Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Sim, L. , Shu, L. , Jegatheesan, V. and Phong, D. D.(2009) 'Effect of Operating Parameters and Cleaning on the Performance of Ceramic Membranes Treating Partially Clarified Sugar Cane Juice', Separation Science and Technology, 44: 15, 3506 — 3537
To link to this Article: DOI: 10.1080/01496390903183295
URL: http://dx.doi.org/10.1080/01496390903183295

Separation Science and Technology, 44: 3506–3537, 2009

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390903183295

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Effect of Operating Parameters and Cleaning on the Performance of Ceramic Membranes Treating Partially Clarified Sugar Cane Juice

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Abstract: The performance of ceramic membranes with pore sizes of 0.05 and 0.10 μm in purifying limed and partially clarified sugar cane juice was investigated under different operating conditions. From various operating conditions and strategies, switching off the permeate for 5 seconds for every 5 minutes (S5sT5 m) by an automated control valve provided higher flux. From the three pH experiments conducted on the 0.05 μm membrane, the best performance was observed at a pH of 7.5. Amongst the four fouling models tested, the cake filtration model fitted the performance of both membranes with higher accuracy at a transmembrane pressure of 0.5 bar. Filtering the cane juice through the membrane reduced the turbidity by 99.7%, color by 15%, and the starch concentration by 80% as well as increased the purity by 1.4%. The effective cleaning chemical composition from experimental results showed that 1% NaOH and 3000 ppm NaOCl solution performed the best but only for the experiments that were treating limed and partially clarified juice at pH 7.5.

Keywords: Ceramic membrane, membrane fouling, purity rise, sugar cane juice, transmembrane pressure (TMP)

Received 11 February 2009; accepted 10 June 2009.

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INTRODUCTION

Currently, the sugar industry relies heavily on conventional clarifiers in clarifying raw sugar cane juice which have higher operating cost and cause associated environmental problems. Furthermore, filtrates from filters that contain impurities are redirected back into clarifiers that further increase the loading on the clarifiers. Therefore more efficient methods in clarifying the sugar cane juice are required in order to reduce the operating costs and the usage of chemicals (lime) is sought. Clarification of sugar cane juice through membrane filtration is one such efficient method that can be employed in the sugar industry.

Sugar mills generally run continuously throughout the season and fed with sugar canes from various sources. This means varying cane variety, soil and growing conditions, weather patterns, and seasonal attributes which would make the task of ensuring consistent production of high clarity and low colored sugar cane juice through the clarification process a challenge to the sugar industry. Membrane filtration promises sugar cane juice with better clarity, lower viscosity, color (1–3), and starch content as well as higher purity. Membrane clarification reduces the color of the juice by 60% (4). Ultrafiltration of clarified sugar cane juice is achievable through a spiral wound or flat sheet filtration system using polymeric membranes or a tubular filtration system using ceramic membranes (5). In a study conducted using ceramic membranes, the flux increased when the transmembrane pressure (TMP) was increased (6). In another study, the 0.1, 0.2, 0.5, 0.8, and 1.4 μm membranes produced 38.0, 27.0 30.0, 52.0, and 62.7 $L/m^2 \cdot h$ of fluxes when treating 60°Brix solution at (85 ± 5)°C (7). Alternatively, another study showed that higher fluxes were obtained as the sizes of the membrane pore decreased (8).

Currently the sugar industry does not deem the application of membrane filtration in clarifying sugar cane juice necessary due to the doubts of the cost-effectiveness of its productivity. This study is the continuation of our previous study on the performance of ceramic membranes with pore sizes of 0.05 and 0.10 μm in clarifying limed and partially clarified sugar cane juice under different operating conditions (9). The performance of the membranes that were operated under a TMP of 0.5 bar to treat sugar cane juice with different pH values and the strategy of stopping the permeate from the membrane for 5 seconds every 5 minutes of filtration (S5sT5 m strategy) were investigated. Further, the efficiency and the cost of several cleaning solutions that were used to recover the fouled membranes were evaluated. Four mathematical models were used to fit the fouling behavior of the membranes. The available literature on the clarification of sugar cane juice by ceramic membranes is limited and therefore the information provided in this paper will give an excellent

overview for researchers who want to work further on the application of ceramic membranes in clarifying sugar cane juice.

MATERIALS AND METHODS

Materials

Ceramic membranes with two difference pore sizes (0.05 and 0.10 μm) were used to filter the limed and partially clarified sugar cane juice under different operating conditions. The membrane with 0.05 μm pore size yielded higher initial and average fluxes among the three membranes (0.02, 0.05, and 0.1 μm membranes) tested in our previous study (9). While, the 0.05 μm membrane best represents the cake filtration model, the 0.10 μm membrane represents the combination of external and progressive internal fouling model compared to the others under higher TMPs and cross-flow velocities (9). Therefore, we have selected both pore sizes to evaluate the performance under lower TMP and cross-flow velocity. Further, the separation is focused on colloidal and macromolecules. It is the main concern in the sugar industry as the separation of the above constituents from sugar cane juice saves energy in the crystallization stage. The specifications of the membrane system and the properties of membranes used are given in Table 1 and the operating conditions of each experimental run are given in Table 2. The experimental setup of the system is shown in Fig. 1.

Table 1. Material characteristics and module details of the membrane system used

Item	Description
Manufacturer	Jiangsu Jiuwu HiTech, Nanjing, China
Membrane type	Tubular
Membrane material	ZrO_2
Membrane support material	α-Alumina oxide
Pore size	0.05 μm and 0.10 μm
Pure water permeability	597 $L/m^2 \cdot h \cdot bar$ (0.05 μm) 533 $L/m^2 \cdot h \cdot bar$ (0.10 μm)
Porosity	35%
Length	500 mm
Number of channels	19
Channel diameter	4 mm
Surface area	0.1193 m^2

Table 2. Summary of operating conditions of the experimental runs

Run	Cross-flow velocity (m/s)	Experimental details	Pore size of the membrane used (μm)
1	3.0	pH = 7.5	0.10
2	1.5	pH = 7.5	
3	3.0	pH = 7.5 Permeate valve was closed for 5 seconds after every 5 minutes of operation (S5sT5 m strategy)	
4	3.0	pH = 7.5	0.05
5	1.5	pH = 7.5	
6	3.0	pH = 9.0	
7	3.0	pH = 5.5 (no lime addition)	
8	3.0	pH = 7.5 S5sT5 m strategy	

A sugar cane variety Q200 was collected from Paluma (Queensland, Australia) and stored inside a cold room at the Mechanical Engineering workshop of James Cook University at $10 \pm 5^{\circ}C$. The sugar cane stored in the cold room was used within 10 days and the characteristics of the feed solution (turbidity, purity, color, starch) of all experiments were similar. Therefore the impact of storing the sugarcane on the feed sugar cane macromolecular properties is inconsiderable. Raw sugar canes were taken out from the cold room and crushed using the sugar cane miller. The raw sugar cane juice was then filtered through a 250 μm sieve to

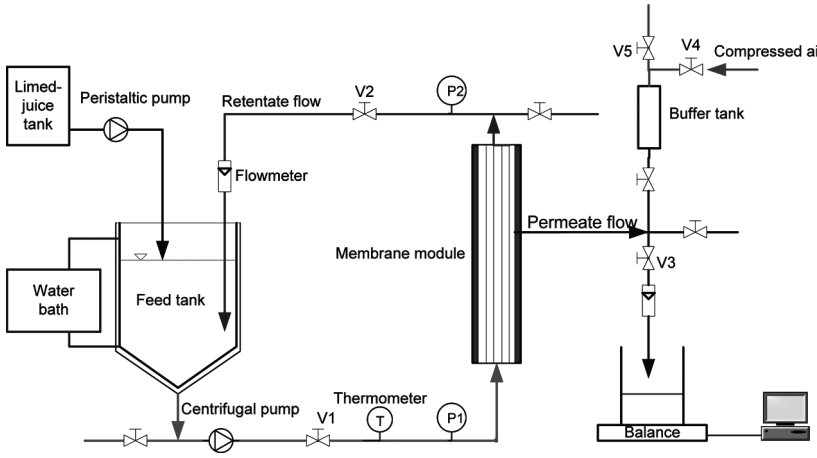


Figure 1. Experimental setup of the ceramic membrane system.

remove large fibers. A total estimate of 50 liters of raw sugar cane juice was treated with lime ($Ca(OH)_2$), and mixed by a stirrer to raise the pH from around 5.5 to 7.5 in all experimental runs except runs 6 and 7. Experimental run 6 was treated with extra lime to raise the pH to 9.0 while run 7 had no lime added to it at all. The limed juice was left unstirred for one hour for the flocculated solid particles to settle. After one hour, the settled juice was filtered through a 125 μm sieve and was diluted with deionized (DI) water to a desired sucrose content level (around 16°Brix). The volume of the diluted juice was around 60 liters and was used as feed for an experimental run. The experimental preparation is labor extensive and from our previous study (9), we have found that running a membrane filtration experiment for 2 to 4 hours of duration will provide sufficient information to evaluate the short term performance of the membrane and in this case we chose to run for 2 hours. The data obtained for flux are sufficient to estimate the steady state flux using the fouling model.

