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Desalination and recovery of iminodiacetic acid (IDA) from its sodium chloride mixtures by nanofiltration

Jianquan Luo[a,b], Shaoping Wei[c], Yi Su[a], Xiangrong Chen[a], Yinhua Wan[a,*]

[a] National Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100080, China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, China
[c] Guangxi Research Institute of Chemical Industry, Nanning 530001, China

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ABSTRACT

The desalination of model solutions containing iminodiacetic acid (IDA) and NaCl was examined using three commercial nanofiltration (NF) membranes (NF270, Desal-5 DL, Nanomax50). Experimental results showed that with all the three membranes, the rejection of IDA increased with the increase of pH from 8 to 11, and negative rejection of Cl^- was found in filtration in a certain range of pH. NF270 was chosen to further investigate the effect of permeate flux, temperature and solutes concentration on the separation of IDA and NaCl. The results showed that IDA rejection decreased with the increase of temperature and salt concentration, and the high concentration of IDA could induce a lower rejection of NaCl. Furthermore, the desalination and recovery were examined with model solution in different operation modes and a laboratory scale test with an industrial fluid was also performed. Under suitable conditions, with NF270, the recovery of IDA could be more than 95% while the NaCl removal was greater than 58%.

1. Introduction

Iminodiacetic acid (IDA) is widely used as a chemical intermediate and a chelating reagent for the production of glyphosate herbicides, electroplating solutions, chelating resin, surfactants, anticancer drugs, etc. [1–3]. There are two major methods to synthesize IDA: direct synthesis via hydrocyanic acid and catalytic dehydrogenization of diethanol amide [4]. In both processes IDA salts (sodium or potassium) are obtained first in the synthetic step. In order to convert these salts into IDA, the conventional methods are neutralization and crystallization by adding concentrated inorganic acids (hydrochloric or sulfuric acid). In this process, the maximum recovery of IDA is around 85% because a massive salt remaining in solutions can obstruct IDA crystallization [5]. As a result, quite a lot of IDA and high concentration of salts would remain in the crystallization mother liquor, hence constituting a pollution problem if it is discharged directly as a waste stream. Therefore, it is necessary to recover the IDA and to reduce the salt in the effluent in order to tackle the problems of low IDA recovery and environment pollution in conventional IDA production.

Generally, 2–6% (w/v) IDA and 8–14% (w/v) NaCl are left in the effluent in conventional IDA production. To recover IDA from the effluent, conventional approach normally consists of evaporation, concentration and crystallization, which is energy intensive and expensive. Recently, Zeng et al. [6] reported the recovery of IDA by electrodialysis at the isoelectric point of IDA, and the total recovery of IDA could be up to 99.4%. However, the pH of solution could change during the electrodialysis, and once the pH value is away from the isoelectric point, most of IDA will be lost. In addition, electrodialysis requires relatively high capital investment and operating cost.

Nanofiltration (NF) is a membrane separation technology based on both charge (Donnan effect) and size (sieving effect). It was reported that NF technology could separate low molecular weight solutes (e.g. glucose, saccharides, amino acid, and peptide) from inorganic salt solutions [7–12], showing great potential in desalination and/or the recovery of valuable organic substances. To our knowledge, there has been no report yet regarding the separation and recovery of IDA and the removal of NaCl using NF technology from the effluent in IDA production.

Although tangential flow (or cross-flow) filtration is widely used in industry and laboratory experiments, it normally consumes relatively large amount of feed solution. Moreover, permeate flux will vary with time if constant pressure (constant transmembrane pressure) operation is employed, therefore, it is impossible to exclude the effect of permeate flux variation when another parameter is being examined. Previous studies [13–15] demonstrated that the problem could be tackled by dead-end filtration at constant permeate flux. In the present study, dead-end filtration at constant permeate flux was employed to examine rapidly the feasibility of

* Corresponding author at: National Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, PO Box 353, Beijing 100080, China. Tel.: +86 10 62650673; fax: +86 10 62650673.
E-mail address: yhwan@home.ipe.ac.cn (Y. Wan).

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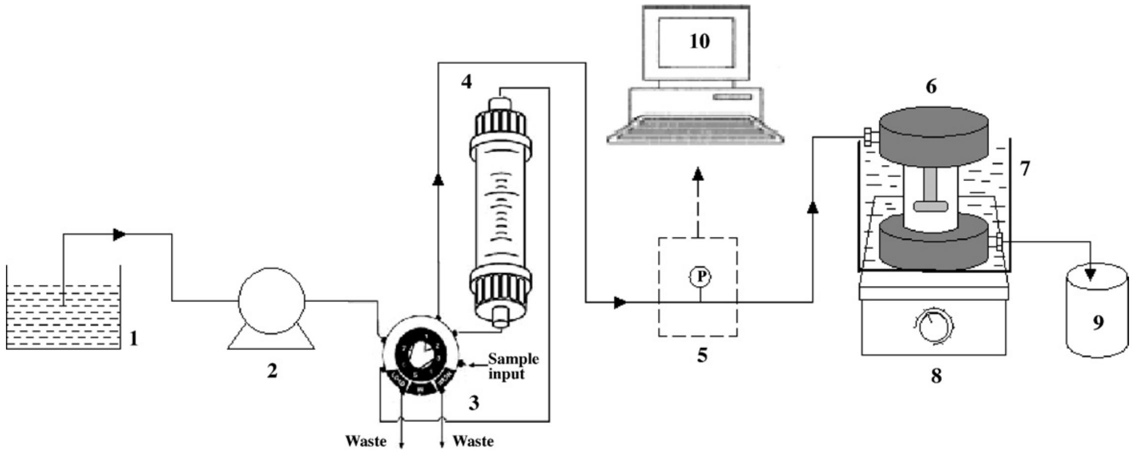

Fig. 1. Schematic diagram of the experimental set-up for nanofiltration.

desalination and recovery of IDA using NF technology with model solutions containing IDA and NaCl and practical effluent in IDA production. Model solutions were used to examine the effect of various operating parameters on the separation of IDA and NaCl, including pH, temperature, permeate flux and concentration of IDA and NaCl. The desalination and recovery of IDA were examined in different operation modes, and a laboratory scale test with practical effluent was also performed. The focus of this work was to identify the suitable operation conditions and operation mode for the efficient recovery of IDA and desalination under high NaCl concentration using NF technology.

