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Desalination of effluents with highly concentrated salt by nanofiltration: From laboratory to pilot-plant

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HIGHLIGHTS
► Highly concentrated salt facilitates solutes to diffuse through NF270 membrane.
► Highly concentrated salt increases concentration polarization.
► Water rinse can regenerate NF270 membrane for desalination of iron dextran.
► Desalination of IDA mother liquor can ensure continuous IDA production.
► Dilution–concentration mode is most suitable for desalination of soy sauce.

GRAPHICAL ABSTRACT

ABSTRACT
Nanofiltration (NF) has been widely used for treatment of industrial effluents, but very few work concerns NF process in concentrated saline solution, especially for NF-desalination aiming at permeation of monovalent salts and retention of organic solutes. In this study, NF270 membrane was chosen to treat model solutions and three industrial effluents with highly concentrated salt (crude iron dextran solution, iminodiacetic acid mother liquor, and raw soy sauce), showing that with increase of salt concentration, the retention of all the solutes decreased while concentration polarization was increased. In the presence of charged organic solutes, inorganic salt retention would decline, even negative retention of monovalent salt was found. Increasing pH would induce membrane swelling in saline solution, which might be caused by the higher local salt concentration around the membrane polymers at higher pH. As NF-desalination of industrial effluents with highly concentrated salt was scaled up from laboratory to pilot-plant, the dead-end stirred filtration at constant flux could provide some important information for pilot-plant tests, such as membrane selection, optimum operating parameters and mechanism analysis, but it was necessary to re-optimize operating mode and method for crossflow filtration at constant pressure, in order to control the concentration polarization at high salt concentration.

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1. Introduction
The biochemical industries, especially pharmaceutical synthesis and food processing, frequently produce crude feeds or waste streams containing highly concentrated salt (e.g. NaCl up to 20%, w/v) [1–8]. These mixtures are produced by salt-adding preparation or by acid- or alkali-catalyzing reactions followed by neutralization. A mass of salt in these industrial fluids induces many problems in their post-treatment, and also increases health risks due to an excessive intake of salt. Moreover, quite a lot of organic products are difficult to be extracted from concentrated saline solution, causing a pollution problem when they are discarded without purification. Therefore, partly removing salt from these effluents is important, not only for the environment, but also for improving product quality. The existing alternative treatment methods, such as crystallization, extraction, ion-exchange and electrodialysis, are usually too expensive to be industrialized and the cost of treatment can eventually undermine the economic viability of...
the whole process with progressing tightening of environmental regulations.

Nanofiltration (NF), as a membrane separation technology using both electric charge (Donnan effect) and pore size (sieving effect), could separate low molecular weight solutes (e.g., glucose, saccharides, amino acid, and peptide) from inorganic salt solutions [5,9,10], and simultaneously concentrate organic solutes and remove inorganic salt, showing a great potential in desalination and/or the recovery of valuable organic substances (permeation of monovalent salts). Moreover, the salt ions could easily pass through the membrane at high salt concentration [10], even the nominal monovalent salt rejection was often negative in mixtures of salts and large charged organic molecules or mixed monovalent–multivalent salts [4,5,11,12], thus greatly decreasing osmotic pressure difference across membrane. Consequently, NF technique has been considered as a promising approach to treat the effluents containing high concentration salt (>1 M).

NF270 membrane was mainly applied in purification of drinking water because of its very high water production capacity [13,14]. Recently, increasing applications of NF270 on industrial effluents were reported [4,5,7,15–18], indicating that this membrane had relatively high retention and permeability as well as strong anti fouling performance. Mänttäri et al. [19] compared NF270 with several other NF membranes (e.g., NTR7450, Desal-5 DL, NF-PES-10) in terms of glucose retention and water permeability, and verified that NF270 had both a relatively high retention (>90%) and a high permeate flux (>12 Lm−2 h−1 bar−1). This abnormally high retention–permeability property made NF270 suitable for desalination of the concentrated ef fl uents. In laboratory scale, NF270 was successfully applied in desalination of three ef fl uents with highly concentrated salt, soy sauce [4], iminodiacetic acid (IDA) [5] and iron dextran complex [7]. Luo et al. [4,5,7] found that, for NF-desalination of these ef fl uents, a dilution operation could improve desalination efficiency, and alkaline pH could enhance salt removal and charged solute retention, and salt concentration affected solute retention and concentration polarization. However, NF process in concentrated saline solution should be elaborated more systematically, and in order to industrialize these applications, pilot-plant tests are needed to be carried out.

