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Membrane performance with a pulp mill effluent: Relative contributions of fouling mechanisms¹

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Abstract

Severe flux decline was observed during ultrafiltration of a pulp mill effluent. Membrane fouling was the result of varying combinations of adsorption, pore plugging and concentration polarization or gel layer formation. A wide range of membrane materials and pore sizes were evaluated, showing the relationship between the membrane material, pore size and the relative contribution of the different fouling mechanisms. Individual resistances were evaluated for adsorption, R_a , pore plugging, R_{pp} , and concentration polarization, R_{cp} , using a series resistance model. These were based on the pure water flux for (1) the new membrane, J_i , (2) after static adsorption with the mill effluent, J_a , (3) the product rate when ultrafiltering the effluent, J_v , and (4) the pure water permeability with the fouled membrane, J_f . These resistances were shown to be misleading in terms of the observed flux loss for cases with significant adsorptive fouling. Adsorptive fouling was underestimated and concentration polarization overestimated. An alternative method, which we shall call flux loss ratios, is proposed, which is based on the flux decline due to a particular mechanisms as a fraction of the overall flux decline. These new measures more accurately reflect the flux decline attributable to each fouling mechanism.

Keywords: Concentration polarization; Fouling; Ultrafiltration; Pulp mill waste; Series resistance

1. Introduction

New and cost effective technologies are required for the treatment of effluents from the pulp and paper industries. Mills have sought to comply with new regulations by reducing waste generation via process modifications or moving towards mill closure [1]. A brief review of large scale membrane

applications in the pulp and paper industries is given by Jönsson and Wimmerstedt [2]. Their implementation in this and other industries has not realized its full potential. This has largely been due to problems associated with fouling resulting in larger membrane surface areas and shorter membrane lifetimes leading to higher installation and operating costs.

Membrane flux decline observed during permeation is the cumulative effect of several mechanisms. These include adsorption, pore plugging [3], steric [4] and viscosity effects, concentration polarization [5,6] and gel layer formation. Flux decline due to

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adsorption can occur in a very short time frame, < 3 h, the extent of which is determined by the membrane material and solute(s) interactions. The degree of pore plugging is determined by the relative size of the solute and pore as well as the operating conditions. Concentration polarization is the formation of a concentration gradient of solutes established at the membrane surface due to the preferential transport of solvent through the membrane. The higher solute concentration at the surface results in a higher osmotic pressure, thereby reducing the effective driving force. This concentration gradient can be established within minutes [7]. Polarization of higher molecular weight solutes can result in gel layer formation [5]. The gel layer presents an additional hydraulic resistance and may become the dominant separating mechanism [8]. The gel forming potential of lignins in pulp mill effluents has been discussed by Ramamurthy et al. [9] and Woerner and McCarthy [10,11].

Minimization of membrane fouling is essential to make membrane processes economically competitive in applications where there is little cost recovery (i.e. pollution abatement). Any attempt to minimize fouling requires an understanding of the causes and their relative contribution. Understanding the fouling mechanisms allows one to make informed decisions and take appropriate action. For example, if adsorptive fouling is primarily responsible for the observed flux loss there is little benefit to improving the mass transfer.

A series resistance model was used to quantify the relative contributions of adsorption, pore plugging and concentration polarization to flux decline. The conventional resistance model was found to be a misleading indicator of the flux loss due to each of these mechanisms. Relative flux loss ratios (FLR) were proposed as an alternative measure. The relative FLRs, D_i , were assigned a fraction of the overall fouling resistance. This fraction was determined by the ratio of the flux loss due to a particular mechanism to the overall flux decline. The waste stream was the plug screw feeder pressate (PSFP) from a semichemical mechanical pulp (SCMP) digester. A membrane selection criteria was developed based on the different fouling contributions and was related to the membrane material properties, pore size and operating conditions.

2. Theory

2.1. Flux models

The basic model used to describe transport across a porous barrier relates the permeation rate, J_v , to the driving force, ΔP , fluid viscosity μ and a resistance term, R :

$$J_v = \frac{\Delta P}{\mu R} \quad (1)$$

In the case of flow through a membrane, the driving force and the flow resistance can be modified due to the occurrence of concentration polarization and fouling. Various flux models have been used to describe the effect of the feed osmotic pressure and contributions of the different fouling mechanisms. The osmotic pressure–adsorption model (OPA) of Ko et al. [6] describes the flux decline due to membrane fouling and the polarized layer:

$$J_v = \frac{\Delta P - \sigma \pi}{\mu(R_m + R_a)} \quad (2)$$

where π is the osmotic pressure, σ is the reflection coefficient and R_m and R_a are the hydraulic resistances due to the membrane and adsorptive fouling respectively. The resistance boundary layer (RBL) model describes the polarized solute layer as an additive serial resistance, R_{RBL} :