The juice volume inside the feed tank was maintained at 20 liters throughout the experiment by pumping the juice through a peristaltic pump from a limed-juice tank which stored the rest of the juice. Sugar cane juice in the feed tank was maintained at (60 ± 5)°C by re-circulating the hot water from the water bath continuously through the water jacket of the feed tank. The juice was circulated through the membrane module by a centrifugal pump. Valves (V1) and (V2) were adjusted to obtain a TMP of 0.5 bar and a desired cross flow velocity (CFV). By closing the valve V1, both TMP and CFV can be decreased. However, by closing valve V2, TMP can be increased and CFV can be decreased. The TMP was the average pressure of values shown on pressure gauges P1 and P2. The retentate was recycled back into the feed tank while the permeate through the membrane was collected in a tank that was placed on an electronic balance (Ohaus-CD33). The balance was connected to a computer that received weight data at one minute intervals. To compute the flux the weight was converted to volume based on the specific weight of the permeate. For experiments utilizing the 5 seconds off of the permeate for every 5 minutes of operation strategy (S5sT5 m strategy) in runs 3 and 8, the automated control switched off the permeate valve (V3) for 5 seconds after every 5 minutes of operation. This is carried out in order to evaluate the effectiveness of short-term flow disturbance on the membrane surface in re-suspending the foulants that are deposited on the surface of the membrane.

Each experimental run was conducted for 2 hours. Two sets of samples from both the feed tank and the permeate were collected at 0 (initial), 0.5, 1, and 2 hours. One set was analyzed immediately while the second

set was stored inside a refrigerator. At the end of each experimental run, the sugar cane juice was drained from the system. The membrane was then rinsed with de-ionized (DI) water and then cleaned with a chemical solution. Membrane Resistance was checked before and after every experimental run by measuring the pure water flux (at 30°C) at a TMP of 0.5, 1.0, 1.5, and 2.0 bar.

Methods

Analytical Methods

The samples collected were brought to the laboratory within 1 to 2 hours after collection and analyzed for Brix, color, turbidity, and Polarity. The starch analysis was performed on secondary samples collected and kept inside a refrigerator by taking out and leaving to defrost before the analysis.

Brix

Brix is a measurement of the mass ratio of dissolved sugar to water in a solution. It is measured with a saccharimeter that measures specific gravity of a liquid or more easily with a refractometer. An example is that a 30°Brix solution refers to a solution with 30 grams of sugar per 100 grams of solution. Brix of limed, partially clarified, and diluted sugar cane juice was measured using a digital refractometer (Palette PR-101, Atago).

Color

Color here refers to the absorption properties of the sugar cane juice. Color of the sugar cane juice was measured using Method GS1-7 (10) where the pH was adjusted to 7 using 0.1 M of NaOH and 0.1 M HCl. Then the juice was filtered using 0.45 μm filter paper and 1% filter aid (Kieselguhr) if necessary. Finally, the absorbance is measured with a spectrophotometer (HP-8453) at the wave length of 420 nm. After obtaining the absorbance value from the spectrometer, the following equation is used to compute the color of the sugar cane juice:

$$Color(IU) = \frac{(10^8 \times As)}{(b \times RDS \times p)} \quad (1)$$

Where, A_s is the absorbance, b is the cell length (=1 cm), RDS is the Refactometric Dry Substances (Brix), and p is the density of the solution (kg/m^3)

Turbidity

Turbidity is the cloudiness or haziness of sugar juice caused by individual suspended solid particles that are generally invisible to the naked eye. Turbidity was measured using Method GS 7–21 (10):

$$Turbidity = 100 \times s \tag{2}$$

$$s = A/b \tag{3}$$

Where, A is the absorbance at the wave length of 900 nm and b is the cell length in cm.

Polarization (Pol. %)

Polarization is a property of transverse waves which describes the orientation of the oscillations in the plane perpendicular to the wave's direction of travel. The dry lead method, as described below, was used to measure the Pol of sugar cane juice (11). Two gram of dry subacetate of lead per 100 mL of solution was added to 250 mL of juice and the precipitates were allowed to settle for approximately 30 minutes. The solution was then filtered and the polarity was measured with a polarimeter (angular degree) at 20°C with a 200 mm length Pol tube.

$$Pol\ percent\ juice = \frac{(Angular\ deg \times 26)}{(34.626 \times apparent\ density\ at\ 20°C)} \tag{4}$$

The purity and purity rise were calculated using the following equations:

$$Purity = \left(\frac{Pol}{Brix}\right) \times 100 \tag{5}$$

$$\text{Purity Rise} = \text{Purity of the Permeate} - \text{Purity of the Feed} \tag{6}$$

Starch

Starch $(C_6H_{10}O_5)_n$ is a polysaccharide consisting of a large number of glucose monosaccharide units joined together by glycosidic bonds. The following method was used to analyse the starch concentration in the sugar cane juice: 1 ml of juice was added to the reagents (1.2 ml of 2 N acetic acid, 0.25 ml of 10% KI and 2.5 ml of 0.001667 M KIO_3 solution) and mixed thoroughly. The optical density of this solution was measured immediately at 600 nm against a blank containing all the reagents and 1 ml of water (12).

Membrane Cleaning

The membrane was cleaned in place after each experimental run using only alkaline cleaning reagents. Prior to chemical cleaning, the membrane was rinsed with DI water for several times, with the permeate valve closed, until the resulting rinse produced clear water with no visible traces of sugar cane juice and flocculants. Each rinse lasted from 5 to 15 minutes. Then the membrane was rinsed with DI water once more with the permeate valve opened. A TMP of 0.2 bar and a cross flow velocity of 1.5 m/s was used for all rinses and chemical cleaning at a temperature of $(50 \pm 5)^{\circ}C$. Finally, pure water flux (at 30°C) of the cleaned membrane was measured at TMPs of 0.5, 1.0, 1.5, and 2.0 bar and if any further cleaning were required, the whole chemical cleaning process was repeated using the same or different concentration of the chemicals.

Particle Size Distribution (PSD) and Zeta Potential

Three secondary permeate samples collected at 0.5, 1.0, and 2.0 hour from experimental run 2 (0.1 μm membrane, CFV:1.5 m/s, pH:7.5, TMP: 0.5 bar) were sent to ATA Scientific Pty Ltd. at Sutherland (New South Wales, Australia) for particle size analysis. The three permeate samples were first tested for particle size using the Malvern Mastersizer 2000 (Laser Diffraction Particle sizer). After measuring the permeate samples on the Mastersizer 2000 it appeared that the samples contained a significant amount of material that is too large to be measured by Dynamic Light Scattering. It was obvious that the samples were unstable and had undergone a significant amount of agglomeration during the transport. For this reason a sample was measured using the Mavlern Zetasizer-Nano system (Dynamic Light Scattering instrument). The zeta potential of the sample was also measured using the Zetasizer-Nano system.

RESULTS AND DISCUSSION

The aim of this study is to evaluate the flux and the quality of clarified sugar cane juice (permeate) obtained by filtering the juice through ceramic membranes and to compare the results obtained under different operating conditions to minimize the fouling of membrane. The secondary objectives of the study include recovering the fouled membrane through appropriate cleaning protocols, approximating the cost effectiveness of each chemical cleaning performed and investigating the fouling mechanisms through mathematical modeling.

Flux

All experiments were conducted for 2 hours and Fig. 2 shows the experimental flux results in the order in which the experimental runs were performed. Table 3 shows the initial, final, and average fluxes obtained in all 8 experimental runs along with the average fluxes for every 30 minutes intervals during the experimental runs. The average flux values were calculated using permeate and sample volumes collected during those intervals. From the results shown in Fig. 2 and Table 3, it is apparent that the initial flux of the experimental runs gradually decreased as more experimental runs were performed on the same membrane.