In this paper, NF270 membrane was applied to desalination of effluents with highly concentrated salt at both laboratory and pilot-plant scales, and the NF-desalination process was divided into three categories — separation of salt and neutral solutes (iron dextran), separation of salt and charged solutes (IDA), and separation of salt and mixed solutes (soy sauce). This NF-desalination application aims at permeation of monovalent salts and retention of organic solutes. The focus of this work was to discuss salt effect on solute retention and concentration polarization, and analyze the relationships and the deviations between laboratory studies and pilot-plant tests. The present work should be very useful for understanding NF process under high concentration salt conditions and to industrialize the desalination of concentrated effluents using NF270 membrane.

2. Materials and methods

2.1. Experimental set-up and procedure

In laboratory studies, the dead-end filtration was carried out in constant flux mode, and this laboratory-scale set-up was described in detail elsewhere [4,5,7], as shown in Fig. 1. This device is fitted with a membrane disk having an effective diameter of 24 mm within the module, with an effective membrane surface area of 4.52×10−4 m². The experiments were performed in three modes: concentration mode, diafiltration mode, and full recycle mode. First, the stirred cell was filled with feed, and then, for concentration mode, feed was continuously pumped into the cell and more and more organic solutes accumulated in retentate; for diafiltration mode, deionized water was injected into the cell with feed and the salt concentration in feed decreased continuously; for full recycle mode, a solution with the same solute concentration as permeate was put into the cell to ensure that the filtrations were performed in a way similar to the total recycling operating mode (i.e., circulating the permeate back to the stirred cell to keep the solution compositions unchanged).

In pilot-plant tests, crossflow filtration was adopted under constant pressure, and the schematic diagram of the pilot-plant NF-system is shown in Fig. 2 [20]. This homemade NF pilot device was equipped with a 100 L capacity feed tank and two multistage pumps (CRN3-36, Grundfos, Denmark). Pressure was measured by both digital and analog manometers, and, as transmembrane pressure (TMP) reference value, the mean value between the inlet and outlet of membrane module was taken, and pressure drop never exceeded 0.9 bar. Temperature was controlled by circulating water. Crossflow flux and permeate flux were determined by rotameters. The membrane module of NF270-4040 was supplied by DOW-Filmtec and consisted of a spiral-wound...
2.2. Membrane and feed solutions

The commercial membrane NF270 was produced by DOW-Filmtec, and based on the manufacturers’ data sheet and literature [13,19,21], the properties of NF270 membrane are shown in Table 1.

The model solutions were prepared by sodium chloride (NaCl), glucose, iminodiacetic acid (IDA), and glutamic acid. Glucose (Amresco, USA), NaCl and IDA (Beijing Chemicals Reagent Company, Beijing, China) were of analytical grade. Soy sauce (Amresco, USA), NaCl and IDA (Beijing Chemicals Reagent Company, Beijing, China) were of biochemical grade and supplied by the Shanghai Kangda Amino-Acid Factory, Shanghai, China. Pilot-plant tests were carried out in local factories and the industrial effluents were obtained directly. Their main characteristics were described in Table 2 [4,5,7].

2.3. Analytical methods

At laboratory scale, the glucose concentration was determined using the 3,5-dinitrosalicylic acid (DNS) method. The pH value and NaCl concentration of the solutions were measured using an ion meter equipped with pH and Cl− electrodes (PX5-216, Precision & Scientific Instrument, China). IDA concentration was measured with a spectrophotometer (UV757CRT, Precision & Scientific Instrument, China) at 235 nm after nitrosation [5]. At pilot-plant scale, all the analysis was conducted by Product Inspection Centre of the factories.

2.4. Calculated parameters

Average observed rejection (Robs) can be calculated by:

\[
R_{obs} (\%) = \left(1 - \frac{C_P}{C_{R,av}}\right) \times 100
\]

where \(C_P\) is solute concentration in permeate, and \(C_{R,av}\) is the average concentration of initial feed and final retentate (g L\(^{-1}\)).

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

\[
\text{Removal} (\%) = \frac{C_f \cdot V_P}{C_f \cdot V_f} \times 100
\]

where \(C_f\) is the solute concentration in the feed, \(V_P\) and \(V_f\) are the volume of permeate and feed, respectively (L).