2. Experimental

2.1. Experimental set-up and membranes

Fig. 1 shows the set-up for NF experiments. The dead-end filtration experiments were conducted with a home-made magnetic stirred cell in concentration or diafiltration mode. The working volume of the cell was 12.8 mL, which could be fitted with a membrane disc having an effective diameter of 24 mm within the module, and the effective membrane surface area was 4.52×10^{-4} m^2. The operation temperature was controlled by water bath. Feed or deionized water was pumped at constant flow rate into the filtration cell using a high performance positive displacement pump (P-500, Pharmacia, Sweden), and the data of transmembrane pressure (TMP) were continuously monitored by a pressure sensor (MLH040BSB09A, Honeywell, USA) and logged into a computer. All the experiments were performed at constant permeate flux conditions so as to exclude the effect of flux variation throughout the experiments, as reported elsewhere [13–15]. Three commercial NF membranes (NF270, Desal-5 DL, Nanomax50) were used in the present work. Based on the manufacturers' data sheet and the literatures [16–19], the properties of these NF membranes are shown in Table 1.

2.2. Solutions

Model solutions containing 0–1.5 mol L^{-1} NaCl and 0–60 g L^{-1} IDA were prepared by dissolving NaCl (MW = 58.5) and IDA (MW = 133) (both were of analytical grade and purchased from Beijing Chemicals Reagent Company, China) in deionized water. Fig. 2 shows the chemical structure and dissociation equilibrium of IDA. As a bivalent organic acid with pK_a of 2.98 and 9.89 [20], the relationship between pH and the acid/base ratio can be described by

Table 1
Property of NF membranes tested.

Membrane	NF270	Desal-5 DL	Nanomax50
Manufacturer	Filmtec (DOW)	Osmonics (GE)	Millipore
Surface material	Polyamide	Polyamide	Polyamide
Molecular weight cut-off	150–200 [16]	150–300 [16]	400 [17]
L_p (L m^{-2} h^{-1} bar^{-1}) 25 °C	13–14[a]	7–8[a]	8–9[a]
Max. temperature (°C)	45	50	50
Max. pressure (bar)	41	40	41
pH range	3–10	2–11	4–10
Isoelectric point (pH)	~5.3 [18]	~4.2 [18]	4.5 [19]

L_p: pure water permeability.
[a] Our own measurement.

the Henderson–Hasselbalch equation [21]:

$$\mathrm{pH} = \mathrm{pK} + \log\left(\frac{\text{proton acceptor}}{\text{proton donor}}\right) \quad (1)$$

The original pH of model solutions was 2.1–2.2 before adjustment. The pH of feed could be adjusted with NaOH (1 mol L^{-1}) to specific values as required. All the feed and deionized water were filtered through 0.22 μm microporous filters (MEMBRANA, Germany) before use.

2.3. Experimental procedure

A fresh membrane was used for each set of experiments. The virgin membranes were soaked in deionized water for at least 48 h prior to use. In order to diminish the effect of pressure on membrane performance in subsequent tests, the membranes were then pre-pressured for at lest 30 min at the flux of 398.2 L m^{-2} h^{-1} with deionized water until a constant pressure (~30 bar) was obtained. To determine solute rejection, about 15 mL model solutions were injected into the injection column (Superloop 50 mL, Pharmacia, Sweden) and then pumped into the stirred cell. Due to the high osmotic pressure induced by the solutes (IDA and salts) near the membrane during filtration, low permeate flux had to be adopted to ensure the TMP would not exceed the pressure limit of the mem-

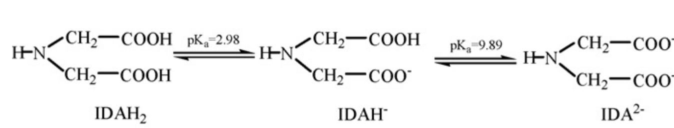

Fig. 2. Equilibrium dissociation of IDA.

brane in the experiments for solute rejection measurement. After 4 min filtration at a constant flux of 33.2 L m^{-2} h^{-1}, filtration permeate and the corresponding retentate were collected for subsequent analysis. To examine irreversible fouling of membrane after filtration, the pure water permeability (L_p) and hydraulic resistance of membranes were determined before and after each set of experiments. In diafiltration test, deionized water was used as diluent and pumped into the cell at certain rate using constant volume diafiltration mode.

2.4. Analytical methods

The pH values and NaCl concentration of the solutions were measured using an ion meter equipped with pH and Cl^- electrodes (PXSJ-216, Precision & Scientific Instrument, China). IDA concentration was measured with a spectrophotometer (UV757CRT, Precision & Scientific Instrument, China) at 235 nm after nitrosation [22].

2.5. Data processing

In NF experiments, the observed rejection (R_{obs}) of a solute by the membrane is defined as:

$$R_{obs}(\%) = \left(1 - \frac{C_P}{C_{R,av}}\right) \times 100 \quad (2)$$

where C_P is the solute concentration in permeate; $C_{R,av}$ is the average concentration in the cell during filtration.

In retention experiments, the values of $C_{R,av}$ were calculated in terms of mass balance equation shown below:

$$C_R V_O = C_{R,O} V_O + C_O V_P - C_P V_P \quad (3)$$

$$C_{R,av} = \frac{C_{R,O} + C_R}{2} \quad (4)$$

where C_O is the solutes concentration of feed, $C_{R,O}$, C_R are the solutes concentration in retentate before and after experiments, respectively; V_O is the volume of the stirred cell; V_P is the volume of permeate.

