



Review Paper

Membrane Fouling Prevention and Control Strategies in Pulp and Paper Industry Applications: A Review

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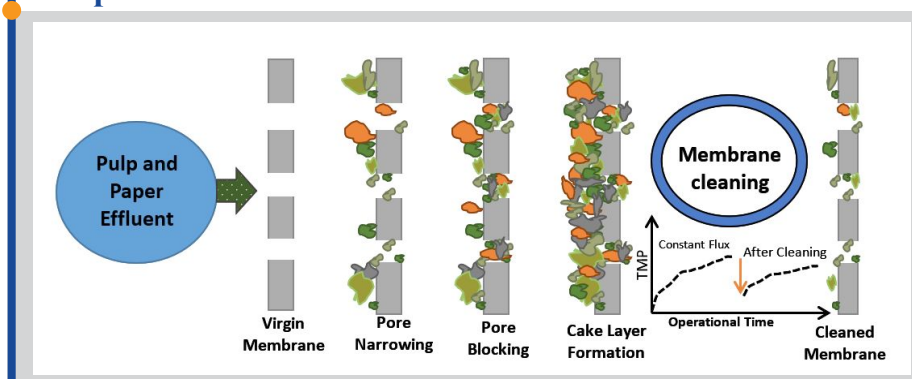
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Graphical abstract



Highlights

- Membrane fouling is a major challenge in pulp and paper effluent treatment.
- Factors affecting membrane fouling are summarized and discussed.
- Physical, chemical, and hydrodynamic fouling control strategies are discussed.
- Optimization techniques for membrane operation are reviewed.

Abstract

Membrane separation technologies have recently received much attention, from lab-scale studies to full-scale operations, in the forest industry. However, membrane fouling comprises a significant obstacle to their broad application. Thus, to ensure cost-effective operation of membrane separation processes, the improved elucidation of membrane fouling and establishment of effective fouling control strategies are critical. Membrane fouling decreases process performance efficiency, thereby increasing operational and maintenance costs. Although much research has been conducted in this field, a review has not yet been undertaken to address membrane fouling in pulp and paper mill applications. Further, membrane fouling is still not fully understood. In this review, a survey of the present state of fouling management strategies in the pulp and paper industry (PPI) is presented alongside the latest advances and innovative methods in fouling management. This article also discusses the key parameters that affect membrane fouling, fouling characterization techniques, as well as fouling mechanisms and strategies that are employed for fouling control. In addition, future research opportunities related to membrane fouling control strategies in both low-pressure membranes and MBRs are proposed.

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1. Introduction

Membrane technologies have been utilized for the treatment of PPI effluent and sludges since the late 1960's. Recently, they received increasing attention due to their short processing steps, distinctive fractionation, reduced chemical utilization, considerable energy savings, as well as the capacity for being incorporated into existing operating units [1–3]. However, due to the complexity and high fouling tendency of forest product process streams and effluents, membrane fouling remains a significant impediment and challenge toward the adoption of this technology on a large scale [4,5]. Fouling leads to a decrease in membrane filtration capacity, an increase in the frequency of membrane cleaning, and a reduction in membrane lifespan; thus, leading to higher operating and membrane replacement expenditures [2,4,6]. Accordingly, significant research has been devoted to addressing membrane fouling. These studies have focused on various aspects, including fouling characterization [7], fouling mechanisms [4], pretreatment methods [8], and fouling prevention and cleaning regimes [9–11].

The feasibility of applying membrane filtration processes is contingent on the ability to run the process over a long service period at acceptable permeate flow rates. However, as is typical with the use of membrane technologies, they are vulnerable to flux decline due to pore narrowing and plugging, and cake layer formation [12]. These issues are caused by compounds such as extracellular polymeric substances (EPS), soluble microbial products (SMPs), and dissolved inorganic materials. During the direct filtration of pulp and paper process wastewater, organic and inorganic fouling of the membrane are the most dominant mechanisms, as wood hydrolysate contains various substances, including carbohydrates, extractives, and lignin. Both organic and inorganic fouling types (sludge flocs, EPS, SMPs, and struvite) were observed in membrane bioreactors (MBRs), where cake layer was the main fouling mechanism [13–16]. Further, decreased flux was observed under both thermophilic and mesophilic operating environments.

Since membrane fouling is very complex, strategies for its reduction must be individually customized, as each specific effluent has its own unique properties. Therefore, in regard to the implementation of membrane technologies in the forest industry, special membrane fouling control strategies as well as fouling prevention measures are required. To date, plenty of research efforts have been devoted to the design of experiments toward the elucidation of membrane fouling problems [11,17], hence many mitigating strategies have been proposed and developed. Although much research has been conducted on this matter with several review papers available, none have yet undertaken to address the fouling problems that occur during the filtration of paper mill effluents, and membrane fouling is still not fully understood. It is well known that preventive membrane fouling strategies and membrane cleaning cycles depend on the type of effluent being treated, as well as the specific membrane employed. Further, each feed/membrane system exhibits a particular type of fouling phenomenon [18]. Pulp and paper industry (PPI) related effluents are heterogeneous; thus, it seems important to review the findings obtained in relevant works to provide an overview of the

results, which may facilitate a complete fouling understanding and ease its control. This article comprises a critical review of membrane fouling in the PPI inclusive of prevention and control strategies, conventional standard approaches, as well as new and emerging technologies.

2. The concept and mechanism of membrane fouling

Membrane filtration involves complex interactions between the membrane surface, processing conditions, and effluents under treatment. These interactions often affect each other, which result in a multifaceted effect on the surface of the membrane, known as the phenomenon of membrane fouling. From a practical perspective, fouling is defined as a reduction in the active area of the membrane due to the reversible or irreversible deposition or adsorption of foulants on the surface of the membrane or inside its pores. Fouling initiates a decrease in permeate flux, increase in transmembrane pressure (TMP), and loss of membrane performance. Therefore, frequent cleaning, larger membrane areas, and regular maintenance are required to maintain a given flux and TMP. As depicted in Figure 1, the primary fouling mechanisms include pore blocking, the adsorption of feed components, and cake formation. Pore obstruction is accountable for early sharp flux reduction due to the accumulation of large suspended materials on the surface of the membrane, while the formation of the cake layer is the reason for steady long-term flux deterioration [19]. Cake layer is the main mechanism that causes fouling in anaerobic membrane bioreactors (AnMBRs). Fouling may be classified either on the reversibility of fouling, or from the aspect of the origin of foulant materials. In terms of the source of foulants, fouling can be categorized as organic fouling, particulate fouling, bio-fouling, or inorganic fouling. During the recovery of hemicellulose, lignin, or other inhibitors removal, organic and inorganic mechanisms comprise the primary types of fouling. Considering the reversibility or attachment strength of particles to the surface of a membrane, fouling may be classified as either reversible or irreversible.

2.1. Membrane fouling in pressure-driven membrane processes

Widely used membrane technology in forest industry applications are based on pressure-driven membrane technologies: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). MF has a high capacity to successfully clarify process water and remove large suspended particulates; hence, it is employed as a prefiltration step for membranes that contain smaller pores, to prevent fouling or separate solids of different sized classes [3,20,21–24]. Both UF and NF membrane separation processes are commonly applied for the recovery, fractionation, and purification of hemicelluloses from pulp and paper effluents, while NF and RO membranes are employed for the removal of fermentation inhibitors,

exclusion of small molecules, and concentration of sugars (see Table 1). However, fouling remains an obstacle to their more extensive applications particularly in the filtration of acidic effluents, with hydrophobic membranes.

Table 1 summarizes a number of studies that were carried out with pressure-driven membrane technologies in the treatment of pulp and paper effluents. Based on the literature, wood extractives (lipid extracts including fatty acids, resin acids, steroids, and phenolic extracts including lignans,

tannins), lignin and its degradation products, and polysaccharides are foulants that are commonly found during the filtration of pulp and paper effluent and processing water. The removal of these materials before filtration has been shown to enhance the filtration capacity. In their partly dissociated forms, these foulants may severely foul membranes (mainly hydrophobic membranes) at lower pH values, in contrast to alkaline wood hydrolysates.

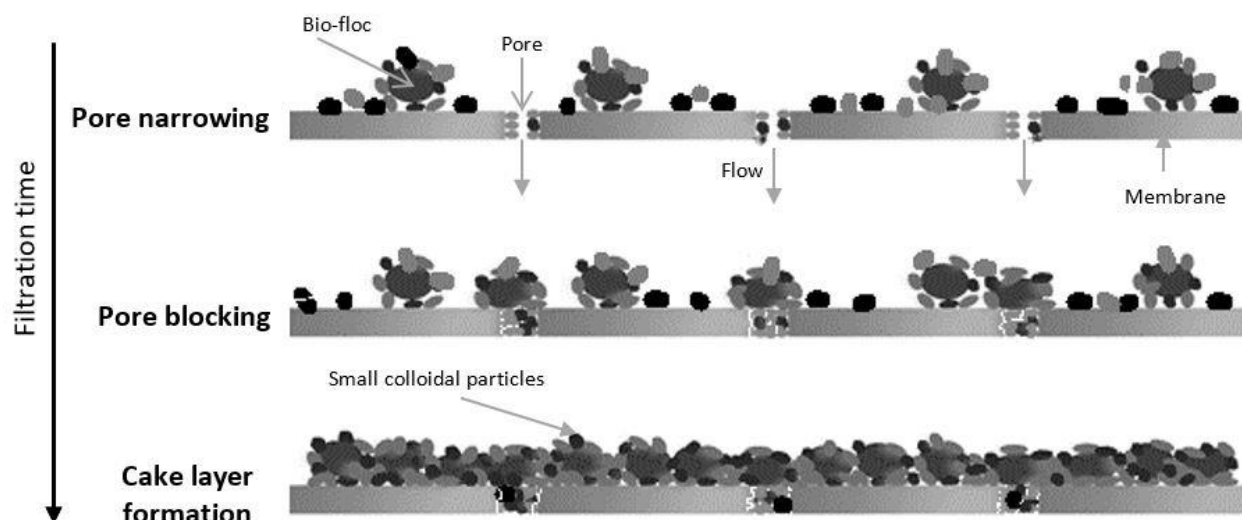


Fig. 1. Representation of porous membrane fouling mechanisms.

As is evident from Table 1, different membrane materials and a varied range of pore sizes have been investigated. It was revealed that membranes with tighter pore structures fouled to a lesser degree than did membranes with looser pore structures. Here again, it was observed that when the pore sizes were relatively small, the fouling was mainly due to adsorption; however, when the membrane cut-off was increased, pore plugging was a dominant fouling mechanism. In MF, pore blocking was the dominant membrane fouling mechanism as the effluent comprised large, suspended macromolecules that plugged the large pores of the MF membrane. However, in the cases of UF and NF, absorptive fouling was observed. A wide array of membrane materials may be applied in the treatment of PPI effluents, including regenerated-cellulose (RC), polyamide (PA), sulfonated

polyethersulfone (SPES), polyolefin (PO), cellulose acetate (CA), polysulfone (PS), polyethersulfone (PES), polypiperazine amide (PPA), and polyvinylidene fluoride (PVDF), (see Table 1). Hydrophobic membranes such as PS, polyamide-imide, and polyether-imide are more prone to fouling than hydrophilic membranes. It was also discovered that fouling was more serious with membranes that had higher contact angles, in contrast to those with lower contact angles. Due to the different chemical compositions of membranes and applied hydrodynamic process conditions, a wide range of fouling control strategies have been developed, including feed pretreatment strategies, several cleaning approaches/cleaning agents, and various physical mitigation measures. These fouling control approaches are discussed in detail in the following sections.