3. Results and discussion

3.1. Salt effects on solute rejection and concentration polarization

3.1.1. Salt with neutral solutes

Significant researches regarding the effect of inorganic salt on the transfer of neutral solutes through NF membranes demonstrated that solute rejection decreased in the presence of salts [9,21–25]. It can be seen in Fig. 3 that, glucose retention decreases with increase of NaCl concentration, and the magnitude of the variation is larger when salt concentration is less than 1 M, especially at low permeate flux. As reported by Escoda et al. [25] and Luo and Wan [21], salt ions resulted in both pore swelling and solute dehydration, thus increasing pore radius and decreasing solute size, which made neutral solutes diffuse through membrane more easily. At low permeate flux, diffusive transfer was more important, and accordingly, the effect of salt concentration on solute retention was more obvious.

As shown in Fig. 4, the transmembrane pressure (TMP) increases linearly with permeate flux at all salt concentration, indicating that shear rate at membrane surface is high enough and concentration polarization does not grow severer with increase of flux under this condition. According to the boundary layer theory, when concentration...
polarization layer did not increase with permeate flux, TMP could be expressed as follows:

\[ J_v = \frac{1}{N_v} \frac{\Delta \Pi_b}{R_m + R_{cp}} \]  

\[ TMP = N_b (R_m + R_{cp}) J_v + \Delta \Pi_b \]  

where \( J_v \) is volumetric flux per unit area of membrane, and \( N_b \) is solvent viscosity, \( R_m \) the intrinsic membrane resistance, \( R_{cp} \) the resistance of concentration polarization layer, \( \Delta \Pi_b \) the osmotic pressure difference between bulk and permeate. By fitting the data in Fig. 4, some linear equations could be obtained, where the slopes at different salt concentrations represented the product of solvent viscosity and total filtration resistance, \( N_b(R_m + R_{cp}) \), and the intercept denoted osmotic pressure difference, \( \Delta \Pi_b \). As seen in Fig. 4, total filtration resistance and osmotic pressure increase with salt concentration (suppose solvent viscosity is not changed). Membrane resistance decreased at higher salt concentration due to pore swelling effect [21,25], and thus the real reason why the total filtration resistance increased was the augment of concentration polarization. In fact, the solution viscosity would slightly increase due to the addition of much salt [7,25], which decreased back diffusion of solutes in boundary layer and thus aggravated concentration polarization [7]. At the same time, an increasing of concentration polarization at higher salt concentration would increase the glucose accumulation at the membrane surface and make more glucose molecules permeate through the membrane, thus causing a decrease of \( R_{obs} \) of glucose. Moreover, the total osmotic pressure difference between bulk and permeate increased with salt concentration because glucose molecules and salt ions at membrane surface went up, more obviously than those at permeate side.

### 3.1.2. Salt with charged solutes

The effects of inorganic salt on charged solutes included pore swelling and salting-out, as well as charge screening, and therefore, with increasing salt concentration, the IDA retention decreased more evidently when compared with glucose retention (no electrostatic effect), as shown in Fig. 5. The effects of NaCl concentration on charge screening could be interpreted with the Deby screening length (\( \kappa^{-1} \)), where \( \kappa^{-1} \) is inversely proportional to the square root of electrolyte concentration [23]. With increasing NaCl concentration, \( \kappa^{-1} \) decreased and this would increase the transmission of IDA and in turn reduce rejection.

When 30 gL\(^{-1}\) IDA was used as solute for NF process, the relationship of TMP and permeate flux still kept linear at all the investigated salt concentrations. As shown in Fig. 6, the slopes of the TMP-flux equations increase with salt concentration, indicating that concentration polarization grows severer at higher salt concentration, but their intercepts show a reverse trend, that \( \Delta \Pi_b \) decreases when adding salt (see Eq. (4)). This could be explained by the fact that, NaCl retention was very small in the presence of large charged solutes [5], and thus \( \Delta \Pi_b \) due to NaCl increased little with rise of salt concentration, while IDA retention declined much at higher salt concentration, and therefore, with increasing salt concentration, \( \kappa^{-1} \) decreased and this would increase the transmission of IDA and in turn reduce rejection.