$$J_v = \frac{\Delta P}{\mu(R_m + R_{RBL})} \quad (3)$$

Wijmans et al. [12] have shown that the osmotic pressure model is equivalent to the RBL model under certain assumptions. Purely series resistance models represent both the fouling and polarization flux declines as serial resistances [3,8,13–15] and have the form:

$$J_v = \frac{\Delta P}{\mu \left(R_m + \sum_{i=1}^n R_i \right)} \quad (4)$$

The resistances R_i can be attributed to various fouling or flux decline mechanisms, yielding a flux model of the form:

$$J_v = \frac{\Delta P}{\mu(R_m + R_a + R_{pp} + R_{cp})} \quad (5)$$

where R_a , R_{pp} and R_{cp} refer to adsorptive fouling, pore plugging and concentration polarization or gel layer formation, respectively. A model of this form was used to evaluate the relative contributions of each fouling mechanism during ultrafiltration of PSFP.

We have chosen to use a purely phenomenological model such as Eq. (5) because detailed information on the osmotic pressure of a complex mixture such as PSFP was not available. Series resistance flux models were also used by Belfort et al. for ultrafiltration of cell culture media [3]. Pouliot et al. [14] used a series resistance model similar to Eq. (5) but called R_{pp} and R_{cp} irreversible and reversible fouling resistances.

A disadvantage of series resistance models is that they account for osmotic pressure and gel formation in the same manner, as an additive resistance. The former represents a flux decline due to a reduction in the driving force while the later represents a hydraulic resistance to flow. The model is insensitive to the actual mechanism but still provides information on the contribution of either mechanism to flux decline. The lack of physical data and possibility of both osmotic pressure effects or gel layer formation supports the use of Eq. (5).

2.2. Evaluation of resistances

The serial resistances due to each fouling mechanism are calculated from the flux loss under different operating conditions. The following fluxes were measured:

- J_i the pure water flux for a new membrane
- J_a the pure water flux for a membrane which has been fouled by static adsorption
- J_f the pure water flux for a membrane which has been fouled by permeation of the actual PSFP effluent
- J_v the flux with PSFP under a given set of operating conditions

The flux loss between J_i and J_a is attributable to adsorptive fouling. Pore plugging accounts for the difference between J_f and J_a . The difference between J_v and J_f represents the flux loss due to polarization effects.

The pure water permeability (J_i) is used to evaluate R_m for a new membrane using Eq. (1). The

additive resistance due to adsorptive fouling can be determined from the ratio of J_i and J_a :

$$\frac{J_i}{J_a} = \frac{R_m + R_a}{R_m} \quad (6)$$

from which

$$R_a = \left(\frac{J_i}{J_a} - 1 \right) R_m \quad (7)$$

The permeate viscosity is constant since the fluxes are based on the permeation of pure water.

The R_a term is based on the pure water permeation rate after contacting the membrane with the feed material, J_a , in the absence of a transmembrane pressure. The contribution of R_a may be underestimated by this procedure as adsorption is evaluated at the bulk concentration. The higher concentration at the membrane surface as a result of concentration polarization may also lead to greater adsorption. Adsorption at the membrane surface/pore entrance may prevent further adsorption within the membrane, as suggested by Brink et al. [16]. There is also a potential for more adsorption during permeation when adsorbants have access to the internal pore structure. In these situations, the added resistance due to pore plugging would be overestimated as it would include some additional resistance due to adsorption. The procedure outlined above is preferred due to the susceptibility of high MWCO membranes to pore plugging with PSFP.

The remaining resistances can be calculated sequentially in a similar fashion:

$$R_{pp} = \left(\frac{J_i}{J_f} - 1 \right) R_m - R_a \quad (8)$$

$$R_{cp} = \left(\frac{J_i}{J_v} - 1 \right) R_m - R_a - R_{pp} \quad (9)$$

using the resistance terms determined in the previous step and assuming that differences in the permeate and pure water viscosities are negligible in determining R_{cp} .

The serial resistances attributed to each fouling mechanism are dependent on the experimental procedure and operating conditions. For example, material deposited on the membrane surface was removed using only recirculating water, the membrane surface

was not physically or chemically cleaned. The pore plugging resistance may be overestimated if any surface deposits were not removed.

The R_{pp} and R_{cp} terms are expected to be a function of the operating conditions, namely the transmembrane pressure (TMP), cross flow velocity (CFV) and temperature. The absolute resistance of the membrane, R_m , is assumed to be constant after an initial 5 h precompression with reverse osmosis (RO) treated water. The adsorptive fouling resistance, R_a , may be a weak function of the TMP and CFV and a stronger function of pH, temperature and other variables. The TMP can be expected to have a strong effect on R_{pp} and R_{cp} while the CFV would influence R_{cp} .

