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Short chemical cleaning of polymeric ultrafiltration membranes fouled by sugarcane juice polysaccharides

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ABSTRACT

This work examines chemical cleaning of PS and PES ultrafiltration (UF) membranes fouled by sugarcane juice and its polysaccharide component. Six commercial membranes in the MWCO range of 30–100 kD were examined. The juice polysaccharide fraction was used as the model foulant and short cleaning duration (up to 20 min) was investigated. A combination of 2% w/v NaOH and 200 ppm NaOCl resulted in adequate water and juice flux recovery. However, NaOCl exposure affected the membrane properties, leading to flux enhancement, with repeated UF-cleaning operations surprisingly resulting in progressively higher product flux. Among the membranes investigated, those with low water flux (< 100 L/m^{2}h) fouled less and were more amenable to chemical cleaning.

Keywords: Sugarcane juice; Ultrafiltration; Polysaccharides; Fouling; Chemical cleaning

1. Introduction

Membrane fouling, due to deposition of the rejected material on the surface and within the pores, results in flux decline and change in membrane selectivity. Strategies like feed-pretreatment, adjusting the operation parameters and membrane surface modification can minimize fouling but cannot completely eliminate it. Thus, cleaning is an integral part of membrane applications. Membrane cleaning can involve one or a combination of methods viz. physical (e.g. ultrasound, sponge balls, back pulsing), biological (e.g. enzymatic treatment) and chemical (acids, alkalis, disinfectants, detergents). For food processing applications like ultrafiltration (UF) of milk, whey and juices, chemical cleaning is most common [1–5]).

Developing an optimal membrane-cleaning strategy for a given application is important since it has a direct impact on the process economics. Appropriate chemicals usage causes less damage to membrane surface thereby extending its lifetime and reducing the frequency of membrane replacement. The key parameters affecting cleaning efficiency are the concentration, temperature, hydrodynamic conditions and the time. For most chemical cleaners, 30–60 min is generally prescribed for complete action [6]; moreover, prolonged chemical cleaning may actually refoul the membrane. Thus, there have been several reports on short chemical cleaning cycles (up to 30 min) for membranes fouled by multi-component feed streams in various applications viz. food and beverage industry [1,4,7,8], wastewater treatment [9] and industrial effluents [10–12].

Clarification of sugarcane juice by UF using polymeric membranes is characterized by significant fouling and flux decline [13–16]. Among the different components present in sugarcane juice, the polysaccharides fraction is known to cause membrane fouling [17]. Alkaline hypochlorite is a recommended cleaning agent for polysaccharide or protein fouled membranes [6]. In passion fruit juice UF, membrane fouling caused by cellulose and hemicellulose along with other small carbohydrates was

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removed using sodium hydroxide [7]. Treatment with 0.1% NaOH for 5 min followed by 10 min water wash was able to restore the initial pure water permeability. Polysaccharide removal efficiency by NaOH was enhanced with increasing time of action on PES membrane [18]. Strugholtz et al. [19] evaluated the performance of different cleaning chemicals and their combinations as well as the effect of temperature on MF membranes fouled in water treatment application. The cleaning solutions analysis using liquid chromatography–organic carbon detection (LC-OCD) revealed the maximum removal of polysaccharides by 50 ppm NaOCl solution at 20°C. A combination of hypochlorite with caustic was found to be less effective in this case. In sugarcane juice UF using polyethersulphone (PES) and polysulphone (PS), a combination of 0.5% HCl and 0.1% caustic at 50°C resulted up to 80% water flux recovery within 20 min [20].

This work investigates the efficacy of short chemical cleaning cycles for various PES and PS membranes fouled by sugarcane juice and its isolated polysaccharide fraction. The relationship between the membrane pure water flux, extent of fouling and flux recovery after cleaning is also examined.

2. Experimental

2.1. Materials

Commercially available PS and PES UF membranes in the 30–100 kDa range were investigated (Table 1). The sugarcane juice samples, after clarification with lime, were obtained from a local sugar mill in northern India. The juice samples were stored in a freezer at –70°C and required volumes were brought to room temperature prior to membrane filtration. Samples once used were discarded and a fresh lot used for the subsequent experiment. The polysaccharide fraction was prepared from the juice sample as described in Section 2.2.2. The cleaning solutions were prepared fresh by dissolving a known amount of the required chemical viz. sodium hypochlorite (NaOCl) (BDH, Mumbai, India) or sodium hydroxide (NaOH) (Qualigens ExcelaR, Mumbai, India) in reverse osmosis (RO) water.

2.2. Methods

2.2.1. Juice analysis

Protein was calculated from the total nitrogen, estimated by Kjeldahl method [21]. The total carbohydrate was estimated colorimetrically by Dubois assay [22] and dextran was analyzed using Roberts' copper method [23].

2.2.2. Juice polysaccharide preparation

The polysaccharide fraction was isolated from sugarcane juice by precipitation with hydrochloric acid and ethanol. The detailed procedure is described elsewhere [24]. The precipitated fraction was freeze dried and stored for further use. All experiments were conducted using freshly reconstituted solution of the freeze dried fraction in RO water.

2.2.3. UF experiments

UF was conducted in a stainless steel SEPA ST cell (Osmonics, USA) with a filtration area of 16.9 cm^2. Prior to UF, the clarified sugarcane juice was centrifuged at 6000 rpm for 18 min to remove suspended particulate matter. Experiments were carried out with a volume reduction of 33%. The flow rate was measured in terms of the time required to collect a given volume of permeate. The feed, retentate and permeate were subsequently analyzed for protein, total carbohydrates and dextran content. For the UF of polysaccharide solution, 30 ml of the

Table 1
Membranes screened

	Membrane	Material	Supplier	NMWCO (kD)		Pure water flux (L/m^2 h)	
				Supplier	Experimental [24]	Supplier[a]	Experimental[b]
1.	UFPES50	PES	Permionics, India	50	b.t.l.[c]	NA	527
2.	UF-PES-030H	Permanently hydrophilic PES	Microdyn-Nadir, Germany	30	18	100–250	33
3.	UF-PES-050H	Permanently hydrophilic PES	Microdyn-Nadir, Germany	50	29	250–500	259
4.	UF-PS-100H	Permanently hydrophilic PS	Microdyn-Nadir, Germany	100	>100	300–600	146
5.	GR51PP	PS	Alfa-Laval, Denmark	50	>60	NA	35
6.	GR40PP	PS	Alfa-Laval, Denmark	100	37–50	NA	139

[a] 3 bar, 20°C, 700 rpm; [b] 1 bar, ambient temperature (25–28°C), 0 rpm; [c] beyond test limit

feed solution at a concentration of 1.5mg/ml was used to obtain 10 ml of permeate.