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salt concentration, solute retention decreased, causing a reduction of osmotic pressure difference across membrane; but at high flux (area C), TMP was governed by concentration polarization, and the greater resistance of concentration polarization layer due to higher salt concentration, resulted in a higher TMP at the same permeate flux; the moderate flux (area B) was regarded as a transition zone. Moreover, the severer concentration polarization at both higher salt concentration and higher flux also resulted in a decrease of IDA observed retention.

3.1.3. Effect of organic solutes on salt
The electrostatic effect of NF is the main separation mechanism for inorganic salt, and thus with increasing NaCl concentration, the retention itself decreases due to its greater charge screening effect on NF membrane, as shown in Fig. 7. The addition of neutral solute (glucose) did not affect the NaCl retention, but when charged solute (Glutamic acid) was added, NaCl retention decreased largely at low salt concentration. This was caused by the Donnan effect, as the accumulation of glutamic acid (as an amphoteric electrolyte, it was negatively charged at pH=5.2 [21]) near the membrane surface would result in more Cl⁻ ions in the permeate side, i.e. lower rejection of NaCl (because the salt ions with smaller size and less charge passed through the membrane more easily). And this effect would be fully screened by a high ionic strength, and hence, when salt concentration increased more than 1 M, NaCl retention for these three solutions was almost the same. Meanwhile, the presence of organic solutes in saline solution would aggravate the concentration polarization, thus increasing TMP.

3.2. Separation of salt and neutral solutes: desalinization of iron dextran complex
Iron dextran is a kind of hematinic used for both human and animal. It is a complex of ferric oxyhydroxide with dextrans of 5000 to 7000 Da (average molecular weight) in a viscous solution (3.8 mPa.s, 20 °C). The crude products of iron dextran contain 10 – 18% (w/v) NaCl because large amounts of sodium hydroxide and hydrochloric acid are used in its production. With NF270 membrane, iron dextran was almost completely rejected, while salt rejection was so small (Robs = 1 – 2%) that salt ions could pass through the membranes easily. Desalinization of iron dextran by NF technology was a secure, environment-friendly and highly efficient process, but severe concentration polarization might limit its application [7].

3.2.1. Concentration polarization in concentrated saline solution
Luo et al. [7] reported that the behavior of concentration polarization during NF of iron dextran could be attributed to the viscosity effect resulting from salt concentration. That is, solution viscosity increased with salt concentration, which lowered the diffusion coefficient and decreased the back diffusion of iron dextran molecules from boundary layer to bulk solution. As result, more iron dextran molecules accumulated at membrane surface and a “denser” concentration polarization would be expected. As shown in Fig. 8a, under a constant flux operation in laboratory, higher TMP profiles appear in NF of iron dextran with higher salt concentration, and when NaCl concentration is up to 2.5 M, the TMP keeps increasing with time, suggesting continuous iron dextran accumulation in the concentration polarization layer or even the formation of gel layer [7]. These results from the real industrial effluent confirmed the opinion obtained from model solutions, and we can conclude that, higher salt concentration resulted in greater concentration polarization.

In order to control the concentration polarization in concentrated saline solution, the pump was intentionally paused for about 1 s at different time intervals during NF operation (intermittent pump pause), and as shown in Fig. 8b, this operation can effectively prevent the continuous increase of TMP at high salt concentration by accelerating iron dextran molecules to disperse away from the membrane surface. Another strategy to decrease concentration polarization was “programmed flux increase” operation, as permeate flux was increased in step (8.85 → 11.1 → 13.3 → 15.5 Lm⁻² h⁻¹, each flux lasted 60 min). When flux increases to 15.5 Lm⁻² h⁻¹, a quite stable TMP profile is obtained, and after 60 minutes running, the TMP value

![Fig. 7. NaCl retention and TMP variation at different salt concentrations for three solutions. Glucose = 15 gL⁻¹, glutamic acid = 10 gL⁻¹, flux = 26.5 Lm⁻² h⁻¹, pH = 5.2, T = 25 °C, stirring speed = 1400 rpm.](image)

![Fig. 8. TMP variation of NF270 with time for iron dextran solution (a) with different salt concentrations; (b) with different operation strategies. Full recycle mode; flux = 15.5 Lm⁻² h⁻¹; T = 20 °C; stirring speed = 1200 rpm.](image)
is much lower than that for fixed flux operation, as seen in Fig. 8b. Therefore, for the pilot-plant equipment under constant pressure mode, intermittent pressure release and crossflow surge might be adopted to periodically remove concentration polarization layer, and gradually increasing TMP could be used to control the formation of polarization layer.