Table 1

Fouling prevention and control strategies in the mechanical operation of membrane processes with different effluents and process waters.

Processed materials	Membrane type and pore size (kDa)	Membrane module and its material ^a	Scale	VRF ^d	Temp (°C)	TMP (bar)	Fouling mechanism	Main foulants	Fouling control strategies	Ref.
Prehydrolysis Liquors of Poplar Chips	MF/UF 0.22 and 0.45 μm/ > 1	Flat sheet PVDF/CA	Lab	1–23	20	3.99	–	High molecular weight lignin	NaOH addition + MF	[3]
Pulp and paper mill process water	UF 30/50	– RC/PES	Lab	– ^b	40	1/2	Adsorptive fouling	Wood extractives	–	[4]
Pulp and paper mill effluent	UF 30/50	Flat sheet RC/PES/polyamide,	Lab	–	50–70	–	–	Extractives (lignans, resin, and fatty acids)	–	[7]
Birch and Spruce hydrolysate	UF 5/10	– –/PS/RC	Lab	0.66*	55	3/5.5	–	Degradation products of lignin and extractives	Various pretreatment	[8]
Pulp and paper effluent	UF	Tubular PES	Lab	–	30	5	Adsorptive fouling	Phenolic compounds	Combined mechanical and chemical cleaning	[9]
Pulp and paper mill circulation water	MF/UF 20/30/50	Flat sheet PES/ RC/PVDF	Lab/ pilot	5/2	50/ 46/78	0.5/2	–	–	Vibration	[20]
Pulp and paper wastewater	MF/UF/RO 0.14 μm/500/100	Tubular/spiral-wound Zirconium oxide/PS/PES/Pol yamide thin-film	Lab	0.8*	30	11/28/20	–	–	Cross-flow velocity/ combined physical and chemical	[21]

										cleaning	
Process Water from the thermomechanical pulping mill	MF/UF/NF 0.2 µm/5/	Spiral wound ceramic /PES	Lab	0.5–0.99*	80/80/50	6/20	–	Extractives and solids	Pretreatment with drum filter and MF	[22]	
Wheat bran arabinoxylan solution	MF/UF 0.2 µm/10	Tubular α-alumina oxide and titanium dioxide	Lab	0.3*	80/	0.4–1.6	Gel formation	Gel-forming substances	Prefiltration by MF + cross-flow velocity	[23]	
Process water from thermomechanical pulping	MF/UF 0.04, 0.1, 0.5 µm/5	Spiral wound	Lab	0.98*	60	1.5 – 4	–	Suspended solids and colloidal extractives	Prefiltration by MF	[24]	
Paper mill waters	UF 8–200	Flat sheet/ tubular RC/PVDF	Pilot	–	40 – 52/ 39 – 41	0.1 – 2.7	Pore plugging	Lignin residuals	Shear forces by rotating at 400 or 470 rpm	[25]	
Spent sulfite liquor (SSL)	UF 30	– PS/PES/RC	Lab	–	50	1.5/5.25/8.2 5	Deposition	Phenolic compounds	Cleaning with sodium hydroxide and Ultrasil 11 (Henkel Ecolab)	[26]	
Chemithermomechanical pulp mill process waters	UF 30/50	– RC/PES	Lab	–	40	1/2	Adsorptive fouling	Lignin, extractives, and hemicelluloses	–	[27]	
Pulp mill effluent	UF 1–7	– PVDF/ PS/ PES	Lab	–	50	3.5	Adsorptive fouling	Lignin, resin, and fatty acids	–	[28]	
Pulp and paper mill wastewater	NF 10/30	Flat sheet PES	Lab	2/3/4	25/35/45	12/24/36	Cake layer formation/ pore plugging	–	Operating conditions optimization	[29]	
Model substance for pulp and paper mill and bleaching effluent	NF	Flat sheet SPES/ ^c Aromatic polyamide	lab	–	25	4 – 12	Gel formation	Vanillin and humic acid	–	[30]	
Paper wastewater	NF	– Flat sheet	Batch	–	25/30	5	Concentration polarization	Nonbiodegradable pollutants	Cross-flow velocity	[31]	
Fatty acid solution	UF 20	Flat sheet PES	Lab	–	22 – 23	1	Adsorptive fouling	Fatty acids	–	[32]	
Model substance for pulp and paper mill waters	NF 5/7	Flat sheet SPES	Lab	–	40	8	Dense layer formation due to humic acid adsorption	Polysaccharides and humic acid	Ultrasil 10 cleaning	[33]	
Glucose solution and pulp plant effluent	NF	Flat sheet –	Lab	–	65	8/25	–	–	Cross-flow velocity /chemical cleaning	[34]	
Kraft black liquor	UF	– Cellulose triacetate	Lab	–	–	2.9/4.9/6.9/7 .8	Gel formation/ pore-plugging	–	Centrifugation and MF pretreatment + shear enhanced filtration	[35]	
Hardwood Kraft black liquor	UF/NF 4–100	Tubular PES/PS/PVDF	Lab	0.7–0.9*	60	2/25	–	–	Cross-flow velocity	[36]	
Hemicellulose hydrolyzate	NF 5	Flat sheet PS	Lab	–	45	10/20	Fouling layer formation	–	Feed prefiltration by paper-filter, flushing, and chemical cleaning	[37]	
Masonite Wastewater	UF 10	Flat sheet composite fluoropolymer/RC/PES	Lab	0.7–0.99*	50	10	–	Organic molecules	Alkaline the cleaning agent, 0.5wt% Ultrasil 10 pH adjustment	[38]	
Paper machine whitewater	NF 0.4/1	Flat sheet PES	Lab	1.55/2.09/ 2.28/3.0	25	8–32	Pore blocking and cake formation/ concentration polarization	–	–	[39]	
Effluent from alkaline peroxide mechanical pulping	U 2–100	Flat sheet PO/PES	Lab	0.13–0.98*	25/40/55	1/2/3	–	–	Pretreatment with 150 µm bed screen/ Cross-flow velocity	[40]	
pulp and paper mill wastewater	NF/RO	Flat sheet/ Spiral wound PA/	Lab	12–15/ 5–8	17/40	10	adsorption	–	Cross-flow velocity/pH	[41]	

Biologically treated pulp and paper wastewater	UF 5	Flat sheet PES	Lab	3/4/5	25	4/6/8	Deposition	Organic foulants	Through optimizing the operating conditions	[42]
Eucalyptus and pine wood hydrolysates	UF 4/5	– PS/PES	Lab	2	45/60	2/5.5	Adsorptive fouling	Ligneous material	Pretreatment with polymeric adsorbents	[43]
Pre-hydrolysis liquor	NF/RO 0.15/0.3/0	– -PA	Lab	5	–	6.9/20.7/34. 5	–	Lignin and polyphenolic compounds	Pretreatment with activated carbon adsorption	[44]
Softwood kraft black liquor	UF/NF 20/0.2 – 1	Tubular Al ₂ O ₃ /TiO ₂ / Composite	Lab	0.85 – 0.95*	90/70	2/20/5–35	Cake Layer	Lignin	Membrane flushing and cleaning by alkaline agents	[45]
Aspen and Maple wood hydrolysate	NF/RO 0.1–0.5	Spiral wound/Flat sheet PA/CA/ PPA	Lab	5	40	35/21	Deposition/Concentration polarization	Sugars, organic acids, furfural, and phenols	Cross-flow velocity/cleaning by NaOH	[46]
Spent sulfite liquor	MF/UF/NF 0.05–0.2 µm/1–20	Tubular Al ₂ O ₃ /TiO ₂	Lab	0.2/0.2 1/0.35*	60–70	2/1	–	–	Crossflow velocity/chemical cleaning	[47]
Spent sulfite liquors	UF 1/5/15	Ceramic TiO ₂	Pilot	0.78/0. 45/ 0.15*	20	1.8 – 2	Gel layer formation	–	Flushing and cleaning by 0.1 N NaOH	[48]
Wood extract (auto-hydrolyzate)	UF 30/10	Cellulose based UF membranes	Lab	17/9.2/ 6.4/5.2/ 3.6	65	1/2	Concentration polarization and gel layer formation	Lignans and lipophilic wood extractives	Oxidation by gas-phase pulsed corona discharge (PCD) + high shear rate	[49]
Birchwood chips extract	UF 5	Flat sheet PS	Lab	0.66*	60	5.5	Gel layer	Ligneous and hemicellulosic compounds	Different pretreatments based on adsorption	[50]
Spent sulfite liquor	UF/NF 10/5/3/0.5	Flat sheet RC	Lab		54–75	20.8–31			Vibratory share-enhanced filtration	[51]

^a RC = regenerated cellulose, PVDF = polyvinylidene fluoride, PES = polyethersulfone, SPES = sulfonated polyethersulfone, PO = Polyolefin, PPA = polypiperazine amide, PA = polyamide, CA = cellulose acetate, PS = polysulfone,

^b – shows value not available or not reported.

^c /= means multiple values used

^d Volume Reduction Factor (VRF), while the values indicated by the asterisk (*) are volume reduction percent

2.2. Membrane fouling phenomenon in Membrane Bioreactors (MBRs)

Over the last few years, the treatment of forest industry effluents and process waters by MBRs has been intensively reported in the literature. Both aerobic membrane bioreactor (AeMBR) [16,52,53] and AnMBR [13–15,54,55] processes have been used under mesophilic (15–40°C), or thermophilic (40–70°C) conditions. The membrane units were fitted in either the primary bioreactor vessel (submerged MBR) or in an isolated tank following the biological treatment step (side-stream MBR). MBRs demonstrated excellent results, having a smaller environmental footprint, reduced sludge generation, high COD removal, and increased biogas production. However, the control of membrane fouling continues to hamper the economic viability of MBRs as a result of high maintenance costs, energy requirements for air scouring, and chemical supplies for membrane cleaning.

Both mesophilic and thermophilic MBRs suffer from fouling problems. However, thermophilic submerged anaerobic membrane bioreactors (SAnMBRs) face severe membrane fouling as higher temperatures induce increased SMP release [56]. Further, thermophilic bacteria have poorer biofloculation settleability and higher EPS production in contrast to mesophilic bacteria [57]. Concentrations of EPS were found to be 2.5 times higher in thermophilic over mesophilic operations. Because of their heterogeneous nature, EPS deposit onto the surface of the membrane and form a thin gel layer, which represents an important barrier to the permeable flux. Many researchers consider EPS as key foulants in MBRs, where their generation is correlated to parameters, e.g., temperature, solid retention time (SRT), sludge age, organic loading rate (OLR), and substrate composition. EPS have been categorized as bound EPS and soluble EPS; and typically contain a mixture of macromolecular polyelectrolyte polysaccharides such as proteins, nucleic acids, and humic compounds. Soluble EPS are typically associated with irreversible fouling.

