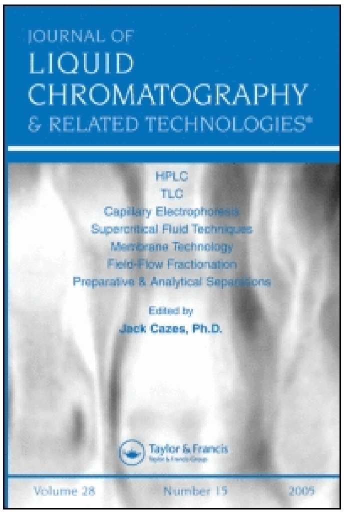

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Separation of Polysaccharides from Industrial Syrup Using Tubular Membranes

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Abstract: The mass-transfer plot and gel-polarization aging of a number of tubular membranes made of hydrophilic polymers, ceramic, and sintered stainless steel was compared under their recommended operating temperature, transmembrane pressure, shear velocity, and cycle time for the separation of polysaccharides from composite industrial syrup. The results showed that more than 98% of the polysaccharides that correlate with the turbidity in the syrups were separated from the syrups. At the same time, the purity of the syrup was increased by up to 3% after membrane ultrafiltration. The comparison clearly showed that there were distinct differences in performance between different tubular membranes.

Keywords: Separation, polysaccharides, hydrophilic polymer membranes

INTRODUCTION

The issue of polysaccharides in sugar crystallization and recovery has been known for a long time in the industry.[1–6] At least two types of polysaccharides were found in industrial process syrups. The naturally occurring starch and cellulose found in industrial syrups come from the original sucrose-producing plants and may not be completely removed in the industrial processes. The dextrans found in industrial syrups are products of bacteria

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that may not be completely avoided. The level of total polysaccharides in industrial syrups depends on the raw materials, as well as the process stage. The recovery streams tend to concentrate the polysaccharides, while the product streams are separated on purpose from polysaccharides. The polysaccharides cause increase in viscosity and decrease in rate of diffusion and crystallization and thus create lower recovery and lower yield of sucrose. Polysaccharides are also responsible for high turbidity and poor filterability of process syrups.

Polysaccharides from various industrial syrups can be separated from the syrup by different membranes.[1,6] Although the membrane is capable of separating polysaccharides from smaller molecules, such as sucrose, the cost associated with the membrane material remains to be an issue in commercial-scale operations. It is highly desirable to develop membrane materials suitable for this application to achieve highest product throughput (flux of membrane) and life cycle of the membranes.

This study explores the performance of several tubular ultrafiltration membranes in their ability to separate polysaccharides from low purity industrial syrups. Tubular ultrafiltration membranes made of hydrophilic polymers, ceramic, and sintered stainless steel were investigated. The flux of the membranes was studied as a function of operating temperature, membrane pore size, transmembrane pressure, cycle time, shear velocity, and feed characteristics. The results should provide insights into the ultrafiltration process of polysaccharide separation.

EXPERIMENTAL

More than two industrial process syrups, containing at least a low-purity syrup that contained more than 1% polysaccharides and a high purity syrup that contained less than 0.1% polysaccharides, were used to blend together to make the composite syrup for this study. This composite syrup was made such that it was possible to carry out membrane experiments for different membranes, under different experimental conditions, over a period of several months, without significant variations in the nature of the testing syrup. The final solid content of the composite syrup was adjusted to 40% (w/w).

The CMF hydrophilic polymer membranes of different tubular diameters (1.5 and 3.0 mm, respectively) were manufactured by Dow Chemical Filmtec Division (Midland, MI). The Carre/SCEPTER A5180-19 (nominal pore size 0.1 μm) sintered stainless steel tubular membranes were manufactured by Graver Technologies (Glasgow, Delaware). The Membralox tubular ceramic membranes of different nominal pore sizes (0.05, 0.1, and 0.2 μm, respectively) were products of U.S. Filter (Warrendale, PA). These membranes have had major success in many industries, and it was our desire to compare their characteristics and developing applications in new markets. Table 1 summarizes the types of major commercial ultrafiltration/microfiltration membranes that were included in this study.

