Journal of Membrane Science 509 (2016) 105–115

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Refining sugarcane juice by an integrated membrane process: Filtration behavior of polymeric membrane at high temperature

Jianquan Luo*, Xiaofeng Hang, Wei Zhai, Benkun Qi, Weijie Song, Xiangrong Chen, Yinhua Wan*

State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, PR China

ARTICLE INFO

Article history:
Received 15 December 2015
Received in revised form
12 February 2016
Accepted 24 February 2016
Available online 27 February 2016

Keywords:
Juice clarification
Decoloration
Ultrafiltration
Nanofiltration
Membrane fouling

ABSTRACT

Application of membrane filtration to sugarcane juice refining is appealing because it can eliminate the usage of chemicals, achieve continuous and automated production, as well as produce superior quality of juice. However, some technical problems, such as low permeate flux, high sucrose loss in membrane retentate and serious membrane fouling, are impeding this technological upgrading in sugar industry. In this work, an integrated membrane process consisting of a tubular loose ultrafiltration (UF), a spiral-wound tight UF and a spiral-wound NF was developed to refine the raw sugarcane juice at pilot-plant scale. With a super high volume reduction ratio (VRR) of 20, the loose UF was able to be operated at a flux from 30 to 70 L m^{-2} h^{-1}, and the tight UF could run at a flux from 10 to 40 L m^{-2} h^{-1}; at the same time, the color removal kept more than 95%. Moreover, diafiltration operation could recover most of sugar in the UF concentrates, leading to a high sucrose recovery of up to 98% in two-stage UF. A novel cascade diafiltration mode was proposed to save water by 25% compared with the separated diafiltration. Mathematical models could well predict the diafiltration efficiency for the loose UF but not for the tight UF. Permeate flux of the loose UF was dominated by membrane fouling while for the tight UF, osmotic pressure played a more important role in the flux decline. With a suitable cleaning strategy, the performance of this integrated membrane process can be nearly regenerated although the temperature jump between filtration and cleaning (60–30 °C) might result in some foulants accumulating in the membrane system. These results would serve as a valuable guide for process design and practical operation in subsequent industrial application.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The manufacture of plantation white sugar contains several successive steps: (1) juice extraction from cane or beets by crushing; (2) clarification and decoloration of raw juice; (3) concentration of clarified juice by multi-effect evaporation; (4) syrup sulphitation; (5) crystallization [1–3]. The second step plays a vital role in the sugar quality and productivity [4]. Conventional purification treatment involves addition of lime and sulfur dioxide, followed by boiling the treated juice, and the resulting sludge is then removed by sedimentation and vacuum filtration [2,3]. However, due to the addition of chemicals as well as manual and batch operation, this traditional refining method suffers from inferior and unstable product quality, high operation and reagent costs, and serious environmental problems caused by solid waste [1,4]. Therefore, alternative processes, such as activated carbon adsorption [5,6], electrodialysis [7], ion exchange [8] and membrane filtration [4,9], were explored to solve the above-mentioned problems. Among these methods, membrane filtration, particularly ultrafiltration (UF) is considered as the most promising one because it can eliminate the usage of chemicals, achieve continuous and automated production, and produce superior quality of juice [1,10].

Although research on the purification of sugarcane juice by membrane filtration began in the early 1970s [11], the use of membranes for this application is rare in Chinese sugar mills, and, indeed, the world [1,12]. In fact, there are three technical limitations impeding this technological upgrading in sugar industry. First, there was a trade-off between permeate flux and color removal [13,14]. For instance, Hamachi et al. found that when color removal increased from 37% to 55% by using the membrane with smaller pore size, the steady flux decreased by 69% [13]. In a pilot-plant test, Ghosh and Balakrishnan observed a low permeate flux of 7 L $m^{-2}h^{-1}$ with a color removal of 47% [15]. To break this trade-off, the development of high-performance membrane (higher porosity and stronger antifouling performance) and

* Corresponding authors.
E-mail addresses: jqluo@ipe.ac.cn (J. Luo), yhwan@ipe.ac.cn (Y. Wan).

http://dx.doi.org/10.1016/j.memsci.2016.02.053
0376-7388/© 2016 Elsevier B.V. All rights reserved.

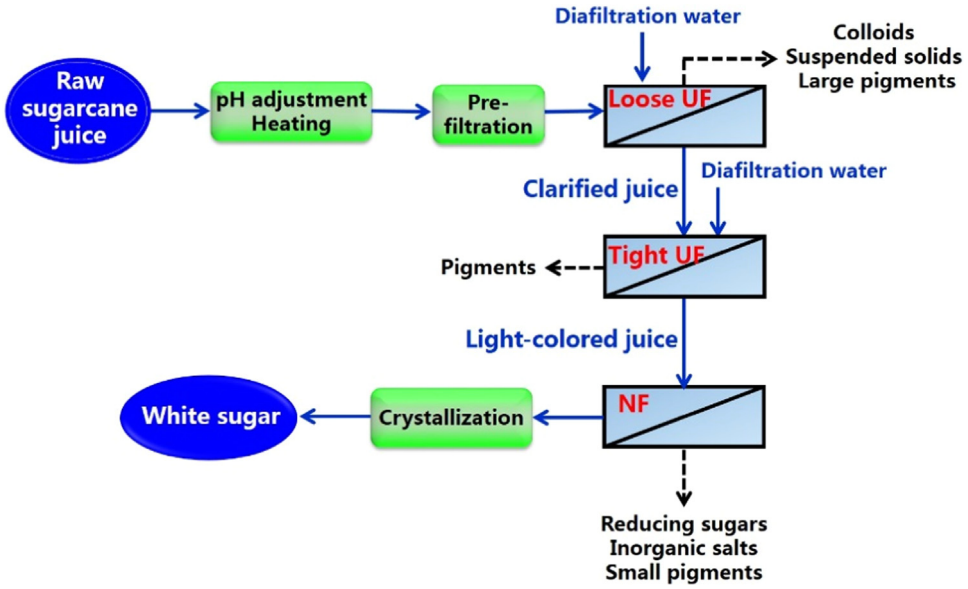

Fig. 1. Schematic diagram of sugar production from sugarcane juice by an integrated membrane process.

Table 1
Characteristics of raw sugarcane juice after pH adjustment and pre-filtration.

Index	Value
Brix (%)	12.9–15.2
Purity (%)	62.7–70.5
Sucrose (%)	8.2–10.4
Color (IU/560 nm)	15000–30000
Turbidity (MAU/560 nm)	21000–41000
Reducing sugar (%)	1.7–3.2
Conductivity ash (%)	0.019–0.020
pH	6.9–7.5
Density (g mL^{-1})	1.07

process integration are required. Second, the sugar loss in the UF concentrate would debase the benefit of this technology since UF membrane could retain some sugar [3,14]. Additional chemical treatment for the UF concentrate would introduce harmful agents into the juice, thus reducing the added-value of the by-products. Diafiltration operation may recover most of the residual sugar without adding chemicals [16], while there has few report yet regarding the sugar recovery from the UF concentrate [9]. Third, due to the high viscosity and complex composition of raw sugarcane juice, severe membrane fouling (e.g. cake layer and pore narrowing) and flux decline would occur with processing time, especially at a high Brix of juice [12,17,18]. Saha et al. claimed that polysaccharide fractions in sugarcane juice mainly contributed to membrane fouling [19], and they also modified commercial UF membranes with poly(ethylene glycol) methacrylate (PEGMA) monomer to control the fouling caused by polysaccharides in sugarcane juice [20]. Moreover, Balakrishnan and co-workers made great efforts to scale up the trials in the sugar mills [2,15,21], and they applied spiral wound UF modules (20 kD, polyethersulphone) to clarify the raw sugarcane juice (10 m^3/h) for more than 180 h, however, the flux is too low to meet the demand of industrialization [15]. Therefore, in order to industrialize this technology, more efforts regarding membrane selection/integration, residual sugar recovery, fouling mechanism and membrane cleaning should be made at pilot-plant scale.