All experiments were performed at ambient temperature, at a constant pressure of 1 bar in a dead-end filtration mode. A fresh membrane disc was used for each experiment and the membrane washing and water flux measurements were performed using RO water. After juice/polysaccharide UF, the fouled membrane was rinsed with RO water to remove loosely bound foulants before measuring the fouled membrane water flux.

The fouling was estimated in terms of the normalized pure water flux (PWF) J_1/J_0 where J_0 and J_1 is the PWF of the pristine and the fouled membranes respectively. A high J_1/J_0 ratio indicates low fouling. The membrane propensity to foul was expressed as J_{p2}/J_{p1}, where J_{p1} and J_{p2} is the juice flux at the beginning and end of UF respectively [25]. A high J_{p2}/J_{p1} value indicated a lower propensity to foul.

The rejection of juice component "*i*" was calculated using the following expression:

$$R_i(\%) = \left(1 - C_{i,p} / C_{i,f}\right) \times 100 \qquad (1)$$

where R_i is the rejection of component *i*, and C_p and C_f is the concentration of *i* in the permeate and the feed respectively.

The deposition of specific juice component on the membrane was estimated by mass balance.

$$D_i = C_{i,f} V_{i,f} - C_{i,p} V_{i,p} - C_{i,r} V_{i,r} \qquad (2)$$

where *D* is deposition in mg of the component *i* on the membrane, *C* is concentration of foulants (mg/ml) and *V* is volume (ml). The subscripts *f*, *p*, *r* stand for feed, permeate and retentate respectively. The methods followed to estimate the concentration of juice components have been described in section 2.2.1.

2.2.4. Membrane cleaning

2.2.4.1. Pristine membrane washing

The pristine membranes were washed thoroughly to remove any preservative before UF. The membrane disc was dipped in 100 ml RO water and sonicated for 3 min (Toshibha, 1.5L50, India). The pH, conductivity and total dissolved solids (TDS) content of the water was monitored after each wash using pocket-sized testers (Eutech, Singapore). The procedure was repeated till the properties of the wash water were observed to be within ±0.5 units of the fresh RO water values. All washing and PWF measurements were conducted using RO water.

2.2.4.2. Chemical cleaning

Known concentrations of the reagents (200 ppm NaOCl and up to 2.0% w/v NaOH) were examined alone, in sequence and in combination as cleaning agents. The choice of the reagents was based on our previous findings [20,26] and literature recommendations [6]. The fouled membrane disc was immersed in 50 ml of the appropriate cleaning solution for a fixed time period and shaken intermittently. The disc was thereafter removed from the cleaning solution and rinsed repeatedly with fresh RO water while monitoring the pH, conductivity and TDS of the wash solution. Washing was considered to be complete once the wash water characteristics were within ±0.5 units of the fresh RO water values. Subsequently, the flux of the chemically cleaned membrane (J_c) was measured.

All the fouling and cleaning experiments were done in duplicate. The normalized PWF of the chemically cleaned membrane was expressed as J_c/J_0.

2.2.5. Scanning electron microscopy (SEM) analysis

SEM was done using Leica Stereoscan 440 (U.K.). The pristine membrane samples were washed with water following the method described in section 2.2.4.1. The fouled membranes were rinsed with water to remove loosely bound components. All membrane samples were dried overnight at 30ºC before preparing 3×3 mm strips for silver sputter coating. The silver coated strips were used for recording the SEM images.

3. Results and discussion

3.1. Juice fouling

Fig. 1a shows the sugarcane juice flux and the corresponding fouling for the selected membranes. These membranes displayed an average flux of greater than 6 L/m^{2}h and the fouling was low-to-moderate (J_1/J_0 of 0.47–0.75). The only exception was UFPES50, which showed considerable fouling (J_1/J_0 of 0.38). This was however selected because it was the best among the locally manufactured Permionics membranes. Interestingly, the J_{p2}/J_{p1} ratio is low (≤0.31) for all the membranes indicating that these have a high propensity towards juice fouling (Table 2). Since the experiments were conducted in a constant pressure dead-end mode, the rejected components in the feed matter were expected to contribute significantly to the filtration resistance due to a combination of concentration polarization and membrane fouling thereby resulting in flux decline. An analysis of the fouling by the resistance-in-series model indicated that cake filtration was the dominant phenomenon [17].

The membrane selectivity was analyzed in terms of the rejection of the non-sugar components viz. protein, carbohydrate and dextran. All the selected membranes displayed high rejection of the non-sugar components (Fig. 1b). Furthermore, a significant amount of the rejected protein component was deposited on the membranes (Fig. 1c). The deposition was relatively lower for GR40PP and UFPES50 membranes. The dextran deposi-