The first set of experimental runs on both membranes (run 1 and 4) used the same operating conditions such as the CFV of 3 m/s, TMP of 0.5 bar, pH of 7.5, and temperature of $(60 \pm 5)^{\circ}$C. Figure 3(a) shows the normalized flux of experimental run 1 and 4 and both results showed similar patterns. Figure 3(b) shows the normalized flux obtained for the second set of experimental runs on both membrane experiments (run 2 and 5) with a CFV of 1.5 m/s, TMP of 0.5 bar, pH of 7.5, and temperature of $(60 \pm 5)^{\circ}$C. Again, similar patterns were observed for both membranes. For experimental runs 3 and 8 which had the operating conditions such as a CFV of 3 m/s, TMP of 0.5 bar, pH of 7.5, and temperature of $(60 \pm 5)^{\circ}$C, along with the addition of the S5sT5 m strategy applied. Figure 3(c) shows the normalized flux of experimental runs 3 and 8, again both results showed similar patterns. The pH experiments consisted of

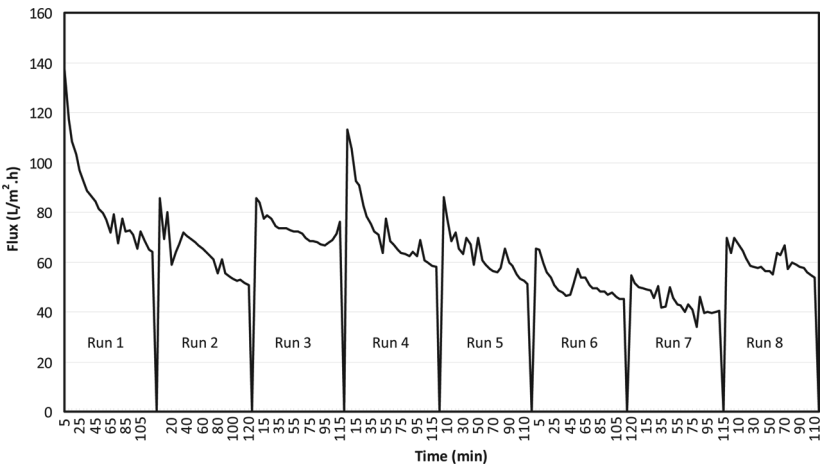


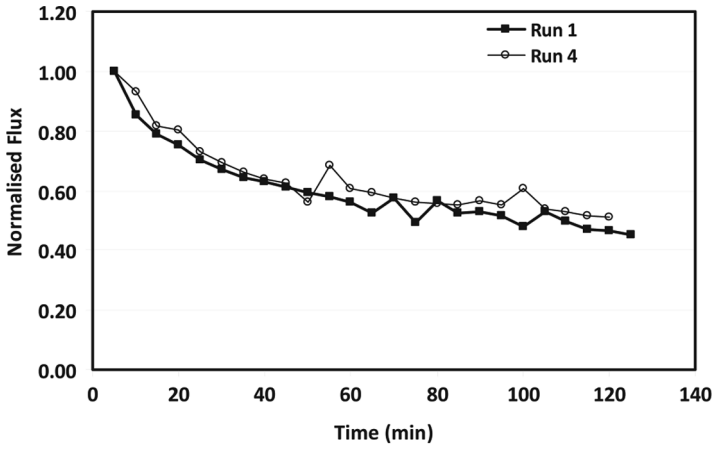
Figure 2. Experimental flux obtained under different operating conditions (runs 1 to 3 for 0.10 μm membrane and runs 4 to 8 for 0.05 μm membrane).

Table 3. Summary of initial, final, and average fluxes

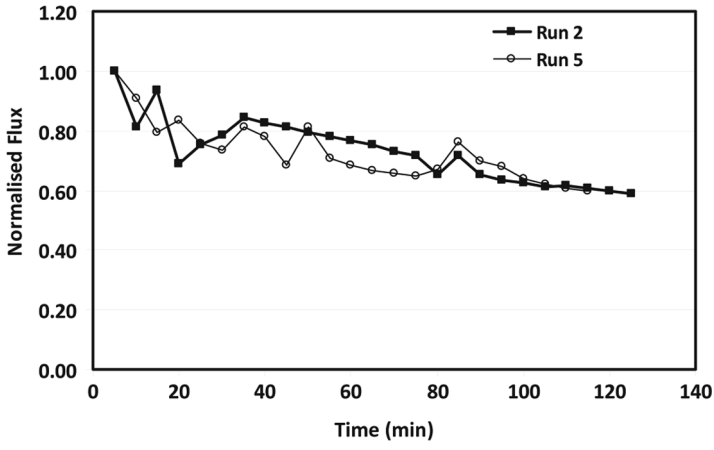
Run	Initial flux $L/m^2 \cdot h$	Final flux $L/m^2 \cdot h$	Average flux $L/m^2 \cdot h$	Average flux for every 30 minute time period $L/m^2 \cdot h$			
				1st 30 minutes	2nd 30 minutes	3rd 30 minutes	4th 30 minutes
1	137.4	62.3	82.4	109.2	82.8	73.5	67.7
2	85.4	50.4	62.5	70.8	68.6	60.0	52.5
3	85.6	76.0	73.0	79.6	72.9	68.8	70.2
4	113.1	58.0	72.7	93.8	71.3	64.2	61.4
5	86.0	51.3	62.6	72.1	64.2	58.7	54.1
6	65.6	45.2	51.3	58.4	49.6	50.9	46.5
7	54.7	40.9	44.3	50.6	45.8	40.6	40.9
8	69.9	52.8	59.9	66.1	57.5	60.8	56.5

experimental runs 4, 6, and 7. Figure 3(d) shows the normalized flux of these runs.

From the experimental runs 1, 2, 3, 4, 5, and 8 it can be concluded that at a TMP of 0.5 bar, low CFV (=1.5 m/s) provided initial fluxes

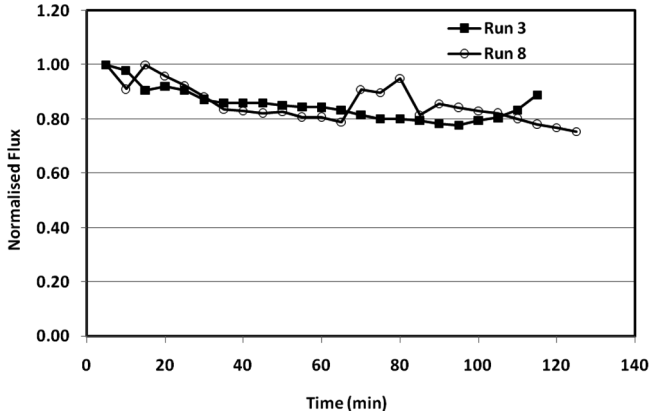


(a)

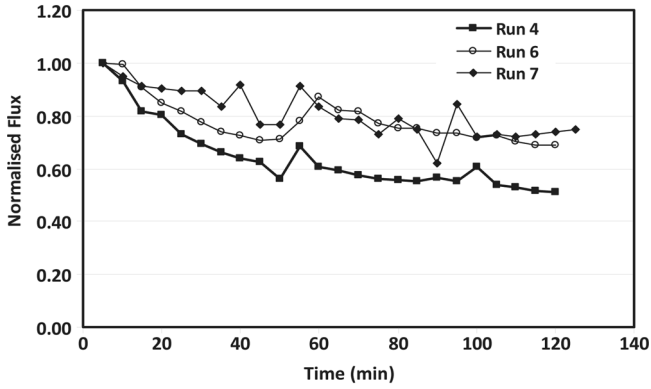


(b)

Figure 3. Temporal variation of normalized flux for 0.05 and 0.10 μm membranes at a TMP of 0.5 bar: (a) CFV = 3.0 m/s and pH = 7.5 (run 1 for 0.10 μm and run 4 for 0.05 μm membrane); (b) CFV = 1.5 m/s and pH = 7.5 (run 2 for 0.10 μm and run 5 for 0.05 μm membrane); (c) CFV = 3.0 m/s and pH = 7.5, S5sT5 m strategy (run 3 for 0.10 μm and run 8 for 0.05 μm membrane); (d) CFV = 3.0 m/s and pH = 5.5 (run 7), 7.5 (run 4) and 9.0 (run 6) for 0.05 μm membrane.



(c)



(d)

Figure 3. Continued.

of 85.4 and 86.0 $L/m^2 \cdot h$ for 0.10 and 0.05 μm membranes, respectively. However, when the CFV was increased to 3.0 m/s, the corresponding initial fluxes were 137.4 and 113.1 $L/m^2 \cdot h$, respectively. This indicates that the CFV is an important factor in determining the initial flux. Also the increase in CFV increased the initial flux obtained through 0.10 μm membrane more compared to the initial flux obtained through 0.05 μm membrane. Further, in another study conducted by our group found the initial fluxes of 140.7 and 165.4 $L/m^2 \cdot h$ for 0.10 and 0.05 μm membranes at a TMP of 1 bar and a CFV of 3.0 m/s, respectively (9). Thus, the TMP affects the initial flux obtained through 0.05 μm membrane more compared to the initial flux obtained through 0.10 μm membrane.