On the other hand, due to the high viscosity of the sugarcane juice and the pretreatment demand, the purification of sugarcane juice by membrane filtration should be carried out at above 50 °C in sugar mills. This provides an opportunity to study filtration behavior of polymeric membrane at high temperature, since the relevant literature was quite scarce. Poly (phthalazine ether sulfone ketone) (PPESK) membrane is thermostable and commonly applied at high temperature. Generally, the permeate flux of PPESK membrane was increasing with temperature, while the retention started to decline when the temperature was more than 60 °C [22,23]. For other membrane materials, such as polyethersulfone, polysulfone, regenerated cellulose and polyamide, Kowalska et al. found that the retention was decreasing when temperature increased from 25 to 55 °C [24]. Manttari et al. claimed that an increase in temperature decreased the retention until a critical temperature of the membrane was exceeded (~60 °C), and after that temperature the flux even decreased and the retention increased [25]. At elevated temperature, the higher permeate flux could be explained by the lower feed viscosity, while the greater diffusion coefficient and larger effective pore diameter of membrane might cause a reduction in retention [26]. However, the concentration polarization would be reduced at higher temperature (faster back diffusion), which might increase the observed retention. Moreover, the severe fouling formation at high temperature was also likely to be responsible for the retention augment mentioned by Manttari et al. [25]. These previous studies mostly focused on the permeate flux and retention of the membranes [10]. To the best of our knowledge, there has been no report regarding the fouling behavior and cleaning strategy when the membrane is operated at high temperature (~60 °C).

The present work aimed at establishing an integrated membrane process to obtain both high color removal and satisfactory permeate flux in refining sugarcane juice. As shown in Fig. 1, a loose tubular UF (with big pore size) was applied to remove colloids, suspended solids and large pigments in sugarcane juice, and a tight spiral wound UF (with small pore size) was employed to further decolorize the clarified juice, and then a spiral wound nanofiltration (NF) was used to concentrate the final UF permeate and at the same time decrease the contents of reducing sugar, salts and small pigments in the syrup. Efforts were also made to recover sugar from the UF retentate by different diafiltration operations. Moreover, flux behavior and fouling mechanisms during the UF/NF concentration process at high temperature were illustrated, and membrane cleaning and long-term operation stability of sugarcane juice refining by membrane filtration at pilot-plant scale were investigated.

2. Materials and methods

2.1. Sugarcane juice and chemicals

Raw sugarcane juice was directly taken and used from a local sugar mill in Zhanjiang, Guangdong Province, China. Raw sugarcane juice was pretreated by pH adjustment using NaOH solution in order to retard microbial growth and sucrose conversion. Subsequently, the sugarcane juice (pH = 7.2 ± 0.3) was heated to 70 °C, and then filtrated by a filter-bag with 50 μm pore size to remove some precipitates and solids. Fresh raw sugarcane juice was used for each set of experiments. The characteristics of the raw sugarcane juice after pH adjustment and pre-filtration are shown in Table 1.

All chemicals used for pretreatment, cleaning and sterilizing were of food grade, provided by the local sugar mill. The proprietary cleaning agent was composed of alkali and surfactant, and a concentration of 0.2–0.3% (*w*/*v*) (pH = 11.6 ± 0.3) was used in the present work except elsewhere stated. 500 ppm (pH = 11.3 ± 0.2) was applied for loose UF cleaning. NaOH solution (pH = 11) and citric acid solution (pH = 2) were also used for tight UF cleaning. When the membrane systems were stopped for more than 24 h, the membrane modules were filled with 1% (*w*/*v*) $NaHSO_3$ solution to prevent bacterial growth.

2.2. Equipment and membrane modules

Homemade pilot devices for tubular and spiral wound membrane modules were used in the experiments, equipped with 100 L capacity feed tanks, as displayed in Fig. 2. For tubular membrane system, a centrifugal pump (CRN5-8, Grundfos, Denmark) was furnished for both feeding and cleaning, and the transmembrane pressure (TMP) was adjusted by the retentate valve. TMP was read from manometers, which was kept at 0.24 ± 0.04 bar during the sugarcane juice treatment. Crossflow/permeate velocities were measured by rotameter, but due to the dark color of raw juice, the crossflow velocity value could not be obtained. While for spiral wound membrane system, two multistage pumps (CRN3-36, Grundfos, Denmark) were furnished for feeding and cleaning, respectively. Pressure was measured by pressure sensor and displayed on the panel, which was maintained at 10.5 ± 0.5 bar for tight UF and at 20.5 ± 0.5 bar for NF during the refining process, respectively. The crossflow velocity was kept at around 65 L min^{-1} and 35 L min^{-1} for tight UF and NF, respectively. Operating temperature was controlled at approximately 60 °C by circulating cooling water except for cleaning procedure.

For tubular membrane device, eight modules were equipped with a total membrane area of 2 m^2, and polyvinylidene fluoride (PVDF) tubular UF membrane with pore size of 30–50 nm was purchased from X-Flow, Netherlands. For spiral wound membrane device, only one of pressure vessels loaded with a UF or NF module (effective membrane area of 5 m^2) was used for each test. Polyethersulphone (PES) UF membrane with pore size of ~5 nm and polyamide NF membrane with pore size of ~0.5 nm were provided by Sepro Membranes, USA. All the membrane modules used were of food grade.

2.3. Experimental procedure

All new membrane modules were rinsed by boiled water (cooled to around 30 °C and then filtrated by a filter-bag with 50 μm pore size) for 1 h before use. First, the raw sugarcane juice after pretreatment was filled into the feed tank of the loose UF system, which was operated under concentration mode with volume reduction ratios (VRRs) of 5–20 and then under diafiltration mode with boiled water (60 °C) as diluent. Second, the clarified juice (permeate of loose UF) was transported to the tight UF system, and after concentrating at VRRs of 10–20, the diafiltration operation was also carried out to recover sugar residue. In order to simplify this process, all the UF permeate during diafiltration was not used as feed for the subsequent steps. Third, the light-colored juice (permeate of tight UF) was concentrated by NF at VRRs of 1.7–2.5. The raw juice and purified products at different stages were collected for analysis, and all the analyses were conducted immediately.

Two typical diafiltration modes were employed in this work: dilution-concentration and constant volume diafiltration (CVD) [27]. For dilution-concentration mode, the UF concentrate was diluted with water (the same volume as the concentrate) and then concentrated to its original volume; while for CVD, water addition velocity was the same as the permeate flux and the feed volume

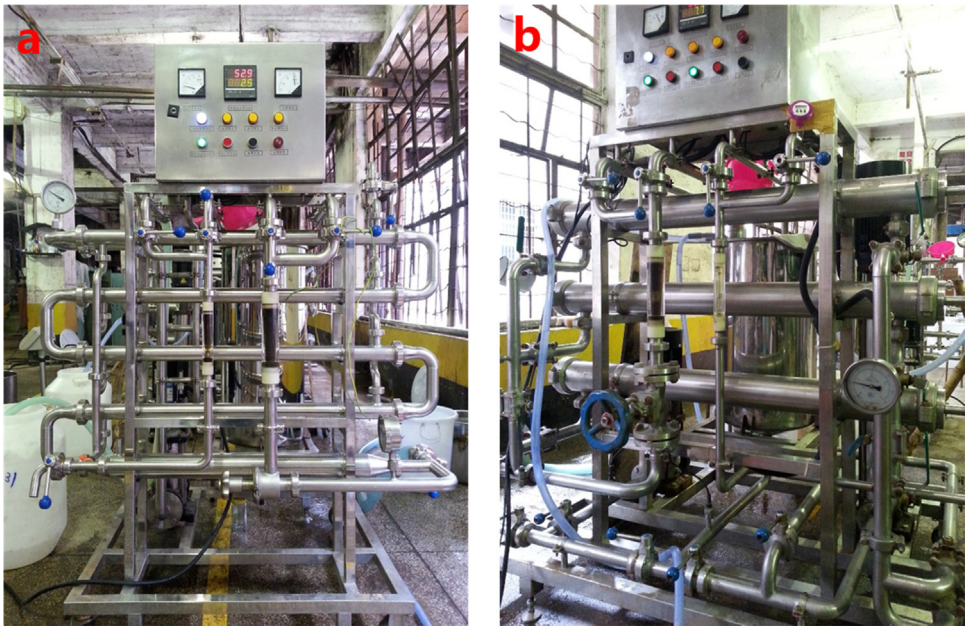

Fig. 2. Photographs of the pilot equipment for (a) tubular loose UF module (clarification of raw sugarcane juice) and (b) spiral wound tight UF and NF modules (decolorization and concentration of sugarcane juice).

was kept constant during diafiltration. Because diafiltration operation was applied to both loose and tight UF systems, there are two different approaches to conduct the CVD: separated and cascade diafiltrations. For separated one, fresh water was added into both loose and tight UF concentrates and this process was carried out intermittently. For cascade one, fresh water was only added into loose UF concentrate and the resulting permeate was used as diluent for the tight UF, making this process continuous.