In diafiltration test, the concentrations of solutes in the retentate (C_R) during filtration can be calculated by measuring their concentrations in the feed and permeate, respectively.

$$C_R = \frac{C_O V_O - C_P V_P}{V_O} \quad (5)$$

The IDA recovery (%) is represented as:

$$\text{Recovery } (\%) = \frac{C_R}{C_O} \times 100 \quad (6)$$

The salt removal (%) is represented as:

$$\text{Removal } (\%) = \frac{C_P V_P}{C_O V_O} \times 100 \quad (7)$$

3. Results and discussion

3.1. Effect of pH

The existing state of IDA in solution could be in three different forms (e.g. $IDAH_2$, $IDAH^-$, IDA^{2-}), depending on solution pH. In terms of Eq. (1), the molar fractions of different forms at different pH values could be calculated using respective pK_a values (see Fig. 2) and the results are shown in Fig. 3 (full lines). As the separation performance of NF membranes depends on both the sieving (steric-hindrance) effect and the Donnan (charge repulsion) effect, it would be reasonable to find that the observed rejection of IDA was closely correlated to its existing states because of Donnan effect. Fig. 3 shows the effect of pH on IDA rejection with three NF membranes. As can be seen from Fig. 3, when Desal-5 DL membrane was used, the rejection of IDA increased significantly with the increase of pH in the range of 2–5. This could be because the fractions of $IDAH^-$ increased significantly with increasing pH, thus a loose concentration polarization would be expected. Meanwhile, the surface charges of membrane changed from positive to negative as the isoelectric point of the membrane is around pH 4.2 [18,23], thus the electrostatic repulsion between the membrane and solutes would increase accordingly. The rejection of IDA with Desal-5 DL also increased significantly in the range of pH 8–11. The reasons could be that the negative charge at membrane surface as well as the concentration of IDA^{2-} increased remarkably with increase in pH, therefore strong Donnan effect would be expected. However, as pH increased from 5 to 8, the rejection of IDA decreased slightly, though the molar fractions of ionic species of IDA dominated and remained approximately constant and a strong electrostatic repulsion between the membrane and solutes was expected. This could not be explained by Donnan effect alone. It was reported that in NF operation, the membrane skin could swell with increase of pH [18], and the swelling could be much more susceptible to pH in concentrated salt solutions [7,24–26]. In this case, the decrease of IDA rejection resulted from membrane swelling could be more pronounced than the increase of IDA rejection caused by electrostatic repulsion effect, as a result, a net decrease in IDA rejection was found. As for the case of pH > 8, IDA has strong negative charge, electrostatic repulsion effect could be more pronounced than membrane swelling effect, and consequently leading to the increase in IDA rejection. Concentration polarization could be another factor affecting the observed rejection of IDA. When pH increased from 2 to 11, the fractions of charged IDA molecules or the charge of IDA molecules increased accordingly, resulting in an increase in electrostatic repulsion between IDA molecules, therefore, the formation of looser concentration polarization layer could be expected. As a result, the wall concentration of IDA would decrease with the increase in pH, and subsequently a decrease in observed transmission or an increase in the observed rejection of IDA would be expected.

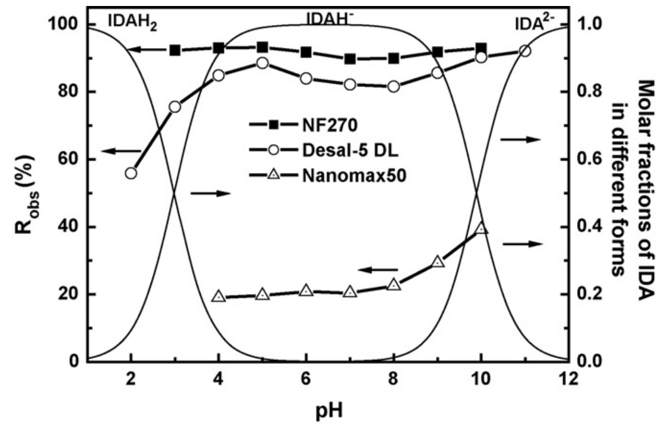

Fig. 3. Effect of pH on IDA rejection with three NF membranes. IDA: 30 g L^{-1}, NaCl: 1.37 mol L^{-1}, flux: 66.37 L m^{-2} h^{-1}, T: 25 °C, stirring speed: 1200 rpm.

When NF 270 membrane was used, the rejection of IDA was more or less constant (around 90%), this could be due largely to its molecular weight cut-off close to the molecular weight of IDA, and size effect could be the dominated factor affecting IDA transmission through the membrane. However, the change in IDA rejection with increase of pH could still be found, particularly when pH > 8, which was less significant than that of Desal-5 DL, as can be seen from Fig. 3. This phenomenon was probably due to the difference in “pore size” of the membrane skin layer between Desal-5 DL and NF270 membranes, and much greater charge effect on rejection

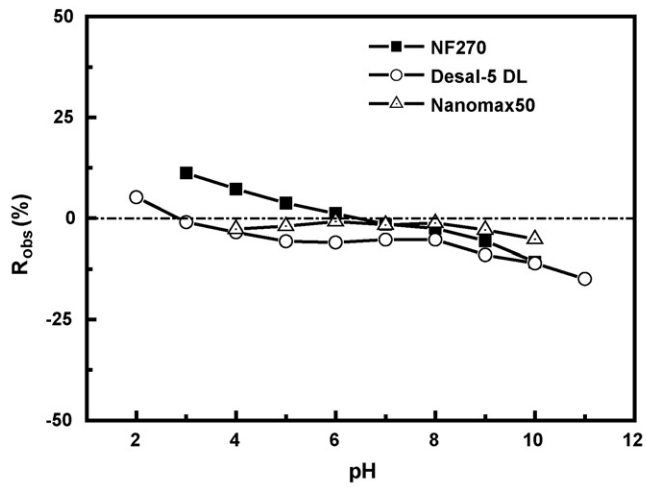

Fig. 4. Effect of pH on NaCl rejection with three NF membranes. IDA: 30 g L^{-1}, NaCl: 1.37 mol L^{-1}, flux: 66.37 L m^{-2} h^{-1}, *T*: 25 °C, stirring speed: 1200 rpm.