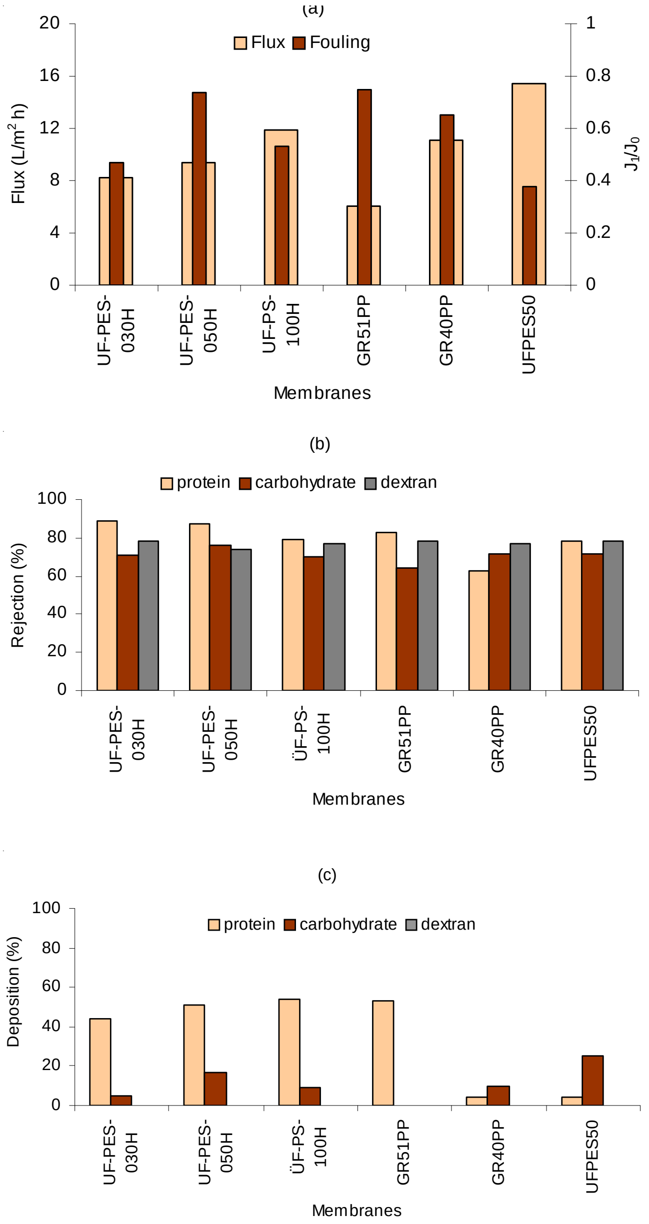

Fig. 1. UF performance of different membranes with sugarcane juice (a) flux and fouling (b) rejection of non-sugars (c) deposition of non-sugars.

Table 2
Flux and fouling characteristics of the selected membranes

Membrane	$J_{p,\text{avg.}}$ (L/m² h)	J_1/J_0	J_{p2}/J_{p1}
UFPES50	15	0.38	0.26
UF-PES-030H	8	0.47	0.30
UF-PES-050H	9	0.74	0.22
UF-PS-100H	12	0.53	0.17
GR51PP	6	0.75	0.31
GR40PP	11	0.65	0.24

tion was negligible (<0.04%) for all the membranes and thus this component appears to have remained almost completely in solution. In our earlier works [17,24] we observed that the juice polysaccharide fraction, containing protein moieties, caused membrane fouling. This protein fraction present in the precipitated juice polysaccharide estimated by BCA assay was about 6.4% (w/w). Therefore, the juice polysaccharide fraction was selected as the model foulant for the chemical cleaning studies discussed in the following sections.

3.2. Membrane cleaning

3.2.1. Action of NaOCl

The effect of 200 ppm NaOCl solution was studied with all the six membranes for varying cleaning duration. Table 3 compares the normalized pure water flux (J_1/J_0) after fouling by the polysaccharide fraction and the corresponding normalized cleaned membrane water flux (J_c/J_0). In general, the J_c/J_0 ratio increased with increasing cleaning duration. The exception was UF-PES-050H, which displayed a J_c/J_0 ratio less than the corresponding J_1/J_0 value after 20 min cleaning. This could either be an experimental anomaly; alternately, it indicated possible re-deposition of the removed foulant on the membrane surface during the cleaning and subsequent water flux measurement process. Also there was slight reduction in J_c/J_0 value for UF-PES-030H membrane after 20 min cleaning compared to 15 min cleaning. This was possi-

Table3
Action of sodium hypochlorite solution

Membranes	Time (min)	J_1/J_0	J_c/J_0
UF-PES-030H	5	0.77	0.84
	10	0.86	0.92
	15	0.90	1.05
	20	0.82	0.99
UF-PES-050H	10	0.37	0.72
	15	0.59	0.98
	20	0.45	0.42
UFPES50	10	0.51	0.55
	15	0.36	0.60
	20	0.33	0.76
GR51PP	10	0.81	0.90
	15	0.57	0.91
	20	0.99	1.29
GR40PP	10	0.49	0.54
	15	0.60	0.88
	20	0.62	0.92
UF-PS-100H	10	0.75	0.90
	15	0.61	0.77
	20	0.53	1.05

bly linked to the marginally higher fouling of that particular membrane disc (J_1/J_0 of 0.82) compared to the one exposed for 15 min to the cleaning solution (J_1/J_0 of 0.90).

Of the membranes investigated, UF-PES-030H and GR51PP are low flux membranes (pristine membrane PWF < 50 L/m^2 h). These membranes fouled less (J_1/J_0 of 0.57–0.99) and displayed good PWF recovery ($J_c/J_0 \geq 0.84$) even for very short cleaning duration (5 min). For the remaining membranes with moderate to high pristine membrane PWF (about 150 L/m^2 h and above), fouling was relatively higher (J_1/J_0 of 0.33–0.75). The corresponding J_c/J_0 ratio was variable (0.54–1.05). For a given membrane type, there was a variation in J_1/J_0 ratio which was attributed to the inherent heterogeneity in the membranes. This kind of variation in pristine membrane PWF was also observed by Susanto and Ulbricht [27]. For each membrane type, 3–6 discs from sheets of the same lot number were used. An examination of the average PWF value and the standard deviation of the pristine membrane discs showed that the variation was more pronounced in the higher PWF UFPES50 and UF-PES-050H membranes (Table 4). Subsequent experiments with the UF-PES-050H membranes (Section 3.2.2 onwards) were performed with discs having PWF variation within 15%.