To evaluate the fouling or cleaning effect of each test, water permeability (L_p) of membrane modules was measured before and after feed filtration and cleaning, respectively. All the membrane modules were cleaned by water and then different chemical agents after each test. For PVDF tubular membrane, it was cleaned with 0.3% cleaning agent solution for 40 min without pressure and then 500 ppm NaClO solution was used for deep cleaning (40 min) at 0.1 bar. For PES and polyamide spiral wound membranes, they were cleaned with 0.2% cleaning agent solution for 40 min at 1 bar. Other cleaning conditions were also adopted for comparison. All cleaning temperatures were kept at 30–35 °C.

2.4. Analytic methods

Sucrose concentration, color, turbidity, reduced sugar concentration and conductivity ash were analyzed by Product Inspection Centre of Guangdong Hengfu Group Sugar Industry Co., Ltd, according to the National Standard of the People's Republic of China GB 317-2006 [28], where color and turbidity were determined by spectrophotometer at absorbance 560 nm rather than 420 nm. Juice Brix was measured by a digital refractometer (A1701000, ATAGO, Japan) after filtration through Whatman filter paper. Purity was defined as the ratio of sucrose concentration to Brix. The pH values were measured by a pH meter (PHS-3C, REX, China).

3. Results and discussion

3.1. Membrane separation performance and product properties

As shown in Table 1, the raw sugarcane juice after pretreatment still contains a large amount of impurities, such as colloids, suspended solids, pigments, reducing sugar and inorganic salts, and thus the purity was only 62.7–70.5%. Due to the presence of colloids and suspended solids, it was prone to foul the membrane not only on the membrane surface but also in the flow channels of membrane modules. Therefore, tubular membrane module was selected to remove the main foulants in the first stage because it has large flow channels and enables super high crossflow velocity (80–100 L min^{-1}) (i.e. strong antifouling performance). As listed in Table 2, after the loose UF treatment, Brix, purity, sucrose, reducing sugar and conductivity ash did not change significantly, while color and turbidity greatly decreased from 19488 to 6077 IU and from 29122 to 261 MAU (milli attenuation units), respectively. This indicated that the large pigment molecules (i.e. fat-soluble pigment coagulations), most colloids and suspended solids were removed by the loose UF. The resulting permeate could be directly treated by spiral wound UF membrane module (high membrane packing density but respectively low antifouling performance) with smaller pore size to further remove the pigments. After the tight UF treatment, color in the juice decreased to 800 IU and turbidity was only 4.4 MAU, and this also was confirmed by the appearance comparison between the loose and tight UF permeates (Fig. 3). However, since this tight UF could retain sucrose to some extent, Brix, purity and sucrose concentration also declined (Table 2), leading to lower sugar productivity in crystallization stage. It is worth mentioning that the reducing sugar concentration in the tight UF permeate increased slightly due possibly to the sucrose conversion. Finally, NF was used to concentrate the light-colored juice. As shown in Table 2, Brix and sucrose are expectedly elevated because NF can almost fully retain sucrose. Purity became higher due to the partial removal of reducing sugars, small pigments and salts. Surprisingly, the color value of the NF retentate obviously decreased compared with that of the tight UF permeate, though the appearance looked more yellow for the NF retentate as displayed in Fig. 3. Because concentration mode was used in this trial, the color substance in NF retentate would not be lower than that in the feed (i.e. tight UF permeate). According to the color determination method [12,28], the color value was inversely proportional to the refractometric dry substances (Brix). As Brix of the NF retentate increased by 62% compared with that of the tight UF permeate, the color value was correspondingly decreased. Moreover, compared with the tight UF permeate, the sucrose concentration in the NF retentate increased by 74% while the reducing sugar concentration only raised by 50% (remembering that sucrose conversion to reducing sugars might be proceeding during the refining process), implying that this NF membrane could partly separate sucrose and reducing sugars. Most salts could pass through the NF membrane because conductivity ash only increased by 5% after NF concentration. As shown in Fig. 3, the NF permeate is clear and nearly colorless, and the total sugar concentration in the permeate is only about 0.1–0.3% (w/v). A mass balance of sucrose across the filtration process was provided in Supplementary information (Fig. S1).

Table 2 also shows the improvement of the final product (NF retentate) compared with the raw juice. Purity increased by 4.38%, indicating that sucrose productivity would enhance and more sucrose crystal could be obtained from the juice during the multi-effect evaporation, which greatly increased the benefits of this process. The sucrose concentration was improved by 50%, meaning that lots of water in the juice was removed and energy requirement in the multi-effect evaporation could be decreased. The color and turbidity removals were 96.55% and 99.99%, respectively,

Table 2
Characteristics of products in all stages.

Index	Raw juice	Loose UF permeate	Tight UF permeate	NF retentate	Comparison of NF retentate and raw juice (%)
Brix (%)	14.1 ± 0.9	14.0 ± 0.8	12.6 ± 1.5	20.4 ± 1.1	+44.68
Purity (%)	66.2 ± 4.0	66.3 ± 5.4	64.5 ± 5.3	69.1 ± 2.4	+4.38
Sucrose (%)	9.39 ± 0.9	9.25 ± 0.8	8.1 ± 1.4	14.1 ± 0.5	+50.16
Color (IU/560 nm)	19488 ± 2011	6077 ± 173	800 ± 121	673 ± 134	−96.55
Turbidity (MAU/560 nm)	29122 ± 1011	261 ± 131	4.4 ± 3.7	4.25 ± 3.0	−99.99
Reducing sugar (%)	1.55 ± 0.19	1.48 ± 0.3	1.6 ± 0.3	2.4 ± 0.3	+54.84
Conductivity ash (%)	0.02 ± 0.001	0.02 ± 0.001	0.02 ± 0.001	0.021 ± 0	+5.00

Experimental conditions: the raw sugarcane juice after pH adjustment and pre-filtration was concentrated by the loose UF membrane with a VRR of 6, and the loose UF permeate was concentrated by tight UF membrane with a VRR of 10, and then the tight UF permeate was concentrated by the NF membrane with a VRR of around 2. VRR was the volume ratio of initial feed and concentrate.

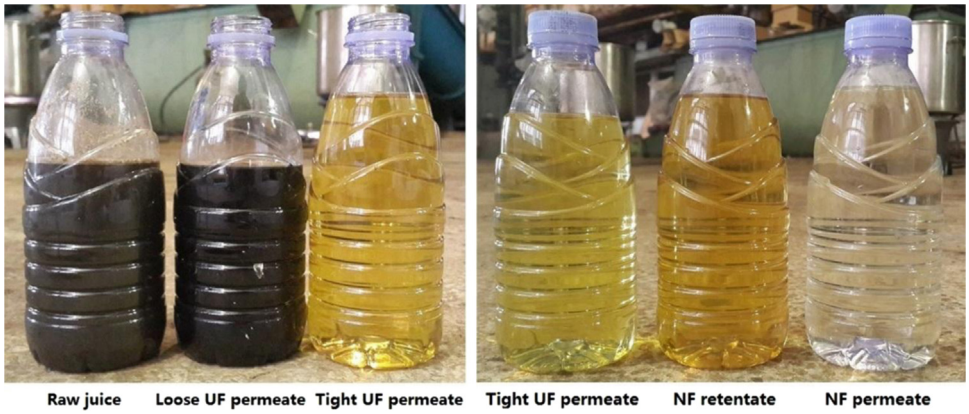

Fig. 3. Images of sugarcane juice products after loose UF clarification, tight UF decolorization and NF concentration.

which were the highest in the reported results regarding membrane filtration of sugarcane juice [1]. The color value of the final product was below 800 IU, and Saska mentioned that a decolorized syrup should have no more than 800 IU color for successful refining to white sugar having a color below 25 IU [4], which was defined as superior grade of white sugar in China [28]. Therefore, due to the superior permeate quality, this integrated membrane process (two-stage UF followed by NF) could replace the traditional method for clarification and decoloration of raw sugarcane juice. However, during this two-stage UF process, concentration factor (i.e. VRR) could not exceed 25 in order to keep a satisfactory flux, and thus a quite large quantity of concentrated juice (about one tenth of the total volume) with a high concentration of sucrose was produced (i.e. the UF retentate or UF concentrates), which would be a big sugar loss if such UF concentrates were discarded without treatment. In order to further improve the economic benefits of this technology, recovery of residual sugar in UF concentrates by diafiltration was carried out in the following study.