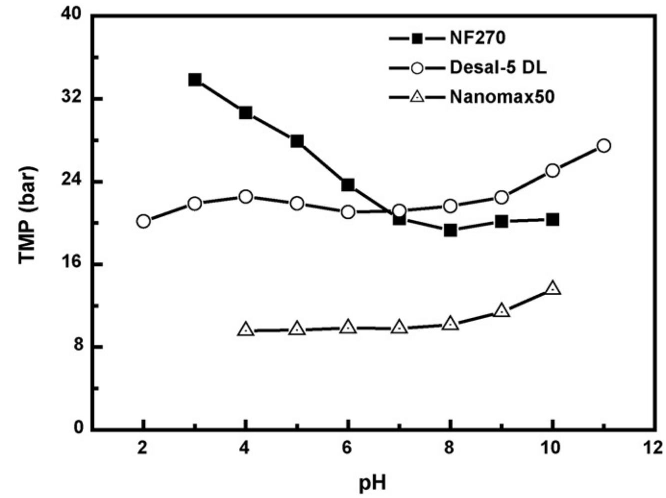

Fig. 5. Effect of pH on TMP with three NF membranes. IDA: 30 g L^{-1}, NaCl: 1.37 mol L^{-1}, flux: 66.37 L m^{-2} h^{-1}, *T*: 25 °C, stirring speed: 1200 rpm.

of IDA ions existed for the Desal-5 DL membrane. Again, the IDA rejection could be the comprehensive result of membrane swelling, electrostatic interactions between IDA molecules and membrane, and concentration polarization.

When Nanomax50 membrane was used, as expected, a lowest rejection for IDA among three NF membranes was found in the pH range examined and most IDA would pass through the membrane since its MWCO is 400, much higher than the molecular weight of IDA. Therefore, manipulating the electrostatic repulsion between the membrane and IDA molecules would be the most effective method if this membrane was used to recover IDA, as demonstrated in the separation of albumin from immunoglobulins (IgG) by ultrafiltration [27]. As shown in Fig. 3, the rejection of IDA with Nanomax50 increased gradually with the increase of pH when pH > 8. Since Nanomax50 membrane had negative charges at pH > 4.5 and IDA^{2-} concentration increased sharply at pH > 8, therefore there existed an increasing electrostatic repulsion between the membrane and solutes. The increase of IDA rejection when pH > 8 indeed illustrated the significance of Donnan effect in NF of IDA solution with the Nanomax50 membrane.

Fig. 4 shows the effect of pH on NaCl rejection with three membranes. It was found that NaCl rejection decreased gradually when pH increased from 2 to 11, and negative NaCl rejection was found for all the NF270, Desal-5 DL, Nanomax50 membranes when pH > 6. This phenomenon was also found in the filtration of other fluids [8,28,29]. This could be attributed to a number of mechanisms, such as the charge repulsion effect, the charge equilibriums and the competition for permeation between co-ions with different diffusion, size and charge [28]. In our case, the membranes were negatively charged at pH > 6, Cl^- could pass through the membrane more freely than IDA^- and IDA^{2-} since the later two possess bigger size or higher charge, resulting in chloride enrichment in the permeate.

Fig. 5 shows the effect of pH on TMP with three membranes. As shown in Fig. 5, except for NF270, when the pH increased, the trends of TMP variation were similar with IDA rejection trends. NF270 has the highest rejection of IDA and NaCl at pH < 7 (Figs. 3 and 4), resulting in the highest TMP in the present work due to concentration polarization caused by the retained IDA and NaCl. When pH > 7, the NaCl rejection of NF270 became negative and the difference of IDA rejection between NF270 and Desal-5 DL was small (Figs. 3 and 4). Therefore, the highest TMP with Desal-5 DL at pH > 7 could be due to its lowest water permeability (see Table 1). Because NF270 showed a highest recovery of IDA, it was chosen to further examine the feasibility of recovering IDA under the conditions similar to the practical effluent in IDA production (e.g. pH 5.0–5.2).

3.2. *Effect of permeate flux*

Permeate flux is a key operating factor affecting membrane filtration since it could significantly affect concentration polarization and membrane fouling during filtration operation, as well as separation of the solutes in solution. Fig. 6 shows the effect of permeate flux on the rejection of IDA and NaCl at pH 5.2. With the increase of flux, IDA rejection was almost constant while NaCl rejection increased slightly and negative rejection of NaCl was found at flux <33.19 L m^{-2} h^{-1}. Similar results were also found by Yunoki et al. [8], they reported that the apparent rejection of Cl^- decreased with decreasing permeate flux. As shown in Fig. 6, the relation between TMP and flux showed a perfect linearity, suggesting that the filtration was operated below the “critical flux” [30]. Measurement of membrane resistance before and after filtration suggested that membrane fouling could be negligible (data not shown).

3.3. *Effect of temperature*

Increasing temperature will lead to an increasing mass transfer of both water and solutes, thus affecting the concentration

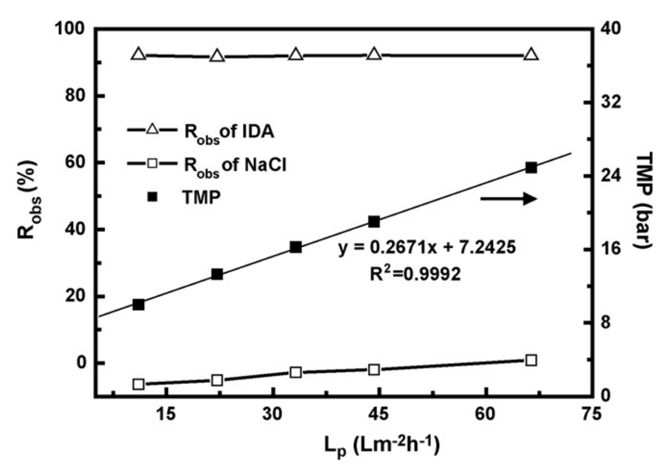

Fig. 6. Effect of permeate flux on solute rejection and TMP with NF270. IDA: 30 g L^{-1}, NaCl: 1.37 mol L^{-1}, pH 5.2, *T*: 25 °C, stirring speed: 1200 rpm.