Similarly, at a TMP of 0.5 bar, low CFV (=1.5 m/s) provided average fluxes of 62.5 and 62.6 $L/m^2 \cdot h$ for 0.10 and 0.05 μm membranes, respectively. However, when the CFV was increased to 3.0 m/s, the corresponding average fluxes were 82.4 and 72.7 $L/m^2 \cdot h$, respectively. Thus, the CFV is an important factor in determining the average flux as well and again the increase in CFV increases the average flux obtained through 0.10 μm membrane more compared to the average flux obtained through 0.05 μm membrane. Also, our previous study (9) gave average fluxes of 60.6 and 81.9 $L/m^2 \cdot h$ (for 2 hours) for 0.10 and 0.05 μm membranes at a TMP of 1 bar and a CFV of 3.0 m/s. This indicates that increase in TMP affects more adversely the average flux obtained through 0.10 μm membrane compared to the average flux obtained through 0.05 μm membrane. This is possible as the rate of fouling of the membrane may be higher for 0.10 μm membrane compared to 0.05 μm membrane.

When the S5sT5 m strategy was applied in experimental runs 3 and 8, the final flux obtained was the highest (76.0 $L/m^2 \cdot h$) for 0.10 μm membrane and second highest (52.8 $L/m^2 \cdot h$) for 0.05 μm membrane. This indicates that the strategy of closing the permeate valve intermittently helps in reducing the fouling and thus reducing the rate of decline in the flux. It is interesting to note that the experimental runs applying the S5sT5 m strategy were conducted last for both membranes thus having lower initial fluxes. However, the normalized flux values obtained for experimental runs 3 and 8 over a period of 2 hours (Fig. 3(c)) were higher compared to the normalized fluxes obtained in other experimental runs which did not undergo the S5sT5 m strategy. This indicated that applying the S5sT5 m strategy is useful in reducing the rate of fouling.

Experimental runs 4, 6, and 7 were conducted to investigate the effect of pH on the initial, average, and final flux when filtering the sugar cane juice through 0.05 μm membrane. From Fig. 3(d) it can be seen that normalized flux values were better at pH 5.5 and 9.0 compared to at pH 7.5. However, from Table 3 it can be seen that the highest initial, average, and final flux were obtained at pH 7.5. This indicates that the membrane performs better in treating sugar cane juice at pH 7.5.

Clarified Sugar Cane Juice Quality

Table 4 shows the typical values of sugar cane juice quality in the feed and the permeate obtained from experimental run 2. From Table 4, it can be seen that turbidity of the juice was almost completely removed by the membrane and the starch removal was also high. Figure 4(a) shows the color reduction percentage from the feed to permeate in all 8

Table 4. Typical quality parameters of feed and permeate streams obtained for run 2

	Brix (%)		Pol		Purity		Turbidity (ICUMSA, 900 nm)		Color at 420 nm		Starch: concentration (at 100° Brix) (mg/L)		pH	
Time (Hr)	F	P	F	P	F	P	F	P	F	P	F	P	F	P
0	16.5	16.4	14.9	15	90.3	91.5	117.9	0.6	8780	7900	452.1	68.4	7.23	7.19
0.5	16.6	16.4	14.8	14.9	89.2	90.9	128.9	0.7	8800	7880	530.8	74.2	7.18	7.12
1	16.5	16.5	14.8	15	89.7	90.9	162.9	0.8	9380	8080	651.4	73.1	7.10	7.07
2	16.5	16.3	14.7	14.8	89.1	90.8	182.9	1.0	10020	8210	752.2	75.9	7.18	7.15

F-Feed; P-Permeate.

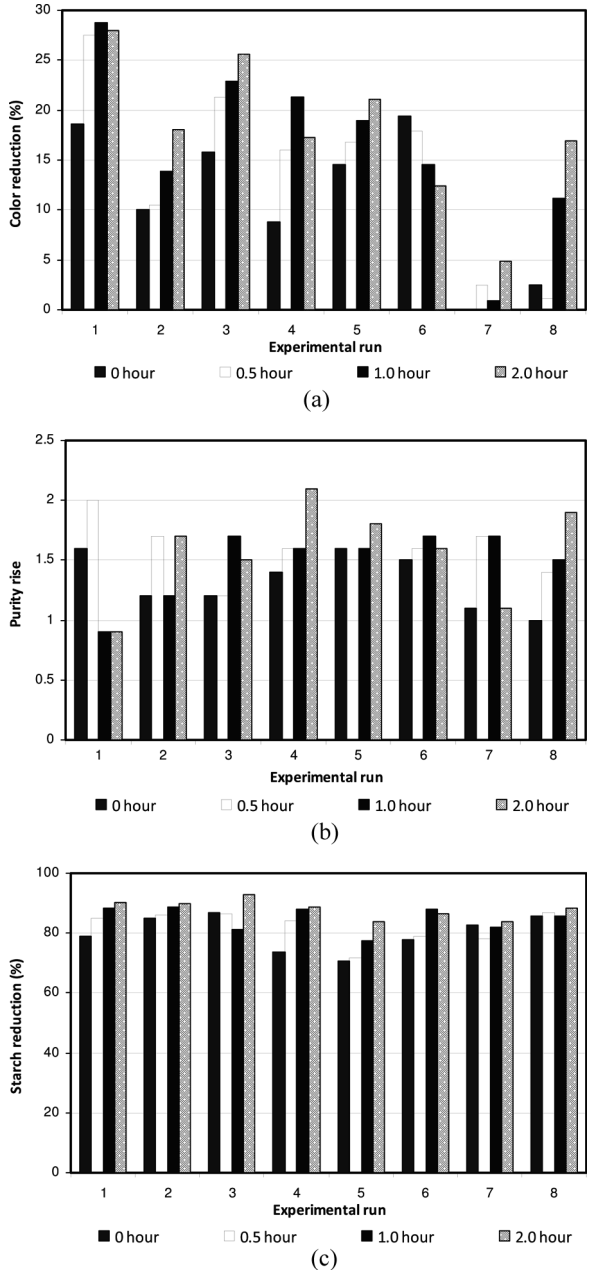


Figure 4. Performance of 0.05 and 0.10 μm membranes in treating sugar cane juice; (a) Percentage reduction of color; (b) Percentage rise in purity; (c) Percentage removal of starch.

experimental runs. Run 6 which was conducted at a pH of 9.0 showed a different trend than the rest of the runs; in run 6, the percentage reduction in color decreased with time instead of increasing like in all the other experimental runs. Experimental run 7 which did not have any lime (pH = 5.5) showed a very low percentage of color removal. It can be concluded that at lower pH no significant color removal is achieved by membrane filtration.

Figure 4(b) shows the percentage of purity rise in all experimental runs. Although the percentage of purity rise is small, it can be seen that generally it increased throughout an experimental run. Figure 4(c) shows the percentage removal of starch in all experimental runs. Generally the starch removal increased throughout an experimental run. Overall, filtering the sugar cane juice through the ceramic membrane could reduce the turbidity by 99.7%, color by 15%, and starch concentration by 80% as well as raise the purity by 1.4%.

Membrane Resistance and Cleaning of Fouled Membranes

For the experimental runs on the 0.10 μm membrane, different chemicals and concentrations were trialed to observe their effectiveness on cleaning the fouled membrane but for all experimental runs on the 0.05 μm membrane, 1% NaOH and 3000 ppm free chlorine was used as the cleaning chemical solution; the same chemical concentration was used if additional chemical cleaning was required. All chemical cleaning lasted for 30 minutes and were operated while the permeate valve was closed. The pH of the solution that is passed through a membrane is an important factor in deciding the service lifespan of the membrane (13), thus cleaning solutions with trial chemical composition that limits the pH to 11 were performed on the 0.10 μm membrane. But these trials failed to lower the initial resistance of the membrane values within acceptable recovery ranges and therefore were no longer performed on the 0.05 μm membrane. A summary of the chemicals used for cleaning along with their relative performance in recovering the membrane and an estimated cost of cleaning chemicals used are given in Table 5.

After each experimental run, the membrane resistance was measured after rinsing as well as chemical cleaning and the values of membrane resistance obtained are given in Table 6. Although rinsing with water would have definitely reduced fouling, the membrane resistance after rinsing was much higher compared to the resistance of the membrane at the beginning of the experimental run. However, chemical cleaning provided a recovery of the membrane which ranged from 76.7 to 98.9% for 0.10 μm membrane and 83.1 to 103.7% for 0.05 μm membrane.