In MBRs, fouling may result in the development of a thin gel layer, as well as a thick cake with multiple layers; where each layer can have different characteristics and structures. For example, a dense and compressed layer can form as is observed when filtration is operated at a high flux compared to a loose gel layer formed at a lower flux [55,58]. This is because large suspended particles, small colloidal particles, macromolecules, and proteins can be quickly trapped on the membrane surface, due to increased applied

pressure and flow rate. Further, particle size plays a key part in defining the type of cake layer that forms on the membrane surface. Particle dimensions typically decrease when operating at thermophilic temperatures compared to mesophilic temperatures [16]. It is generally assumed that soluble colloidal material is responsible for blocking the pores, while the suspended solids initiate the formation of the cake layer. Typically, when foulants are similar to or smaller than the pores of the membrane, adsorption and pore blocking mechanisms occur; however, when the foulants are larger than the pores of the membrane, a cake layer is likely to form on the membrane's surface [59]. Lin et al. [15] considered the attachment of bacterial clusters and/or small flocs to the surface of the membrane as the starting stage of the cake layer formation process. Gao et al. [14] mentioned that the fouling of a SAnMBR could be greatly affected by the buildup of colloidal materials due to sludge floc breakage resulting from high pH shocks. Simstich et al. [16] analyzed the elements found in the cake layer and concluded that calcium, aluminum, barium, and iron have higher tendencies to deposit on the surface of the membrane, whereas sodium, potassium, as well as silicon, had a lower probability of being found in the fouling layer.

Table 2 summarizes the extent of membrane fouling mechanisms that anaerobic and aerobic MBRs may be subject to. Formation of the cake layer was a dominant fouling mechanism, although the concentration polarization mechanism was also observed. All fouling types including organic, inorganic, and biofouling were seen in these studies. The biofouling of membranes is associated with pore closure, the adsorption of EPS, and cake layer formation. Inorganic fouling is the result of the deposition of colloids, struvite, and salts of Ca²⁺, Al³⁺, Ba²⁺, and Fe³⁺. Membrane fouling was observed in both AnMBRs and AeMBRs. However, due to fluctuation in pH (via phosphate concentrations, or CO₂, and the production of high ammonia), AnMBRs exhibited a higher fouling tendency than did their aerobic counterparts.

Different membrane materials such as polymers or ceramics were employed for the treatment of PPI process waters and effluents, as shown in (see Table 2), where PVDF is the primary polymer used in MBRs. These membrane materials exhibited various fouling propensities due to different pore sizes, morphologies, and hydrophobicities. PVDF showed some superiority over polyethylene (PE) membranes as related to the irremovable fouling reduction in MBRs. Both hollow fiber and flat sheet (plate-and-frame) membrane modules have been applied in PPI effluent and process water

treatment. Hollow fiber membranes are found to be more susceptible to fouling, requiring regular rinsing and chemical cleaning [60]. However, hollow fiber membrane modules are typically inexpensive to produce, permit high packing densities and can bear strong backwashing [60]. Polymeric membranes were seen to be mainly fouled by both biomass and struvite, while

ceramic membranes were fouled mostly by struvite ($MgNH_4PO_4 \cdot 6H_2O$) [61]. Numerous approaches have been proposed to control fouling issues, including physical techniques (backwashing and hydrodynamic conditions), chemical cleaning, and operation under sub-critical flux. These methods are further described in the subsequent sections.

Table 2
Fouling of MBRs during the treatment of pulp and paper effluents and sludge.

Process	Wastewater type	Scale	Membrane module and material	Configuration	Fouling type	Mechanism	Main foulants	Control strategies/cleaning	Ref.
SAnMBR	Kraft evaporator condensate	Lab		Submerged	Biofouling	Cake formation	EPS/ SMP/ sludge flocs	Biogas sparging	[13]
SAnMBR	Thermomechanical pulping whitewater	Lab	MF 70 kDa Flat-sheet PVDF	Submerged	Organic	Cake formation	EPS/ polysaccharides/ proteins/ fine flocs	Gas sparging	[14]
SAnMBR	Kraft evaporator condensate	Lab		Submerged	–	Cake formation	Microbial flocs, EPS,	–	[15]
ThAeMBR	Paper mill deinking wastewater	Lab	MF 0.04 μ m Flat-sheet PES	Submerged	Inorganic	Cake formation	Salts of Ca, Al, Ba, and Fe	High cross flow velocity	[16]
AeMBR	Kraft pulp condensates	Lab	UF 0.03 μ m Hollow fiber Polymeric	Submerged	–	Concentration polarization	–	Aeration	[52]
ThAeMBR	Pulp and paper wastewater	Lab	MF 0.3 μ m Flat-sheet PVDF	Submerged	Inorganic	Cake formation	–	Fine and coarse bubbles	[53]
ThAnMBR	Kraft evaporator condensate	Lab	Flat-sheet PVDF	Submerged	Organic/inorganic	Cake formation	The protein fraction of EPS	Biogas sparging	[55]
ThAeMBR	Thermomechanical pulping pressate	Lab	MF 0.3 μ m Flat-sheet PVDF	Submerged	Organic	Cake Layer	EPS	Aeration	[58]
–	Synthesized paper mill wastewater	Lab	MF/UF 0.3 μ m/ 30 Flat sheet PVDF	External	Organic	Pore blocking	Biological suspension	Tangential flow/ Flushing	[62]
ThAnMBR	Kraft evaporator condensate	Pilot	UF	External	–	–	–	High velocity	[63]
ThAeMBR	Simulated newsprint white-water	Lab	UF 0.05 μ m Tubular ceramic	External	Organic/inorganic	Gel layer formation/ pore blocking	Colloidal Particles	Chemical cleaning by $HClO_3$ followed by 10% HNO_3 and $NaOH$	[64]
–	Synthetic paper mill wastewater	Lab	MF Flat sheet PVDF	External	Biofouling	–	–	Tangential flow	[65]
AeMBR	Paper mill wastewater	Pilot	MF 0.1, 0.4 μ m Flat sheet Poly-olefin hollow-fiber	Submerged	Biofouling	Pore blocking	–	Coarse bubble	[66]
AeMBR	Paper mill wastewater	Pilot		Submerged	–	–	–	Prefiltration/Aeration	[67]
ThAnMBR	Kraft evaporator condensate	Lab	MF 0.3 μ m Flat-sheet PVDF	Submerged	Organic	Cake layer and pore clogging	Larger colloidal particles (1–10 μ m).	On/off cycle and physical cleaning	[68]
SAnMBR	Kraft evaporator condensate	Lab	MF 0.3 μ m Flat-sheet PVDF	Submerged	Biofouling	Cake layer	–	Biogas sparging	[69]
ThAeMBR	Paper mill white-water	Lab	UF 0.02 μ m Polymeric	Submerged	–	–	–	Immersion of the membrane unit for 24 hours in a 0.5% $NaOCl$ solution	[70]
ThAnMBR	Thermomechanical Pulping wastewater	Lab	Flat-sheet PVDF	Submerged	Biofouling	Cake layer	EPS, bacteria	Biogas sparging	[71]
AnMBR	Pulp and paper pressate wastewater	Lab	UF 0.04 μ m Hollow fiber PVDF	Submerged	Organic	Cake layer formation	EPS, polysaccharides and humic acids	High biogas sparging rate	[72]
ThAnMBR	Prehydrolysis Liquor	Lab	MF 0.4 μ m Flat sheet Chlorinated-PES	Submerged	–	Cake Layer	Deposition of colloids	Relaxation period/ scouring/ biogas sparging	[73]

SMP = soluble microbial products

ThAnMBR= thermophilic anaerobic membrane bioreactor

ThAeMBR= thermophilic aerobic membrane bioreactor

– = indicates value not reported or not available.

3. Parameters affecting membrane fouling

Membrane fouling is a complex phenomenon resulting from the joined effects of various factors. These factors are segregated into three categories and are explained below, namely: process conditions (pH, temperature, TMP, volume reduction factor (VRF), hydrodynamic conditions), treated materials (hydrophobicity, molecular shape, concentration), and membrane characteristics (surface chemistry, pore size, morphology, hydrophobicity, zeta potential). It is widely assumed that membrane-solute interactions and membrane surface chemistries are key toward understanding the phenomenon of fouling [74]. In other words, membrane fouling has been found to be directly associated with the physiochemical properties of processed materials, membrane features, and process conditions. Thus, membrane/module characteristics and operating parameters must be carefully considered during process design, as effluents from pulp and paper mills are usually characterized by extreme parameters (e.g., high temperature and pH) and high organic strength; otherwise, burdensome cleaning procedures will be required. Figure 2 provides an overview of the key factors that affect the membrane fouling problem, and these parameters are discussed in the following section.

3.1. Membrane characteristics

Appropriate membrane selection is vital to minimize fouling, in that membrane hydrophobicity, pore size, and its distribution, and surface roughness can influence the propensity of membranes to foul, and thus have an impact on their subsequent cleaning regimens. These properties are explained below:

Pore size is among the most critical membrane characteristics that affect fouling phenomena. The effects that pore sizes have on membrane fouling may be correlated to the particle size of the treated feed [60]. It has been observed that membranes with large pore sizes are more sensitive to fouling during the effluents treatment than membranes with smaller pore sizes. Nuortila and Nyström [25] reported that looser membrane pores (cut-off values $> 100 \text{ kg mol}^{-1}$) were more susceptible to fouling compared to tighter membrane pores (cut-off value $< 100 \text{ kg mol}^{-1}$) in the treatment of a paper mill effluent [25]. In an opposite trend, the largest pores employed for MF membranes were found to be more susceptible to fouling than the smaller pores used in UF and NF membranes. It was reported that when the particles in the feed solution were smaller than the dimensions of the membrane pores, the pores could be expected to clog. However, in contrast to large porous membranes, the smaller porous membranes rejected a wide range of treated materials, which resulted in cake formation. In general, fouling due to cake layer formation was more reversible during the cleaning cycle. [60].

Among the membrane characteristics that affect the extent of fouling is the membrane surface charge. Membrane surface charge imparts multiple effects during membrane filtration and is contingent on membrane material and pH value. Numerous compounds contained within forest industry effluents and process waters may be charged and dissociated under the predominant conditions. Thus, the charge properties of the membrane surface can be affected by the adsorption of ions and charged particles. The membrane charge can be measured by zeta potential measurements or membrane potential measurements. During effluent treatment, it has been observed that the impact of electrostatic attraction on membrane fouling could be decreased by utilizing a membrane with a weak charge only, as effluents from pulp and paper mills contain both negatively and positively charged materials [26,27,75]. Additionally, it was found that the carboxylic acid from wood extractives of the pulping industry became charged at pH values of > 4 , which initiated dissociation [75]. Polymer membranes were found to be positively charged at a pH of < 4 and were negatively charged at pH between 4 and 6.

Another factor that has proven to have an important impact on permeate flux and membrane fouling was membrane morphology. The extent of membrane fouling and its subsequent cleanability may be controlled by membrane surface morphology (roughness) [26]. It was discovered that membranes with rougher surfaces had higher fouling tendencies than did membranes with smoother surfaces. For example, Knudsen et al. [76] found that the PVDF membrane with a rougher surface was fouled more rapidly than a thin film composite membrane which possessed a smoother surface during the ultrafiltration of white water from a recycled paper-processing mill. This was because rougher surfaces attracted particulates much more easily than did smooth surfaces; however, following the formation of a cake layer, the consequences of the roughness of the surface became less significant.