It was observed that in some of the cases, the action of NaOCl resulted in a higher PWF of the cleaned membrane in comparison to the pristine membrane value (i.e. $J_c/J_0 > 1$). One possible reason is the increased hydrophilicity of the membrane after NaOCl treatment [28]. Moreover the PS / PES membranes used in the studies were known to contain polyvinylpyrrolidone (PVP) as an additive. Hypochlorite reacts with the pyrrolidone ring of PVP, causing chain scission of PVP molecules that thereafter leach out of the membrane matrix during washing [29]. In addition to removing residual PVP in the membranes, hypochlorite treatment also modifies the membrane pore size or pore size distribution as observed by SEM analysis and rejection studies on BSA and other smaller solutes [30]. Furthermore, action of hypochlorite can make the membrane surface smoother [31], introduce greater negative charge and a larger effective pore size, both of which increase with further exposure [32]. Change in membrane morphology correlating membrane damage has also been reported for PS membrane after prolonged treatment with NaOCl [33]. However, all these reported studies employed higher NaOCl concentration (400–6000 ppm) and the exposure was also longer (1–48 h). It is thus interesting that the membrane properties were adversely affected even at short exposures to low NaOCl dosage.

It is pertinent to note that $J_c/J_o > 1$ has been reported with other cleaning agents as well viz. sodium dodecyl sulfate (SDS, $C_{12}H_{25}OSO_3Na$) cleaning of PS ultrafilters fouled by fermentation broth of glutamic acid [34], commercial cleaning agents like Ultrasil 75 and Ultrasil 91 in the cleaning of PS and PES membranes fouled with whey protein concentrate[35]. No explanation was provided in these studies.

3.2.2. *Action of NaOH and NaOCl*

Fig. 2 shows the effect of sequential cleaning (0.5% w/v NaOH followed by 200 ppm hypochlorite) on UF-PES-050H membrane. This membrane was chosen since the fouling was relatively high (Table 3) and the properties were well characterized. It was expected that action of alkali would hydrolyze the surface deposits thereby exposing the pores to the subsequent NaOCl treatment [36]. The NaOH treatment was investigated for various durations (up to 20 min) while the subsequent NaOCl cleaning was conducted for a fixed time of 15 min considering best PWF recovery in the previous experiments (Table 3).

In all the experiments, the extent of membrane fouling was consistent (J_1/J_0 ratio between 0.52–0.54). Irrespective of cleaning time, treatment with NaOH alone restored up to 80% of the pristine membrane water flux (J_{NaOH}/J_o between 0.68–0.78). Therefore, initially cleaning with 0.5% w/v NaOH was less effective compared to 200 ppm NaOCl since 15 min cleaning with NaOCl resulted in nearly complete PWF recovery (Table 3). Strugholtz et al. [19] reported a similar observation. In their study on cleaning of PES membrane fouled by constituted natural organic matter (NOM) solution containing polysac-

Table 4
Variation in pristine membrane PWF

Membranes	PWF (L/m^2 h)			
	Average	Std dev	Minimum	Maximum
UFPES50	410.52	234.28	170.07	700.49
UF-PES-030H	36.91	7.53	31.66	50.45
UF-PES-050H	234.20	110.13	147.52	386.79
UF-PS-100H	146.33	41.02	88.57	181.78
GR51PP	34.04	4.07	29.49	38.09
GR40PP	138.95	37.07	97.18	167.95

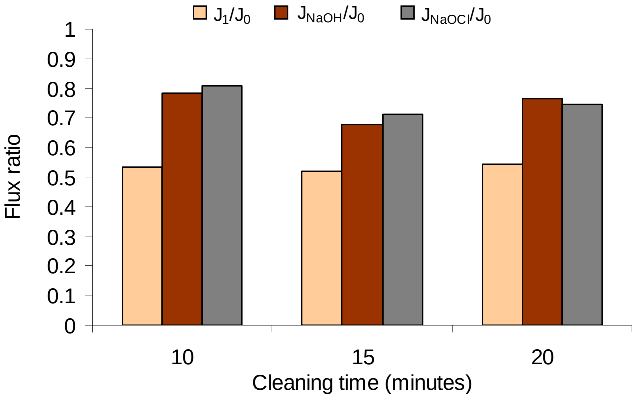

Fig. 2. Action of sequential chemical cleaning (0.5% NaOH followed by 200 ppm NaOCl).

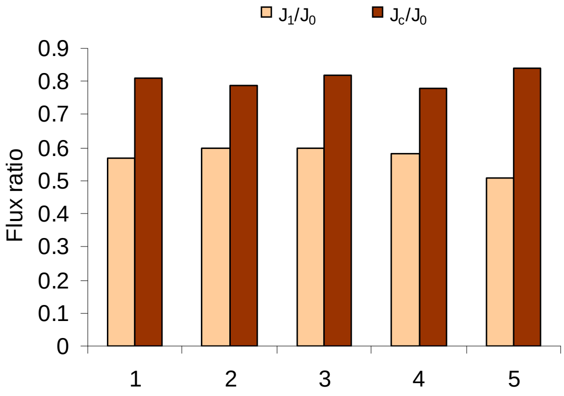

Fig. 3. Multi-step chemical cleaning (description in section 3.2.2).

charides and humic acids, NaOCl displayed higher polysaccharides removal compared to NaOH. This was attributed to the oxidizing capacity of NaOCl and was experimentally confirmed by the decreased aromaticity (i.e. decreased double bonds) of the organic components obtained in the NaOCl wash solution. The action is expected to be analogous for sugarcane juice polysaccharides, which are also associated with aromatic phenolic components [37].

After NaOH cleaning, additional treatment with NaOCl had almost no effect upon the PWF. This was possibly because the maximum removal of organic foulants that could be affected by 0.5% (w/v) NaOH had already occurred and the remaining foulants were associated/bound with inorganic components. Sugarcane juice polysaccharide contains significant amount of calcium [24], which is known to bridge organic colloids to the membrane surface [38]. Furthermore, as demonstrated with alginate solution, polysaccharides can form a gel in the presence of calcium ions that can then adsorb onto the membrane [39]. Both NaOH and NaOCl are not effective in removing inorganic foulants [19,40]. Moreover, the action of NaOH could also modify the charge characteristics [28] thereby modifying membrane–foulant interaction.