Table 5. Summary of experimental cleaning runs

Run	Cleaning chemicals	Number of cleaning runs	Performance	Estimated cost of chemical cleaning (AU$)
1	0.5% NaOH	1	Unsatisfactory	0.52
	1% NaOH+3000 ppm free chlorine (NaOCl)	1	satisfactory	1.45
2	pH adjusted to 11 using: 150 ml NaOH (1%) + 200 ppm free chlorine (NaOCI)	1	Unsatisfactory	0.18
	1% NaOH+3000 ppm free chlorine (NaOCl)	1	satisfactory	1.45
3	pH adjusted to 11 using: 125 ml NaOH (1%) +l000 ppm free chlorine (NaOCl)	1	Unsatisfactory	0.27
	1% NaOH+3000 ppm free chlorine (300 ml NaOCl)	1	satisfactory	1.45
4	1% NaOH +3000 ppm free chlorine (300 ml NaOCl)	1	Satisfactory	1.45
5	1% NaOH +3000 ppm free chlorine (300 ml NaOCl)	1	Satisfactory	1.45
6	1% NaOH +3000 ppm free chlorine (300 ml NaOCl)	2	Satisfactory	2.90
7	1% NaOH +3000 ppm free chlorine (300 ml NaOCl)	3	Satisfactory	4.35
8	1% NaOH +3000 ppm free chlorine (300 ml NaOCl)	2	Satisfactory	2.90

• Cost calculated using: NaOH = AU$ 8.6/kg (technical grade) and NaOCI = AU$1.4/liter (active chlorine 12%).

• Constant operating protocol for all cleaning runs: TMP = 0.2 bar, cross-flow velocity = 1.5 m/s Temperature = 50°C, Duration = 30 minutes.

Table 6. Membrane resistance before and after the experimental runs

Run	Initial resistance (m^{-1})	Resistance after the rinse (m^{-1})	Resistance after the chemical cleaning (m^{-1})	Recovery (%)
1	6.943×10^{11}	2.873×10^{12}	7.574×10^{11}	91.7
2	7.191×10^{11}	4.281×10^{12}	9.379×10^{11}	76.7
3	9.379×10^{11}	4.356×10^{12}	9.487×10^{11}	98.9
4	10.030×10^{11}	3.821×10^{12}	6.690×10^{11}	150.0
5	6.690×10^{11}	4.591×10^{12}	6.451×10^{11}	103.7
6	6.451×10^{11}	5.949×10^{12}	7.385×10^{11}	87.4
7	7.385×10^{11}	3.603×10^{12}	7.917×10^{11}	93.3
8	7.917×10^{11}	5.397×10^{12}	9.523×10^{11}	83.1

Further, progressive increase in the initial membrane resistance was found for 0.10 μm membrane after each experimental run (runs 1 to 3) while that was not the case for the resistance of the 0.05 μm membrane (runs 4 to 8). This indicates that 0.10 μm could be affected more by irreversible fouling compared to 0.05 μm membrane. This was evident from our previous study as well (9).

Generally, 1% NaOH and 3000 ppm free chlorine performed better compared to other chemical combinations (either 0.5% NaOH solution or 200 ppm free chlorine solution at a pH of 11) in recovering the membrane. However, at a pH of 5.5, three chemical runs of 1% NaOH and 3000 ppm free chlorine solution were required to obtain 93.28% of membrane recovery. Similarly, at a pH of 9.0, two chemical runs of the above solution were required to recover the membrane. Thus, the pH of the sugar cane juice solution that is fed into the ceramic membrane could affect the fouling and rate of recovery of the membrane significantly.

Fouling Models

So far there has not yet been an intensive study of membrane fouling of limed and partially clarified sugar cane juice and therefore one of the aims of this study is to verify the validity of the existing fouling models. The four existing models tested in this study are (14,15):

- Cake filtration model
- Pore narrowing model (progressive internal fouling)
- Combination of external and progressive internal fouling
- Complete pore block model

Cake Filtration Model

This model assumes that after filtering sugar cane juice through a membrane, the macrosolutes rejected by the membrane form a solid layer known as cake on the surface of the membrane with a resistance R_c to filtration which will increase proportionally to the volume V_f of the filtered juice.

Thus the total filtration resistance, R_t at time t may be written as:

$$R_t = R_{m0} + R_c + \frac{\alpha C_w V_f}{A_0} \tag{7}$$

Where R_{m0} is the intrinsic membrane resistance, α is the specific cake resistance per unit mass, C_w is the rejected particle concentration near the membrane, and A_0 is the total membrane area. Thus the filtration flow rate can be given by:

$$Q_f = \frac{dV_f}{dt} = \frac{P_{tm}A_0}{\mu_f\left[R_{m0} + \left(\frac{\alpha C_w V_f}{A_0}\right)\right]} \tag{8}$$

Where μ_f is the permeate viscosity, and P_{tm} is the transmembrane pressure. Assuming that R_{m0} and αC_w remains constant, the following equation between the filtration time and the volume of juice filtered can be obtained by integrating the above equation.

$$\frac{t}{V_f} = \frac{1}{Q_0} + \frac{\alpha C_w V_f}{2A_0 R_{m0} Q_0} \tag{9}$$

Where $Q_0 = P_{tm}A_0/\mu_f R_{m0}$ is the initial flow rate of the permeate.

Pore Narrowing Model Detailing (Progressive Internal Fouling)

This model assumes that a fraction of the microsolute which penetrates the pores gets adsorbed onto the inner pore surface and by doing so narrowing the pores. The rate of reduction of pore radius, r can be expressed as:

$$2\pi NLr\frac{dr}{dt} = -CQ_f \tag{10}$$

Where L denotes the membrane thickness, N is the total number of pores, C is the dimensionless parameter characterizing the fraction of solute which gets adsorbed, Q_f is the permeate flow rate, and t is the time.

Integrating the above equation with respect to time yields:

$$\pi NL(r_0^2 - r^2) = CV_f \tag{11}$$

Where r_0 refers to the initial radius of membrane pores. Using Poiseuille's law in the pores and substituting r^2 from the above equation, we obtain:

$$Q_f = Q_0\left(1 - \frac{C_v}{V_p}\right)^2 \tag{12}$$

Where $V_p = \pi N r_0^2 L$ is the total initial pore volume. Integration of the above equation with respect to time yields:

$$\frac{t}{V_f} = \frac{1}{Q_0} + \frac{C_t}{V_p} \tag{13}$$

By combining Eqs. (12) and (13) one can obtain:

$$\frac{1}{\sqrt{Q_f}} = \frac{1}{\sqrt{Q_0}} + \frac{C\sqrt{Q_0}}{V_p}t \tag{14}$$

Combination of External and Progressive Internal Fouling Model

Since the sugar solution contains both rejected solutes and microsolutes, a combination of internal and external fouling might be expected. In this model, the cake filtration model is modified to include the membrane resistance R_m from the pore narrowing model which increases with time and may be expressed as:

$$R_m \approx R_{m0}\left(1 + 2cV_f/V_p\right) \tag{15}$$

Replacing this equation into the cake filtration model equation, the following expression could be obtained:

$$Q_f = \frac{P_{tm}A_0}{\mu_f\left[R_{m0} + \left(\frac{\alpha C_w}{A_0} + \frac{2C}{V_p}\right)V_f\right]} \tag{16}$$

This equation can be further expressed as:

$$\frac{1}{Q_f} = \left[\frac{\mu_f}{P_{tm}A_0}\right]\left(\frac{\alpha C_w}{A_0} + \frac{2C}{V_p}\right)V_f + \left[\frac{\mu_f R_{m0}}{P_{tm}A_0}\right] \tag{17}$$

Complete Pore Blocking Model

Of all four models, this is the more drastic form of internal fouling which can occur if particle sizes are equal or close to the pore diameter and result in a complete pore block of the membrane. Thus the surface area

of the membrane, A is reduced over the time as given below:

$$A = A_0 - \sigma V_f \tag{18}$$

Where σ is a parameter representing the plugging potential of the suspension which can be expected to be proportional to the particle concentration. Here the flux decay is assumed to be solely due to a reduction in the membrane area and not to an increase in resistance. The permeate flux Q_f can be expressed as:

$$Q_f = Q_0\left(1 - \frac{\sigma V_f}{A_0}\right) \tag{19}$$

Integrating the above equation with time would yield:

$$V_f = \frac{A_0}{\sigma}(1 - \exp(-\sigma J_0 t)) \tag{20}$$

Where J_0 is the initial permeate flux. By combining Eqs. (19) and (20), the following equation can be obtained:

$$Q_f = Q_0 \exp(-\sigma J_0 t)) \tag{21}$$

Rearranging this equation into a more suitable form for graphical plot would yield the following:

$$\ln[Q_f] = \ln[Q_0] - \sigma J_0 t \tag{22}$$

All four models mentioned above were used to fit the experimental data obtained from the experimental runs 1, 2, 4, 5, 6, and 7. Data obtained from runs 3 and 8, which utilizes the S5sT5 m strategy, are unsuitable for the fitting of these mathematical models as these models assume that no outside disturbances affect the normal operating conditions of the membrane. Of the four mathematical models tested, the pore narrowing model and the complete pore blocking model did not fit the experimental data. However, cake filtration model and the combination of external and progressive internal fouling models fitted the experimental data to very good extent (Tables 7 and 8). Figures 5(a) and 5(b) shows the cake filtration model fitting to the experimental data obtained from 0.10 and 0.05 μm membranes respectively; Figs. 5(c) and 5(d) shows the combination of external and progressive internal fouling model fitting to the experimental data obtained from 0.10 and 0.05 μm membranes respectively. Between the two models, the cake filtration model fitted well to the experimental data obtained from both membranes indicating the