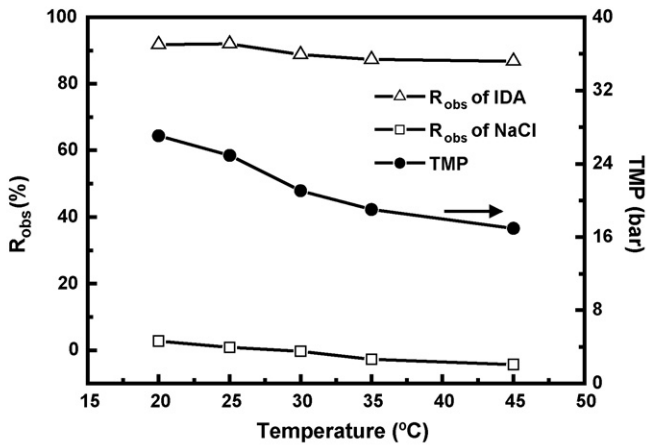

Fig. 7. Effect of temperature on solute rejection and TMP with NF270. IDA: 30 g L^{-1}, NaCl: 1.37 mol L^{-1}, pH 5.2, flux: 66.37 L m^{-2} h^{-1}, stirring speed: 1200 rpm.

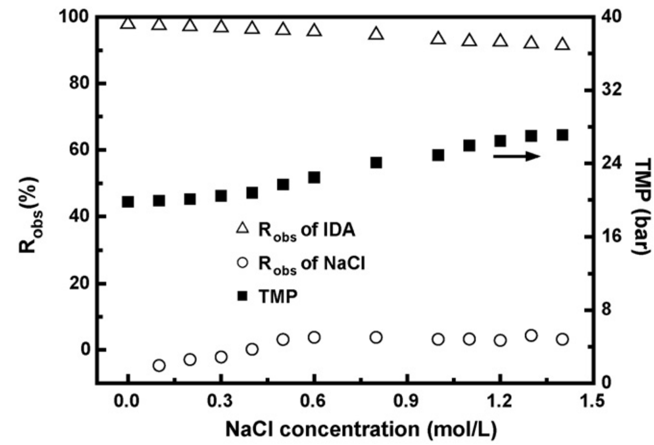

Fig. 8. Effect of NaCl concentration on solute rejection and TMP with NF270. IDA: 30 g L^{-1}, pH 5.2, flux: 66.37 L m^{-2} h^{-1}, *T*: 25 °C, stirring speed: 1200 rpm.

polarization, flux and solutes rejection. Fig. 7 shows the effect of temperature on the rejection and TMP obtained at flux of 66.37 L m^{-2} h^{-1}. As the temperature went up, the TMP in filtration decreased significantly at constant flux, this could be attributed to an increase in water diffusion and a decrease in the viscosity of the solution with increasing temperature. However, higher temperature inevitably resulted in some changes in solutes observed rejections (Fig. 7). The reasons could be, firstly, higher temperature accelerated the solutes diffusion through the membrane because of the higher diffusivity of solutes and the lower viscosity of solution. Secondly, because the layer of adsorbed water molecules on the pore walls became thinner at higher temperature, the hydrodynamic drag forces inside the pores would be decreased as the effective pore diameter increased with temperature, as reported by Tsuru et al. [31] and Goulas et al. [32], thus the solutes could more easily pass through membrane pores. Thirdly, with increasing temperature, there was a decrease in concentration polarization due to the increase of the diffusivity of solutes molecules, as a result, the concentration of solutes at membrane surface would be reduced, and a decrease in TMP and the observed rejection of IDA would be expected. Nevertheless, IDA can be largely retained by NF 270 while NaCl can pass through the membrane freely due to the dominant size effect, therefore, the changes in IDA and NaCl rejection were not remarkable.

3.4. Effect of NaCl and IDA concentration

It is well known that the existence of salt can affect the solutes permeation in NF due to charge screening effect and salt induced membrane swelling, as reported by Freger et al. [7,25] and Bouchoux et al. [33]. As shown in Fig. 8, when NaCl concentration increased from 0 to 1.4 mol L^{-1}, the IDA rejection decreased gradually from 98.8% to 90.8%. The possible explanation could be the increase of membrane permeability due to membrane swelling [33,34] or/and charge screening effect under higher salinity conditions [24]. At pH 5.2, IDAH$^-$ would be the dominant species in solution. The effects of NaCl concentration on charge screening could be interpreted with the Debye screening length (κ^{-1}), where $\kappa^{-1} \propto 1/C^{1/2}$, and *C* is the concentration of the electrolyte solution [26]. With increasing NaCl concentration, the Debye screening length (κ^{-1}) will decrease and a “denser” concentration polarization layer will be formed. All these will increase the transmission of IDA and in turn reduce the rejection. Moreover, the increase in TMP with NaCl concentration could also be attributed to the formation of the denser concentration polarization layer.

As far as NaCl rejection was concerned, the rejection increased with increasing NaCl concentration in the range from 0 to 0.4 mol L^{-1}, and when NaCl concentration was more than 0.4 mol L^{-1}, the rejection was more or less constant. On the whole, NaCl could not be retained by the membrane.

Fig. 9 shows the effect of IDA concentration on solute rejection and TMP. As shown in Fig. 9, with an increase in IDA concentration, there was a slight decrease in IDA rejection, while the decrease in NaCl rejection was more pronounced. The decreasing IDA rejection with increasing IDA concentration in feed could be attributed to the increased wall concentration of IDA due to concentration polarization.