The various tubular membranes were mounted in the experimental pilot skid shown in Fig. 1. The piping and the pump were all made of stainless steel to avoid any rust contamination on membrane surfaces. The composite syrup was first transferred to the feed tank. The syrup was delivered by the pump, serving both as feed pump and recirculation pump, to pass through a shell-and-tube heat exchanger and a 300 mesh stainless steel screen filter, before it entered the inlet of the tubular membrane element. The mesh screen was used as a standard practice to protect the membrane surface from scratching by any large particles in the composite syrup. The retentate efflux was recirculated to the feed tank. The permeate efflux was directed to a separate sample collector. The average transmembrane pressure was controlled by the permeate valve shown in the figure. The transmembrane pressure was calculated as the difference between the average retentate-side pressure and the permeate side pressure, as recorded by the three pressure gauges mounted on the membrane element. The temperature of the retentate efflux was controlled by adjusting the exhaust steam pressure at the shell-and-tube heat exchanger. The cross flow velocity on the membrane surface was controlled by the retentate valve. A lid was used to cover the feed tank to minimize the loss of water vapor, which could introduce significant error in calculating feed concentration.

The experiment was carried out both in a batch mode and in a feed-and-bleed mode. The batch mode experiment, with permeate bleed and without

Table 1. Tubular membranes for polysaccharide separation

Membrane	Tubular diameter (mm)	Nominal pore size (μm)	Materials	Manufacturer
Filmtec CMF-1.5	1.5	0.2	Modified hydrophilic polymer	Dow Chemical
Filmtec CMF-3.0	3.0	0.2	Modified hydrophilic polymer	Dow Chemical
Carre A5180-19-0.1	19	0.1	Sintered stainless steel	Graver Technologies
Membralox-4.5-0.05	4.5	0.05	α-Alumina based ceramic composite	U.S. Filter
Membralox-4.5-0.1	4.5	0.1	α-Alumina based ceramic composite	U.S. Filter
Membralox-4.5-0.2	4.5	0.2	α-Alumina based ceramic composite	U.S. Filter

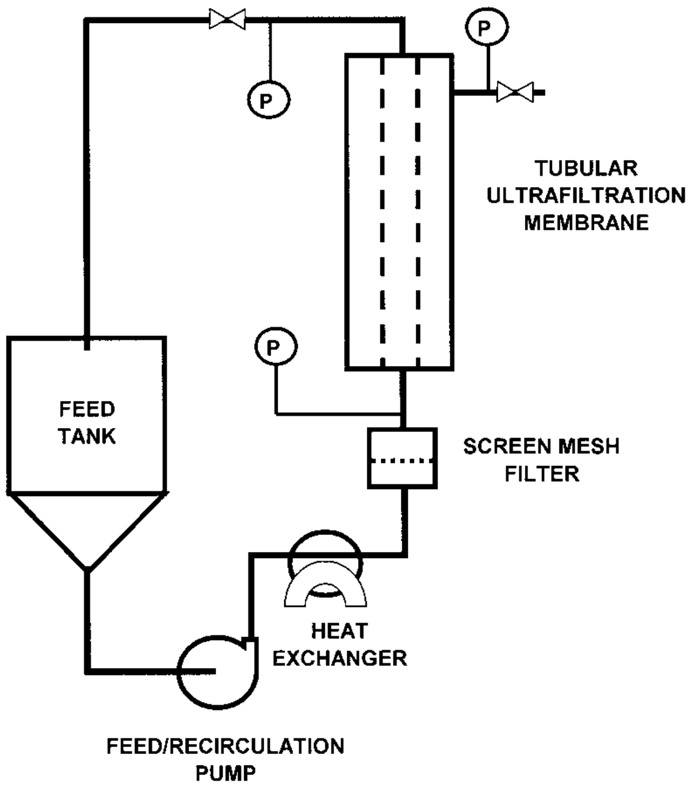

Figure 1. The experimental apparatus used to study membrane flux under different operating conditions with control of shear volocity, temperature, and transmembrane pressure.

adding fresh syrup to the feed tank, provides a standard mass-transfer plot. It provides a condition nearest to the constant and fully developed gel-polarized layer on the membrane surface with steadily increasing concentration. The well-known film theory predicts that under such conditions, the throughput or the flux of the membrane is controlled by the mass transfer between the bulk and the surface. The ideal behavior of mass-transfer controlled flux should linearly decrease as the natural log of the bulk concentration.[3,7,8]

When the permeate efflux was returned to the feed tank, the batch mode provided the full recycle and, thus, a true constant concentration situation. We took advantage of this methodology to research on the gel-polarization aging effect for a given concentration of interest. Indeed, this information could be useful in industry for sizing up ultrafiltration equipment, which requires defined cycle time and cleaning/regenerating down times.