3.2. Recovery of residual sugar in UF concentrates by diafiltration

3.2.1. Mathematical models for diafiltration

3.2.1.1. Dilution-concentration mode. UF concentrates were first diluted with the same volume of water and then concentrated to its original volume. During the concentration step, the solute mass in the retentate is equal to the feed (diluted solution) mass minus the mass in the permeate:

$$C_r V_r = C_f V_f - C_p V_p \tag{1}$$

where C_r, C_f and C_p are the solute concentrations in retentate, feed and permeate, respectively, V_r, V_f and V_p are the volume of retentate, feed and permeate, respectively.

Average observed retention (R_{obs}) of solutes is defined as:

$$R_{obs}(\%) = \left(1 - \frac{C_p}{C_{r,av}}\right) \times 100 \tag{2}$$

where $C_{r,\,av}$ is the average solute concentration in retentate for one concentration cycle.

$$C_{r,av} = \frac{1}{2} \times \left(\frac{1}{2} C_{r,n} + C_{r,n+1}\right) \tag{3}$$

where $C_{r,\,n}$ and $C_{r,\,n+1}$ are the retentate concentrations in the n and $n+1$ cycles, respectively. Here $C_{r,\,n} = 2C_{f,\,n+1}$.

Assuming that solute retention is constant during diafiltration, substituting Eq. (3) into Eq. (2), following equation can be obtained:

$$\frac{C_{r,n+1}}{C_{r,n}} = \frac{R_{obs} + 3}{6 - 2R_{obs}} \tag{4}$$

3.2.1.2. Constant volume diafiltration (CVD). During the CVD, the loss of solute from the feed is equal to the mass in the permeate, that is,

$$V_f dC = -C_p dV \tag{5}$$

Substituting Eq. (2) into Eq. (5), and then integrating it at $V=0$, $C=C_f$, gives,

$$\frac{C_r}{C_f} = \exp\left[(R_{obs} - 1)\frac{V}{V_f}\right] \tag{6}$$

3.2.1.3. Cascade diafiltration. In cascade diafiltration, fresh water is only added into loose UF concentrate and the obtained permeate is then used as diluent for the tight UF in CVD mode. The variation of solute concentration in loose UF retentate can be expressed by Eq. (6). Because the sucrose retention of loose UF (R_{obs1}) is zero, the sucrose concentration in the permeate of loose UF was the same as that in its retentate, which can be described as:

$$C_{p1} = C_{r1} = C_{f1} \exp\left(-\frac{V}{V_{f1}}\right) \tag{7}$$

The removal of sucrose in tight UF stage is equal to the mass difference between loose and tight UF permeates, that is,

$$V_{f2} dC_{r2} = (C_{p1} - C_{p2}) dV \tag{8}$$

According to Eq. (2), the permeate concentration in tight UF stage can be calculated by:

$$C_{p2} = C_{r2}(1 - R_{obs2}) \tag{9}$$

Substituting Eqs. (7) and (9) into Eq. (8), and then integrating it at $V=0$, $C_{r2}=C_{f2}$, gives,

$$\frac{C_{r2}}{C_{f2}} = \frac{C_{f1}}{C_{f2}\left(1 - R_{obs2} - \frac{V_{f2}}{V_{f1}}\right)} \exp\left(-\frac{V}{V_{f1}}\right) + \left(1 - \frac{C_{f1}}{C_{f2}\left(1 - R_{obs2} - \frac{V_{f2}}{V_{f1}}\right)}\right) \exp\left(\frac{R_{obs2} - 1}{V_{f2}} V\right) \tag{10}$$

where subscripts 1 and 2 represent the loose and tight UF, respectively.

More detailed information about equation derivations can be found in Supplementary information.

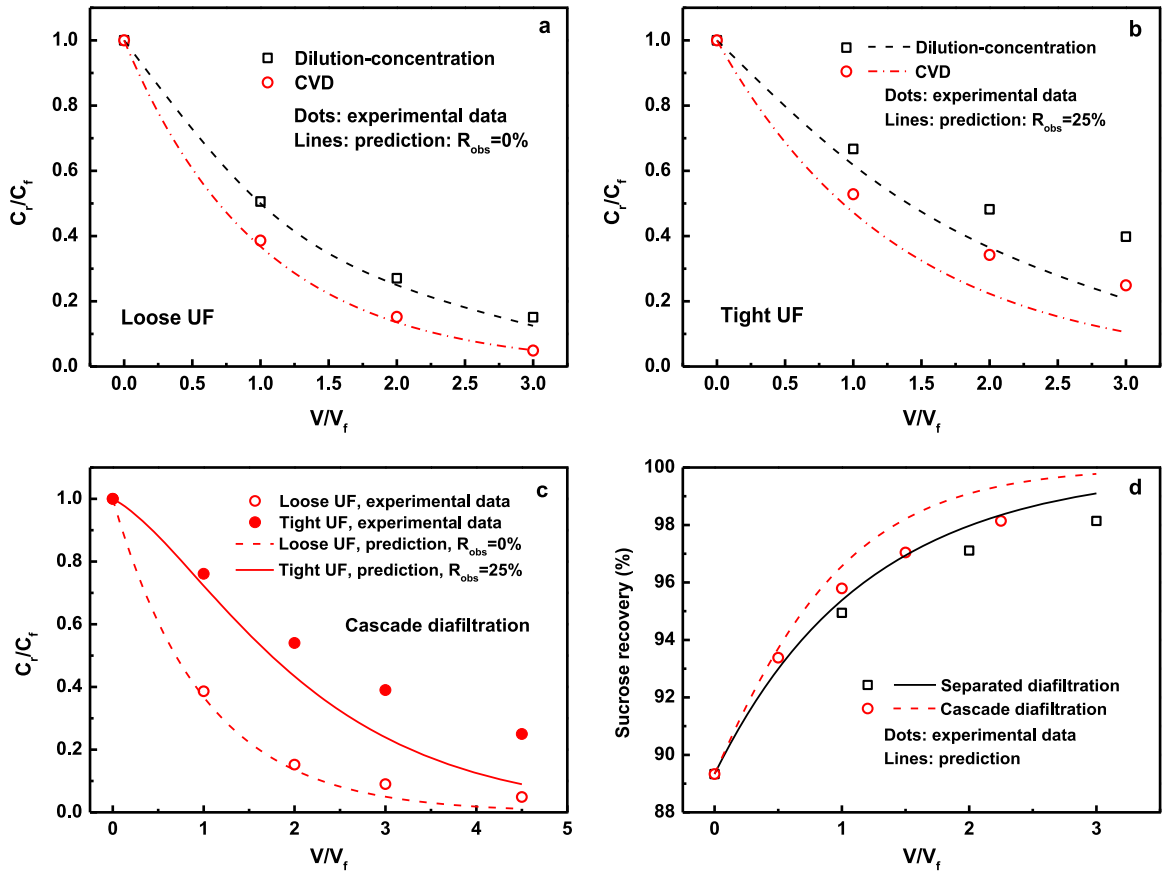

Fig. 4. Diafiltration of UF retentate for recovery of sucrose: comparisons of experimental and prediction results in dilution-concentration and CVD modes for (a) loose UF and (b) tight UF membranes; (c) experimental and prediction results in cascade diafiltration; (d) comparison of sucrose recovery in separated and cascade diafiltrations. Assuming the ratio of retentate concentrations in loose and tight UF was 0.6, their retentate volumes were the same and VRR for the loose and tight UF were 25 and 24, respectively.