It has also been frequently seen that the hydrophilicity of membranes may considerably affect membrane flux and fouling. Based on the literature review, many studies verified that fouling issues might be reduced through

the utilization of hydrophilic membranes [9,20,26,28,77]. Maartens et al. [9] examined the fouling of PES UF membrane during the treatment of PPI effluent, whereas Weis et al. [26] investigated the fouling problems of PS, PES, and RC UF membranes when they treated SSL. Puro et al. [27] studied the fouling of PES and RC membranes during the UF of chemothermomechanical mill wastewaters. The results of these studies have discovered that by changing the hydrophilic properties of the membranes, the level of foulants that is absorbed onto the membranes could be reduced. This may be attributed to the hydrophobic nature of wood extractives, which represent the most common foulant species that are present in PPI process water and effluent treatment. It has also been found that fouling was less serious with membranes that had lower contact angles over those with higher contact angles. Conversely, Persson et al. observed higher levels of fouling on hydrophobic PES membranes when treating thermomechanical pulping process streams [77].

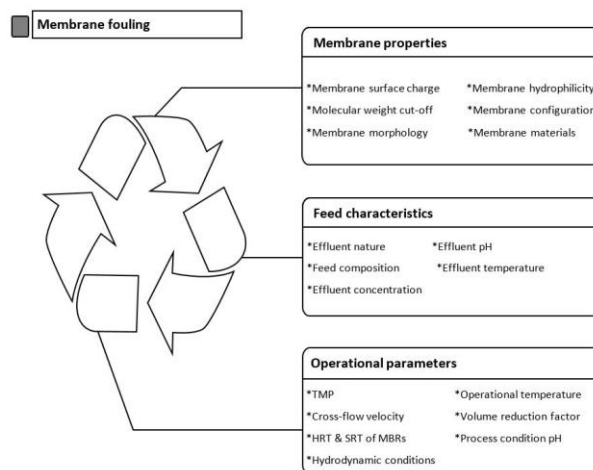


Fig. 2. A simplified diagram of the parameters that affect membrane fouling

3.1.1. Merits of ceramic membranes

Currently, two of the most commercially available membrane materials are polymers and ceramics. Ceramic membranes were extensively used to recover lignin-derived materials from Kraft black liquor. Regarding membrane fouling control, there are several advantages of ceramic membranes that make them perfect candidates for the treatment of PPI effluents under highly variable conditions (e.g., wide pH range, chemically harsh nature, and high temperatures). The greatest benefit of ceramic membranes is the opportunity of applying short backflushing using permeate streams in reverse through the membrane to reduce fouling. Further, several ceramic membranes are more foulant resistant due to their low protein adsorption. Another benefit of inorganic membranes is that they permit in-situ physical/chemical cleaning at elevated temperatures with the use of strong chemicals (chlorine, hydrogen peroxide, ozone, and inorganic acids), whereas organic membranes can only withstand relatively mild conditions. Moreover, several inorganic membranes are less vulnerable to biological and microbial degradation compared to their polymeric counterparts. Furthermore, inorganic membranes require less feed stream pretreatment due to their inherent abilities (rigid porous structure, ease of cleaning after fouling, temperature and chemical resistance, lower susceptibility to biological attack), which is a factor that strongly favors inorganic membranes. The costs of pretreatment of feed can significantly contribute to overall operating expenses. Although they possess several inherently positive qualities, ceramic membranes are mechanically heavy and are considerably expensive to produce, in contrast to polymeric membranes. However, high production costs can be compensated for by their long working life.

3.2. Process conditions

The identification of optimal process conditions for effluent treatment is a challenging task due to the complexity of the fouling phenomenon in PPI. In the literature, several studies have been conducted toward addressing the effects of operating conditions e.g., pH, temperature, TMP, cross-flow velocity, and VRF on membrane fouling [2,29,62,78]. TMP is the best indicator for the evaluation of membrane performance; hence, it is frequently employed to measure membrane fouling at different scales (lab-scale, pilot-

scale, and full-scale applications) [78]. Another criterion that may be used for the evaluation of fouling involves relating the differences between pure water permeate flux prior to and following filtration of effluent. In addition, a new approach termed "TMP balance" was also developed to measure the pressure loss due to foulants, which facilitated the direct assessment of membrane fouling under diverse flux values [78]. Conversely, the operation of membranes close to the threshold flux, which is defined as the change between low and high fouling grades, was found more applicable, as it applies less stress to the membrane, while reducing the number of chemical cleaning cycles, and the requirement for membrane replacement. If a system is running above critical flux levels, a cake layer will progressively form, and thus a further increase in TMP is needed to sustain the membrane flux. This concept was further investigated and pronounced by Luo et al., which was based on the conceptual model of particle deposition [79]. They defined the threshold flux as, "at and below threshold flux, adsorption and reversible fouling are nearly stable, and the fouling rate is low and almost constant, regardless of the permeate flux; while above threshold flux, reversible fouling increases with increased permeate flux" [79].

Among process conditions, cross-flow velocity [18,21], hydrodynamic, and VRF [8,29,42] also have roles to play in the mitigation of fouling. The effects of cross-flow velocity on membrane fouling have been intensively studied, where the obtained results revealed that this could be considered a practical approach to diminish fouling and concentration polarization [2,62]. In contrast, VRF, which may be defined as the ratio between the size of the permeate and the initial size of the treated feed has a significant influence on the amount of hemicelluloses and lignin that can be held back by the membrane. However, in reported results, VRF was shown to affect membrane fouling only slightly, which likely could be attributed to the lower range of VRF used in the experiments [29]. Another popular approach for minimizing fouling is to control the hydrodynamic conditions during the operation of the membranes. Several studies have verified that hydrodynamic conditions directly affect the fouling of SAnMBRs [13,14,54,69]. Table 3 shows the impacts of operating conditions on membrane fouling control.

3.3. Feed characteristics

Effluents related to the generation of forest industry products are highly complex and consist of heterogeneous mixtures of various woody materials (cellulose, hemicelluloses, lignin, and extractives), with the addition of chemicals used in the pulping process, depending on the pulping processes. Therefore, the characteristics of pulp and paper effluents may vary, and different foulants can be anticipated during membrane filtration, whether organic or inorganic.

Table 4 shows the physicochemical properties of various pulp and paper effluents. Different pulping conditions result in the generation of a variety of effluents such as black liquor (BL), spent sulfite liquors (SSL), prehydrolysis liquors (PHL), and process water compounds. The compositions of forest product effluents are very complex and varied, as they contain different wood-based compounds. Dal-Cin characterized semi-chemical mechanical pulp mill process water and reported 432 mg/L of resin and fatty acids, 2,400 mg/L of soluble lignin, 1,900 mg/L of insoluble lignin, and 920 mg/L of volatile acids [28]. Puro et al. reported (660-3060 mg/L) of suspended solids, (20-80 mg/L) of lignans, (90-820 mg/L) of sugar, and (9-66 mg/L) of lipophilic extractives for groundwood mill circulation water [7], whereas, Olsson reported (61.4 mg/g) of lignin, (3.14 mg/g) of hemicelluloses for BL [80]. BL is very alkaline (pH 13-14) and contains molecules of organic materials and pulping chemicals as inorganics. Reportedly, the content of phenolic hydroxyl groups is higher in the BL from Kraft pulping, compared to BL from organosolv and ethanol processes. In contrast, SSL is extremely acidic (pH~2) and contains significant amounts of various monosaccharides derived from hydrolyzed hemicelluloses. Humpert et al. [81] reported (4.7-9.3 g/L) acetic acid, (~1 g/L) extractives, (59-120 g/L) liginosulfonate, (0.03-2.00 g/L) furfural, and (9.1-60 g/L) sugars for SSL. Yang et al. [82] reported (10.2 g/L) lignin, (11.2 g/L) acetic acid, (1.43 g/L) furfural, and (50.33 g/L) sugars for industrial PHL.

The temperature of process water in the generation of forest products may vary from 10 °C to 90 °C, or sometimes even higher [75], where extreme processing conditions may limit the viability of some membrane materials. In the case of MBR applications, operating at high temperatures is very important because wastewaters from the forest product industry typically have a high temperature. However, thermophilic MBRs have the issue of membrane fouling due to high heat, which induces the additional release of EPS. The concentrations and pH of the effluents of paper mills also vary considerably, contingent on the pulp production process, the raw material used, and the manufactured paper grade [27]. An increase in pH value reportedly enhances the solubility of numerous colloidal materials such as phenolic compounds, thereby increasing their filterability and decreasing their

adhesion to the surface of the membrane. Also, the size of the molecules affects the solubility of the solute, and hence, the likelihood of precipitation on the membrane [83]. The concentration of the solution also influences membrane resistance, and a noticeable increase in fouling is observed when reaching the saturation concentration point of the treated material [84].

Table 3
Effects of process conditions on membrane fouling control.

Treated effluent	Process	T (C°)	PH	Fouling parameters	Influences on the fouling	Ref.
Kraft evaporator condensate	SAnMBR	37±1	7	Hydrodynamic conditions	Biogas sparging rate ↑, cake formation rate ↓ permeate flow rate ↑	[13]
Thermomechanical pulping whitewater	SAnMBR	37±1	7.0±0.2	Hydrodynamic conditions	Biogas sparging ↑, cake layer formation ↓, fouling rate ↓	[14]
Thermomechanical pulping whitewater	SAnMBR	–	–	Microbial flocs (small flocs vs. large flocs)	Small flocs have a higher level of EPS compared to larger flocs, thus, EPS ↑, fouling rate ↑	[15]
Deinking wastewater of paper mill	ThAeMBR	50	6.3-7.3	Small sized flocs	Floc size ↓, the particle layer density ↑ → pressure drop ↑	[16]
Pulp and paper mill circulation water	Mechanical filtration	46/50/78	5	Permeate flux	Vibration ↑, Fouling rate ↓ Permeate flux ↑	[20]
Circulation water from pulp and paper mill	Mechanical filtration	46/50/78	5	Temperature	Temperature ↑, permeate flux ↑	[20]
Paper mill wastewaters	Mechanical filtration	40-52/39-41	4-7.8	Permeate flux	Shear forces ↑, surface fouling ↓, permeate flux ↑	[25]
Mill wastewaters	Mechanical filtration	25-45	4-10	Permeate flux	Permeate flux ↓ when temperature ↑ due to increased foulants	[29]
Kraft pulp condensate	ThAeMBR	55	7	Temperature	Temperature ↑, fouling rate ↓	[52]
Thermomechanical pulping pressate	ThAeMBR	51±1	6.9±0.1	HRT	HRT ↓, permeate flux ↑, fouling rate ↑	[53]
Pressate from thermomechanical pulping	ThAeMBR	51±1	6.9±0.1	Hydrodynamic conditions	Coarse bubbles ↑, cake layer formation ↓, Fouling rate ↓	[53]
Thermomechanical pulping pressate	SAnMBR	37/42/47/55	7±0.2	Temperature	Temperature ↑, sludge floc size ↓ permeate flux ↓	[54]
Kraft evaporator condensate	ThAnMBR	55/37	7	Temperature	Temperature ↑, floc size ↓, EPS release ↑ → filtration resistance ↑	[55]
Kraft evaporator condensate	SAnMBR	37±1	7.0±0.2	Hydrodynamic conditions	Biogas sparging rate ↑, cake layer formation ↓, critical flux ↑, fouling rate ↓	[69]
Thermomechanical pulping wastewater	AnMBR	35±1	7.0±0.2	Hydrodynamic conditions	Biogas sparging rate ↑, cake formation rate ↓ permeate flux ↑	[72]

In the PPI, effluents and process streams contain thousands of mixtures, which might lead to both organic and inorganic fouling. Aside from the woody materials, diverse chemical compounds are utilized in the conversion of lignocellulosic materials, and different additives are employed in the manufacturing of the final products. Therefore, the identification of foulants and ways through which they affect the membrane performance remains a challenging task [74]. Few researchers have studied the influence of organic compounds on membrane filtration. The organic matter present in the pulping mill effluents is likely to interact with a given membrane, where this interaction can be either internal or external [83]. Based on the literature, lignin and wood extractives have the highest propensity to act as foulants. It was found that the fouling by wood extractives mainly originates from fatty and resin acids [85]. Also, a small fraction of lignans was also observed in the fouled membranes [7]. Weis et al. [26] reported that resin and fatty acids, and to some extent lignans, were the principal wood extractives that initiated membrane fouling during the filtration of pulp and paper mill wastewaters.