The relative resistance of each component is often expressed as a function of the total resistance:

$$\%R_m = \frac{R_m}{R_t}, \quad \%R_a = \frac{R_a}{R_t}, \quad \%R_{pp} = \frac{R_{pp}}{R_t},$$

$$\text{and } \%R_{cp} = \frac{R_{cp}}{R_t} \quad (10)$$

The values for the resistance terms depend, of course, on the membrane and the degree of fouling. They also depend on the order of numerical calculation and are determined by the experimental procedure. This is shown schematically in Fig. 1. The curved line represents the inverse relationship between the flux and total hydraulic resistance. A hypothetical example is used where adsorption, pore plugging and concentration polarization are responsible for the same absolute flux loss. The R_a term is relatively small compared to both R_{pp} and R_{cp} , even though the observed flux loss was equivalent for each mechanism. The inferences made based on these relative resistances can be misleading under certain conditions. Examples will be presented in the results section highlighting the different cases that can be encountered.

2.3. Fouling contributions based on flux loss ratios

We suggest an alternative approach, using flux loss ratios, to estimate the relative contributions of the fouling mechanisms. The FLR's are based on the

Fig. 1. Flux as a function of the total resistance. A constant flux decline is assumed due to each fouling mechanism. The additive resistance of each mechanism is not proportional to the flux decline.

ratio of the absolute flux decline for a given mechanism to the overall flux loss. The adsorptive FLR is calculated as

$$D_a = R_f \times \frac{J_i - J_a}{J_i - J_v} \quad (11)$$

The remaining relative fouling terms are determined in a similar manner:

$$D_{pp} = R_f \times \frac{J_a - J_f}{J_i - J_v} \quad (12)$$

$$D_{cp} = R_f \times \frac{J_f - J_v}{J_i - J_v} \quad (13)$$

The overall fouling resistance is obtained from:

$$\frac{J_i}{J_v} = \frac{R_m + R_f}{R_m} = 1 + \frac{R_f}{R_m} \quad (14)$$

in which the permeate and pure water viscosity are assumed equal. As with the serial resistances, it is useful to compare the FLRs to the overall resistance,

R_t . We can define the relative RFLs (from this point on the RFL are relative RFLs) as:

$$\begin{aligned} \%D_m &= \frac{R_m}{R_t} \times 100, \quad \%D_a = \frac{D_a}{R_t} \times 100, \\ \%D_{pp} &= \frac{D_{pp}}{R_t} \times 100, \quad \text{and} \quad \%D_{cp} = \frac{D_{cp}}{R_t} \times 100 \quad (15) \end{aligned}$$

The flux loss ratios are not the serial resistances normally associated with the series resistance model in Eq. (5). However, the flux loss ratios can be expressed as a function of the resistances determined with, Eqs. (7), (8) and (9). The denominator in Eqs. (11), (12) and (13) can be written as:

$$\begin{aligned} J_i - J_v &= \frac{\Delta P}{\mu} \left(\frac{1}{R_m} - \frac{1}{R_m + R_f} \right) \\ &= \frac{\Delta P}{\mu} \frac{R_f}{R_m(R_m + R_f)} \quad (16) \end{aligned}$$

from which Eq. (11) can be written as:

$$\begin{aligned} D_a &= R_a \frac{\Delta P}{\mu} \left(\frac{1}{R_m} - \frac{1}{R_m + R_a} \right) \frac{\mu}{\Delta P} \frac{R_m(R_m + R_f)}{R_f} \\ &= R_a \frac{(R_m + R_f)}{(R_m + R_a)} \quad (17) \end{aligned}$$

$$D_{pp} = R_{pp} \frac{R_m(R_m + R_f)}{(R_m + R_a)(R_m + R_a + R_{pp})} \quad (18)$$

$$D_{cp} = R_{cp} \frac{R_m}{(R_m + R_a + R_{pp})} \quad (19)$$

The flux loss ratios are compared to the serial resistances in Fig. 2. When the absolute flux loss is equal for each of the three fouling mechanisms, the flux loss terms, D_i , are also equal. This is equivalent to transforming the inverse relationship between flux and pressure into a straight line with a negative slope determined by the end points (J_i , R_m) and (J_v , R_t). The flux loss ratios make simultaneous use of all the available information regarding fouling due to each mechanism. The discrepancy between the two methods is greatest when there is significant adsorptive fouling. The series resistance model can grossly underpredict the significance of adsorption. Experimental and theoretical results will be used to illustrate this in the Results and Discussion.