3.2.2. *Comparison of different diafiltration modes*

Fig. 4a and b shows the comparisons of dilution-concentration and CVD modes for the loose and tight UF, respectively, indicating that CVD is more efficient than dilution-concentration in both cases, which is coincident with our previous results [27]. It should be pointed out that in both diafiltration modes, the prediction lines (Eqs. (4) and (6)) were in good agreement with experimental data for the loose UF, while the sucrose recovery efficiency obtained from the experiments was much lower than the prediction results for the tight UF, especially at higher value of V/V_f. It was confirmed that sucrose could easily pass through the loose UF even with fouling layer, while for the tight UF, the average sucrose retention during the concentration process was about 25%. Even if a higher sucrose retention from 35% to 55% was used to fit the model for the tight UF, the prediction results still deviated from the experimental data (the four points could not "fall on" one prediction line at the same time), implying that the sucrose retention was changing (or increasing) during the diafiltration. There are three possible mechanisms responsible for this phenomenon. First, the Stoke's radius of sucrose is 0.471 nm [29], and the tight UF with 5 nm pore size is supposed to not retain sucrose molecules. However, some sucrose molecules possibly combined with other solutes (e.g. polysaccharides), which could be partly rejected by the tight UF membrane. Most importantly, these conjugated sugars had different sizes/molecular structures and the percentage of larger ones in the total sugar was increasing with diafiltration. Second, with the decrease of sugar concentration in the UF concentrate, the viscosity was decreasing and concentration polarization became lower. Third, permeate flux was increasing during diafiltration, thus enhancing the solvent convection transport and also amplifying the "dilution effect" on the permeate. These three possible reasons would result in an increase in the observed sucrose retention by tight UF and a deviation between experimental data and prediction results.

In order to further save water consumption, a new diafiltration mode, named cascade diafiltration was proposed, where the permeate obtained from the loose UF was then used as diluent for the tight UF. Compared with separated CVD, the diafiltration efficiency in both experimental and prediction results did not change for the loose UF (Fig. 4a and c). While for the tight UF, since its diluent contained some sucrose, the diafiltration efficiency by cascade diafiltration significantly decreased at the beginning, but when V/V_f was 4.5, the value of C_r/C_f was similar to that for separated CVD at $V/V_f=3$ (Fig. 4b and c). Because no fresh water was added into the tight UF concentrate for cascade diafiltration, 25% of water was saved. The cascade diafiltration process for the tight UF was also predicted with the Eq. (10), where $C_{f1}/C_{f2}=0.6$ (the tight UF can retain some sucrose) and $V_{f2}/V_{f1}=1$ (VRRs for the loose and tight UF are 25 and 24, respectively). The prediction results still deviated from the experimental data, being similar to that in separated CVD (Fig. 4b and c). Fig. 4d also shows the comparison of sucrose recovery in the whole process (two-stage UF) by using separated and cascade diafiltrations, indicating that our proposed diafiltration mode was more efficient according to both experimental and prediction results.

3.3. *Flux decline and fouling mechanisms for UF membranes*

Membrane fouling is a big challenge to be solved in sugarcane juice purification by membrane filtration. In this work, a two-stage

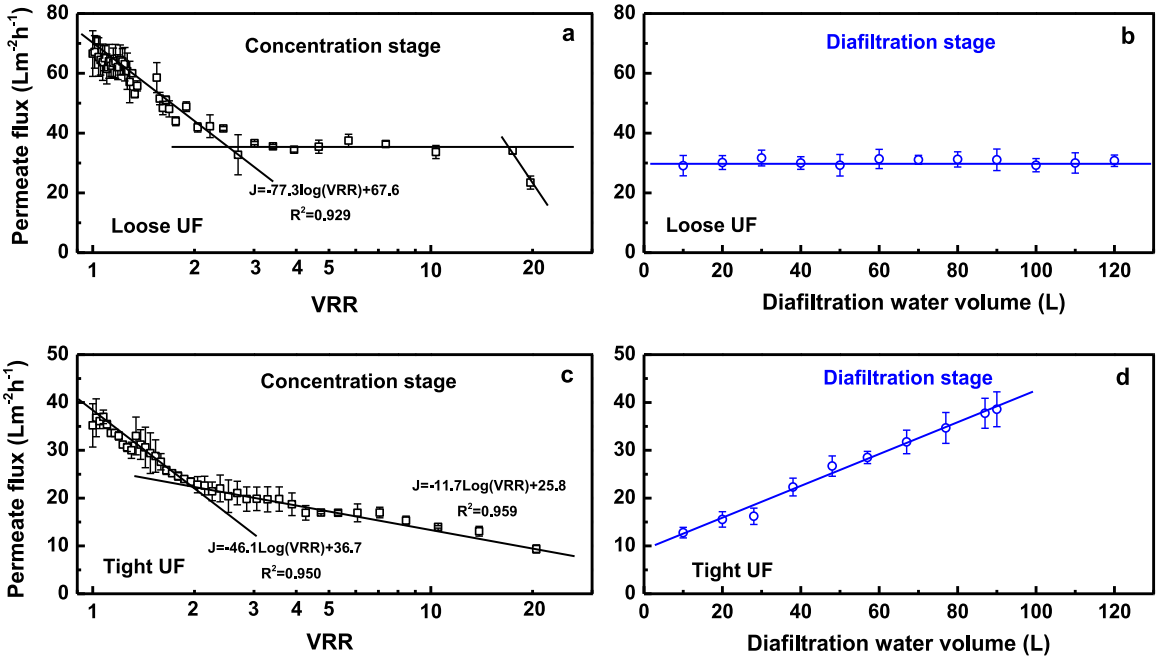

Fig. 5. Permeate flux as a function of volume reduction ratio (VRR) in semi-log coordinates for (a) loose and (c) tight membranes during concentration stage, and permeate flux variations with water usage during diafiltration stage for (b) loose and (d) tight membranes (separated CVD mode was used).

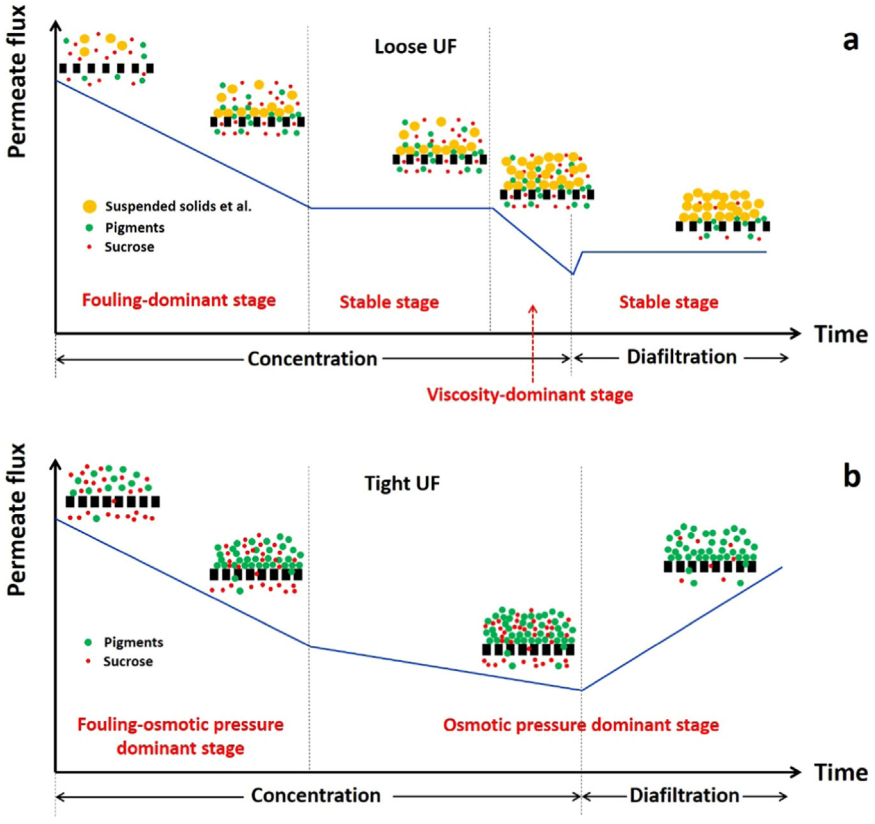

Fig. 6. Flux behavior and mechanisms during the sugarcane juice refining by (a) loose and (b) tight membranes.