The feed-and-bleed mode was used to study the continuous ultrafiltration process. The method was widely used for actual commercial operations as well as experimental research. Because of the above mentioned gel-polarization aging effect, this continuous process is not theoretically a steady-state. In order to maintain a constant throughput, one must take measure to overcome the growing mass transfer resistance. Increasing transmembrane pressure is one typical way to do so, but is limited by both compressibility of the gel-polarization layer and by the mechanical strength of the membranes. Increase in temperature reduces shear viscosity and, thus, increases diffusion rate of molecules through porous media such as membrane structures. However, the polymer materials of the membranes, such as cellulose acetate, should be used below the glass transition temperatures. Sintered metal and ceramic membranes are expected to be more tolerant for high service temperatures.

At the end of each experiment cycle, the membrane elements were thoroughly flushed with water free of ionic contaminations. We use pure water flux test at 1 bar transmembrane pressure and room temperature to investigate the degree of the membrane fouling. The change in the indicator was used to quantitatively express the membrane fouling against the value we obtained for the brand new membrane element. We attempted to use this ratio as the fouling index and compared our experimental data with the index before and after we conducted the cleaning procedure. It was expected that the fouling index would also predict the mass-transfer plot. We used the cleaning procedures recommended by the individual membrane manufacturers to regenerate the membranes after the flush. The membranes were cleaned in place using the feed tank and the pump with chemicals recommended by individual membrane manufacturers.

The composite syrup was adjusted by a number of industrial syrups and analyzed for consistency in turbidity and polysaccharides concentration using conventional industry-standard lab methods. The concentration of total dissolved solids was measured using a standardized refractometer. The concentration of polysaccharides was correlated with the simple turbidity measurement. The purity of the syrups was calculated by dividing polarimetric sucrose concentration by refractometric solids. We followed the convention used by the membrane manufacturers and expressed our bulk concentration of polysaccharides as the dimensionless volume concentration ratio (VCR) defined as the ratio of the initial volume of the feed liquid to the transient volume. If the membranes reject the polysaccharides, the polysaccharides concentration will simply equal the VCR value times the initial concentration, which was adjusted to roughly a constant for our composite syrup blended from industrial syrups of different purities. The concentration of polysaccharides was correlated with both turbidity NTU units, and the actual VCR values were referenced for polysaccharides concentration in this study.

RESULTS AND DISCUSSION

We observed, consistently, that the pump was generating substantial viscous heating during most of our experimental measurement. The need of the steam in the shell-and-tube was indeed minimal. The steam was typically needed at the beginning of each experiment. As advised by the membrane manufacturers, we first established a strong cross flow (turbulent range shear velocity) before we gradually ramped up the transmembrane pressure by slowly opening the permeate valve and, thus, avoided the premature fouling of the membranes.

The aging effect was clearly observed for all the tubular membranes. Typically, once we experienced the initial fall in flux, we then started to observe the more established gel-polarization behavior. This was reflected in the change from an initially stiff slope in the flux against a time curve to a smaller slope (as if it were second-order transition). This is illustrated in Fig. 2. Although the polysaccharides concentration was at its low level