Fig. 2. Comparison between resistances obtained based on the series resistance model (R_i) and flux loss ratios (D_i).

The fouling resistance terms are not independent. Reducing or eliminating one of the resistances does not imply a proportional change in flux. As an example, the flux of a given membrane has a high J_i but has significant fouling by adsorption, accounting for a flux loss of 90%. The membrane and solute interactions are then reduced by either changing the solute properties or modifying the membrane (without changing R_m). The flux loss by adsorptive fouling for this system is now negligible. However, J_v will not increase by the amount recovered with the lower adsorptive fouling. The solute transport to the surface will be larger and a greater flux loss due to concentration polarization would be expected. The extent to which this occurs depends on how close the system is to the limiting flux.

The flux loss ratios and series resistances are both evaluated for a fixed set of operating conditions. The values of the $\%D_i$ or $\%R_i$ terms will change as the operating conditions are varied. An illustrative example would be one where the transmembrane pressure was varied. We shall assume that there is no adsorption or pore plugging occurring. At a low pressures,

concentration polarization is minimal and $J_v \approx J_i$. In this case $\%D_m$ dominates. As the pressure is increased the limiting flux is reached through either osmotic pressure effects or gel formation. J_v is now considerably lower than J_i at the same pressure and $\%D_{cp}$ dominates over $\%D_m$. Changing the shear rate can affect the contribution of the remaining flux loss ratios. Reducing the shear can increase $\%D_{cp}$ causing a reduction of $\%D_a$ and $\%D_{pp}$. The flux loss ratios can be used to qualitatively predict changes in flux under different operating conditions, as with the conventional series resistance model. When $\%D_{cp}$ dominates, increasing the shear rate will increase J_v , reducing $\%D_{cp}$ and increasing $\%D_a$ and/or D_{pp} .

3. Experimental

3.1. Materials

The feed material used in this work was the plug screw feeder pressate (PSFP) from an SCMP pulp mill. Samples of PSFP were taken during regular operation of the pulp mill and refrigerated at 2°C until tested. The feed was used as received except for prescreening with a 400 mesh to remove large fibres. Non-screened PSFP contains much larger particles including wood fibres up to 1–10 mm in length. A summary of the constituents is given in Table 1.

The particle sizes covered a broad range from 0.1 to 20–60 μm as determined by dynamic light scattering (Granulometer HR 850 and Malvern Zetasizer 3). The upper limit was set by the pre-screening which is equivalent to $\sim 37 \mu\text{m}$. The molecular weight distribution of soluble PSFP components, as determined by GPC, ranges from $\sim 4.0 \times 10^6$ to $< 100 \text{ Da}$, Fig. 3. Sugars, polysaccharides, soluble and insoluble lignins are major components and account for the wide molecular weight distribution and

Fig. 3. Molecular weight distribution of PSFP as determined by GPC. Molecular weight is shown for selected peaks.

high total organic carbon (TOC) of this effluent. Attempts to synthesize PSFP using pure components were not successful. Permeation experiments correlated poorly with the actual feed [17], prompting this course to be abandoned.

The membranes used represent a broad range of materials and pore sizes. Materials included polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), polysulfones (PS), polyether-imide (PEI), polyamide-imide (PAI), cellulose and several thin film composites (TFC). Molecular weight cut offs (MWCO) ranged from nanofiltration (300 Da) to the upper limit of ultrafiltration ($> 500 \text{ KDa}$). Membranes were procured from commercial sources or manufactured in our laboratory using an automated casting machine [18].

3.2. Procedures

Ultrafiltration and pure water permeability measurements were performed using thin channel flat sheet test cells and have been described elsewhere

Table 1
Composition of PSFP, 100 mesh filtrate

pH	Conductivity ^a ($\mu\Omega$)	DS ^b (mg/l)	SS ^c (mg/l)	TOC ^d (mg/l)	BOD ^e (mg/l)	RFA ^f (mg/l)	Lignin sol (mg/l)	Lignin insol (mg/l)	Volatile acids ^g (mg/l)	Sugars (mg/l)
5.7	5100	12600	1700	5670	5250	432	2400	1900	920	2680

^a Electrical conductivity. ^b Dissolved solids. ^c Suspended solids. ^d Total organic carbon. ^e Biological oxygen demand. ^f Resin and fatty acids. ^g Primarily acetic acid.

Fig. 4. Test sequence for evaluating J_i , J_a , J_f and J_v .

[19]. The cells are circular with a impinging feed at the center of the membrane, promoting mixing at the membrane surface beyond that expected at the mean cross flow velocity of 0.8 m/s ($N_{Re} = 800$). The effective permeation area is $14.5 \times 10^{-4} \text{ m}^2$. Permeation with PSFP was performed at 345 kPa (50 psi) and 50°C.