Maartens et al. [9] treated effluent from PPI with UF, and they found that the foulants in the effluents were of a phenolic nature. Puro et al. [4] analyzed the fouling of UF, which was initiated by process wastewater that originated from a mixture of hardwood and soft wood materials. The researchers found that sterols participated remarkably in the fouling of a RC membrane, although their quantity in wastewater was low. Chen et al. [86] characterized membrane foulants in fine paper mill effluent filtration using a PES UF membrane. Their results indicated that the reversible foulants represented 85.52% of the total foulants and were primarily derived from the resins, whereas irreversible adsorptive foulants represented 14.48% and were generated from coating chemicals. Ramamurthy et al. [87] studied membrane fouling due to fatty and resin acids using tall oil. From the flux measurements, they revealed that fatty and resin acids initiated the formation of the gel layer on membrane surfaces in the presence of high molar mass solutes.

Overall, wood extractives are the primary foulant species in membrane processes during the treatment of PPI effluents. Lipophilic extractives are characterized by their hydrophobic nature [4], and they are negatively charged in the pH range of from 2–11 [88] (see Table 4). According to Allen [88], colloidal wood resin particles are spherical in shape, and their particle size distribution is very similar in different types of pulps [88]. The range of particle diameters for the lipophilic extractives was 0.2–2 μm (~0.5 μm on average) [88], as they formed colloidal droplets in wastewater [89]. The molecular weights of hemicellulose, lignin, and wood extractives vary widely, dependant on the cooking conditions and biomass species. For example, the hemicelluloses molecular weights of the SSL are in the range of 8000–19600 g/mol; while the average molecular weight of liginosulfonate is between 235 and 1030 g/mol [90]. The molecular mass distribution of hemicellulose in thermomechanical mill wastewater is in the range of 0.2–2 kDa; whereas the molecular mass of lignin is in the range of 0.5–4 kDa [91]. The molecular mass of lignin in BL is typically from 0.8–9.9 kDa [92]. The molecular weights of wood extractives are low compared to hemicelluloses and lignin (see Table 4). However, fine particulate matter contains a higher rate of negatively charged ionic groups on its surface than in other particle size fractions [89]. Based on a survey of the literature, alkaline treatment (e.g., mechanical pulping, sulfite pulping, and oxidative bleaching treatment) was found to increase the charge density, which was attributed to the existence of galacturonic and sulfonic acids [89]. Also, the alkaline condition of BL may naturally change hydrophobic lignin into hydrophilic due to the existence of hydroxyl groups that generally dissociate at a higher pH. In general, different types of effluent and process water from pulp and paper mills have been treated; however, the foulant species present in the membranes have not, as yet, been well characterized.

4. Fouling characterization

The characterization of fouling is an essential part of the membrane filtration process, as it not only provides valuable insights into the mechanisms of fouling but also better elucidates the factors that initiate membrane fouling. Several scientists have developed fouling indicators for the improved prediction of fouling issues in membrane filtration processes, where different techniques have been employed. However, in pulp and paper effluent treatment, few studies have characterized membrane fouling. For example, Carlsson et al. [85] used a surface spectroscopic method for a membrane fouling study in pulp mill effluent treatment. They observed that fatty acids were the dominant foulant materials in the membranes rather than resin acids. Maartens et al. [9] characterized the nature of foulants adsorbed onto the surface of the membranes fuelled by PPI effluent using a colorimetric staining technique, and subsequently reported that foulants in PPI wastewater were phenolic compounds of hydrophobic characteristics. Similar results were reported when Puro et al. [7] studied the organic foulants originated from the pulping effluent (groundwood mill circulation water). The researchers found that fatty acids and resin, in addition to traces of lignans, were dominant foulant compounds on the surface of the membranes. However, hydrophobic membranes were severely affected by these acids and lignans than were the hydrophilic membranes.

Conversely, the extent of membrane fouling and the fouling type were also determined by the membrane hydrophobicity and surface morphology (roughness, pore size, pore size distribution). Weis et al. [26] analyzed the zeta potentials, roughness, and membrane contact angles when they studied the cleaning of UF membranes following exposure to SSL effluent. It was found that both hydrophobicity and roughness were associated with long-term fouling tendencies. In another study, Puro et al. [27] evaluated the membrane roughness by topographic imaging and used a sessile drop method for contact angle measurement; whereupon they reached conclusions similar to that of Weis et al. [26], that the hydrophilicity and morphology of membranes have an evident influence on fouling. Although some researchers have attempted to characterize membrane fouling, comprehensive data on principle foulants remains unavailable due to the complex composition of the wood hydrolysate. Multiple lignins and extractive degradation products are released during hydrolysis processes. Overall, the development of new methods for the characterization of fouling is necessary for a better clarification of the membrane fouling problem. Further, the adoption of a membrane autopsy technique in the PPI is required to elucidate the nature of membrane fouling toward the determination of the causes of membrane failure.

Table 4
Physico-chemical properties of different pulp and paper effluents and process waters [4,7,28,49,50,80,81,82,88-92].

Component	Type of effluent and process water				Molecular weight (g/mol) ^c	Charge	Hydrophobicity/ Hydrophilicity
	Spent sulfite liquors (SSL)	Black liquors (BL)	Prehydrolysis liquors (PHL)	Process water from thermomechanical pulping			
Total Solid content (g/L)	128–220	12–15	80.5	3.3–4.9			
Acetic acid (g/L)	2.7–9.3	5–6	1.2–11.2	–	60		
Lignin (g/L)	50–120 ^a	0.6–71	0.10–10.2	0.8–3.5	220–9500	N ^d	Hydrophobic/ Hydrophilic
Hemicellulose (g/L)	15–22%	0.1–30	0.5–25.92	0.8–1.5	1000–19500	N	Hydrophobic
Monomeric sugar							
Arabinose (g/L)	1.0–7.8	0.80 mg/g	0.11–0.85	0.075–0.11	–	–	Hydrophilic
Xylose (g/L)	0.8–26.7	1.07 mg/g	0.05–49.2	0.01–0.02	150	N	
Mannose (g/L)	4.0–16.2	–	0.06–0.8	0.07–0.88	–	–	
Galactose (g/L)	0.2–5.34	1.00 mg/g	0.13–0.70	0.11–0.516	–	–	
Glucose (g/L)	1.7–3.28	0.23 mg/g	0.28–1.16	0.046–0.30	–	–	
Rhamanose (g/L)	~1	–	0.01–0.44	0.001	–	–	
Total sugars (g/L)	7.5–60	1–6 wt %	0.6–50.33	0.090–1.9	–	–	Hydrophilic
Extractives (g/L)	~1	0.5–2.1	–	0.009–0.066	on order of 10 ²	N	Hydrophobic
Fatty acids (g/L)	~ ^b	–	–	0.0048–0.432	–	N	Hydrophobic
Resin acids	–	–	–	0.0023–0.77	–	N	Hydrophobic
Phenolic compounds (g/L)	–	0.67–3.99 mmol/g	0.026–0.286	0.009–0.066	2975	N	Hydrophilic
Furfural (g/L)	0.03–2.00	–	0.01–1.47	–	96.09	–	
Sterols	–	–	–	0.0011–0.03	–	N	Hydrophobic
Lignans	–	–	0.042	0.02–0.11	–	N	Hydrophilic
Volatile acids (g/L)	–	–	–	0.920–2.1	–	N	
Ash (g/L)	19.8–20.8	28.13–39	1.0–1.5	0.9	–	–	
Temperature (°C)	–	50–90	–	50–70	–	–	
pH value	1.7–3.4	12–14	3.5–4.5	3.3–6.5	–	–	
Charge density	–	N	N	N	–	–	

^a liginosulfonate

^b – indicates value not available or not reported.

^c Weight Average molecular weight (Mw)

^d N = Negative charge

5. Fouling management strategies

Various fouling control strategies have been employed for the control of membrane fouling including, chemical methods (e.g., coagulation, chemical cleaning, and membrane surface modification), hydrodynamic methods (e.g., vibrating membrane, high shear, and rotating disk), physical methods such as ultrasound, and physical cleaning techniques.

5.1. Pretreatment strategies

The management of membrane fouling through the incorporation of pretreatment methods has gained increasing popularity in membrane technologies. In the literature, many pretreatment options have been employed to diminish membrane fouling, and increase permeates quality. Some of these pretreatment processes may degrade, inactivate, or remove the foulants (lignin and wood extractives) prior to membrane filtration. The effectiveness of these pretreatment methods is strongly associated with the applied pretreatment agent, the dosage used, temperature, feed properties, and membrane characteristics. This review discusses pretreatment processes, which are mainly applied in the pretreatment of the wastewaters and effluents from pulp and paper mills, namely, coagulation, pH adjustment, activated carbon adsorption, laccase addition, MF, and ozone oxidation. Table 5 summarizes the impacts of these pretreatment strategies on membrane fouling.

5.1.1. pH adjustment

The pH has a significant result on the filtration process, as it defines the electronic polarity of particles. Commonly, the population of negative charges increases when the pH increases; however, the population of positive charges diminishes [93]. Pulp and paper mill effluents can be extremely alkaline or acidic; hence, modification of the treated effluent pH can change solute–membrane interactions to diminish membrane fouling. Reportedly, membrane fouling was observed to be more severe under acidic conditions than alkaline conditions. Gönder et al. [29] observed reduced membrane fouling at the alkaline condition (pH 10) when they examined the application of NF membranes in the separation of biologically treated effluents. This phenomenon is attributed to the increased strength of electrostatic repulsion between the surface of the negatively charged membrane and the negatively charged components of the effluent, which inhibited the adsorption of solutes onto the surface of the membrane [29]. Brinck et al. [32] studied the pH effect on the permeate flux decline of a PES UF membrane when they treated a fatty acid solution. They noted that the solubility of the fatty acid solution at a pH of 5–6 was 100 times greater compared to the neutral fatty acid solution; hence, the membrane fouling due to adsorption was unimportant [32]. Probably, this is one reason why alkaline effluents from bleaching are generally not difficult to filter compared to the acidic effluents [75]. However, large volumes of PPI wastewaters need large quantities of chemicals; thus modifying pH via this method is economically inefficient.

5.1.2. Coagulation

The application of coagulants to facilitate the destabilized particles aggregation in treated feeds has been considered in the paper industry [95]. Coagulation pretreatment was intensively applied in wastewater treatment due to its low cost and comparatively simple operation. However, limited research is accessible as to its use in the reduction of membrane fouling and enhancement of the permeability of pulp mill process water. The efficacy of coagulation is primarily dependent on operating conditions such as pH values, coagulation dose, coagulation type, mixing type and density, in addition to membrane configurations such as module designs, pore sizes, and membrane materials [94]. Coagulants have an optimal pH range; however, pulp mill effluent might be very alkaline or acidic, where adjusting the pH is required for a successful coagulation performance. One potential method might be to utilize the acidic waste portions resulting from the pulping process for this purpose [93].