Table 7. Cake filtration model fitting to the data obtained from experimental runs

Run	1/Q (h/L)	Q (L/h)	Flux ($L/m^2 \cdot h$) Model	Flux ($L/m^2 \cdot h$) Actual	Error (%)	R_0 (m^{-1})	αC_w (m^{-2})
1	0.063	15.873	133.05	137.38	−3.151	6.94×10^1	4.21×10^9
2	0.106	9.434	79.07	85.41	−7.417	7.19×10^1	2.43×10^9
4	0.075	13.369	112.06	113.13	−0.950	10.0×10^{11}	8.0×10^9
5	0.102	9.775	81.93	86.04	−4.769	6.69×10^{11}	3.74×10^9
6	0.133	7.541	63.21	65.60	−3.637	6.45×10^{11}	3.25×10^9
7	0.156	6.427	53.87	54.66	−1.457	7.38×10^{11}	3.62×10^9

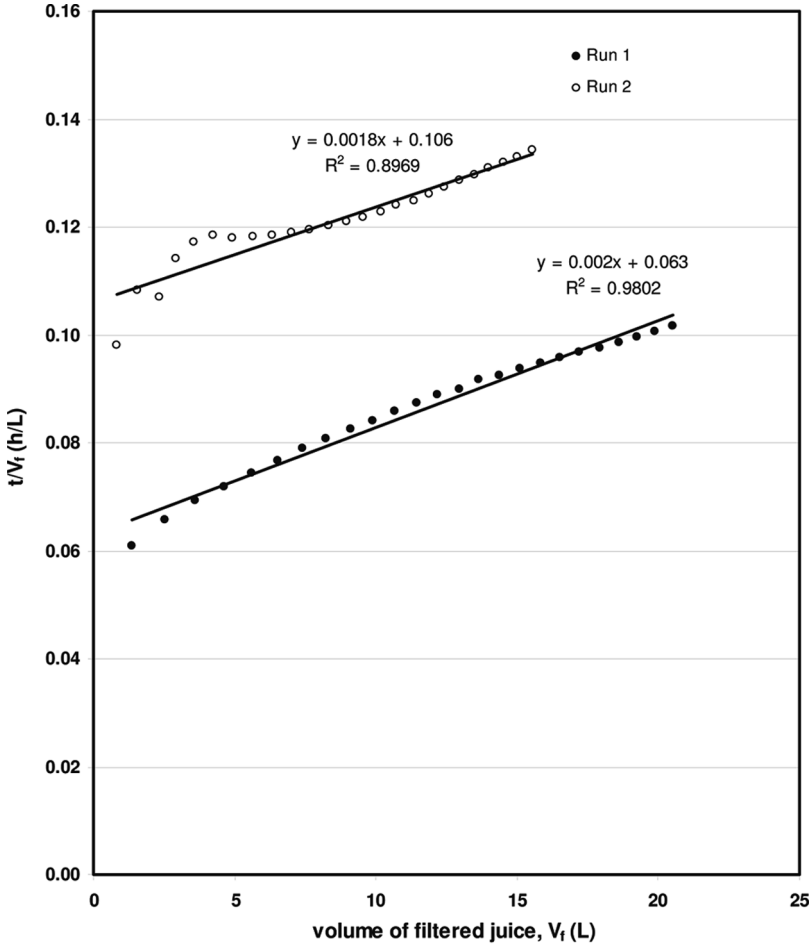
surface fouling of the membrane is significant compared to the progressive internal fouling. This is acceptable as at low TMP the foulants could have been transported less towards the membrane surface and therefore not contributing much for the internal fouling. Our previous study (9) showed that at a TMP of 1 bar and a CFV of 3 m/s, cake fouling model fitted better for the data obtained from 0.05 μm membrane and the combination of external and progressive internal fouling model fitted better for 0.10 μm membrane. Thus, 0.10 μm membrane could be susceptible to internal fouling at higher TMPs. However, 0.05 μm is less susceptible to internal fouling at TMPs of 0.5 and 1.0 bar.

Particle Size Analysis

When the permeate sample collected after 30 minutes of filtration in run 2 was initially measured, it was added directly into the Malvern Mastersizer

Table 8. Combination of external and progressive internal fouling model fitting to the data obtained from experimental runs

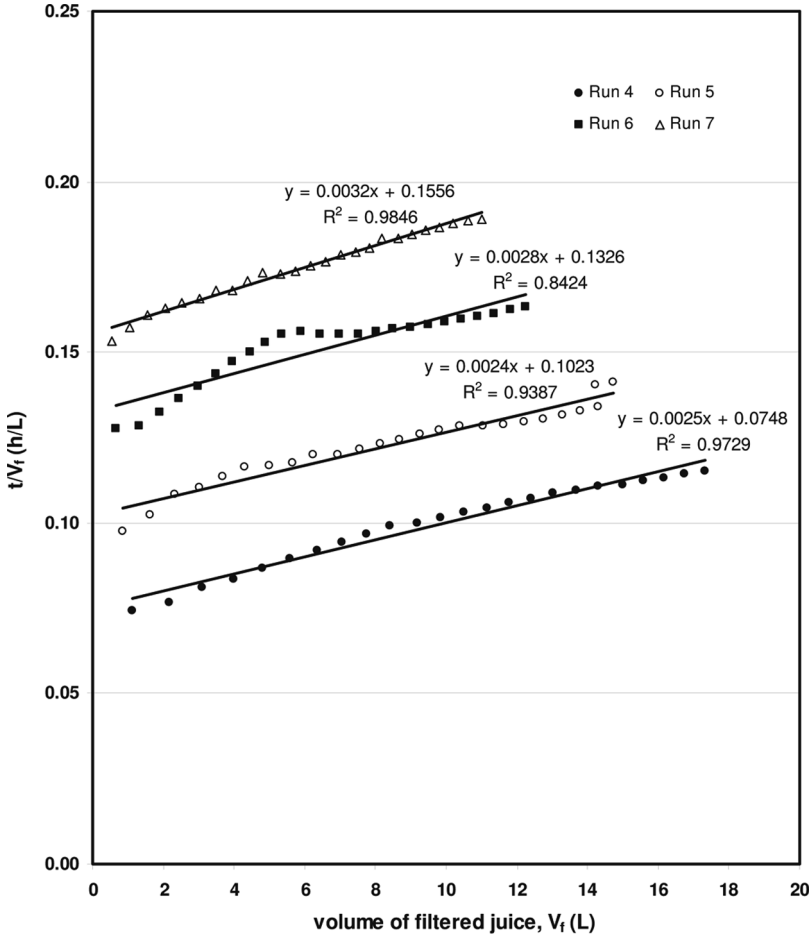
Run	Model input, R_{m0} (m^{-1})	Model output of $[\mu_f R_{m0}/P_{tm}A_0]$ (h/L)	Experimental value of $[\mu_f R_{m0}/P_{tm}A_0]$ (h/L)	Error in the value of $[\mu_f R_{m0}/P_{tm}A_0]$ (%)
1	6.943×10^{11}	0.03686	0.0672	45.152
2	7.191×10^{11}	0.03818	0.1043	63.399
4	1.003×10^{12}	0.05326	0.0818	34.886
5	6.690×10^{11}	0.03552	0.1075	66.961
6	6.451×10^{11}	0.03425	0.1419	75.865
7	7.385×10^{11}	0.03920	0.1590	75.343



(a)

Figure 5. (a) Cake filtration model fitting to the experimental data for 0.10 μm membrane; (b) Cake filtration model fitting to the experimental data for 0.05 μm membrane; (c) Combination of external and progressive internal fouling model fitting to the experimental data for 0.10 μm membrane; (d) Combination of external and progressive internal fouling model fitting to the experimental data for 0.05 μm membrane.