hybrid UF process (tubular module followed by spiral wound one) was employed to “break up” the foulants (i.e. suspended solids, colloid and pigments, etc.). In order to avoid fouling aggravation and guide membrane cleaning, it is required to clarify the flux behavior and fouling mechanisms during the concentration and diafiltration processes. As shown in Fig. 5a and b, for the loose UF, permeate flux falls on a straight line with VRR in semi-log coordinates when VRR was less than 3, which presumably corresponds to the mass transfer limited regime. During this period, membrane fouling formed and became stable. When VRR increased from 3 to 10, a nearly constant flux was observed. While VRR reached to 20, a rapid flux decline occurred due to the viscosity surge. During the diafiltration process (CVD mode), permeate flux kept almost constant, implying that suspended solids, colloids

and large pigments were the main foulants for the loose UF (these molecules' concentration did not change during diafiltration). However, the flux behavior for the tight UF was totally different. Permeate flux was always decreasing with increasing VRR, and then it was unexpectedly increasing during the diafiltration.

Based on the flux behavior shown in Fig. 5, a schematic presentation on the possible mechanisms of flux decline and membrane fouling for the loose and tight UF was proposed in Fig. 6. There were four flux stages in the loose UF (Fig. 6a). During the fouling-dominant stage, suspended solids, colloids and large pigments would deposit on the membrane and form a cake or gel layer, and at the same time, some smaller foulants (e.g. pigments) also adsorbed in the membrane and blocked the pores, resulting in an obvious flux decline. When the flux decreased to "critical or threshold flux" [30,31], the flux decline stopped and a stable stage occurred. However, with increase of the retained solute concentration, the viscosity was increasing, and subsequently the flux went to viscosity-dominant stage, where flux decline appeared again. After that, water was added and the feed volume kept constant, where sucrose and small pigments were washed out through the membrane but the retained solutes stayed unchanged, inducing a stable flux stage again. Meanwhile, there were only two flux stages in the tight UF (Fig. 6b), and osmotic pressure caused by small pigments and sucrose played an important role in its flux behavior. As shown in Fig. 6b, at the beginning of concentration process, fouling formation (e.g. pigments adsorption in/on the membrane) and osmotic pressure increase were responsible for the rapid flux decline. Then, the membrane fouling became stable and permeate flux was governed by the osmotic pressure. In the osmotic pressure dominant stage, permeate flux first decreased due to the accumulation of small molecules in the concentrate, and during the diafiltration, permeate flux kept increasing due to the continuous removal of sucrose and small pigments from the retentate.

In one concentration-diafiltration cycle, with a super high VRR of 20, the loose UF was able to be operated at a flux from 30 to 70 L m^{-2} h^{-1}, and the tight UF could run at a flux from 10 to 40 L m^{-2} h^{-1}. At the same time, the color removal maintained more than 95%. If such performance can be regenerated by a suitable cleaning strategy, this integrated membrane process is promising to be industrialized.

3.4. Membrane cleaning and operating stability

Since the membrane materials and fouling mechanisms were different for these three membrane modules (UF+UF+NF), different cleaning strategies were carried out according to their manufactures' instructions. Based on the juice composition, organic fouling was considered as the main fouling type. Thus, an alkaline cleaning agent, together with some chemicals, such as NaClO, NaOH and citric acid, were selected to clean the membranes. Table 3 shows the preliminary cleaning results by different strategies. For the tubular loose PVDF UF, the combined strategy with cleaning agent followed by NaClO was the best choice. The cleaning mechanisms were speculated as follows: cleaning agent could first remove the cake or gel layer on the membrane, and then NaClO oxidized the foulants in the pores; on the one hand, if NaClO was used directly, the tight cake or gel layer could act as a protective or "sacrifice" layer, preventing the "attack" to the foulants in the pores; on the other hand, the single strategy with cleaning agent was also not able to remove this stubborn pore fouling. As for the tight UF, the main fouling mechanism might be the pigment adsorption on the membrane because most foulants were retained by the loose UF, and our cleaning agent could recover the permeability thoroughly. However, NaOH could not remove such fouling in 1 h, and citric acid would aggravate the permeability loss.

Table 3
Effect of cleaning strategy on membrane permeability recovery.

Membrane modules	Cleaning strategies	Results[a]
Tubular loose UF (PVDF)	Only cleaning agent	+
	Only NaClO	−
	Mixture of cleaning agent and NaClO	+
	Cleaning agent followed by NaClO	+++
Spiral-would dense UF (PES)	Only NaOH	−
	Only citric acid	−−
	Only Cleaning agent	+++
Spiral-would NF (Polyamide)	Only Cleaning agent	+++

[a] +++ indicates full recovery of membrane permeability; + indicates part recovery of membrane permeability; − indicates negligible cleaning effect; −− indicates permeability drop after cleaning.

Fig. 7 shows the membrane permeability recovery by chemical cleaning for the loose UF, tight UF and NF. It can be seen that cleaning agent concentration had a significant influence on the cleaning efficiency for the loose UF, and if the cake or gel layer was not fully removed by the cleaning agent, the residual fouling layer would consume NaClO in the second cleaning step, resulting in an insufficient permeability recovery (Fig. 7a). When elevating cleaning agent concentration, the cumulative fouling after incomplete cleaning could also be removed. For the tight UF, acidic cleaning produced a permeability drop, while soaking with a low concentration of NaClO for 30 min would enhance the membrane permeability, implying that the membrane pores were susceptible to the pH and oxidizer. For the NF, since the sugars (i.e. sucrose, glucose and fructose) were the main components in its feed, membrane fouling was not significant, and cleaning agent could easily regenerate the membrane performance. The slight permeability loss at the first two days could be caused by the membrane compression at high pressure.

Fig. 8 shows the initial permeate flux variation in the first fifteen days for these three membranes. Although the membrane permeabilities could almost be recovered by the proposed cleaning strategies, the initial permeate fluxes during sugarcane juice purification were decreasing in the first four days, indicating that there was still some fouling accumulating in the modules. From the tenth day, the raw sugarcane juice quality became inferior (higher color and turbidity due to different batch of sugarcane), and thus the permeate flux decreased obviously. While the permeate flux of NF was almost constant from the fourth day, suggesting that the separation performance of NF was irrespective of raw juice quality. Anyway, with regular chemical cleaning once a day, this integrated membrane process could be operated stably at pilot-plant scale for 45 days (results not shown).

3.5. Role of high temperature on sugarcane juice refining by polymeric membranes

A high operating temperature of 60 °C had a significant effect on membrane performance and juice quality, as listed in Table 4. For each parameter examined, both positive and negative effects of high temperature could be found, and these could be the reasons why high permeate flux, low solute retention, and serious fouling were not observed as expected [26,32–35]. For instance, at a high TMP of 10 bar, the permeate flux of the tight UF even went down to 10 L m^{-2} h^{-1} while it was increasing to the original value again after diafiltration, implying that membrane fouling was not important in this case. Here, osmotic pressure played a vital role in such flux variation because the calculated osmotic pressure was increased by 11.7% compared with the case at room temperature (see Table 4). Moreover, it can be seen from Figs. 7 and 8 that