3.2.2. Pilot-plant test

Using two NF270–4040 crossflow modules, a pilot-plant test was carried out under constant pressure mode. It was found that, the operations of intermittent pressure release and pressure programming were not very effective for reducing concentration polarization of iron dextran in practical applications. The reason was that, for this highly viscous feed, crossflow rate was limited due to the pressure drop (<0.9 bar), and thus the shear rate on the membrane was much lower than that for dead-end stirred filtration; accordingly, concentration polarization was easy to form and it was mainly affected by the viscosity and running time. Moreover, intermittent operation of a pump would cause higher operational cost as well as damage on the pump itself, so it might be not cost effective in practical applications.

Increasing temperature could decrease concentration polarization and thus enhance permeate flux in pilot-plant test because viscosity was reduced at higher temperature and the back diffusion of iron dextran was increased. So the operating temperature here was more than 35 °C, much higher than that in laboratory studies (20 °C). Moreover, at such high temperature, the effect of salt concentration on solution viscosity and concentration polarization could be negligible, different from that in laboratory studies.

In order to obtain qualified product by one-step NF operation, the crude iron dextran solution should be simultaneously concentrated and desalted by NF270. Iron dextran concentration should be increased by 200% and salt concentration had to be decreased by 90%. The arrangement of concentration step and diafiltration step would affect solution viscosity and desalination time, which had a huge impact on concentration polarization and permeate flux. Fig. 9 shows the results of three different operating modes at pilot-plant scale. The best strategy (c) was that, first, 120 kg feed was concentrated to be 60 kg, then diafiltration step was carried out and 120 kg water was used as diluent, finally the desalted feed was concentrated to be eligible product. This operation had relatively high permeate flux and the least processing time due to the lightest concentration polarization. The concentration step can improve the desalination efficiency of subsequent diafiltration, but excessive concentration factor will result in a sharp flux decline due to viscosity increase (i.e. concentration polarization aggravates), as shown in Fig. 9a.

After each desalination process, membrane modules were rinsed using crude feed at high crossflow rate and zero TMP, but membrane permeability failed to be recovered. However, the same operation using water could fully remove concentration polarization layer and the separation performance of NF270 could be totally recovered without chemical cleaning, indicating that this process was sustainable and very appropriate to be applied in industry.

3.3. Separation of salt and charged solutes: desalination of iminodiacetic acid (IDA) mother liquor

Iminodiacetic acid (IDA) is an important chemical intermediate as well as a chelating reagent. Usually, IDA salts are obtained first in its synthesis process, and the subsequent acidification produces a massive inorganic salt in the mother liquor, which obstructs IDA crystallization and generates a waste stream containing IDA. Luo et al. [5] reported that the observed retention of IDA by NF270 was more than 90% while NaCl could pass through almost freely. Consequently, treatment of IDA mother liquor by NF can recover IDA and remove salt at one-step, and thus tackle the problems of low IDA recovery and environmental pollution in conventional IDA production.

3.3.1. pH effect on charged solutes retention

As a divalent organic acid, the ionization state of IDA varies with pH, and in terms of Henderson–Hasselbalch equation,

$$\text{pH} = \text{pK}_a + \log \left( \frac{\text{proton acceptor}}{\text{proton donor}} \right)$$

the molar fractions of different forms (e.g. IDA$^+$, IDA$^{2−}$, IDA$^{3−}$) at different pH values could be calculated using respective pK$\text{a}$ values ($\text{pK}_a = 2.98$, $\text{pK}_a = 9.89$) [5] and the results are shown in Fig. 10 (full lines). Luo et al. [5] found that with increase of pH, the electrostatic repulsion between IDA and NF270 increased while their steric hindrance decreased due to membrane swelling [23], and the variation of IDA retention with pH was governed by a competition of these two influences. It can be seen from Fig. 10 that, when pH increases from 5 to 7, IDA retention declines due to the dominant sieving effect, while pH rises from 8 to 10, IDA retention goes up due to the dominant electrostatic effect. Otherwise, IDA was negatively charged more and more with increase of pH, and thus chloride ion could permeate through the membrane much more freely than IDA ions because IDA ions possessed bigger size and charge and due to co-ions competition as well as Gibbs–Donnan equilibrium. Therefore,
NaCl retention decreased at higher pH, even negative rejection was found when pH was higher than 6.