Fig. 9 also shows that NaCl rejection decreased with increasing IDA concentration, similar phenomenon was reported by Yunoki et al. [8] in NF of amino acid and sodium chloride solution. This may be explained by salt induced membrane swelling since increasing IDA concentration could also increase the salinity of the solution, thus making the membrane more permeable for NaCl. The increase in TMP with increasing IDA concentration could be due to concentration polarization alone since no detectable fouling was found by measuring the membrane resistance before and after filtration.

3.5. Diafiltration process

To evaluate the feasibility of NF for desalination of IDA, a continuous constant volume diafiltration (CVD) was conducted with

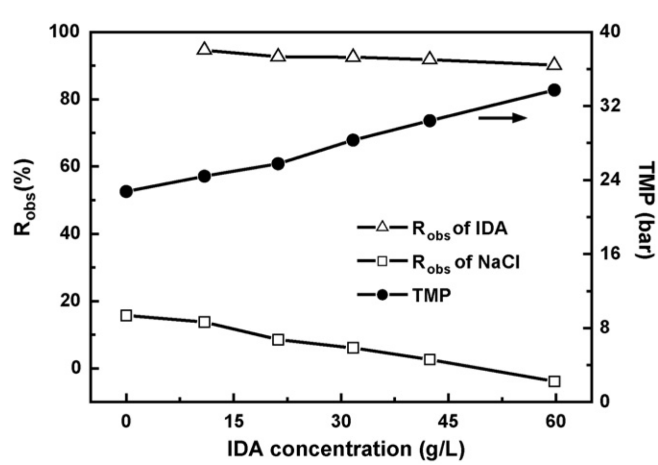

Fig. 9. Effect of IDA concentration on solute rejection and TMP with NF270. NaCl: 1.37 mol L^{-1}, pH 5.2, flux: 66.37 L m^{-2} h^{-1}, *T*: 25 °C, stirring speed: 1200 rpm.

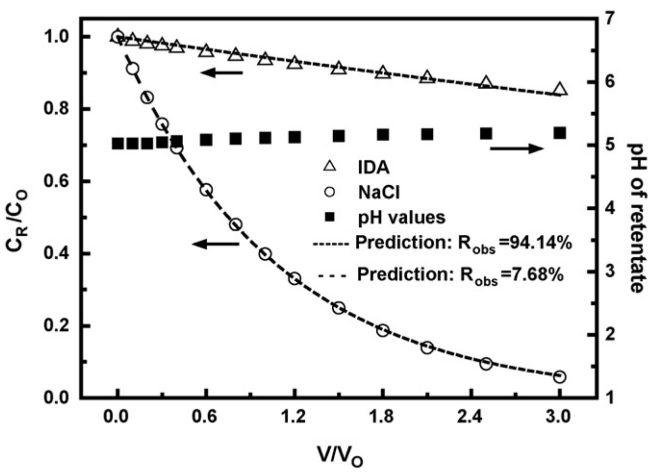

Fig. 10. Effect of V/V_0 on C_R/C_O and pH during diafiltration with NF270. $C_{O,\,IDA}$: 30 g^{-1}, $C_{O,\,NaCl}$: 1.37 mol^{-1}, pH 5, flux: 66.37 L m^{-2} h^{-1}, T: 25 °C, stirring speed: 1200 rpm.

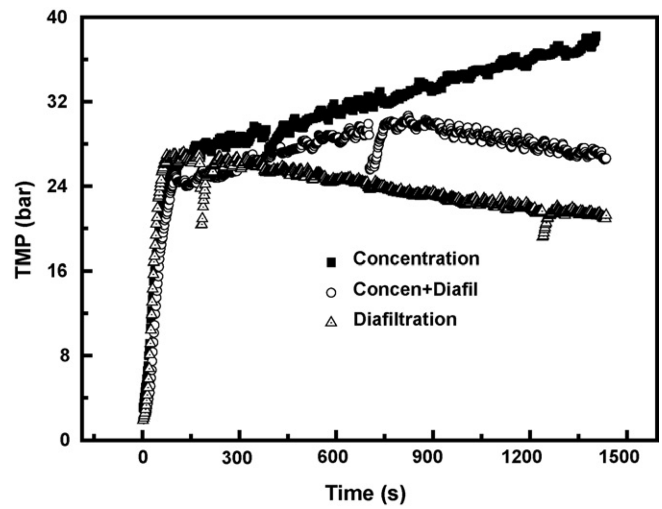

Fig. 11. TMP profiles during desalination in different modes.

the model solution containing IDA and NaCl. The experiment was carried at a constant flux of 66.37 L m^{-2} h^{-1} at 25 °C and the stirring speed kept at 1200 rpm. The initial IDA concentration was 30 g L^{-1} with pH 5.0. Fig. 10 shows the variation of pH and solute concentration in the retentate during dialfiltration. Based on the experimental results in Fig. 10, when diafiltration volume number (V/V_0) was 3, the recovery of IDA in retentate could be 85.2%, and 94.2% of NaCl was removed (only 5.8% NaCl in total remained in the solution). Moreover, unlike electrodialysis, pH only changed slightly during diafiltration, which could be easily adjusted by adjusting the pH of diluent if required.

A process simulation for diafiltration can be performed simply based on mass balance and rejection equations. For a constant volume system, the loss of a solute in the cell was equal to that found in the permeate, that is,

$$V_0 \mathrm{d}C = -C_\mathrm{p} \mathrm{d}V \tag{8}$$

Supposing the rejection was constant, by substituting Eq. (2) into Eq. (8), the following equation can be obtained at $V = 0$, $C = C_0$,

$$\frac{C_\mathrm{R}}{C_\mathrm{O}} = \exp\left[(R_\mathrm{obs} - 1)\frac{V}{V_0}\right] \tag{9}$$

where R_{obs} was the average rejection obtained from Fig. 8. The simulation results are shown in Fig. 10. It can be seen that the predicted values of solutes concentration agreed well with the experimental data, suggesting that this mathematical model could predict the concentration of solutes in retentate and provide a guide for process control in industrial production.