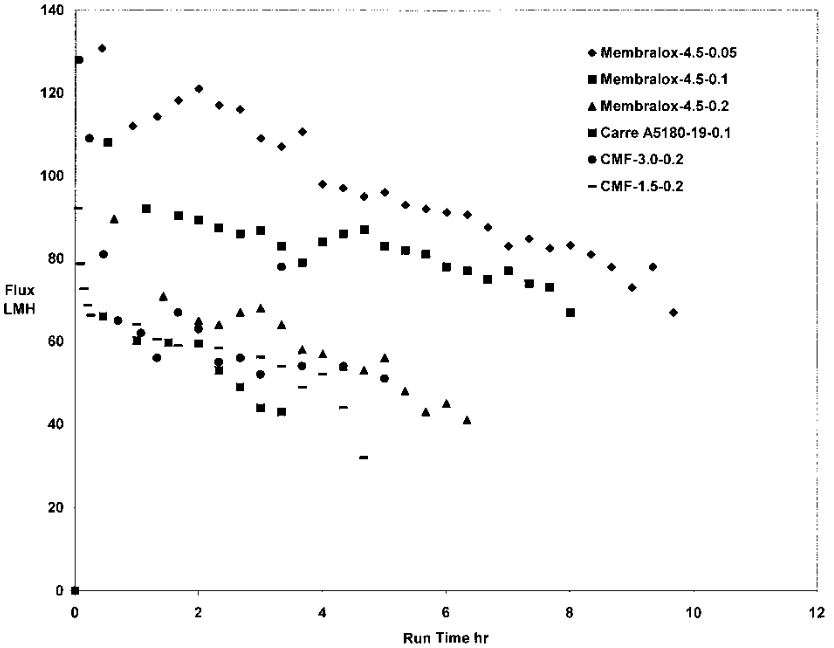

Figure 2. The gel-polarization aging curve for different membranes at their corresponding optimal conditions. The ramp-up period to reach the final transmembrane pressure was controlled at 30 min for all membranes. The polysaccharides concentration was referenced by VCR = 2 with total recycle. The operating temperature was controlled at 85°C for all the membranes. The final transmembrane pressure was controlled at 1.1, 3.0, and 9.7 bar for polymer, ceramic, and metal membranes, respectively.

(referenced as VCR = 2), the aging trend was apparent. The decay in flux is normally understood by membrane experts to be the results of gradual build-up of a gel-polarization layer and its compression under transmembrane pressure on the surface of the skin layer of the membrane structure. It is believed that the high shear velocity (5 m/sec) created by the recirculation pump suppresses the growth of the polarization layer, but is not adequately strong enough to remove such layer.

The industrial practice of overcoming this polarization layer includes back flushing from the permeate side, by reversing the transmembrane pressure momentarily. The effectiveness of the backflush technique in our experiment was found not to be satisfactory. Indeed, the only way to successfully recover the syrup flux was by the extensive chemical cleaning, as recommended by individual membrane manufacturers. Figure 3 illustrates the relative scale of the recovery of the pure water flux after chemical

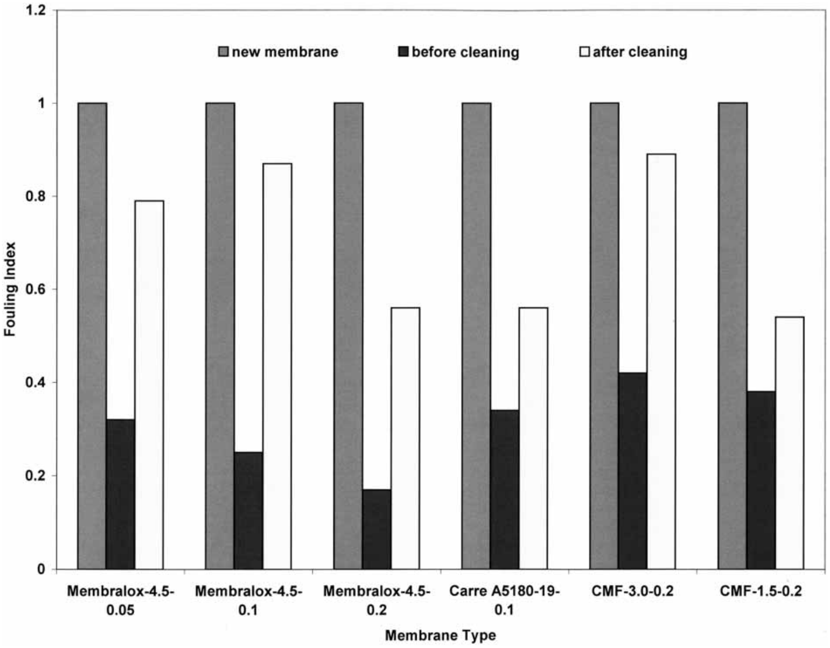

Figure 3. Fouling index of membranes before and after cleaning. The index was measured after 4 hr of continuous operation at constant concentration of VCR = 2. The operating temperature was controlled at 85°C for all the membranes. The ramp-up period to reach the final transmembrane pressure was controlled at 30 min for all membranes. The polysaccharides concentration was referenced by VCR = 2. The final transmembrane pressure was controlled at 1.1, 3.0, and 9.7 bar for polymer, ceramic, and metal membranes, respectively.