Fig. 3 shows the results of multi-step cleaning of fouled UF-PES-050H membrane using NaOCl alone and mixed with 0.5% (w/v) NaOH. Different protocols were examined as listed below.

Protocol 1 (NaOCl + NaOH): 5C → W → 5C → W
Protocol 2 (NaOCl + NaOH): 5C → 5C → W
Protocol 3 (NaOCl + NaOH): 5C → 5C → W → 5C → W
Protocol 4 (NaOCl): 15C → W → 15C → W
Protocol 5 (NaOH): 15C → W

Here, "XC" refers to X min contact with cleaning solution and *W* is RO water rinsing.

Replacing the used cleaning solution with a fresh batch did not show any noticeable improvement in PWF. The J_c/J_o ratio was almost identical (0.78–0.82) for all the protocols tested. Further, a longer, 30 min cleaning with NaOCl alone (protocol 4) did not increase the J_c/J_0 value beyond 0.78. A similar recovery (J_c/J_0 of 0.84) was obtained with a single stage cleaning with 2% w/v NaOH.

The combined action of NaOH and NaOCl for different cleaning durations is presented in Fig. 4. For a fixed concentration of 0.5% (w/v) NaOH and 200 ppm NaOCl, increasing the exposure time from 5 to 20 min increased PWF recovery, with J_c/J_0 value reaching 0.85. The J_c/J_0 ratio was marginally improved (0.89) by further increasing the NaOH concentration to 2% (w/v) without varying the hypochlorite concentration and cleaning for 20 min. This combination was used in subsequent experiments.

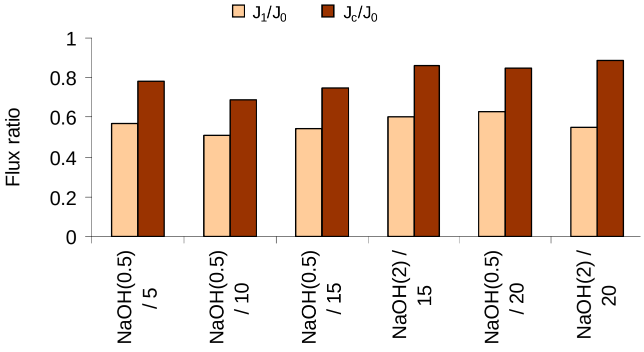

Fig. 4. Action of NaOH and NaOCl in combination (%w/v NaOH/time in min).

3.2.3. Successive UF-cleaning cycles

Fig. 5 shows the flux data for four successive UF-cleaning cycles with both polysaccharide fraction and the sugarcane juice. The fouled membranes were cleaned for 20 min with a mixture of 2% (w/v) NaOH and 200 ppm NaOCl after each UF cycle. The flux recovery is presented in Fig. 6.

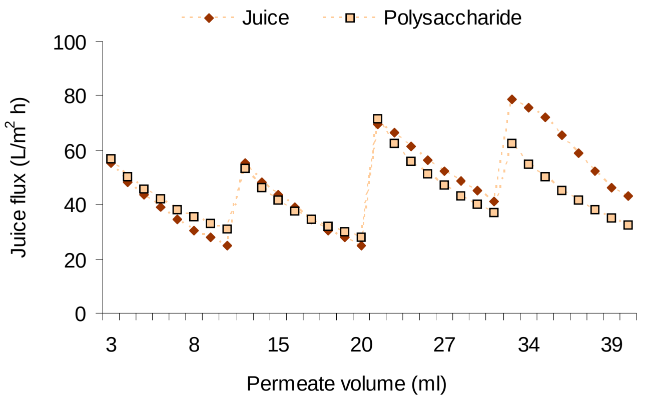

Fig. 5. Successive UF-cleaning cycles: polysaccharide and sugarcane juice flux.

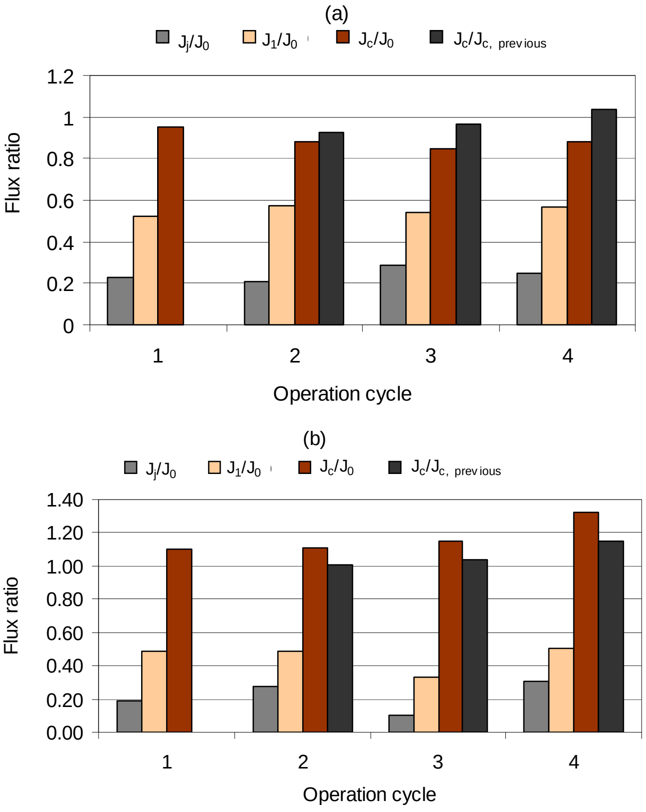

Fig. 6. Fouling and flux recovery with successive UF-cleaning cycles (a) polysaccharide feed (b) sugarcane juice.

The $J_c/J_{c,\ \text{previous}}$ ratio indicates the PWF recovery with respect to the previous UF cycle. Here, $J_{c,\ \text{previous}}$, which was the cleaned membrane PWF for the previous cycle, was also the initial PWF for the next UF cycle. Depending upon the $J_c/J_{c,\ \text{previous}}$ ratios, three different situations are possible.