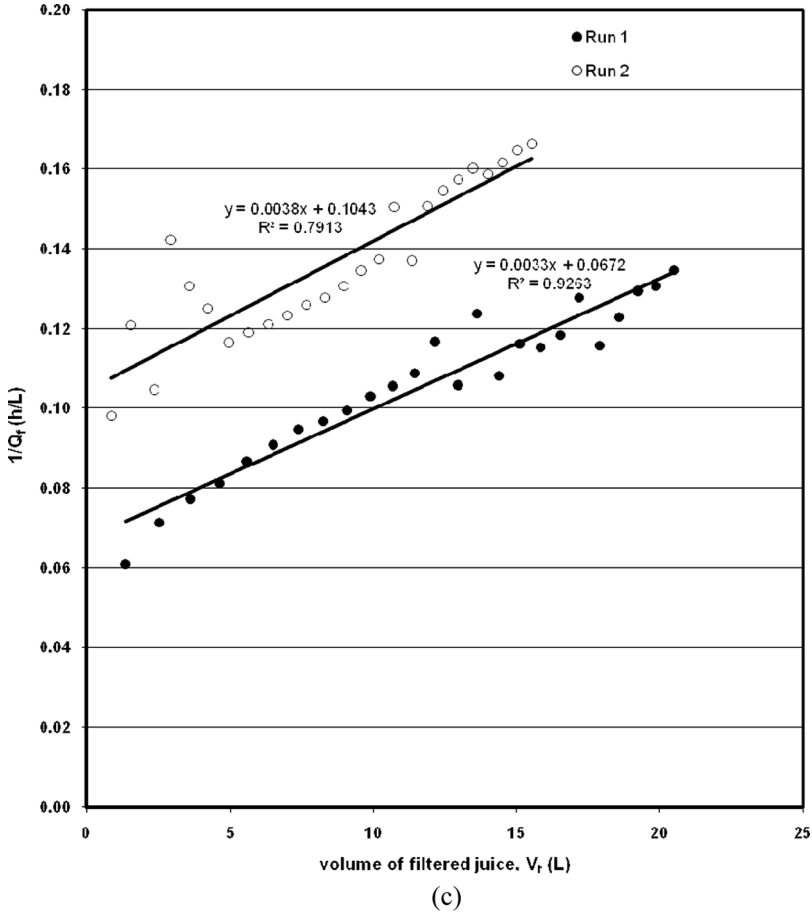
2000 and measured without any pretreatment. The results showed that the sample contained two main groups of particles, with the small particles having a peak at around 1 μm and the larger particles centered on a peak at 25 μm (Fig. 6(a)). In the initial measurement, the larger particles



(b)

Figure 5. Continued.

accounted for nearly 50% of the volume of the sample. Figure 6(a) also shows the results obtained when the same sample was measured several times with only the pump and stirrer moving the sample through the instrument; the particle size was noticed to be reducing over time. This suggested that the larger particles were agglomerates; another aliquot of the sample was sonicated in an external ultrasonic bath before measurement. When the sonicated sample was measured, the peak of the larger particles had disappeared and all had broken down into smaller

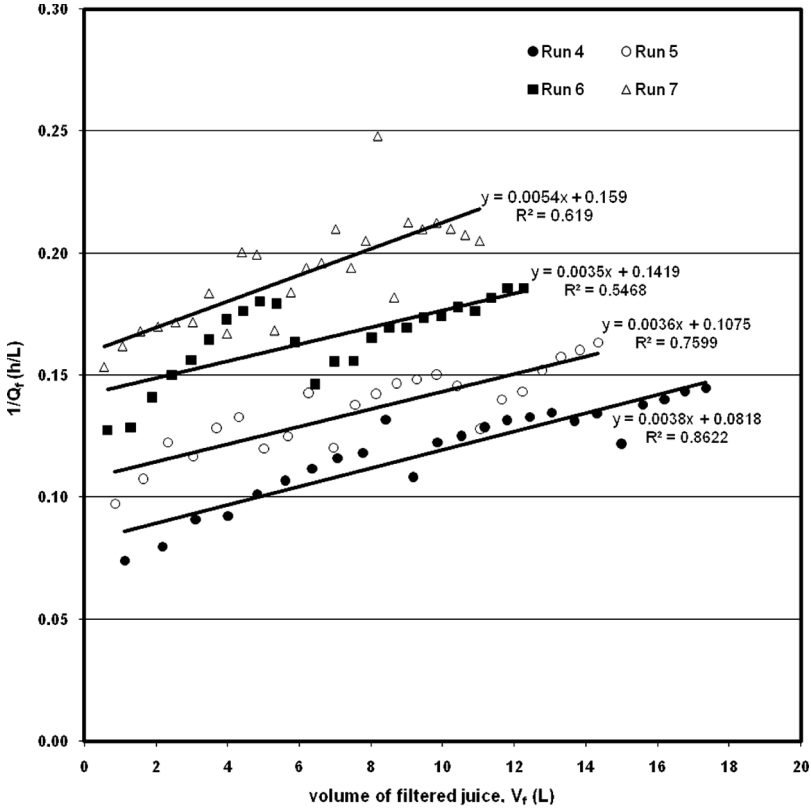


(c)

Figure 5. Continued.

particles (Fig. 6(b)). Similar results were obtained when the permeate samples obtained after 1 and 2 hours of filtration in run 2 (Figs. 6(c) and 6(d)). However, the presence of particles in the permeate that are larger than the pore size of the membrane (0.10 μm) indicates that the particles in the permeate are unstable and had formed flocs that were up to 10 μm in size.

In order to obtain accurate results the samples were analysed through Malvern zetasizer-nano system which is a light scattering instrument that is capable of measuring sub-micron particles. An aliquot of the permeate sample obtained after 30 minutes of filtration in run 2 was filtered



(d)

Figure 5. Continued.

through a 220 nm syringe filter and approximately 5 drops of the filtered sample was added to 1 mL of water. After that the sample is finally introduced into the Zetasizer-Nano system for measurement. Figures 7(a) and 7(b) shows the "intensity distribution" and the "volume distribution" for the same sample. Larger particles scatter much more light than smaller particles, so an intensity distribution is extra sensitive to the presence of large particles. The intensity distribution for this sample shows that there were large particles present that passed through the filter, but there is also a significant amount of smaller particles around 1 nm present. By converting the result to a "volume" distribution, the bulk of the sample by volume is observed to be composed by the

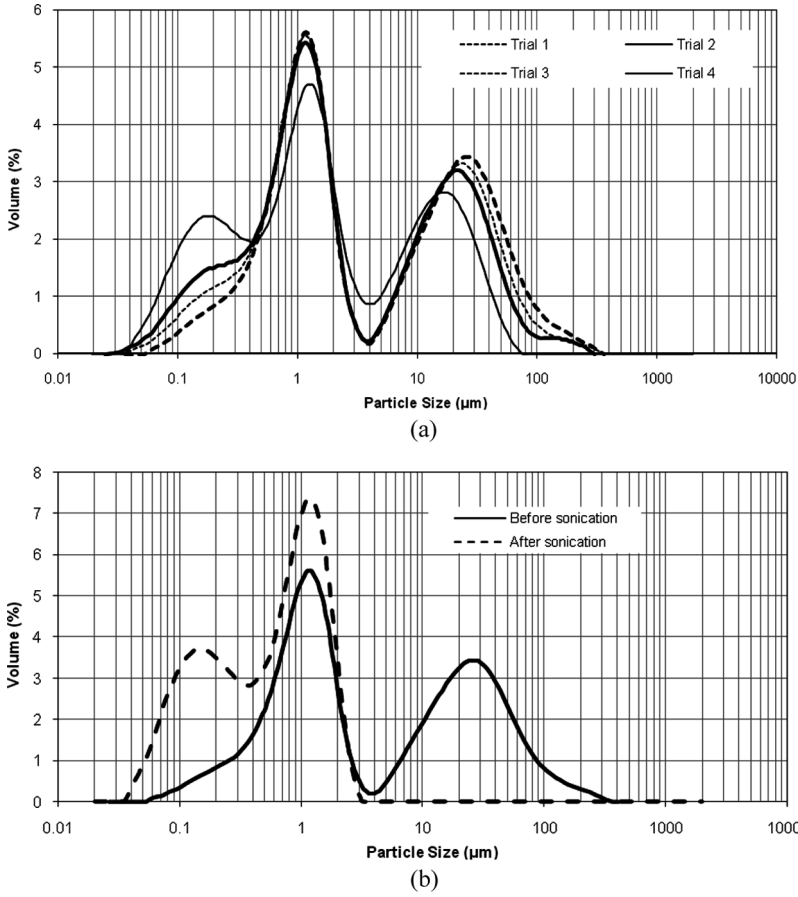
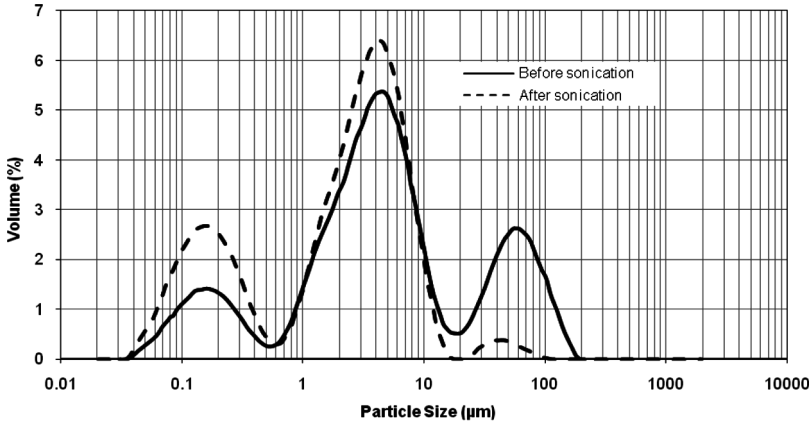