The testing procedure is summarized in Fig. 4 and required the determination of four fluxes.

J_i New membranes were permeated with RO water, for 5 h at 345 kPa and 25°C after which the J_i and retention of a 6K PEG test solute were determined.

J_a Groups of 12 membrane coupons were then contacted with 500 ml of PSFP in the absence of a transmembrane pressure at 50°C for 3 h with gentle stirring at 1 h intervals. Coupons were thoroughly rinsed (not physically cleaned), returned to the test cells and the J_a and 6K PEG retention re-evaluated.

J_v Preheated PSFP (50°C) was then ultrafiltered at 345 kPa for 3 h with the permeate recycled to the feed. The product rate was measured at 1 and 3 h. J_v at 3 h was used to calculate the fouling resistances and flux loss ratios.

J_f The PSFP was replaced with RO water and run for a minimum of 1 h with at least two water exchanges. Membranes were left in contact with water with no TMP overnight. The J_f and 6K PEG

retention were evaluated the following day after permeation with fresh RO water for 2 h.

4. Results and discussion

4.1. Intermediate pure water fluxes and product rates

Plots of the J_a/J_i , J_f/J_i and J_v/J_i ratios as a function of J_i were used to determine the significance of the different fouling mechanisms. Usually one would use the pore size on the ordinate axis. Accurate pore size (or MWCO) evaluation for open membranes is difficult to obtain and is highly dependent on the solute/test conditions. These types of membranes are usually quoted in terms of 100K, 300K, 500K MWCO or 0.1 μm by manufacturers. This resulted in discretized data which made any plot with MWCO as an axis difficult to read. The membrane's J_i was used in place of the MWCO which allowed an approximate, but continuous, representation of membrane performance.

Figs. 5–7 show the flux loss due to adsorption, pore plugging and concentration polarization effects, respectively. The J_a/J_i vs. J_i plot in Fig. 5 shows

Fig. 5. J_a/J_i vs. J_i for various membrane materials.

Table 2

J_a/J_i ratios after static adsorption tests for various membrane materials

Material	J_a/J_i (%)
Regenerated cellulose	102
TFC	102
Modified PVDF	95
Cellulose acetate	91
PVDF	82
PAN	70
PAI	61
Cellulose tri-acetate	53
PEI	30
PES	29
PS	29
Modified PS	29

the loss due to adsorptive fouling. Despite the variability within a class of materials, the overall trends, summarized in Table 2, followed trends observed with protein fouling [6,8]. Polysulfones exhibited severe fouling while regenerated cellulose membranes and some TFCs showed little or no fouling. Hydrophobic materials such as polyetherimide, polysulfones exhibited similar behaviour as reported with proteins [20] with large reductions of the pure water flux. Commercial modified polysulfones developed for protein applications were also prone to severe adsorptive fouling. A detailed discussion of adsorptive fouling with PSFP is available elsewhere [21].

The lower J_f/J_i ratios in Fig. 6, compared to J_a/J_i indicate further fouling. This is due to pore plugging after permeation with PSFP, in addition to adsorption. In particular it can be seen that membranes with high MWCOs (high J_i) are susceptible to pore plugging regardless of the membrane material. The higher the MWCO, the lower the J_f/J_i ratio. Finally, the J_v/J_i vs. J_i plot in Fig. 7 shows flux losses due to the cumulative effect of all the fouling mechanisms. Very few membranes have high values of J_v/J_i and these are mostly regenerated cellulose and TFC's with lower MWCOs. Following the progression of the flux ratios in Figs. 5–7 it can be seen that the material aspect is important to avoid adsorptive fouling and that high MWCO membranes are susceptible to pore plugging. Concentration polarization effects then dominate and prevent high J_v/J_i ratios with high MWCO membranes.

Fig. 6. J_f/J_i vs. J_i for various membrane materials.

The contributions of the various mechanisms can be more clearly seen by examining membranes made from the same material but of different pore sizes. The first example in Fig. 8 shows the intermediate

Fig. 7. J_v/J_i vs. J_i for various membrane materials.

Fig. 8. Intermediate fluxes for YM regenerated cellulose membrane series.

fluxes for a range of YM series regenerated cellulose membranes. The appended number indicates the rated MWCO in 1000's. Each bar represents J_i , J_a , J_f and J_v , respectively.