During the treatment of PPI effluents, foulants may be removed by applying an appropriate coagulant to the wastewater such as a copolymer of methacrylate. When Leiviskä and Rämö [93] investigated the coagulation of wood extractives, they reported 92% removal of extractives, using acrylamide and methacrylate of the dosage range between 102–142 mg/L as copolymers. Hong et al. presented the benefits of coagulation as a pretreatment for the removal of micro-particles in process water prior to membrane filtration [95]. They evaluated the viability of a UF membrane joined with coagulation pretreatment. When treating wastewaters from Kraft pulp mill, they concluded that the use of alum and ferric chloride could significantly improve

the permeate flux for subsequent membrane filtration. Due to the low cost of coagulation, simple handling, and its considerable capacity to minimize fouling, coagulation may be a feasible choice for the PPI. In a similar work, alum greatly enhanced the membrane permeability with a reduced fouling propensity in contrast to commercial cationic coagulant [96]; however, the excessive addition of cationic coagulants resulted in very detrimental effects on the membranes performance.

5.1.3. Activated carbon adsorption

Pretreatment of the feed by activated carbon (AC) adsorption prior to membrane filtration has also been employed to prevent membrane fouling [8,38,44,97,98]. The capacity of AC is dependent on different factors such as its pore size, carboxylic portion, and surface area. Persson and Jönsson [38] and Koivula et al. [8] reported that the pretreatment of forest industry effluents by AC before filtration had positive impacts on the improvement of permeate flux and reduction of membrane fouling. However, pretreatment methods must be tailored separately, as pulp and paper effluents possess different characteristics contingent on the pulping process employed. Shen et al. [97] studied a combined procedure of AC adsorption, treatment by ion exchange resin, and concentration by a membrane process to facilitate the membrane filtration. It was concluded that removal of lignin and other organics with large molecular mass from the prehydrolysis liquor (PHL) by adsorption to AC, not only decreased fouling but also greatly facilitated the subsequent membrane filtration process. Ahsan et al. [44] assessed hemicellulose and acetic acid recovery from PHL by combining an AC treatment, NF, and RO. To alleviate the fouling problem, PHL was initially exposed to adsorption on the AC, whereafter the processed PHL was filtered by a NF membrane to recover the hemicelluloses, and the acetic acid rich permeate solution was filtered by a RO membrane. They concluded that AC was a good adsorbent for the removal of lignin; thus, lignin removal can improve following NF and RO processes [44].

Persson and Jönsson [38] reported complete pure water flux recovery when they investigated various measures to decrease fouling during the UF of effluent from the Masonite mill. Although the fouling was successfully minimized using AC, it would be very expensive to utilize this technique in full-scale operations because of the high cost of AC (2000 €/metric ton) [38]. Lowering the pH of pulp and paper wastewater to decrease membrane fouling can be a less expensive method in comparison with AC; however, this depends on the buffer capacity of the wastewater. Alternatively, charcoal adsorption has also been used for the removal of phenolic compounds from wood hydrolysate. Parajó et al. reported 75% removal of the phenolic compounds when they treated hydrolysate from *Eucalyptus globulus* [99], while Miyafuji et al. reported on the high removal of phenolic compounds from spruce wood hydrolysate [100].

5.1.4. Addition of activated and inactivated laccase

Laccase, which is blue copper and contains polyphenol oxidase, has also been used as a pretreatment material to minimize fouling. In the literature, the addition of laccase to wastewater was reported to ease the removal of phenolics, via their precipitation, in pulp and paper mill effluent [101,102]. A successfully combined process of laccase pretreatment and membrane separation technology has been reported by Strand et al., Ko and Fan, and Ko and Chen [50,102,103]. Ko and Fan [102] treated secondary effluent from a Kraft pulping mill with laccase prior to filtration. Amid the initial 180-minutes of filtration, the addition of activated laccase reduced the permeability of the membrane by 4–14% due to the development of a gel layer. However, once the steady state was established, no further flux decline occurred, and the membranes can be employed to eliminate the pollutants without a major fouling problem. The fouling reduction may be described by the fact that laccase lifted the molecular weight of the wastewater to a higher range, where the minimization of components with lesser molecular masses facilitated subsequent membrane separation [102]. In another study, Strand et al. [50] combined laccase mediated enzymatic degradation coupled with adsorption on bentonite when they treated lignin and hemicelluloses. Laccase together with bentonite reduced the number of complexes and increased the quantity of high molecular weight compounds, which resulted in higher permeate flux. They attributed the formation of large ligneous compounds to the lignin oxidation (by laccase) to phenoxy radicals, whereas the formation of large hemicellulose compounds was attributed to the linkage between lignin and hemicelluloses. However, Krawczyk et al. attributed the development of large molecular masses of hemicelluloses to the enzymatic cross-linking between laccase and hemicelluloses [32]. Compared with other enzymes pretreatment, laccase is appropriate for a wide variety of uses, such as the delignification processes and detoxification of wastewater.

5.1.5. Pre-filtration

In the treatment of forest industry effluents, a MF is applied prior to UF and NF membrane processes for the reduction of membrane fouling. Krawczyk et al. [23] examined the effect of MF as a pretreatment stage on effluent viscosity and UF capacity during the separation of hemicelluloses extracted from wheat bran. MF led to a substantial improvement in permeate flux during the UF, while the loss of hemicelluloses was considerable. Contrary results were obtained by Thuvander and Jönsson [24], who found that MF (0.1 μm pore size) eliminated colloidal extractive compounds while a large quantity of high molecular weight hemicelluloses passed through to the permeate [24]. The type and properties of hydrolysate might be behind these conflicting views on the results of MF. Zhang et al. [40] pretreated wastewater from mechanical pulping mills by using a 150 μm bed screen to reduce membrane fouling issues. Bhattacharjee et al. [35] pretreated Kraft BL by centrifugation, followed by MF, to reduce membrane fouling of UF by removing traces of colloidal matter and suspended solids via MF. These pretreatment processes were shown to be very effective in completely returning the water flux of the UF membrane.

5.1.6. Oxidation

The application of advanced oxidation processes can be a very useful alternative in the reduction of membrane fouling. The partial degradation of high molar mass lignin compounds by oxidation has been shown to improve filtration capacity due to the reduction in feed viscosity and minimization of a gel layer formation during concentration filtration. Different oxidation methods, such as pulsed corona discharge (PCD) and ozonation have been studied, and their application before membrane filtration has appeared to diminish membrane fouling. Mänttari et al. [104] treated NF concentrates produced from the forest industry by ozone to increase its biodegradability and reported high performance (two to four-fold biodegradability). However, the purity of permeate has also decreased due to the degradation of concentrated compounds of UF that could permeate the membrane [104,105]. Also, the impacts of ozone on membrane fouling are varied because of the heterogeneous and variable nature of natural organic matter.

On the other hand, foulant oxidation by gas-phase PCD is also used for fouling management. PCD is an effective membrane fouling control alternative in light of the fact that it reduces the molar mass of the lignin compounds and facilitates their permeation through the membrane. Thus, there is an opportunity for the valorization of the permeated lignin. However, due to oxidation, the molecular mass of the hemicelluloses may also be reduced, which may lead to hemicellulose losses. Schlesinger et al. [106] studied the fouling behavior of hemicellulose during the NF of pressate liquor. Irreversible fouling decreased upon oxidative degradation by PCD, suggesting a higher rate of organic materials oxidation in the pressate liquor. However, this oxidation also caused hemicellulose degradation and decreased their average molar masses [106]. Koivula et al. [8] assessed different pretreatment approaches to control membrane fouling during the UF of wood autohydrolyzates, and revealed that the pretreatment of effluents with PCD oxidation to highly decrease UF membrane fouling and enhance the permeability. Mänttari et al. [49] studied filtration capacity enhancement during the separation of galactoglucomannan from process water using gas-phase PCD oxidation. The results of this research exhibited that the PCD oxidation profoundly enhanced the filtration viability of the process water. The positive result on the membrane filterability can be partially elucidated by the reduced viscosity of the oxidized effluents; however, its impact on fouling of the hydrophilic membranes and the purity of the concentrated hemicelluloses have been low. The high hemicellulose purity could be attributed to the removal of lignans and lipophilic compounds, which may

have some effect on the hemicellulose purity. PCD oxidation also decreased the average molar weight of hemicelluloses to some extent [49].

5.1.7. Polymeric adsorbents

Polymeric adsorbents have been employed prior to membrane filtration for membrane fouling control and filtration capacity improvement. Willför et al. [107] developed a process that consisted of the removal of colloidal matter through the addition of a cationic coagulant, and the removal of lignin and lignans by a XAD-7 (uncharged polyacrylate adsorbent), followed by UF with a 20 kDa cut-off to remove low molecular weight materials. The purity of acetyl-galactoglucomannans was as high as 95% due to the removal of lignin and lignans. Koivula et al. [43] introduced XAD16 and XAD7HP amberlite based adsorbent pretreatment to remove absorptive foulants in the separation of hemicelluloses from the paper effluent. XAD-16 comprises an uncharged hydrophobic adsorbent, which is used to adsorb hydrophobic molecules, while XAD-7 is an uncharged adsorbent that has been employed to adsorb non-polar compounds. The outcomes of this work proved that XAD adsorbents offer a viable pretreatment technique for improving filtration capacities, while reducing membrane fouling. Both applied adsorbent enhanced the membrane filtration capacity to ~90%. Although this method was proven to improve the flux, it was also associated with major hemicellulose loss. Thus, selective polymeric adsorbents were required to decrease hemicellulose losses due to adsorption. These adsorbent materials are characterized by their preference for aromatic substances. However, the cost of the adsorbents required to achieve a given filtration flux should be considered as well.

Several studies with different aims have demonstrated the effectiveness of XAD and DAX in lignin removal from a lignocellulosic suspension. Schwartz and Lawoko [108] studied the separation of acid-soluble lignins derived from hardwood chips hydrolysate and stated that 90% of acid-soluble lignin could be isolated with the Amberlite XAD-4 resin. Westerberg et al. [109] employed a hydrophobic polymeric XAD-16 resin to remove lignin and lignans from galactoglucomannan, and demonstrated high performance. Using XAD-4 resin, lignin compounds were removed in significant amounts from wood hydrolysates, without carbohydrate loss [110].

Table 5 summarizes the effectiveness of pretreatment practices on membrane fouling. Several potential pretreatment methods for the removal of foulant compounds may be found in the literature, and many of them show significant effects on reversible and irreversible fouling. Pretreatment approaches such as oxidation by PCD, coagulation by alum, and prefiltration by MF and AC have shown great potential for the reduction of fouling. For example, it has been found that the removal of colloidal extractives by prefiltration reduces the effluent viscosity, and thus, the possibility for these complexes to build a gel layer during the effluent concentration process. Moreover, hybrid processes, for instance, combining oxidation and UF are characterized by a reduced quantity of waste produced, high energy efficiency, and the possibility that lignin may also be separated from hemicellulose–lignin complexes. However, pretreatment procedures must be separately optimized for each process water due to their variable characteristics. Furthermore, the accurate characterization of feed water is required to determine the appropriate pretreatment method. Moreover, some pretreatment methods, such as polymeric adsorbents and AC have shown hemicellulose losses due to hemicellulose–lignin linkages. Thus, the links between hemicelluloses and lignin must be broken prior to adsorption to reduce hemicellulose losses in the pretreatment step. Another strategy toward decreasing the adsorption of hemicelluloses might be through the application of selective adsorbents and optimizing their amounts.