3.6. Operation modes

There were two conventional approaches for achieving solute recovery and salt removal: concentration and diafiltration [24,35]. To compare the performance under different operation modes, the membrane filtration was carried out at constant flux, and the filtration time was kept the same, therefore, the total volume to be processed (feed plus diluent) was the same (e.g. 25.6 mL in total, see Table 2). Table 2 shows the experimental results in diafiltration and concentration modes under the specific operating conditions. When concentration mode was used, the obvious advantages were that more feed could be processed and there was no water consumption. Moreover, IDA recovery was higher than that obtained in diafiltration mode, but its NaCl removal ratio was less than that in diafiltration mode. However, the TMP profile during concentration (Fig. 11) shows that it kept increasing rapidly and reached 38 bar (very close to the pressure limit of the membrane) very quickly, suggesting that concentration mode could be impractical in application. In diafiltration process, the TMP was much lower than that in concentration process, but it consumed quite a lot of water and the process efficiency was much lower in terms of feed being processed in a definite time duration.

To combine together the advantages of concentration and diafiltration modes, a new operation mode which employs both concentration and diafiltration was examined, as reported by Castino and Wickramasinghe [36]. The objective was to increase processing efficiency, reduce water consumption and ensure membrane filtration being performed in an acceptable TMP range. In the experiment, 19.2 mL feed was firstly concentrated to 12.8 mL, then the diafiltration step was performed with 6.4 mL deionized water in a CVD mode. The experimental results are also shown in Table 2 and Fig. 11. It can be seen that the new mode had much higher feed processing capability, much lower water consumption than diafiltration mode, and lower TMP than concentration mode. Therefore, the new operation mode could be more suitable for IDA recovery and desalination in terms of IDA recovery (95.8%), NaCl removal (58.4%) and relatively low TMP (<30 bar).

When the new operation mode is employed, water usage can be minimized by maximizing the feed volume processed in concentration step. However, as the feed is concentrated, the concentration of IDA in retentate will increase, hence leading to an increase in TMP. Therefore, there exists an optimum concentration factor in this new operation mode to obtain the least water usage while keeping the TMP not exceeding the pressure limit of the membrane during

Table 2
Effect of operation modes[a].

Operation modes	Feed volume (mL)	Water usage (mL)	IDA recovery (%)	NaCl removal (%)
Diafiltration	12.8	12.8	95.7	60.7
Concentration	25.6	0	96.8	49.5
Concentration + diafiltration	19.2	6.4	95.8	58.4

[a] Feed: IDA: 30 g L^{-1}, NaCl: 1.37 mol L^{-1}, pH 5.2, flux: 66.37 L m^{-2} h^{-1}, T: 25 °C, stirring speed: 1200 rpm.

operation. As for the pilot-scale test under constant pressure conditions, optimization of operation mode should involve minimizing the desalination time [36]. This work is still in progress.

An industrial feed sample supplied by a plant was also tested for IDA recovery and desalination using the new operation mode. The sample contained 45.5 g L^{-1} IDA, 112.6 g L^{-1} NaCl, pH 5.2. With the same processing procedure mentioned above, the recovery of IDA was about 95.6%, NaCl removal was 60.3%.

4. Conclusions

NF was employed to examine the desalination and recovery of IDA from its sodium chloride mixtures by NF at different pH, permeate flux, temperature and solutes concentration. Different operation modes were also studied. The conclusions can be summarized as follows:

(1) pH of solution played a key role in IDA recovery and NaCl removal. NF270, Desal-5 DL showed high rejection of IDA when pH > 4, and negative rejection of Cl^- was found in filtration at a certain range of pH for all membranes examined. In terms of TMP profile, IDA recovery and desalination performance, NF 270 was more suitable for IDA recovery and NaCl removal from the effluent in IDA production.

(2) When NF270 was used, at pH 5.1 ± 0.1, IDA rejection decreased slightly with the increase of temperature, NaCl and IDA concentration. Low flux, high temperature and high IDA concentration favored the transmission (or removal) of NaCl.

(3) IDA recovery and desalination by diafiltration could be simulated using a simple model, the experimental data agreed well with the calculated values. For practical purpose, a new operation which combines concentration and diafiltration modes was proposed and tested for IDA recovery and NaCl removal, showing great potential in IDA recovery and desalination in terms of IDA recovery (95.8%), NaCl removal (58.4%) and relatively low TMP (<30 bar).