- $J_c/J_{c,\ \text{previous}} > 1$ could be due to removal of foulants remaining on the membrane as a result of incomplete cleaning in the previous cycle and/or change in membrane properties (e.g. increased hydrophilicity, enlarged pores etc.) as a result of the cleaning step.
- $J_c/J_{c,\ \text{previous}} < 1$ indicates build-up of foulants due to incomplete removal in the current cycle and/or membrane re-fouling resulting in PWF decline.
- $J_c/J_{c,\ \text{previous}} = 1$ indicating negligible irreversible fouling; alternately, incomplete chemical cleaning compensated by increased membrane hydrophilicity/pore enlargement.

It was observed that membrane fouling with polysaccharides was nearly identical in all the cycles (J_1/J_0 of 0.52–0.57) (Fig. 6a). The PWF recovery was reasonably high with the highest J_c/J_0 value (0.95) in the first cycle. In subsequent cycles, the J_c/J_0 stabilized at marginally lower values (0.85–0.88) thereby indicating that all the active fouling sites on the membrane were possibly irreversibly occupied at this stage. It was also observed that the $J_c/J_{c,\ \text{previous}}$ value progressively increased with each cleaning cycle. The value was below unity in the first two cleaning cycles (corresponding to the 2nd and 3rd UF cycles) but was above 1 after the last cleaning. The normalized polysaccharide flux (J_j/J_0) dropped initially (0.21) and then increased (0.28 and 0.25). Interestingly, the J_j/J_0 values in the 3rd and 4th UF cycles were higher than the value recorded when the pristine membrane was charged first time (0.23).

The drop in the J_c/J_0 value after the first UF cycle indicated the occurrence of irreversible membrane fouling. This was supported by a decrease in the feed flux J_j/J_0 in the next (2nd) cycle. Thereafter, for the 3rd and 4th cycles, though J_c/J_0 remained almost unchanged, both $J_c/J_{c,\ \text{previous}}$ and the feed flux increased, indicating that the membrane was gradually becoming more hydrophilic. This possibly reduced the membrane-polysaccharide- interaction as reflected by the marginally higher J_1/J_0 values (0.54–0.57) in the second, third and fourth UF cycles compared to that in the first cycle (0.52).

Fouling was higher with sugarcane juice compared to polysaccharide fraction (J_1/J_0 of 0.42) (Fig. 6b). This was expected in view of the multi-component nature of the juice. Surprisingly, the corresponding PWF recovery was also higher ($J_c/J_0 > 1$). It was argued that the membrane-juice foulants interaction was relatively weaker than the membrane-polysaccharide fraction interaction. $J_c/J_{c,\ \text{previous}}$ value was consistently over 1 and increased in each subsequent UF-cleaning cycle indicating increasing membrane hydrophilicity and pore enlargement. The juice flux also increased with repeated cleaning and was eventually higher than the polysaccharide flux (Fig. 5).

Fig. 7 shows the SEM images of this membrane under different conditions. The pristine membrane surface was relatively smooth (Fig. 7a) and the cross-section displayed clear pore channels (Fig. 7b). No difference was visible after one UF-cleaning cycle (Fig. 7c and 7d); however, repeated UF-cleaning cycles resulted in an increase

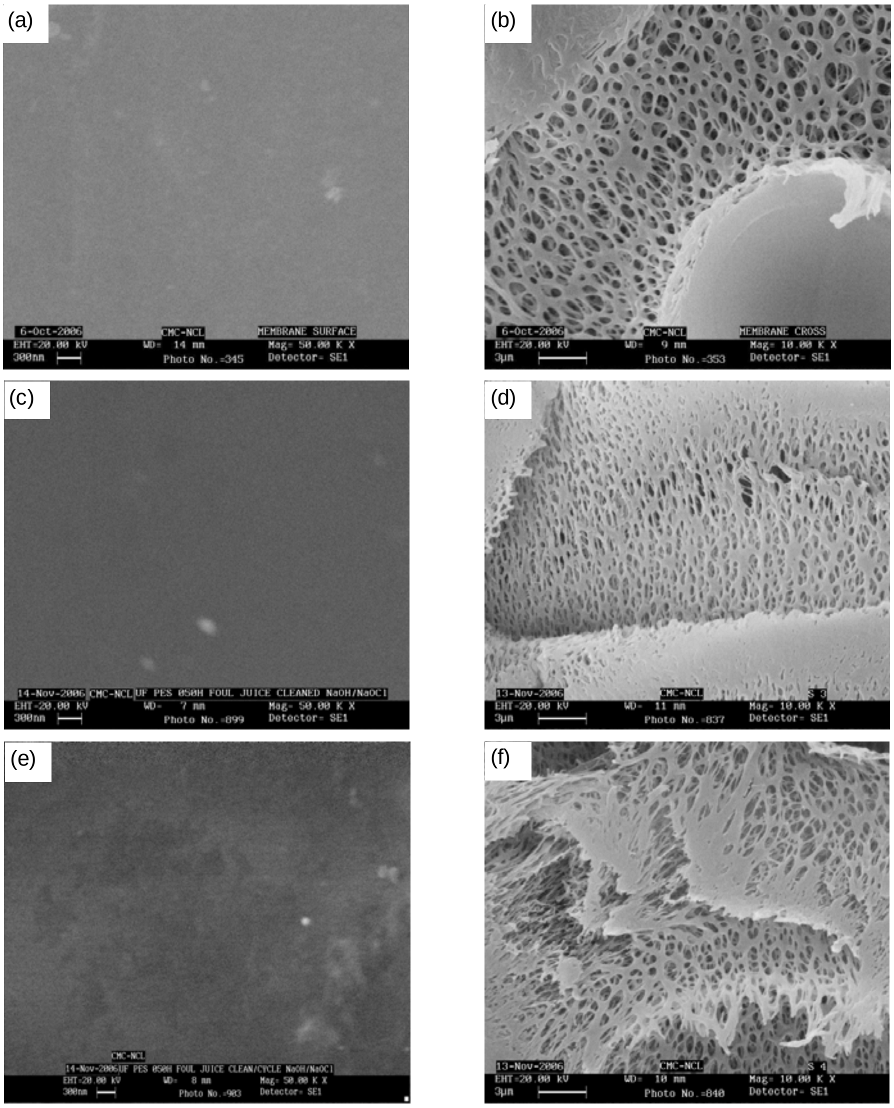

Fig. 7. SEM pictures of UF-PES-050H membrane at different stages (a) Pristine (surface) (b) Pristine (cross-section)(c) Cleaned (surface)(d) Cleaned (cross-section)(e) Cleaned, after 4 UF-cleaning cycles (surface) (f) Cleaned, after 4 UF-cleaning cycles (cross-section).

in membrane surface roughness (Fig. 7e) and pore elongation (Fig. 7f). Thus, repeated, short duration exposure to alkaline hypochlorite was confirmed to cause membrane pore enlargement leading to increased flux.