Table 5
Advantages and disadvantages of feed pretreatment methods.

Raw material	Pretreatment Method	Advantages	Disadvantages
Birch and spruce sawdust hydrolysate	Centrifugation at room temperature	Centrifugation stage improved membrane permeability due to the removal of lipids, grease and colloidal substances [111].	No significant influence on the filtration capacity was observed [8].
Spruce hydrolysate	Hemp adsorption	–	No vital influence on the foulants adsorption was observed [8].
Masonite process stream/Birch and spruce sawdust hydrolysate	pH adjustment	Reduced membrane fouling was observed at pH 10 [29]. Fatty acids foul membranes intensively under acidic conditions [32].	The large volume of process waters requires many chemicals, making the modification of pH economically inefficient.

Masonite process stream/Birch and spruce hydrolysate/PHL	Activated carbon (AC) adsorption	Resulted in reduced fouling and higher permeate flux of both hydrophobic and hydrophilic membranes [38]. Facilitated the subsequent membrane filtration process [97]. Membrane filterability was improved [8,44].	Sometimes modification of AC required the improvement of its absorption performance. Slight hemicellulose losses were observed during the removal of lignin from prehydrolysis liquor [112].
Birch and spruce sawdust hydrolysate/ Wood auto-hydrolysate	Oxidation by pulsed corona discharge (PCD)	PCD oxidation considerably enhanced the separation of the wood hydrolysate and reduced membrane fouling [8]; however, its influence on the fouling of the hydrophilic UF membranes was small [49].	As a result of oxidation, the average molecular mass of the hemicelluloses was slightly reduced [49].
PHL/Kraft pulp mill effluent	Addition of activated laccase	Membrane filterability increased [113]. Polymerized pollutants removed without significant fouling [102].	Gel layer was built on the surface of the membrane at the onset of the filtration [102].
Kraft pulping effluent	Addition of Inactivated laccase	–	Addition of inactivated laccase caused additional flux decline [97].
Hemicelluloses hydrolysate from the thermomechanical pulping mill	MF	Colloidal extractives were removed by MF with a pore size of 0.1 μm . Also, a large quantity of high molecular weight hemicelluloses passed to permeate [24].	Hemicelluloses loss was considerable [24].
The effluent of PPI	Ozonation	Permeate flux improved under higher ozone dosages [104].	Permeate flux somewhat dropped over time under lower ozone dose [104].
Wood extractives removal from chemical pulp bleaching filtrate/ kraft pulp mill wastewaters	Coagulation	Higher wood extractives removal (92%) [72]. Both ferric chloride and alum improved the permeate flux significantly for subsequent membrane filtration [95,96].	Excessive addition of cationic coagulant resulted in a very negative result on membrane performance [96]. Required proper dose, cost, and residual issues.
Birch and pine/eucalyptus wood hydrolysates	Polymeric Adsorbents (Amberlite XAD16, XAD7HP, and XAD4)	High molecular weight lignin was removed efficiently, filtration capacity was significantly improved, and membrane fouling was decreased [43,108].	It was found that polymeric adsorbents caused significant hemicellulose losses [43]. Also, XAD4 adsorbent treatment decreased the quantity of monosaccharides [108].
Wood extract	Laccase treatment combined with adsorption on bentonite	Laccase together with bentonite reduced the amount of the complexes and increased the molecular masses of treated materials; this resulted in the higher permeate flux [50].	–

5.2. Optimization of operating conditions

Operating conditions must be optimized to attain high filtration capacities and low fouling tendencies. Although few studies have been conducted with regard to improved operating conditions, these experiments were typically carried out in a way to examine one factor at a time; which may lead to incorrect conclusions due to disregarding the interactions of certain factors. To overcome this problem, Gönder et al. [29] and [42] utilized a Taguchi experimental design method to boost the process environment that represented pH, temperature, TMP, and VRF for the treatment of pulping effluent using NF and UF processes. These studies aimed to minimize membrane fouling, while increasing the quality of the permeate. In a NF study, the authors believed that operating at a temperature of 25 °C, TMP of 12 bar, VRF of 4, and pH of 10 could result in minimum membrane fouling in wastewater treatment from PPI. It was observed that the pH factor contributed significantly to the response parameters. It is generally believed that the Taguchi method, which studies all the variables with the reduced number of tests, is an efficient approach to optimize process parameters. The simultaneous handling of multiple experimental variables can lead to an improved understanding of the complex fouling phenomena.

Regarding MBRs, a number of recent improvements in the control of membrane fouling such as the manipulation of sludge characteristics through operating parameters (SRT, HRT, F/M (food/mass), DO (dissolved oxygen), and OLR have been considered to reduce the effects of fouling from sludge [59]. Reportedly, SMP concentrations were decreased with increasing SRT. Le-Clech et al. [60] attributed the high fouling rate at short SRT to increased amounts of EPS production. Higher dissolved oxygen is associated with an improved filtration of sludge suspension; hence to maintain low SMP, adequate oxygen supply is needed in the MBR [59]. Changing the biological characteristics of the mixed liquor is another potential solution to the fouling problem in MBRs.

5.3. Membrane surface modification

Recently, increased attention has been accorded to the modification of membrane properties to improve membrane antifouling characteristics. Several techniques such as heterogeneous chemical modification, polymer grafting on membrane surfaces, adsorption of hydrophilic polymers, and plasma treatment have been used. However, regarding membrane applications in the forest industry, few articles describe membrane surface modification [9,114,115,116]. Both increased surface charge and increased surface hydrophilicity were applied to decrease membrane fouling. Understanding the charge properties of treated foulants is vital for the development of fouling-

resistant membranes. Several researchers have attempted to diminish fouling by modifying the surface charges of membranes. Singh et al. [114] treated coating plant effluent with a UF membrane comprised of PES polymer, and the fouling was lower in the modified membrane using sulfonated poly (phenylene oxide) in contrast to control [114]. Nuortila-Jokinen and Nyström [25] compared different membranes in the treatment of paper mill wastewaters, at laboratory and pilot scales, and found that membranes modified with NaCl or UV-irradiation increased the flux; however, at the same time the membranes were fouled [25]. This finding may be partly described by the fact that UV-irradiation probably destroyed the surface of the membrane in such a way that a higher rate of foulant adsorption on the surface of the membrane took place.

Reportedly, membrane processes with increased hydrophilicity are less prone to fouling. Maartens et al. [9] modified tubular UF PES membranes by the non-ionic surfactants (Pluronic® F108 and Triton® X-100), during the filtration of pulp and paper effluents. They found that raising the hydrophilicity of the membrane processes by the adsorption of surfactants prior to filtration decreases the foulants adsorbed on the surface of the membranes, as the foulants in the paper industry effluent are of hydrophobic nature. The flux of the fouled coated membranes was efficiently recovered using the sponge balls and non-ionic detergent. However, the surfactants layer on the membrane was washed off with the non-ionic detergent. In this way, the membranes required recoating following the cleaning step. Consequently, approaches that facilitate surface modifier stability during the cleaning process are required. Belfer et al. [117] modified the properties of a NF by in situ oxidation using hydrophilic polymers. The modification of the NF membrane surface with hydrophilic polymers led to reduced fouling due to the lower adsorption of organic compounds. Dal-Cin et al. [116] modified the UF membranes surface with potassium persulfate. The surface-modified membrane considerably reduced adsorptive fouling, and the flux of the pure water was improved to 70% following the reaction with potassium persulfate, in contrast to 20% for an unmodified membrane.

Table 6 summarizes the effects of membrane modification on the reduction of fouling. Pulp and paper-related foulants tend to adsorb more to hydrophobic surfaces than hydrophilic ones. The modification of membranes with a sulfonate, or the mixing of hydrophobic and hydrophilic polymers, has shown to increase the antifouling characteristics of membranes. These studies also revealed that the modified membrane was highly resistant to foulants than virgin membranes, and increasing the hydrophilicity of the membrane, or applying a surface charge could significantly reduce fouling. However, some of these methods had drawbacks due to complex chemical reactions, and it was not possible to apply them to large-scale operations due to the associated increased costs.

Table 6
Effects of membrane surface modification on membrane fouling.

Membrane material	Modification type	Modifying material	Experiment	Reference
Polyethersulphone	Increased Surface Hydrophilicity	Non-ionic surfactants (Triton® X-100 and Pluronic® F108)	Filtration of pulp and paper effluents: increasing membrane hydrophilicity can decrease the quantity of phenolic foulants.	[9]
(1) NTR-7450: sulfonated polyethersulphone (2) NTR-7450: sulfonated polyethersulphone (3) NTR-7250: substituted polyvinyl alcohol	Increased Surface Charge	(1) NTR-7450UV: 20 min UV-irradiation. (2) NTR-7450M : 0.1% dextran sulfate (DexSu) solution. (3) NTR-7250m: 0.1% NaCl solution.	Purification of paper mill water: modification with NaCl and UV-irradiation enhanced the flux, but did not stop the fouling.	[25]
Polysulfone	Increased Surface Charge	Coated with sulfonated Poly (phenylene oxide)	Filtration of paper wastewaters: the modified membranes reduced the fouling in contrast to the untreated membranes.	[114]
Polyethersulphone and polyethersulphone-polyacrylate polymers blend	Decreased Surface Roughness	Smooth surface vs. rough surface	Paper industry effluent: the modified membranes showed lower adhesion compared to the conventional membranes; additional fouling was observed on the rough surface compared to a smooth one.	[115]
Polysulfone	Increased Surface Hydrophilicity	Potassium persulfate treatment	Effluent from paper mill: the modified membranes considerably decreased adsorptive fouling, and the pure water flux was improved significantly compared to the not modified membranes.	[116]
Polyamide and poly Piperazine-based membranes	Increased Surface Hydrophilicity	Potassium persulfate or potassium metabisulfite redox grafting	Pulp and paper mill effluent filtration: membrane modification with a polyethylene-glycol ester of methacrylic acid (SIGMA) exhibited a considerable reduction in the adsorption of foulants.	[117]
Polyamide (PA) and polyvinylidene fluoride (PVDF)	Increased Surface Hydrophilicity	The tested membranes were modified using a hydrophilic copolymer and surface modification technique	Octanoic acid was utilized as the model solution: the fouling propensity of the modified PVDF membrane was much worse compared to the unmodified PVDF membrane at all concentrations. The treated PA membrane showed a lesser fouling propensity compared to the not modified PA membranes.	[118]

5.4. Physical mitigation measures (hydrodynamic conditions)

In situ fouling control strategies such as vibratory shear, cross-flow filtration, and air scrubbing were successfully developed to reduce membrane fouling and the attainment of high fluxes. First, the shear force produced by the cross-flow velocity can control cake formation during membrane filtration, and permeate fluxes were found to increment directly with increasing crossflow velocity. The velocity of the superficial gas was found to increase the membrane flux linearly from between 0.011 and 0.067 m/s of dyeing and printing paper process waters [119]. The common gas/water ratio for MBRs in high strength wastewater treatment ranges from 10:1 to 50:1 [119]. In MBRs, a cross-flow velocity of 2–3 m/s has been applied to reduce cake layer development [61,119]. As a higher cross-flow velocity can lead to sludge floc disruption, and the generation of reduced particles may aggravate membrane fouling, it also results in significant energy consumption [13]. As is well known, the economic feasibility of the present MBRs generation relies on the rational use of energy.