As shown in Fig. 10, TMP is decreased as pH increases from 4 to 8, and the reason is not only the decline of NaCl and IDA retention, but also maybe the “looser” concentration polarization layer at higher pH (electrostatic repulsion between IDA ions increases). However, TMP kept constant when pH rose from 8 to 10, which was caused by the increase of IDA retention.

As discussed in Nilsson et al. [23], salt effect (salting-out or salting-in) might be the intrinsic mechanism of pH effect on membrane swelling in concentrated saline solution. In their study, glucose retention was almost the same at pH values of 5, 7 and 9 when without salt, while with rise of salt concentration, the retention differences at different pH values were increasing. The mechanism could be explained as follows: in electrolyte solution, charged polymers were surrounded by salt ions due to electrostatic adsorption, inducing that the local salt concentration close to charged group was much higher than the global concentration; remembering that NF270 membrane charge increased with pH, and thus at higher pH, the local salt concentration in membrane went up and membrane swelling due to salt ions was enhanced. Therefore, for treatment of effluents with highly concentrated salt by NF, elevating pH could lower inorganic salt rejection and maybe improve the retention of charged organic solutes due to stronger electrostatic repulsion, but neutral solutes would more easily permeate through the membrane, and at the same time, this salt swelling on polymers might damage the polymeric NF membranes in long-term running.

3.3.2. Processing route for IDA continuous production

An industrial IDA salt effluent supplied by a plant was acidified by hydrochloric acid and about 85% IDA was precipitated by crystallization at a pH of 2.1–2.2 (isoelectric point of IDA) [5]. The supernatant mother liquor was collected and its pH was adjusted to 5.2 by sodium hydroxide. This effluent contained 45.5 g L\(^{-1}\) IDA, 1.94 M NaCl, and after pretreatment by microfiltration (0.22 μm), 19.2 mL feed was concentrated to 12.8 mL and then 6.4 mL water was diafiltrated at 66.37 L m\(^{-2}\) h\(^{-1}\) and 25 °C. The recovery of IDA was about 95.6%, NaCl removal was 60.3%. This desalted effluent could be recycled in acidification step and the inorganic salt would not be accumulated in mother liquor. Moreover, NF was able to decolorize the industrial feed, producing an achromatous permeate only containing a lot of NaCl and little IDA, and this permeate could be discharged directly after a simple treatment.

The similar results were obtained in pilot-plant tests, and membrane fouling was found but could be easily removed by alkaline cleaning. According to laboratory and pilot-plant studies, a processing route for IDA continuous production is proposed as shown in Fig. 11, that the IDA mother liquor is desalted by NF and then returned to acidification tank. By this process, the recycle of IDA mother liquor and the continuous IDA acidification could be achieved. Using multistage NF treatment, IDA recovery was improved a lot and NF permeate could be reused as processing water, indicating that this technology was suitable for IDA production in industry.

3.4. Separation of salt and mixed solutes: desalination of raw soy sauce

Soy sauce is a traditional Chinese food condiment, normally containing a high concentration of sodium chloride (NaCl, 18–20%, w/v). To meet people’s demand for healthy foods, part of NaCl needs to be removed from the raw soy sauce. Luo et al. [4] studied the desalination of soy sauce by NF at laboratory-scale, to show that, NF270 was most suitable for the purpose, and after 53% of the salt was removed from the soy sauce, the content of nutritional components in retentate could meet the Super Class quality standards. However, due to the mass of low molecular weight organic solutes (glucose, saccharides, amino acid, and peptide) and inorganic salt in soy sauce, high osmotic pressure and severe concentration polarization might limit the application of soy sauce desalination by NF. Hence, dilution was a necessary step in order to increase permeate flux and operating mode should be optimized to improve desalination efficiency.

3.4.1. Separation performance

As seen in Table 3, for a pilot-plant test with higher temperature and TMP, the permeate flux is much higher than that in laboratory studies [4,20]. On the one hand, higher temperature resulted in higher solutes removal due to the enhancement of diffusive transport through membrane, causing higher amino nitrogen loss in pilot-plant at 30 °C than in laboratory at 20 °C. On the other hand, higher permeate flux could increase solutes retention and thus lower solutes removal, inducing less amino nitrogen loss in pilot-plant at 30 °C than in laboratory at 25 and 35 °C. Reducing operation temperature could decrease the loss of nutritional components but it would increase the cost and decrease flux, and a moderate temperature and a high TMP was preferred. Accordingly, the dead-end stirred filtration could provide reliable information (e.g. membrane selection and parameter optimization) for industrial application in despite of different TMP profiles and shear force between them.