3.3. Correlation between J_0, J_1 and J_c

Fig. 8 depicts the relationship between J_1/J_0 ratio (normalized flux of the fouled membrane) and the corresponding J_c/J_0 ratio (normalized flux of the membrane after cleaning) for the UF-PES-050H membrane using different cleaning protocols. As J_1/J_0 increased, indicating less loss in membrane water flux after polysaccharide UF, the corresponding J_c/J_0 value also increased. This trend was independent of the cleaning reagent and the duration of the cleaning exercise. This implied that water flux recovery, even for the same membrane type, is dependent on the extent of fouling. The fouling, in turn can vary perceptibly due to inherent heterogeneity, especially with small membrane discs.

The relation between fouling and recovery is further depicted in Fig. 9. This is a plot of J_1/J_0 (indicative of fouling) and J_c/J_0 (indicative of cleaning efficiency) vs. the corresponding pristine membrane PWF (J_0) for all the membranes and cleaning procedures examined in this work. The figure is divided into four quadrants viz.

Quadrant I: Low PWF, low fouling, moderate to high PWF recovery

Quadrant II: Moderate to high PWF, low fouling, moderate to high PWF recovery

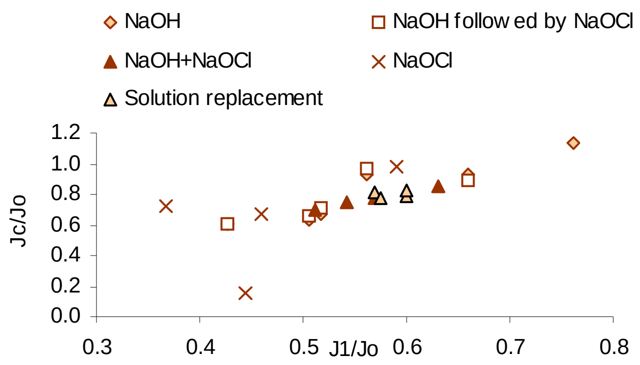

Fig. 8. Fouling vs cleaning for UF-PES-050H membrane.

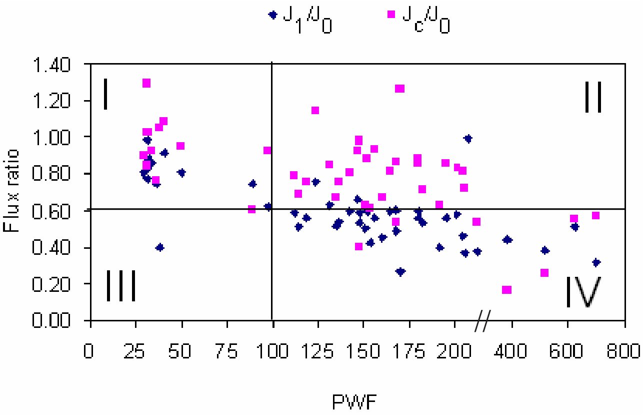

Fig. 9. Comparison of fouling, PWF restoration and pristine membrane PWF.

Quadrant III: Low PWF, moderate to high fouling, moderate to low PWF recovery

Quadrant IV: Moderate to high PWF, moderate to high fouling, moderate to low PWF recovery

When the pristine membrane PWF was below 100 L/m^2 h, membrane fouling with the polysaccharide fraction was typically moderate-to-low (J_1/J_0 value around 0.8) and most fouling data was within quadrant I. The flux could be restored to over 80% of its pristine value as seen from the corresponding J_c/J_0 values clustered in quadrant I. For membranes with PWF in the 100–200 L/m^2 h range, most fouling data points were within quadrant IV and close to quadrant II indicating moderate-to-high fouling. The corresponding PWF recovery after cleaning was moderately high ($0.90 > J_c/J_0$ values > 0.54). For pristine membrane PWF of 200 L/m^2 h and above, the fouling was moderate-to-high ($J_1/J_0 < 0.58$ except few cases) while the flux recovery was poorer (J_c/J_0 ratio typically below 0.7). The corresponding J_c/J_0 values were mostly in quadrant IV (or close to it).

The observations could be explained qualitatively as follows. It is accepted that much of the permeation of water or process fluid initially takes place through the large pores of UF/MF membrane. High membrane PWF implies many large pores in the membrane pore size distribution. Upon UF of the juice polysaccharides, pore blocking/plugging occurred in these large pores thereby leading to a significant PWF drop. Subsequent cleaning was done by soaking the membrane in the cleaning agent and providing gentle, intermittent agitation. The cleaning agent thus had to diffuse through the pores to reach and act upon the foulant. Given the short cleaning cycle (20 min) and the choice of the cleaning agents, only partial cleaning occurred in the limited time. For the low PWF membranes, the large foulant could not readily penetrate into the pores and was restricted to the membrane surface. Thus the PWF drop was not as steep as with the high PWF membranes. Further, during the cleaning cycle, the fouling layers on the membrane surface were easily accessed and hydrolyzed. Thus the PWF recovery was relatively high in this case.