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References

[1] B. Parker, Process for preparing N-phosphonomethyl iminodiacetic acid, US Patent 6,515,168 (2003).
[2] S. Maurizia, V. Sandra, D.A. Salvatore, Recovery of nickel from Orimulsion fly ash by iminodiacetic acid chelating resin, Hydrometallurgy 81 (2006) 9–14.
[3] B. Wasim, P. Brett, Determination of trace alkaline earth metals in brines using chelation ion chromatography with an iminodiacetic acid bonded silica column, J. Chromatogr. A 907 (2001) 191–200.
[4] Q.Y. Zeng, R.J. Xie, Y.F. Wang, Progress in synthesis and separation technology of iminodiacetic acid, Adv. Fine Petrochem. 2 (2001) 23–25 (Chinese).
[5] J.R.G. Ochoa, J.G. Santa-olalla, A.Z. de Diego, J.L.R. Martin, Isolation and purification of iminodiacetic acid from its sodium salt by electrodialysis, J. Appl. Electrochem. 23 (1993) 56–59.
[6] X.J. Zeng, G.W. Yang, X.X. Xu, G. Yang, Recovery experiment of iminodiacetic acid by electrodialysis, Ind. Water Wastewater 33 (2002) 31–32 (Chinese).
[7] V. Freger, T.C. Arnot, J.A. Howell, Separation of concentrated organic/inorganic salt mixture by nanofiltration, J. Membr. Sci. 178 (2000) 185–193.
[8] H. Yunoki, K. Nagata, K.I. Kokubo, A. Ito, A. Watanabe, Effects of the mixture ratio of amino acid and sodium chloride on the rejection of nanofiltration membranes under various operating conditions, J. Chem. Eng. Jpn. 35 (2002) 76–82.
[9] X.L. Wang, C.H. Zhang, P.K. Ouyang, The possibility of separation saccharides from a NaCl solution by using nanofiltration in diafiltration mode, J. Membr. Sci. 204 (2002) 271–281.
[10] S.G. Kang, Y.K. Chang, Removal of organic acid salts from simulated fermentation broth containing succinate by nanofiltration, J. Membr. Sci. 246 (2005) 49–57.
[11] E. Suáreza, A. Loboa, S. Álvarezb, F.A. Riera, R. Álvarez, Partial demineralization of whey and milk ultrafiltration permeate by nanofiltration at pilot-plant scale, Desalination 198 (2006) 274–281.
[12] S.U. Hong, M.D. Miller, M.L. Bruening, Removal of dyes, sugar, and amino acid from NaCl solutions using multilayer polyelectrolyte nanofiltration membranes, Ind. Eng. Chem. Res. 45 (2006) 6284–6288.
[13] R. Ghosh, Y.H. Wan, Z.F. Cui, G. Hale, Parameter scanning ultrafiltration: rapid optimization of protein separation, Biotechnol. Bioeng. 81 (2003) 673–682.
[14] Y.H. Wan, S. Vasan, R. Ghosh, G. Hale, Z.F. Cui, Separation of monoclonal antibody alemtuzumab monomer and dimers using ultrafiltration, Biotechnol. Bioeng. 90 (2005) 422–432.
[15] Y.H. Wan, J.R. Lu, Z.F. Cui, Separation of lysozyme from chicken egg white using ultrafiltration, Sep. Purif. Technol. 48 (2006) 133–142.
[16] E. Sjöman, M. Mänttäri, M. Nyström, H. Koivikko, H. Heikkilä, Separation of xylose from glucose by nanofiltration from concentration monosaccharide solutions, J. Membr. Sci. 292 (2007) 106–115.
[17] V. Antonucci, D. Yen, J. Kelly, L. Crocker, E. Dienemann, R. Miller, O. Almarrsson, Development of a nanofiltration process to improve the stability of a novel anti-MRSA carbapenem drug candidate, J. Pharm. Sci. 91 (2002) 923–932.
[18] M. Mänttäri, A. Pihlajamäki, M. Nyström, Effect of pH on hydrophilicity and charge and their effect on the filtration efficiency of NF membranes at different pH, J. Membr. Sci. 280 (2006) 311–320.
[19] T. Chaabane, S. Taha, M.T. Ahmed, R. Maachi, G. Dorange, Removal of copper from industrial effluent using a spiral wound module–film theory and hydrodynamic approach, Desalination 200 (2006) 403–405.
[20] R. Schneider, F. Zürcher, T. Egli, G. Hamer, Ion chromatography method for iminodiacetic acid determination in biological matrices in the presence of nitrilotriacetic acid, J. Chromatogr. 462 (1989) 293–301.
[21] A.C. Morão, A.B. Alves, M.D. Afonso, Concentration of clavulanic acid broths: influence of the membrane surface charge density on NF operation, J. Membr. Sci. 281 (2006) 417–428.
[22] H.R. Lin, Determination of iminodiacetic acid, Guangxi Chem. Ind. 31 (2002) 36–38 (Chinese).
[23] M.R. Teixeira, M.J. Rosa, M. Nystrom, The role of membrane charge on nanofiltration performance, J. Membr. Sci. 265 (2005) 160–166.
[24] N. Capelle, P. Moulin, F. Charbit, R. Gallo, Purification of heterocyclic drug derivatives from concentrated saline solution by nanofiltration, J. Membr. Sci. 196 (2002) 125–141.
[25] V. Freger, Swelling and morphology of the skin layer of polyamide composite membranes: an atomic force microscopy study, Environ. Sci. Technol. 38 (2004) 3168–3175.
[26] M. Nilsson, G. Tragardh, K. Ostergren, The influence of pH, salt and temperature on nanofiltration performance, J. Membr. Sci. 312 (2008) 97–106.
[27] S. Saksena, A.L. Zydney, Effect of solution pH and ionic strength on the separation of albumin from immunoglobulins (IgG) by selective filtration, Biotechnol. Bioeng. 43 (1994) 960–968.
[28] A. Bouchoux, H.R. Balmann, F. Lutin, Investigation of nanofiltration as a purification step for lactic acid production processes based on conventional and bipolar electrodialysis operations, Sep. Purif. Technol. 52 (2006) 266–273.
[29] M. Vourch, B. Balannec, B. Chaufer, G. Dorange, Nanofiltration and reverse osmosis of model process waters from the dairy industry to produce water for reuse, Desalination 172 (2005) 245–256.
[30] R.W. Field, D. Wu, J.A. Howell, B.B. Gupta, Critical flux concept for microfiltration fouling, 100 (1995) 259–272.
[31] T. Tsuru, S. Izumi, T. Yoshioka, M. Asaeda, Temperature effect on transport performance by inorganic nanofiltration membranes, AIChE J. 46 (2000) 565–574.
[32] A.K. Goulas, P.C. Kapasakalidis, H.R. Sinclair, R.A. Rastall, A.S. Grandison, Purification of oligosaccharides by nanofiltration, J. Membr. Sci. 209 (2002) 321–335.
[33] A. Bouchoux, H.R. Balmann, F. Lutin, Nanofiltration of glucose and sodium lactate solutions variations of retention between single- and mixed-solute solutions, J. Membr. Sci. 258 (2005) 123–132.
[34] G. Bargeman, J.M. Vollenbroek, J. Straatsma, C.G.P.H. Schoren, R.M. Boom, Nanofiltration of multi-component feeds. Interaction between neutral and charged components and their effect on retention, J. Membr. Sci. 247 (2005) 11–20.
[35] W.R. Bowen, A.W. Mohammad, Diafiltration by nanofiltration: prediction and optimization, AIChE J. 44 (1998) 1799–1812.
[36] F. Castino, S.R. Wickramasinghe, Washing frozen red blood cell concentrates using hollow fibres, J. Membr. Sci. 110 (1996) 169–180.