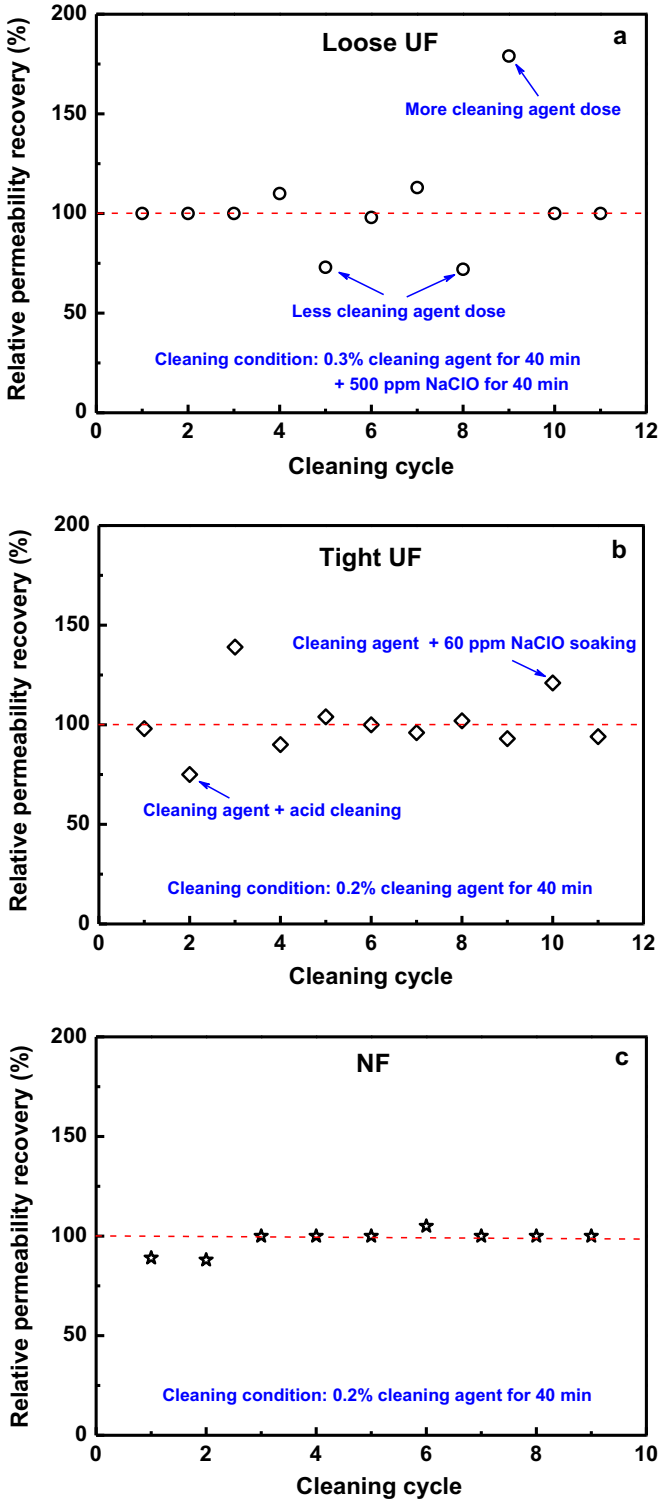

Fig. 7. Membrane permeability recovery after chemical cleaning for loose UF, tight UF and NF. Relative permeability recovery$=(L_{p,c}/L_{p,i})\times 100$, where $L_{p,i}$ and $L_{p,c}$ are the water permeability of membrane before feed filtration and after chemical cleaning, respectively. The time between cleaning cycles was about 24 h (12 h shutdown, 8 h operation, 4 h others).

although the membrane permeability could be almost fully recovered by chemical cleaning, the permeate flux was still decaying in the first four days. This might be caused by the temperature jump between filtration and cleaning (60–30 °C), and the foulants were easier to enter the enlarged pores at high operating temperature, and the following shrinkage at lower cleaning

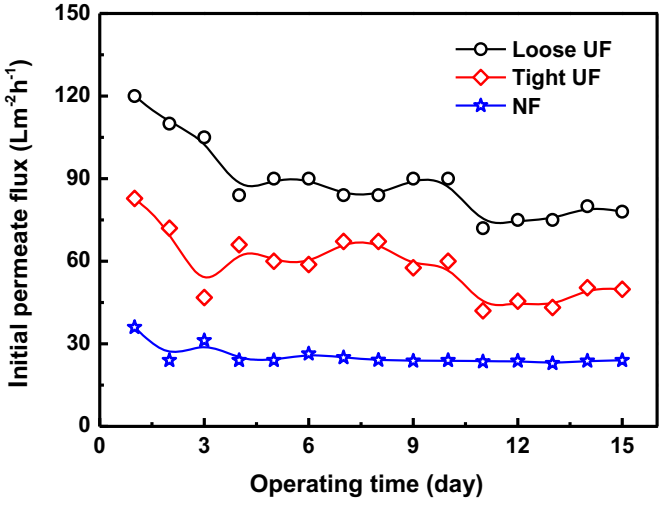

Fig. 8. Initial permeate flux variation with operating time for loose UF clarification, tight UF decolorization and NF concentration.

temperature would induce pore plugging [34,35]. This kind of fouling possibly had negligible influence on the water permeability but resulted in a reduction of permeate flux at high temperature. This high operating temperature could also depress bacteria growth in the membrane system while accelerate Maillard reaction to produce new color during sugarcane juice purification [36].

4. Conclusions

This work demonstrated that an integrated membrane process (two-stage UF followed by NF) could accomplish clarification, decoloration, and pre-concentration of raw sugarcane juice at pilot-plant scale. The color and turbidity removals were up to 96.55% and 99.99%, respectively, and the color value of the final product was below 800 IU, which could be used to produce the superior white sugar by subsequent multi-effect evaporation and crystallization. Diafiltration was carried out to recover the residual sucrose in the UF concentrates, and CVD mode outperformed dilution-concentration mode because the former enabled continuous operation and reduced water consumption. Compared with separated CVD, a novel cascade diafiltration was able to further save water by 25%. Based on mass balance and retention equations, mathematical models were developed for predicting the sucrose recovery efficiency by different diafiltration processes. The simulation results agreed very well with the experimental data for the loose UF but not for the tight UF, as the sucrose retention was increasing during the diafiltration by the tight UF.

For the tubular loose UF, both membrane fouling and viscosity increase might be responsible for the flux decline, while for the spiral-wound tight UF, since the high operation temperature (60 °C) amplified the osmotic pressure effect, osmotic pressure played an important role in its flux variation. A combined strategy with cleaning agent followed by NaClO could almost fully recovered the membrane permeability of the loose UF membrane, while a single cleaning agent enabled to thoroughly recover the permeabilities of the tight UF and NF membranes. However, due to the temperature jump between filtration and cleaning (60–30 °C), there were still some foulants accumulating in the membrane pores, leading to a permeate flux decay in the first several days. With regular chemical cleaning once a day, this integrated membrane process could be operated stably at pilot-plant scale for 45 days, which is promising to be industrialized.

Table 4
Role of high temperature (60 °C) on sugarcane juice refining by polymeric membranes.

Parameters affected by high temperature	Mechanisms of action	Consequences caused by high temperature[a]
Permeate flux	Decreasing feed viscosity and membrane resistance	+
	Increasing osmotic pressure (osmotic pressure calculation: $\pi=nRT$, T is temperature)	−
	Decreasing concentration polarization by enhancing the back diffusion of solutes	+
Solute retention	Increasing effective pore size by reducing the thickness of hydration layer on pore wall [26]	−
	Increasing solute diffusion across the membrane	−
	Decreasing concentration polarization by enhancing the back diffusion of solutes	+
Membrane fouling	Decreasing cake layer formation by elevating the solute solubility	−
	Decreasing foulant adsorption on the membrane or pore wall	−
	Increasing pore blocking due to the temperature-induced pore swelling and higher solute diffusion	+
	Due to the temperature jump between filtration and cleaning (cleaning temperature is normally lower than 40 °C when pH is higher than 11), the foulants were easier to enter the enlarged pores at high operating temperature, and the following shrinkage at lower cleaning temperature would induce pore plugging [34,35]	+
Juice quality	Depressing bacteria growth	+
	Accelerating Maillard reaction and increasing color [36]	−

[a] + indicates positive correlation; − indicates negative correlation.