cleaning, as expressed by the fouling index, which was defined earlier. The index was measured after 4 hr of continuous operation at constant concentration of VCR = 2. The operating temperature was controlled at 85°C for all the membranes. The ramp-up period to reach the final transmembrane pressure was again controlled at 30 min for all membranes. The transmembrane pressure was controlled at constant 1.1, 3.0, and 9.7 bar for the polymer, the ceramic, and the metal membranes, respectively. It appears that no chemical cleaning was capable of restoring the membrane to its brand new pure water flux. However, we noticed that even the fouling index was not restored to unity after chemical cleaning; we were able to reproduce the batch and continuous experiments after the fouling index dropped below unity. Therefore, we believe the fouling index was not directly correlated with the syrup flux. The nature of the fouling was rather complicated and would warrant future research regarding the materials science and surface science of the various membranes.

We were impressed that the turbidity NTU units were significantly reduced after the membrane treatment. At the same time, the purity of the syrup was improved after the polysaccharides were separated from the permeate. Figure 4 illustrates the change of turbidity of the composite syrup before and after membrane treatment. Operating conditions were the same

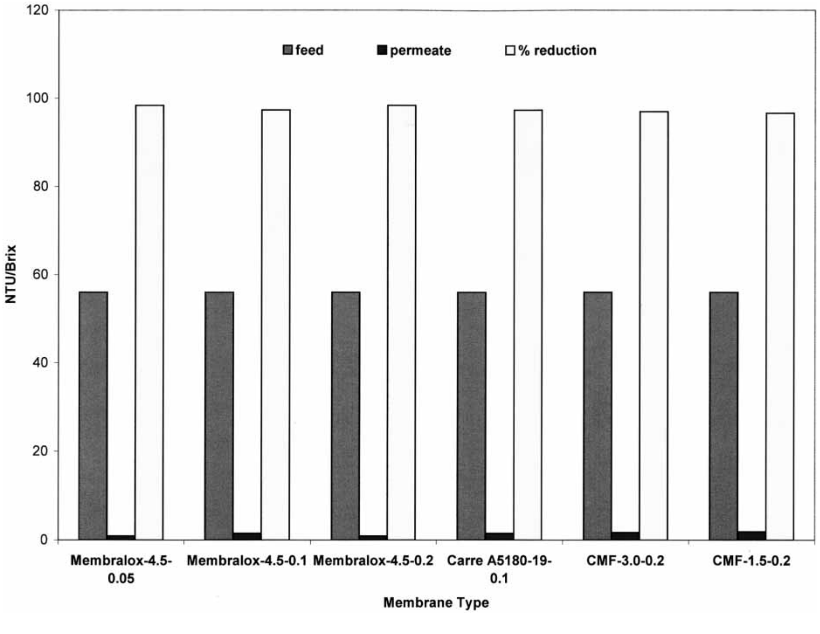

Figure 4. Turbidity change of composite syrup before and after membrane treatment. Operating conditions were the same as Fig. 3.

as Fig. 3. The changes in the sucrose purity of the composite syrup, before and after, membrane treatment is shown in Fig. 5.

We were limited by the membrane manufacturer's recommendation as how high we could apply transmembrane pressure to improve the flux for the polymer membrane to below about 1.1 bar. We observed from the repeated experiments that 5 m/sec and 85°C were optimal for the flux but at different transmembrane pressures for different membranes. Further study on the relationship between the transmembrane pressure and flux improvement or polarization aging is desirable. Higher temperature ideally reduced viscosity as discussed earlier, but promotes sucrose decomposition or colorant generation. We were also limited by the rubber seals for the membrane elements we ventured at higher temperature. Figure 6 shows the mass-transfer plot in which we compare all the membranes at their optimal transmembrane pressures. The flux is plotted as a function of the natural logarithms of the bulk concentration indexed by VCR values. As we can see, the data did not generally show good linearity and, thus, indicating the mass-transfer film theory was not successful. We believe there was really not a fully developed gel-polarization layer whose porosity (compressibility) and concentration would be truly constant at most of operating conditions. However, piece-wise linearity was present indicating the increment of the polarization layer may be rather stepwise, and at each step where the slope in the mass-transfer plot changes, some new mechanism may govern the process. This