3.4.2. Operating mode

In previous study [4], it was found that when using a dead-end filtration at constant permeate flux, the water consumption was the least for single diafiltration mode, but the high osmotic pressure (caused by mixed organic solutes) and the severe concentration polarization (induced by concentrated salt) resulted in very high TMP at a constant

![Fig. 10. Variation of NaCl and IDA rejection as a function of pH. IDA 30 g L\(^{-1}\), NaCl 1.37 M, Flux = 66.4 L m\(^{-2}\) h\(^{-1}\), T = 25 °C, stirring speed = 1200 rpm.](image)

![Fig. 11. Schematic diagram of continues NF-desalination system for industrial application.](image)
permeate flux, and thus the flux had to be reduced due to the limitation of TMP, leading to a prolonged processing time. This implied that in soy sauce desalination with NF270, dilution could be a necessary step in practical application. As shown in Table 4, thanks to the relatively low water consumption and processing time, the combination mode Eq. (2) of dilution–concentration–dialfiltration was regarded as the most suitable for desalination of soy sauce in laboratory.

In pilot-plant tests, after 50 L soy sauce was diluted with different volumes of water, three operating modes, containing concentration followed by dialfiltration, concentration alone, and dialfiltration followed by concentration were carried out respectively, as described in Fig. 12. The data of water usage in Fig. 12 was pre-calculated by the mathematic model proposed in our previous work [4], assuming that the salt concentration in soy sauce decreased to 90 g·L⁻¹. Additionally, no matter which operating mode was used, 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 [20].

Table 5 shows the comparison of desalination results under different operating modes at a constant TMP of 24 bar [20]. Although water consumption in dilution–concentration–dialfiltration (d) mode was more than that in other operating modes, the processing time was relatively low due to its highest permeate flux. This result was not consistent with that from laboratory studies (see Table 4). This could be explained by a fact that, in constant flux mode, TMP was usually neglected when evaluating the desalination efficiency, and only water usage governed the processing time, but in constant TMP mode, the combined effect of water usage and permeate flux determined the desalination efficiency. It can be seen from Table 4 that, although the processing time of dilution–concentration mode (1) was relatively long, its average TMP was much lower when compared with the so-called "best" mode (2). While in pilot-plant tests, permeate flux increased with dilution water, thus reducing processing time [20]. Another essential reason was the different shear forces on membrane between these two membrane modules. In details, for crossflow module with moderate shear rate, concentration polarization was obviously affected by solutes concentration (or viscosity) and dilution step could effectively decrease concentration polarization during desalination, thus enhancing permeate flux not only by a decrease of osmotic pressure.

Finally, the 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 the best choice [20].

4. Conclusions

This work demonstrated that desalination of effluent with highly concentrated salt by NF270 could effectively reject organic solutes while monovalent inorganic salt passed through easily. Three typical industrial effluents with high salt concentration (crude iron dextran solution, iminodiacetate acid mother liquor, and raw soy sauce) were treated by NF270 from laboratory scale to pilot-plant scale. The main findings were summarized as follows:

1. With increase of salt concentration, the retention of all the solutes by NF270 was reduced and the concentration polarization was increased;
2. For charged solutes, at low permeate flux (i.e. diffusive mass transport was dominant), salt ions facilitated the solutes to diffuse through NF270, thus decreasing osmotic pressure and filtration resistance; while at high permeate flux (i.e. convective mass transport was dominant), salt ions aggravated the concentration polarization of organic solutes, thus increasing total filtration resistance.
3. The addition of neutral solutes did not affect salt ion retention, while charged solutes resulted in a drop of salt retention, but this effect would be weakened with increase of salt concentration.

Table 3
Comparison of separation performance between laboratory and pilot-plant tests [4,20].