List of symbols

A	Effective membrane area
C_f	Solute concentrations in feed
C_r	Solute concentrations in retentate
C_p	Solute concentrations in permeate
$C_{r,\ av}$	Average solute concentration in retentate for one concentration cycle.
$C_{r,\ n}$	Retentate concentration in the n cycle
CVD	Constant volume diafiltration
$L_{p,i}$	Water permeability of membrane before feed filtration
$L_{p,c}$	Water permeability of membrane after chemical cleaning
NF	Nanofiltration
V_f	Feed volume
V_p	Permeate volume
V_r	Concentrate volume
R_{obs}	Average observed retention
t	Filtration time
TMP	Transmembrane pressure
PES	Polyethersulphone
PVDF	Polyvinylidene fluoride
UF	Ultrafiltration
VRR	Volume reduction ratio

Acknowledgments

This work was supported by “100 Talents Program” of Chinese Academy of Sciences and the National High-Tech R&D Program of China (2014AA021006). The authors acknowledge the on-site support provided by Guangdong Hengfu Group Sugar Industry Co., Ltd.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.memsci.2016.02.053.

References

[1] V. Jegatheesan, L. Shu, G. Keir, D.D. Phong, Evaluating membrane technology for clarification of sugarcane juice, Rev. Environ. Sci. Biotechnol. 11 (2012) 109–124.
[2] M. Balakrishnan, M. Dua, J.J. Bhagat, Effect of operating parameters on sugarcane juice ultrafiltration: results of a field experience, Sep. Purif. Technol. 19 (2000) 209–220.
[3] P.K. Bhattacharya, S. Agarwal, S. De, U.V.S. Rama Gopal, Ultrafiltration of sugar cane juice for recovery of sugar: analysis of flux and retention, Sep. Purif. Technol. 21 (2001) 247–259.
[4] M. Saska, Method for Producing White Sugar, US Patent US6096136 A, 2000.
[5] H.L. Mudoga, H. Yucel, N.S. Kincal, Decolorization of sugar syrups using commercial and sugar beet pulp based activated carbons, Bioresour. Technol. 99 (2008) 3528–3533.
[6] M. Bernal, M.O. Ruiz, R.M. Geanta, J.M. Benito, I. Escudero, Colour removal from beet molasses by ultrafiltration with activated charcoal, Chem. Eng. J. 283 (2016) 313–322.
[7] A. Baudry, Process of Purifying Sugar-juice by Means of Electrodialysis, US Patent US711375 A, 1902.
[8] R.R. Stevens, Process for Decolorizing Aqueous Sugar Solution, US Patent US4871397 A, 1989.
[9] M. Donovan, R.P. Jansen, R.C. Reisig, M. Hlavacek, G. Walker, J.C. Williams, Sugar cane Membrane Filtration Process, US Patent US6406548 B1, 2002.
[10] A. Cassano, E. Drioli, Integrated Membrane Operations: In the Food Production, De Gruyter, Berlin, 2013.
[11] R.F. Madsen, Application of ultrafiltration and reverse osmosis to cane juice, Int. Sugar J. 75 (1973) 163–167.
[12] W. Li, G.-Q. Ling, P. Huang, K. Li, H.-Q. Lu, F.-X. Hang, Y. Zhang, C.-F. Xie, D.-J. Lu, H. Li, X.-Q. Liang, J.-H. Xiang, Performance of ceramic microfiltration membranes for treating carbonated and filtered remelt syrup in sugar refinery, J. Food Eng. 170 (2016) 41–49.
[13] M. Hamachi, B.B. Gupta, R. Ben Aim, Ultrafiltration: a means for decolorization of cane sugar solution, Sep. Purif. Technol. 30 (2003) 229–239.
[14] J. Gyura, Z. Šereš, G. Vatai, E.B. Molnár, Separation of non-sucrose compounds from the syrup of sugar-beet processing by ultra- and nanofiltration using polymer membranes, Desalination 148 (2002) 49–56.
[15] A.M. Ghosh, M. Balakrishnan, Pilot demonstration of sugarcane juice ultrafiltration in an Indian sugar factory, J. Food Eng. 58 (2003) 143–150.
[16] J. Luo, L. Ding, Y. Su, ShaopingWei, Y. Wan, Concentration polarization in concentrated saline solution during desalination of iron dextran by nanofiltration, J. Membr. Sci. 363 (2010) 170–179.
[17] S. Jacob, M.Y. Jaffrin, Purification of brown cane sugar solutions by ultrafiltration with ceramic membranes: investigation of membrane fouling, Sep. Sci. Technol. 35 (2000) 989–1010.
[18] V. Jegatheesan, D.D. Phong, L. Shu, R. Ben Aim, Performance of ceramic micro- and ultrafiltration membranes treating limed and partially clarified sugar cane juice, J. Membr. Sci. 327 (2009) 69–77.
[19] N.K. Saha, M. Balakrishnan, M. Ulbricht, Polymeric membrane fouling in sugarcane juice ultrafiltration: role of juice polysaccharides, Desalination 189 (2006) 59–70.
[20] N.K. Saha, M. Balakrishnan, M. Ulbricht, Fouling control in sugarcane juice ultrafiltration with surface modified polysulfone and polyethersulfone membranes, Desalination 249 (2009) 1124–1131.
[21] A.M. Ghosh, M. Balakrishnan, M. Dua, J.J. Bhagat, Ultrafiltration of sugarcane juice with spiral wound modules: on-site pilot trials, J. Membr. Sci. 174 (2000) 205–216.
[22] X. Jian, Y. Dai, G. He, G. Chen, Preparation of UF and NF poly (phthalazine ether sulfone ketone) membranes for high temperature application, J. Membr. Sci. 161 (1999) 185–191.
[23] Y. Dai, X. Jian, S. Zhang, M.D. Guiver, Thermostable ultrafiltration and nanofiltration membranes from sulfonated poly(phthalazinone ether sulfone ketone), J. Membr. Sci. 188 (2001) 195–203.
[24] I. Kowalska, K. Majewska-Nowak, M. Kabsch-Korbutowicz, Influence of temperature on anionic surface active agent removal from a water solution by

ultrafiltration, Desalination 198 (2006) 124–131.
[25] M. Mänttäri, A. Pihlajamäki, E. Kaipainen, M. Nyström, Effect of temperature and membrane pre-treatment by pressure on the filtration properties of nanofiltration membranes, Desalination 145 (2002) 81–86.
[26] T. Tsuru, S. Izumi, T. Yoshioka, M. Asaeda, Temperature effect on transport performance by inorganic nanofiltration membranes, AIChE J. 46 (2000) 565–574.
[27] J. Luo, W. Huang, W. Song, X. Hang, L. Ding, Y. Wan, A pilot-plant test on desalination of soy sauce by nanofiltration, Sep. Purif. Technol. 89 (2012) 217–224.
[28] The First Editing Group of China Standards Publishing House (Ed.), China Food Industry Standards Assembly—White Granulated Sugar, China Standards Publishing House, Beijing, 2006, pp. 3–10.
[29] W. Richard Bowen, A. Wahab Mohammad, Diafiltration by nanofiltration: Prediction and optimization, AIChE J. 44 (1998) 1799–1812.
[30] R.W. Field, D. Wu, J.A. Howell, B.B. Gupta, Critical flux concept for microfiltration fouling, J. Membr. Sci. 100 (1995) 259–272.
[31] J. Luo, Z. Zhu, L. Ding, O. Bals, Y. Wan, M.Y. Jaffrin, E. Vorobiev, Flux behavior in clarification of chicory juice by high-shear membrane filtration: evidence for threshold flux, J. Membr. Sci. 435 (2013) 120–129.
[32] T. Steinhauer, S. Hanély, K. Bogendörfer, U. Kulozik, Temperature dependent membrane fouling during filtration of whey and whey proteins, J. Membr. Sci. 492 (2015) 364–370.
[33] X. Jin, A. Jawor, S. Kim, E.M.V. Hoek, Effects of feed water temperature on separation performance and organic fouling of brackish water RO membranes, Desalination 239 (2009) 346–359.
[34] M. Nilsson, G. Tragardh, K. Ostergren, The influence of pH, salt and temperature on nanofiltration performance, J. Membr. Sci. 312 (2008) 97–106.
[35] V. Freger, T.C. Arnot, J.A. Howell, Separation of concentrated organic/inorganic salt mixtures by nanofiltration, J. Membr. Sci. 178 (2000) 185–193.
[36] L.M. López González, I. Pereda Reyes, J. Dewulf, J. Budde, M. Heiermann, H. Vervaeren, Effect of liquid hot water pre-treatment on sugarcane press mud methane yield, Bioresour. Technol. 169 (2014) 284–290.