The qualitative explanation is in agreement with a

Table 5
Membrane resistance before and after polysaccharide fouling and chemical cleaning

Membranes	J_0	J_1	J_C	$R_M = P_T/J_0$	$R_F = (P_T/J_1) - R_M$	$(R_F+R_M)/R_M$	$R_{M,\text{cleaned}}$	$R_{M,\text{cleaned}}/R_M$
GR51PP	33	25.5	34	3.08	0.86	1.28	2.94	0.96
UF-PES-030H	32	27	30	3.13	0.60	1.19	3.33	1.06
GR40PP	132.5	71.5	90.5	0.82	0.62	1.75	1.10	1.36
UF-PS-100H	157.5	90	103.5	0.64	0.50	1.77	0.97	1.51
UF-PES-050H	267.5	129	102.5	0.47	0.40	1.85	0.98	2.08
UFPES50	356	137	127	0.36	0.56	2.58	0.79	2.22

P_T Transmembrane pressure (100kPa)
J_0, J_1, Jc are the PWF of the pristine, fouled and chemically cleaned membrane (in L/m^{2}h)
R_M, R_F, $R_{M,\text{cleaned}}$ are resistance of the new (virgin) membrane, irreversible fouling and the cleaned membrane respectively (in kPa m^{2}h /L)

quantitative assessment based on calculation of the membrane resistance before fouling, after fouling and after chemical cleaning (Table 5). From the table, it is evident that low PWF membranes (J_0 below 100 L/m^{2}h viz. GR51PP and UF-PES-030H) displayed higher membrane resistance (R_M). Addition of the fouling layer with a resistance R_F during filtration caused a much greater flux reduction on the high flux membranes than it does on low flux membranes because of the additivity of the resistances. This is supported by the trend displayed by the normalized resistance of the fouled membrane [(R_F+ R_M) / R_M] wherein the value increases with increasing membrane PWF. Thus it appears that for the low flux membranes, fouling was mostly limited to pore closing/ blocking and cake fouling, which is known to offer greater resistance than pore narrowing [41]. These trends are consistent with SEM analysis in our earlier work [17] wherein low flux UF-PES-030H membrane showed deposition on the surface but none within the pores; in contrast high flux UF-PS-100H clearly displayed deposits within the pores. The chemical cleaning procedure employed was also less effective with increasing PWF as evident by the normalized resistance of the chemically cleaned membrane ($R_{M,\text{cleaned}}$)/R_M) > 1 for the high flux membranes.

The above hypothesis is supported by the SEM images for a high PWF membrane (UF-PS-100H) (Fig. 10). Comparing with the morphology of the pristine membrane, the surface appeared to be only partially cleaned after chemical treatment (Fig. 10c). Furthermore, the membrane cross-section displayed remaining deposits inside the pores (Fig. 10d). It was concluded that chemical cleanliness (removal of foulants on the membrane) was not achieved in this case; this was in agreement with the correspondingly low J_c/J_o (0.66).

4. Conclusions

- Short chemical cleaning cycles (up to 20 min) with a combination of 2% w/v NaOH and 200 ppm NaOCl leads to adequate water and juice flux recovery. However, NaOCl exposure, even for short duration, can cause significant change in membrane properties, including flux enhancement.
- Repeated UF-cleaning operations need not necessarily result in progressively low product flux. Modification in membrane properties (pore enlargement, increased hydrophilicity) can actually result in flux improvement over successive UF-cleaning cycles, as observed with both polysaccharide and sugarcane juice feeds.
- Membranes with low water flux (<100 L/m^{2}h) foul less and are more amenable to chemical cleaning after being fouled with the polysaccharide fraction. In view

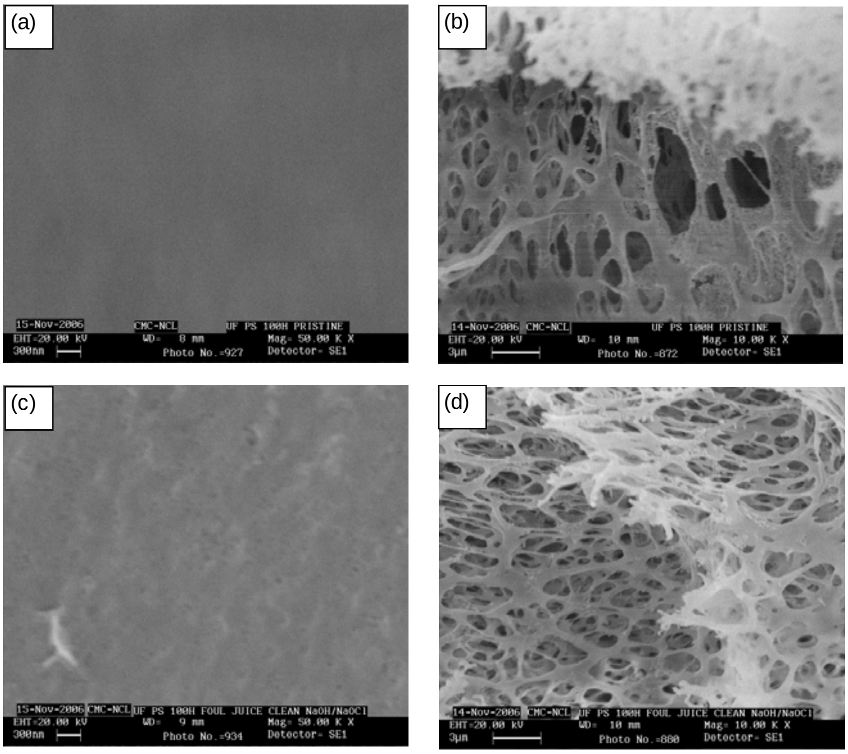

Fig. 10. SEM pictures of UF-PS-100H membrane at different stages (a) Pristine (surface) (b) Pristine (cross-section) (c) Cleaned (surface) (d) Cleaned (cross-section).

of this observation and the presence of a 130 kD component in the polysaccharide fraction, membranes with a NMWCO rating between 30–50 kD appear to be most appropriate for this application.

- The membrane solute-interaction was more pronounced with the model foulant (juice polysaccharide fraction). The presence of other solutes in the feed dilutes this effect. This aspect should be borne in mind in applications with multi-component feed streams, especially since performance evaluations are initially conducted with model solutes.

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