$J_a \sim J_i$ indicates that there was minimal adsorptive fouling with the YM-1. Negligible pore plugging was indicated by $J_f \sim J_i$ and can be attributed to the small pore size of this membrane. There was also minimal flux decline due to concentration polarization, as a result of the low J_i for this membrane. Little flux loss due to adsorption or pore plugging was observed with the YM-10. There was, however, a significant loss due to concentration polarization effects, attributable to the higher J_i . Pore plugging has begun to play a significant role with the YM-30 and concentration polarization was responsible for an increasing flux decline. The YM-100 showed further losses due to pore plugging and concentration polarization. This membrane was tested at 69 kPa whereas the others were tested at 345 kPa. Had it been tested at the higher pressure, losses due to pore plugging would have undoubtedly been greater. It is also important to note that despite the widely varying J_i 's the actual product rate observed with PSFP was similar for all four membranes suggesting that the limiting flux had been obtained for these operating conditions.

The previous example dealt with a membrane material exhibiting very low, if not negligible, ad-

sorptive fouling. At the opposite extreme is polysulfone which strongly adsorbs components of PSFP. Fig. 9 shows the different contributions to flux decline with a series of Victrex polyethersulfone membranes of increasing MWCO, as indicated by the increasing J_i . Adsorption played a significant role in all the membranes, although it decreased as the pore size increased. It was concluded that surface adsorption was likely for lower MWCO membranes and that the adsorbed layer was controlling membrane performance. Adsorption occurred via a pore restriction mechanism with higher MWCO membranes [21].

Pore plugging was a more important factor with the open membranes, as was concentration polarization. Concentration polarization was not a factor for the small pore sizes. The flux through all but the most open membranes was not high enough to establish a significant concentration gradient at the membrane surface. Unlike the YM series, the product rate with PSFP was more dependent on the initial pore size. The effect of adsorption on the polysulfone membranes was similar to shifting the effective pore size downward compared to the regenerated cellulose membranes.

These figures are useful for analysing results but are too cumbersome when considering a large number of membranes. Using a series resistance model allows a large amount of data to be quantified and tabulated. This facilitates identifying trends in membrane performance with respect to materials, pore sizes and test conditions.

Fig. 9. Intermediate fluxes for Victrex PES membrane series.

Table 3

Flux loss ratios for series of regenerated cellulose and polyethersulfone membranes. $%D_m$, $%D_a$, $%D_{pp}$ and $%D_{cp}$ are the flux loss ratios due to the membrane, adsorption, pore plugging and concentration polarization, respectively. YM-100 data obtained at 69 kPa (10 psi). All fluxes temperature corrected to 25°C

Membrane	Manufacturer	Rated MWCO	Material	$%D_m$	$%D_a$	$%D_{pp}$	$%D_{cp}$
YM-1	Amicon	1000	Regenerated cellulose	92	2	0	6
YM-10		10 000		26	18	-13	68
YM-10		30 000		3	18	11	68
YM-100		100 000		5	-10	46	59
V221	NRCC		PES	4	76	17	3
V205				8	82	8	2
V226				3	87	7	3
V222				4	83	11	1
V213				4	52	34	9

4.2. Relative flux loss ratios

The relative flux losses (RFL) for the YM and Victrex series are given in Table 3. The same conclusions are reached regarding the contributions of each fouling mechanism as from Figs. 8 and 9. This is expected as they are derived from the same information. Small negative resistances ($\sim 10\%$ and smaller) are due to experimental error in measuring fluxes and should be considered negligible. The flux loss ratios or serial resistances obtained in replicate

experiments should not be expected to reproduce to a great extent, given the variability of new membrane performance and the permeation experiments in general. Rather the flux loss ratios should be used to identify which, if any, of the three fouling mechanisms are important.

The $%D_a$ term indicates that adsorptive fouling was minimal for the YM series. $%D_{pp}$ and $%D_{cp}$ were significant with both series of membranes for high MWCOs. The greater pore plugging being attributable to the larger pore sizes and concentration

Table 4

Comparison of fouling contributions based on series resistances and flux loss ratios. All fluxes temperature corrected to 25°C

Membrane	Type	J_i (LMH)	J_a (LMH)	J_f (LMH)	J_v (LMH)	Flux loss ratios				Serial resistances			
						$%D_m$	$%D_a$	$%D_{pp}$	$%D_{cp}$	$%R_m$	$%R_a$	$%R_{pp}$	$%R_{cp}$
YM-1	CELL	28	28	28	26	93	0	0	7	93	0	0	7
YM-10	CELL	122	100	115	33	27	18	-12	67	27	6	-4	17
YM-30	CELL	697	575	496	23	3	18	11	68	3	1	1	95
YM-100	CELL	537	593	346	30	5	-10	46	59	6	-1	4	91
V221	PES	78	19	6	3	4	76	17	3	4	12	34	50
V205	PES	110	19	11	8	7	83	7	3	7	35	31	27
V226	PES	355	39	28	15	4	89	3	4	4	34	15	47
V222	PES	670	113	36	29	4	83	12	1	4	22	55	19
V213	PES	795	381	109	34	4	52	34	10	4	5	22	69
XM-50 ^a	ACRYLIC	180	60	10	5	3	66	28	3	3	5	42	50
NTU-2120 ^b	OLEFIN	135	129	47	26	19	4	61	16	19	1	35	45
NA 50 ^c	mod PS	762	143	48	23	3	81	13	3	3	13	32	52
LSY PVD1 ^d	TFC	47	25	28	29	61	47	-6	-2	62	54	-12	-4
ART-1		1000	900	800	700	70	10	10	10	70	8	10	12
ART-2		400	300	200	100	25	25	25	25	25	8	17	50
ART-3		1000	3	2	1	0	100	0	0	0	33	17	50