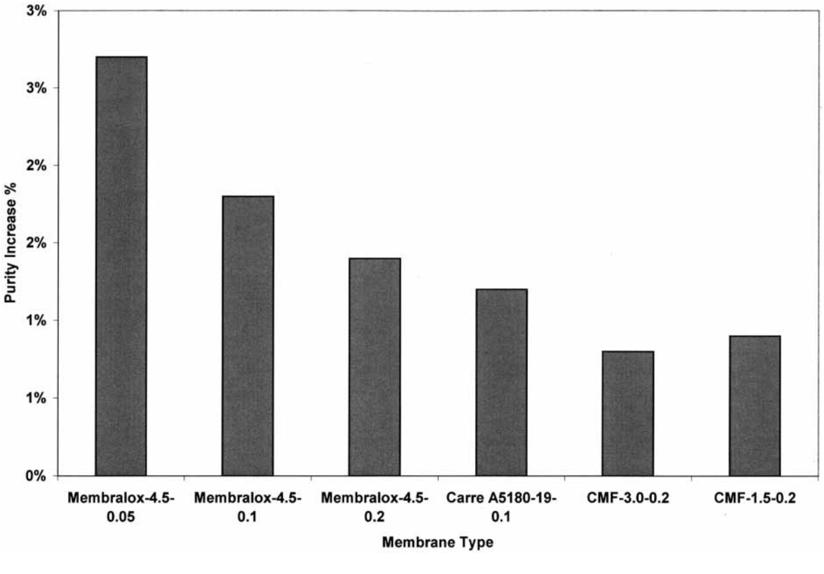

Figure 5. Purity change of composite syrup before and after membrane treatment. Operating conditions were the same as Fig. 3.

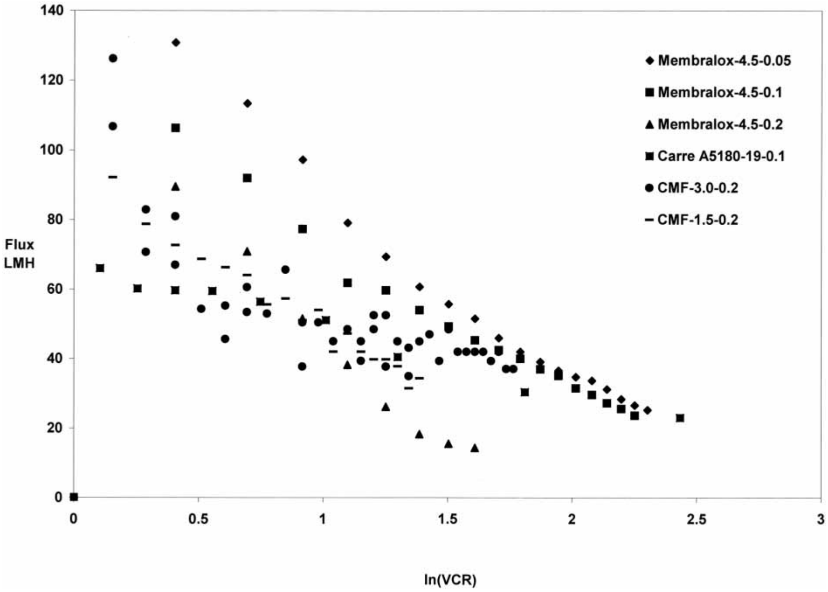

Figure 6. The mass-transfer plot for different membranes at their corresponding optimal operating conditions. The operating temperature was controlled at 85°C for all the membranes. The shear velocity was controlled at 5 m/sec for all the membranes. The transmembrane pressure was controlled at 1.1, 3.0, and 9.7 bar for polymer, ceramic, and metal membranes, respectively.

warrants further theoretical interpretation. We hope what we have achieved from this study provides useful data and insights into such mechanisms.

CONCLUSIONS

From our extensive study with several leading brand commercial tubular membranes, it was shown that ultrafiltration or microfiltration membrane technology is technically adequate in separating polysaccharides and other small colloidal particles from industrial syrups. The purity of the syrup was improved by up to 3% after the treatment of all the membranes used in this study. The turbidity which relates to polysaccharides was reduced by as much as 98% for most of the membranes. The fouling mechanisms of the membranes were complex and the pure water flux based fouling index did not correlate well with the flux behavior of the industrial syrups. The mass-transfer film theory was not very successful in interpreting experimental data with industrial syrups whose fouling mechanisms are to be further understood. The chemical cleaning procedure was the only effective method to restore the flux of the industrial syrups. Backflushing was not found to be very effective for these particular types of materials. Further work on the materials science of the membranes and the fouling mechanisms is needed. This study provides useful insights into these subjects.

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