed that total resistance (R_t) and concentration polarization resistance (R_{cp}) increased significantly with increase in nominal pore size while cake resistance (R_c) and internal fouling resistance (R_{if}) decreased slightly. It was found that the antifouling performance of α-Al_2O_3 ceramic membrane was better than that of ZrO_2 membrane because the former had more charge at the membrane surface at the pH of raw soy sauce. The fouling resistance of the ZrO_2 membrane was dominated by R_{cp}, while the fouling resistance of the α-Al_2O_3 membrane was dominated by R_{cp} and R_c, suggesting that effective control of concentration polarization could lessen membrane fouling. Furukawa et al. [34] investigated UF and MF of soy sauce lees with polysulfone membranes and concluded that the main cause of fouling in the filtration of soy sauce lees was cake layer formation. Since both R_{cp} and R_c could be significantly affected by system hydrodynamics, therefore, one of the main strategies for fouling control could be enhancing the turbulence in the membrane modules through operating condition control and membrane module design.

Fouled membranes need to be cleaned to restore their performances after the flux drops to some minimally acceptable levels. Cleaning can be accomplished by physically removing the foulants from the membranes (e.g., backflushing, mechanical scrubbing) or by using chemical cleaning agents (e.g., acids, alkalis, surfactants, and enzymes) to remove or decompose the foulants. The characterization and identification of foulants are very important in the selection of cleaning solution. Generally, cleaning solutions composed of mineral acids, sodium hexametaphosphate, polyacrylates, and EDTA are suitable for salt precipitates and mineral scalants, while caustics based on NaOH and/or NaClO are used for removing fats and proteins; and enzyme cleaners are used to remove protein and other types of biofoulants in specific instances [38]. Unfortunately, most fouling phenomena are poorly understood and poorly characterized. Zhao et al. [24] studied the foulants deposited on the surface of polysulfone membrane during UF of soy sauce with infrared spectroscopy (IR) and scanning electron microscope (SEM) and found that the main components of the foulants were protein, ash, cell debris, and other suspended solids.

Different cleaning methods were proposed and examined for MF and UF membranes used for soy sauce processing [19–22]. Tian et al. [19] examined hot water (100 °C) backflushing and caustic cleaning (NaOH solution at pH 9–10) for flux restoration of hollow fiber PPESK membranes fouled by soy sauce. Their results suggested that with the use of hot water backflushing, the membrane flux recovery could be more than 96%, while the use of caustic cleaning could completely restore the membrane flux under the experimental conditions tested. Li et al. [20] studied the regeneration of ceramic MF membranes fouled in clarification of raw soy sauce and found that the fouled ceramic membrane could be partially regenerated by water rinsing and satisfactorily regenerated using a four-step cleaning method, i.e. water rinsing for 30 min at 20 ± 3 °C firstly, next 1.5 wt% NaOH cleansing for 40 min at 40 ± 3 °C, then 0.15 mol/L HNO_3 cleansing for 40 min at 40 ± 3 °C, and finally water rinsing again until neutrality. Zhao et al. [24] investigated the regeneration of UF polysulfone membrane fouled by soy sauce using trypsin solution and sodium hydroxide solution and proposed a two-step cleaning protocol with the combined use of the two cleaners.

So far, there has been a little information available on fouling of NF membrane in soy sauce processing. In our laboratory-scale experiments and pilot-scale test on desalination of soy sauce by NF, it was found that the flux declined very fast in the first 2 h and then gradually afterwards. Cleaning was normally required after operation for around 10 h. In our pilot-scale experiments, experiments were performed to restore the flux of the fouled membrane by cleaning with acids, alkalis, and other chemicals. It was found that the flux of the fouled NF membranes by soy sauce could not be recovered completely by caustic cleaning with 0.1% (w/v) NaOH solution or by soaking overnight in the caustic solution, while 0.3% (w/v) homemade composite cleaning agent containing alkali, surfactant, and enzyme could recover the water permeability very effectively. Unlike MF and UF membranes, the pore size of NF membrane is very small, solute adsorption at the membrane surface or within the pore may significantly decrease the diameter of the pore or even block the pore, therefore, internal fouling and pore blocking by low-molecular weight solutes (e.g., amino acid, peptides, and organics) could be the dominating fouling in NF of soy sauce. Multiple interactions with the foulants (e.g., solubilization, dispersion, hydrolysis, and decomposition) would favor the regeneration of the fouled NF membrane, and composite cleaning formulation would be preferred. Moreover, for sterilizing the NF system, it was necessary to perform a thorough washing with 1% (w/v) $NaHSO_3$ solution every week to ensure the product was free of bacteria, and a monthly washing with 2% (w/v) citric acid solution was required to remove inorganic salt precipitates.

4.5 SUMMARY

Membrane technology is playing an important role in improving the quality of soy sauce and ensuring the biosafety of soy sauce. With MF and UF, the turbidity and count of aerobic microorganisms in the product of soy sauce could be significantly reduced, while the nutrients could be retained, thus refined soy sauce with prolonged shelf life and enriched flavor could be produced. With NF membrane technology, low-salt soy sauce could be produced with raw soy sauce containing high NaCl concentration. Due to the high osmotic pressure induced by the high concentration of NaCl in soy sauce, a three-step operation of dilution, concentration, and diafiltration was found to be the suitable operation mode for low-salt soy sauce production.

In processing soy sauce by membrane technology, membrane selection and optimization of operating conditions (e.g., TMP, CFV, temperature, etc.) determine the performance of membrane separation process and the quality of soy sauce products. Selection of the suitable membrane is the first and most important step toward the success of a membrane system since the process efficiency and product quality are largely determined by the membrane. Increasing TMP normally results in a higher initial flux and a much higher fouling rate, and in some cases the permeate flux may decline to less than the flux at lower TMP. Therefore, there is an optimum TMP at which the flux can be a maximum. With increasing CFV, a less rapid flux declines and a higher steady-state flux can be obtained, but a higher energy consumption is required at the same time. Higher temperature favors higher permeate flux, but the membrane and/or product quality may be adversely affected. In optimizing the process parameters for soy sauce filtration, in addition to permeate flux, energy consumption, property of the membrane, and product quality should be taken into account.

Raw soy sauce is very complicated, containing bacteria, bacteria debris, proteins, polysaccharides, amino acids, and inorganic salts. Membrane fouling, resulting in low operating efficiency and even system failure, constitutes a major problem in wider applications of membrane technology in soy sauce industry. Fouling can be controlled to some extent by selecting appropriate membranes and optimizing process parameters. Unfortunately, chemical cleaning is still inevitable to restore membrane performance. It should be pointed out that the cleaning-in-place is a process requirement for soy sauce production. Additional requirement for membrane cleaning increases operational complexity and cost and may reduce the service life of the membrane. There is no doubt that the continued efforts to develop new membranes, new modules, and optimal process design and operation will certainly improve the performance and economics of membrane technology, and thus promote its application in soy sauce industry.

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