<table>
<thead>
<tr>
<th>Index</th>
<th>Laboratory</th>
<th>Pilot-plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>Flux (L·m⁻²·h⁻¹)</td>
<td>6.6</td>
<td>6.6</td>
</tr>
<tr>
<td>Average TMP (bar)</td>
<td>25.6</td>
<td>20.5</td>
</tr>
<tr>
<td>NaCl removal (%)</td>
<td>53</td>
<td>53</td>
</tr>
<tr>
<td>AN removal (%)</td>
<td>20.6</td>
<td>26.1</td>
</tr>
</tbody>
</table>

Table 4
Comparison of desalination results for different operating modes at laboratory scale [4].

<table>
<thead>
<tr>
<th>Operating mode</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water consumption (L)</td>
<td>12.8</td>
<td>10.0</td>
<td>12.0</td>
</tr>
<tr>
<td>Processing time (h)</td>
<td>4.25</td>
<td>3.33</td>
<td>4.00</td>
</tr>
<tr>
<td>Average TMP (bar)</td>
<td>25.55</td>
<td>32.95</td>
<td>24.02</td>
</tr>
<tr>
<td>Amino acid removal (%)</td>
<td>20.2</td>
<td>20.1</td>
<td>22.5</td>
</tr>
<tr>
<td>NaCl removal (%)</td>
<td>53.0</td>
<td>53.0</td>
<td>49.6</td>
</tr>
</tbody>
</table>

Diluted soy sauce (soy sauce: pure water = 1:1) was concentrated to its original volume.

Fig. 12. Description of operating modes and comparison of water consumption. Original feed: 50.0 L soy sauce; Concentration step means that diluted soy sauce was concentrated to its original volume (30.0 L), and at last, low-salt soy sauce was concentrated to 35.0 L for all operating modes.

Table 5
Comparison of desalination results for different operating modes at pilot-plant scale [20].

<table>
<thead>
<tr>
<th>Operating mode</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
<th>f</th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water consumption (L)</td>
<td>36.5</td>
<td>39.0</td>
<td>43.0</td>
<td>50.0</td>
<td>43.0</td>
<td>46.5</td>
<td>49.0</td>
</tr>
<tr>
<td>Processing time (min)</td>
<td>210</td>
<td>138</td>
<td>114</td>
<td>108</td>
<td>111</td>
<td>120</td>
<td>138</td>
</tr>
<tr>
<td>Average permeate flux (L·m⁻²·h⁻¹)</td>
<td>3.25</td>
<td>5.09</td>
<td>6.44</td>
<td>7.31</td>
<td>6.61</td>
<td>6.35</td>
<td>5.66</td>
</tr>
<tr>
<td>Amino nitrogen removal (%)</td>
<td>36.9</td>
<td>35.4</td>
<td>36.9</td>
<td>33.8</td>
<td>35.4</td>
<td>33.1</td>
<td>36.2</td>
</tr>
<tr>
<td>NaCl removal (%)</td>
<td>69.8</td>
<td>67.7</td>
<td>68.1</td>
<td>67.4</td>
<td>68.1</td>
<td>68.1</td>
<td>69.5</td>
</tr>
</tbody>
</table>

TMP = 24 bar; Crossflow = 45 L·min⁻¹; Temperature = 30 °C; Low-salt soy sauce should be concentrated to 35.0 L at last, and the operating modes were described in Fig. 12.
(4) For desalination of iron dextran solution, decreasing salt concentration, intermittent pump pause, and programmed flux increase could effectively reduce concentration polarization in laboratory studies, but these operations did not have an expected effect in pilot-plant tests. However, the optimization of operating mode could decrease concentration polarization and improve permeate flux. Water rinse at high crossflow rate could fully recover membrane performance without chemical cleaning.

(5) Increasing pH induced membrane swelling, but the essential reason might be the higher local salt concentration around the membrane polymers which were charged more at higher pH. The presence of charged solutes IDA could cause a decrease of salt retention, even a “negative” retention. After neutralization, IDA mother liquor was desalted by NF270 and then returned to acidification tank, which could achieve the recycle of IDA mother liquor and continuous IDA production.

(6) For mixed solutes with highly concentrated salt, osmotic pressure and concentration polarization were the two main factors that influence desalination efficiency. The simple dilution–concentration mode was most suitable for desalination of soy sauce by NF270 in industry.

(7) The dead-end stirred filtration at constant flux could be used for membrane selection, operating parameter optimization and mechanism analysis, but it was not fit for the studies of operating mode because its operation laws were different from the tangential flow at constant TMP.

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References