^a XM-50, Amicon 50 000 MWCO. ^b NTU-2120, Nitto 20 000 MWCO. ^c NA 50, Filtron 50 000 MWCO. ^d LSY PVD1, Hydranautics 92% NaCl.

polarization due to the higher fluxes. The membrane itself was a minor resistance for the YM-30 and YM-100 membranes.

The relative resistance of the membrane is negligible for the entire polyethersulfone series. This is due to adsorptive fouling accounting for the major part of the flux loss. Concentration polarization is a relatively small component of fouling due to the already greatly diminished flux. The J_f for the V213 membrane was 109 LMH ($l/m^2/h$) and the product rate corrected to 25°C was 37 LMH. Concentration polarization effects caused a flux decline of 72 LMH. This flux loss was small compared to the > 400 LMH loss due to adsorption. The loss due to adsorption is unavoidable for this material, while that due to concentration polarization may be minimized. As a comparison, the $\%D_{cp}$ for the YM-30 at 68% represents a flux of 473 LMH. There is a greater potential for attaining higher fluxes with this membrane under the appropriate conditions.

4.3. Serial resistance vs. flux loss ratios

The serial resistance and FLR approaches to evaluating fouling contributions were discussed in Section 2.2. Several examples comparing the two methods are highlighted in Table 4. The two methods provide similar conclusions regarding the contribution of fouling mechanisms with the 1 and 10 K MWCO YM regenerated cellulose membranes. There is some disagreement between the 30 and 100 K MWCO membranes. The serial resistances underestimate the flux loss due to pore plugging and adsorptive fouling. The YM-100, in particular, exhibits significant pore plugging. Pore plugging and concentration polarization account for flux reductions of 247 and 316 LMH respectively for this membrane. The series resistance model attributes 90% of the flux decline to R_{cp} . The flux losses are more realistically represented by the flux loss ratios; 46 and 59% of the flux decline to pore plugging and concentration polarization, respectively.

The disagreement between the two methods is considerable for the entire series of polyethersulfone (V series) membranes. The FLR approach indicates adsorptive fouling as being primarily responsible for the flux loss. R_a is greatly underestimated with the sequential method for all these membranes.

The shape of the flux–resistance curve in Fig. 2 shows that a small change in the overall resistance can lead to large changes in flux. Since the adsorptive component of the fouling resistance is determined first, it will tend to be underestimated when using the serial resistances. Subsequent flux losses require an increasingly larger change in the overall resistance. The R_{cp} term will always be overestimated unless the relative difference between J_f and J_v is small.

A set of artificial fluxes can be used to illustrate discrepancies between the two methods more clearly. The examples ART-1 and ART-2 have flux declines of 100 LMH attributed to each fouling mechanism. The initial flux for ART-1 and ART-2 are 1000 and 400 LMH, respectively. The FLRs attribute equal importance to each mechanism in both cases while the serial resistances overestimate R_{cp} . The serial resistance reflects the flux decline from the previous condition. If J_v is one half of J_f , the series resistance model will always predict $\%R_{cp}$ at 50%, regardless of the other intermediate fluxes. This is a direct consequence of the inverse flux–pressure relationship. An exaggerated case is illustrated by ART-3 where adsorptive fouling reduces the pure water flux from 1000 to 3 LMH. J_f and J_v are 2 and 1 LMH, respectively, and R_{cp} is still 50%. The RFLs describe the fouling behaviour more accurately.

4.4. Membrane selection criteria

The membrane which will ultimately be selected will be that which has the highest flux for the required separation. Other important considerations will include the membranes compatibility with cleaning procedures, available configurations, cost, expected lifetime, etc. This may not necessarily agree with the membrane exhibiting desired fouling characteristics. A membrane with high fouling and high flux will be selected over a low fouling membrane with low flux, if both perform the required separation. Ultimately, the total cost of implementation will be the final criterion.