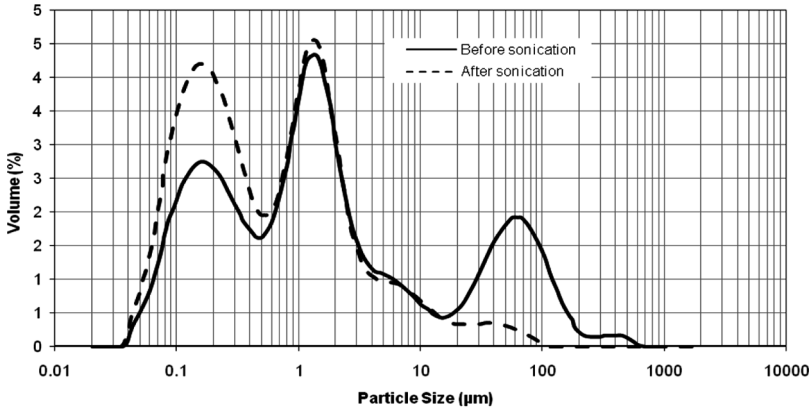
Figure 6. Particle size distribution of permeate samples collected in run 2 (0.10 μm membrane); (a) breakdown of agglomerates when the sample (0.5 hour) was pumped to Malvern Zetasizer repeatedly; (b) Before and after sonication (0.5 hour sample); (c) Before and after sonication (1.0 hour sample); (d) Before and after sonication (2.0 hour sample).

material at 1 nm. This material at 1 nm is almost certainly the sucrose molecules in the solution.

The instability of the particles can be evaluated by analyzing the zeta potential of those particles. Generally speaking, a high zeta potential indicates a stable dispersion while a low zeta potential indicates an unstable dispersion. The permeate sample collected after 30 minutes of filtration in run 2 had a zeta potential of −8 mV which is quite low. Thus,



(c)



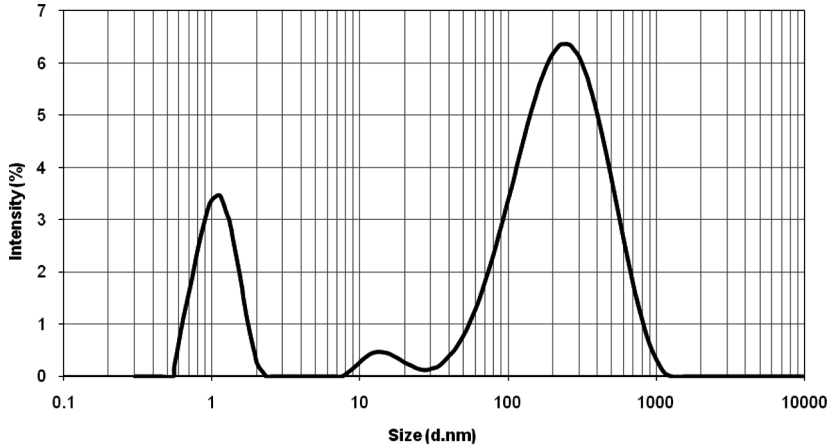
(d)

Figure 6. Continued.

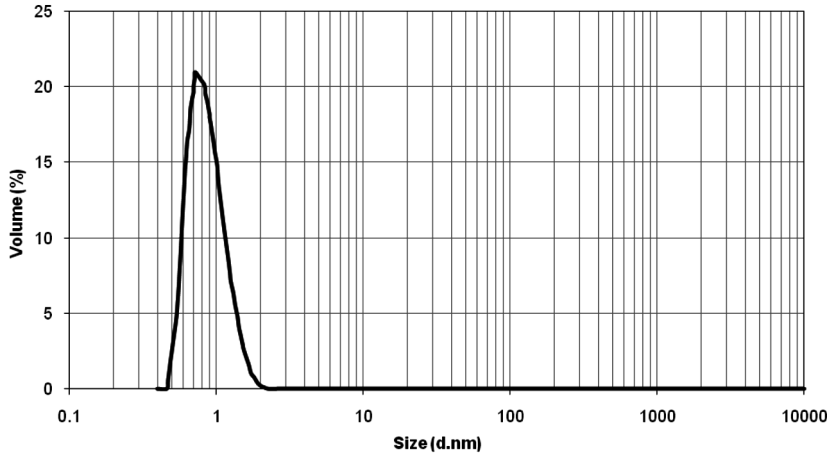
if the permeate is left alone particles in the permeate could form flocs which was observed in this study.

CONCLUSION

The overall performance of ceramic membranes with pore sizes of 0.05 µm and 0.10 µm was investigated under a low TMP of 0.5 bar. When other operating conditions were changed, the following results were



(a)



(b)

Figure 7. (a) Size distribution by intensity after filtered through 220 nm (0.5 hour sample); (b) Size distribution by volume after filtered through 220 nm (0.5 hour sample).

obtained and were compared with the results obtained in a previous study (9):

1. At a lower TMP (0.5 bar), the increase in CFV from 1.5 to 3.0 m/s increased the initial flux (by 32 and 61% respectively) and average flux (by 16 and 32% respectively) obtained through 0.05 and 0.10 μm

membranes. This indicates that the CFV is an important factor in determining the initial and average fluxes obtained through the membranes. Also, the membranes with larger pore size provided higher initial flux. Further, when the initial and average fluxes are compared at a fixed CFV (3.0 m/s) and at TMPs of 0.5 and 1.0 bar (data from previous study (9)) it was found that the initial flux of 0.05 and 0.10 μm membranes increased by 46.2 and 2.4% respectively and the average flux of 0.05 μm membrane increased by 13%. Thus, the TMP affects the initial and average fluxes obtained through 0.05 tim membrane more compared to that obtained through 0.10 μm membrane. This can be attributed to the faster rate of fouling of 0.10 μm membrane compared to that of 0.05 μm membrane which does not help to increase the initial and average fluxes through 0.10 μm membrane significantly.

2. Closing the permeate valve intermittently through the application of the S5sT5 m strategy reduced the rate of fouling of both membranes and provided a higher normalized flux throughout an experimental run.
3. The pH experiments indicated that better initial and average fluxes and permeate juice quality were obtained at a pH of 7.5. Very low color removal was observed at a pH of 5.5. In general, both ceramic membranes reduced the turbidity by 99.7%, color by 15%, and starch concentration by 80%. The purity was increased by 1.4%.
4. Out of the four fouling models used to fit the data obtained from the experimental runs, only the cake filtration model fitted to those data well. At a lower TMP (0.5 bar), even the 0.10 μm membrane would foul due to the deposition of cake on the membrane rather than progressive internal fouling. However, at a higher TMP (1 bar), the 0.05 μm membrane might still foul due to the deposition of cake on the membrane surface but the 0.10 μm membrane would foul due to both deposition of cake and internal fouling (9).
5. The cleaning solution prepared with 1% NaOH + 3000 ppm NaOCl provided better cleaning and recovery of membranes which treated the sugar cane juice. Sugar cane juice with a pH of 5.5 or 9.0 fouled the 0.05 μm membrane more compared to the juice with a pH of 7.5.
6. Sugar cane juice permeate from the ceramic membranes had a zeta potential of −8 mV which makes the particles in the juice to be unstable. Thus, if the permeate is preserved, the formation of flocs is possible which could have a size of 25 μm. This information is essential if the permeate is used for crystallization of raw sugar.

ACKNOWLEDGEMENTS

Sugar Research and Development Corporation (SRDC) funded a project entitled "JCU029: evaluation of membrane technology for clarification of sugar cane juice (2007–2009)" to carry out this work. Mr. Bryn McDonagh of ATA Scientific Pty Ltd, NSW, Australia carried out particle size analysis on the permeate samples and provided valuable suggestions. Messrs. Curt Arrowsmith, Stuart Petersen, and John Ellis of the School of Engineering and Physical Sciences, James Cook University, are also acknowledged for providing assistance in purchasing and installing the membrane system.

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