Selection of the best membrane from a fouling viewpoint would be one where R_m is the dominant term. This type of membrane would be expected to have predictable behaviour in terms of flux stability and separation. Such a membrane would also re-

spond to changes in operating conditions. A minimal $\%D_{cp}$ term suggests that improved mass transfer at the membrane surface would not be beneficial. Higher fluxes would be obtained by increasing the transmembrane pressure. The new set of operating conditions will change the relative contribution of the fouling mechanisms, increasing $\%D_{cp}$. Further increases in the transmembrane pressure will eventually result in smaller flux increases as the limiting flux is approached. For an open membrane such as the YM-100 which had significant pore plugging, higher pressures may have increased $\%D_{pp}$ resulting in flux declines which were not reversible. This was also observed with several membranes which were tested under various operating conditions with PSFP. The membrane will no longer have the same surface properties as the original, the foulants now being an integral part of the membrane. This may make them more susceptible to fouling with a feed such as PSFP because it contains resin acids which can promote the formation of a bound layer due to their binding characteristics [9].

5. Conclusions

A sequential approach to membrane testing allowed identification of the flux loss due to adsorptive fouling, pore plugging and concentration polarization with an SCMP pulp mill effluent. A series resistance model or the flux loss ratios (FLR) facilitated handling large amounts of data and identifying trends in membrane performance with respect to materials, pore sizes and test conditions.

A series resistance model was used to quantify the relative contributions of each fouling mechanism to flux decline. The flux loss ratios are based on the ratio of the flux loss due to each mechanism to the overall flux decline. Flux loss ratios were shown to more accurately describe the flux reduction due to each fouling mechanism. Using experimental and simulated flux data, the series resistance model was shown to underpredict fouling due to adsorption and overpredict concentration polarization.

Understanding the contribution of the fouling mechanisms to flux decline allows selection of the most viable membrane when several choices appear to be suitable based on flux/separation performance.

Selection of an appropriate membrane material will minimize adsorptive fouling while pore plugging is controlled by using a membrane with a suitable MWCO. Adsorptive fouling was severe for PAN, PS, PES, PAI and PEI membranes, typically responsible for a loss of 60 to 80% of their pure water permeability. Regenerated cellulose and several thin film composite membranes exhibited very low adsorptive fouling. These materials, and regenerated cellulose in particular, have been extensively reported in the literature to exhibit low adsorptive fouling with proteins.

Pore plugging was identified by a significant $\%D_{pp}$ term. The wide range of molecular weights of material in PSFP requires careful selection of the pore size and operating pressure. Pore plugging may become more important over long operating times or higher transmembrane pressures resulting in unforeseen flux decline.

Selection of an appropriate pore size requires consideration of the membrane material and solute interactions. Adsorptive fouling with polysulfone membranes reduced the effective pore size and/or reduced the permeability of the membrane. Obtaining similar fluxes with polysulfone and regenerated cellulose membranes required using polysulfone membranes with larger initial MWCOs.

Higher fluxes can be obtained by optimization of the operating conditions or module design. Higher transmembrane pressures would be beneficial with membranes for which $\%D_m$ dominates and $\%D_{cp}$ is minimal. Increased shear rates would be advantageous when $\%D_{cp}$ is large. Little improvement can be obtained if adsorption or pore plugging dominate.

6. List of symbols

CFV	cross flow velocity (m/s)
$\%D_a$	flux loss ratio due to adsorption (–)
$\%D_{cp}$	flux loss ratio due to concentration polarization (–)
$\%D_m$	flux loss ratio for the membrane (–)
$\%D_{pp}$	flux loss ratio due to pore plugging (–)
FLR	flux loss ratio
J_a	pure water flux after static adsorption (l/m ² /h)
J_f	pure water flux after J_v (l/m ² /h)

J_i	pure water flux for a new membrane ($1/\text{m}^2/\text{h}$)
J_v	flux for a new membrane with PSFP as feed ($1/\text{m}^2/\text{h}$)
LMH	flux ($1/\text{m}^2/\text{h}$)
PSFP	plug screw feeder pressate
$\%R_a$	relative resistance due to adsorption (–)
$\%R_{cp}$	relative resistance due to concentration polarization (–)
$\%R_m$	relative resistance of the membrane (–)
$\%R_{pp}$	relative resistance due to pore plugging (–)
TMP	transmembrane pressure (kPa)

6.1. Greek Symbols

ΔP	transmembrane pressure drop ($\text{kg}/\text{m}/\text{s}^2$)
μ	permeate viscosity ($\text{kg}/\text{m}/\text{s}$)
π	osmotic pressure ($\text{kg}/\text{m}/\text{s}^2$)
σ	reflection coefficient (–)

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