Secondly, the use of turbulence promoters for membrane fouling mitigation and permeate flux improvement has also been studied. Turbulence inducers are typically employed to create feed instability and disturb foulants, using mechanical vibration and rotation. These strategies were found to be highly effective in different membrane processes, such as MF [20,23], UF [35,36], NF [34,36,41], as well as in various membrane modules, i.e., tubular, hollow fiber and flat sheet. Although turbulence promoters increase the mass transfer in the system and reduce reversible fouling, they can be costly due to considerable energy consumptions. In the paper industry, a number of studies have been conducted to examine the influence of turbulence inducers on the membrane fouling during filtration processes. For instance, the vibratory shear-enhanced process (VSEP) has been developed for effluent treatment to minimize flux reduction due to concentration polarization as well as membrane fouling [120]. The vibration technique directly moves the membranes instead of moving the effluent, consequently, reducing the materials that may adhere to the membrane. When applying enhanced membrane shear-rates, Huuhilo et al. [20] observed that the lower the trans-membrane pressure and the higher the vibration amplitude, reduced fouling occurred when PPI circulation water was treated. Bhattacharjee et al. [35] studied the capability of UF in BL treatment in a stirred rotating disk unit. Membrane rotation initiated higher turbulence on the feed part, which resulted in greater membrane flux and reduced membrane fouling. Increasing the speed of disk rotation up to 450 rpm improved the membrane flux by 60% following one hour of UF, contrasted to a non-stirring system; while increasing the speed of the feed stirring to 1000 rpm, resulting in an increase of 33% in the starting flux and a 68% rise in the steady-state flux, contrasted with a nonrotating stirrer [35]. Pateraki et al. [51] treated spent sulfite liquor with NF membrane, using a VSEP filtration unit that was equipped with a vibratory system to prompt high shear adjacent to the membrane's surface to minimize fouling. This vibratory system induced high shear rates on the

surface of the membrane, which led to high throughputs and reduced membrane fouling.

Finally, several researchers investigated membrane fouling management and permeate flux enhancement via air sparging. Bubbling appears to be a straightforward approach to produce shear stress on the surface of the membrane in submerged reactors to control membrane fouling. The aeration also delivers oxygen to the microorganisms and maintains the suspension of solids. In the case of a submerged MBR, the membrane scouring can be performed by the aeration at the bottom of the membrane unit. It has been suggested that the biogas generated by SANMBRs can be injected back into the system to accomplish a similar purpose. Sparging with biogas products might be preferable to minimize some concerns such as changes in oxidation likelihood, and the toxification of anaerobic organisms. Lin et al. [13] stated that biogas sparging could efficiently decrease membrane fouling of a SANMBR treating Kraft mill evaporator condensate. However, in some cases, increased aeration intensity will break sludge flocs and release more EPS; thus, biogas sparging rate should be optimized regarding bubble intensity and duration.

5.5. Membrane cleaning strategies

Membrane cleaning procedures may be classified as physical, chemical, and combined physical/chemical. Physical cleaning methods followed by chemical cleaning methods are a common practice in membrane filtration.

5.5.1. Physical cleaning

In physical cleaning, mechanical works are employed to get rid of foulants from surfaces of membranes. Typical physical cleaning methods comprise, sponge ball cleaning, forward flushing, backwashing, reverse flushing, and air flushing. Backflushing is commonly applied, and its parameters are time, frequency, and intensity. Backflushing/relaxation can eliminate the majority of the reversible fouling and the gel polarization layer on the membrane. Ebrahimi et al. [47] carried out a series of filtration experiments to study the impacts of different backflushing frequencies on MF permeate flux, during the treatment of sulfite pulp effluent. MF ceramic membranes respond well to backflushing under a backflush pressure of 4 bar and duration of ~10 seconds. The result of backflushing was more noticeable when the backflush frequency was extended, and with a backflushing frequency of 120 minutes, the average flux increased up to 48%. In another study, the cross-flow system was combined with a backwashing unit (backwash for 5 min and pressure 10 psi) to diminish the fouling problem for a given membrane [121]. The flux of MF membranes was dramatically improved via backwashing, during the filtration of a mixture of cellulase and lignocellulosic particles [121]. Sjöman et al. [37] assessed the impacts of fouling on NF membrane performance for xylose recovery from different hemicellulose hydrolysate feeds. The application of water flushing by itself,

following filtration was not sufficient to remove fouling. This was likely due to irreversible fouling; hence, combined flushing and chemical cleaning might be useful in this case.

In MBR applications, backwashing was applied using the reactor permeate to disrupt clogged pores and remove the formed cake layer from the surface of the membrane. Similarly, intermittent reverse washing coupled with air was also used for an AnMBR. Although this technique is commonly applied in most MBRs, heavy backwashing is not a suitable choice for the flat sheet submerged membranes [60], as they are not structurally supported, and therefore, are prone to tearing. Backwashing also has the drawbacks of energy and permeate consumption. Air flushing is also applied for MBRs and demonstrated excellent performance in flux recovery. However, air backflushing has issues of membrane breakage and rewetting [60].

5.5.1.1. Ultrasonic cleaning

Li et al. [10] studied the effectiveness of three cleaning techniques (ultrasonic, forward flushing, and ultrasound combined) with forward flushing to treat effluent from a Kraft paper mill using MF membranes. An ultrasonic method was successfully used as an in-situ method for elimination of the fouling of the flat-sheet MF membrane [10]. It was found that ultrasound along with forward-flushing was an operative method to retrieve the permeate flux and expel the formed fouling layers. A higher cleaning efficiency was achieved under low temperature and high forward flushing. The cleaning effectiveness of ultrasonic and ultrasound combined with forward flushing were 87% and 97.8%, respectively. In another study, Li et al. [122] employed the ultrasonic method to evaluate membrane fouling and subsequent cleaning regime during the UF of paper mill effluent. They concluded that the ultrasound method could assess the fouling layer formation rate under different operating conditions. These studies presented valuable evidence on flux improvement by ultrasonic irradiation and ultrasound measurement of membrane cleaning; however, studies on ultrasonic membrane cleaning are limited, and this technique may also increase membrane cost.

5.5.2. Chemical cleaning

Among anti-fouling strategies, chemical cleaning remains the preferred method because, regardless of pretreatment and physical cleaning applications, membranes need periodic cleaning to remove the fouling that cannot be removed through physical cleaning. Chemical cleaning is a well-recognized measure, which may be conducted either in situ or ex-situ. Membrane manufacturers suggest different cleaning chemicals (organic acids, NaClO, and caustic soda). Adoption of the best cleaning method relies primarily on the membrane configuration, membrane chemical resistance, and type of adsorbed materials. Despite this fact, chemical cleaning sometimes damages membrane materials, modifies membrane characteristics, and causes secondary pollution. Foulant characterization is fundamental toward applying the most effective cleaning procedure. The consideration of chemical cleaning conditions such as chemical concentration, pH, pressure, cleaning duration, and membrane materials, is significant. In contrast to polymeric membranes, ceramic membranes are typically more robust and allow for in-situ cleaning under high temperatures and the use of strong chemicals.

Liu et al. and Ebrahimi et al. developed chemical cleaning strategies for ceramic membranes [113,64], and a four-step method was designed for ceramic membranes by Liu et al. for the treatment Kraft spent liquor using MF and UF [123]. This process consisted of washing for half an hour with tap water, washing for half an hour with 0.2 mol/L sodium hydroxide, 0.5-hour heating in an oven at 550°C, and 0.5-hour wash with 0.2 mol/L HCl solution; where after the flux was totally recovered to its original level [123]. Organic membranes cannot be fully regenerated; however, using the same procedure without the furnace step, the flux can be recovered by 50%–80% of the original clean water flux [123]. A similar five-step protocol was established for ceramic membranes by Pizzichini et al. for the filtration of PPI effluent using MF and UF [21]. This procedure was comprised of washing for 20 minutes with tap water, one-hour wash with a 0.5 M sodium hydroxide at 60°C, an additional 20 minutes wash using tap water followed by half an hour wash with 0.5% HNO₃, and finally, 20 minutes wash using RO permeate. This process was able to restore 60-70% of the original flux. Mänttari et al. [34] applied an alkali cleaning procedure that consisted of a 0.2 w% Ultrasil 10 solution at a pH value of 11.6 when studying the results of temperature and pretreatment on NF membrane performance. The ultrasil solution was circulated for 20 minutes at 2 bar and 40 °C followed by a relaxation period of 10 minutes. Ebrahimi et al. [47] conducted a systematic series of filtration experiments to study the chemical cleaning effectiveness of the inorganic membranes. Using alkaline agents, approximately 98% of the original pure water flux was recovered for a 20-kDa membrane [47]. The cleaning

frequency of the membrane process can range from 7 to 180 days, depending on the degree of fouling, while the lifetime of the membrane component can range from between 1 and 5 years [46].

MBR suppliers such as Mitsubishi, Zenon, Memcor, and Kubota provide different reagents to address both organic (NaOCl 0.01-0.5%) and biological (citric acid 0.2–0.3% and oxalic acid 1%) foulants. Sodium hypochlorite, at a concentration of 0.3%, is the primary agent for the removal of organic foulants, while citric acid is applied for the cleaning of inorganic foulants [124]. To recover the flux of membrane bioreactors, chemical cleaning is typically performed by removing the membrane and circulating chlorine-free HClO₂ in tap water for 20 min followed by 20% NaOH solution and 10% HNO₃ intermittently with tap water.

5.5.3. Combined physical and chemical cleaning

Chemical cleaning may be combined with back-flushing through the addition of low concentrations of chemicals in a process known as chemically enhanced backflushing [12]. Another possible solution includes the combination of two cleaning schemes (membrane rinsing and chemical cleaning) [125]. The washing of membranes at operational temperatures by the collected permeate was successful, as the permeate has a similar pH value as the treated effluent. Following rinsing, the membrane was washed with a 0.25 wt% Ultrasil 11, alkaline cleaning agent at 60 °C and 0.5 bar. Washing was repeated until the original clean water flux was totally recovered [125]. Rinsing with deionized water was only revealed to recover between 70%–80% of the original water flux, while coupling rinsing with chemical cleaning with Ultrasil 11 recovered 90%–95% of the initial flux value, during UF of the Kraft BL [126]. Figure 3 shows the summary of membrane fouling control strategies.

6. Conclusion and future research

6.1. Conclusion

A state-of-the-art review of several types of fouling control strategies for both MBRs and mechanical filtration processes was conducted. Further, the main parameters affecting membrane fouling in addition to fouling characterization techniques were discussed and documented. The reviewed studies imparted interesting insights into the phenomena of fouling in the treatment of PPI effluent, and different fouling control strategies were established to prevent fouling and recover membrane flux. However, many contradictory observations and results have been reported, which may be attributed to the fact that each work was performed under different operating conditions, in addition to different membrane geometry. Among the reviewed fouling control strategies, pretreatment exhibited not only the decrease of fouling but also the improvement of membrane filterability. However, better elucidation of fouling mechanisms and foulant types is key toward the development of more efficacious and easier pretreatment methods. Chemical cleaning also remains a vital step in sustaining membrane permeability, and several cleaning regimes have been applied. Furthermore, operational condition optimization and hydrodynamic condition control are critical for attaining high filtration capacities and lower membrane fouling.

6.2. Future research works

Although membrane fouling has been the topic of considerable research, several fouling control strategies such as feed pretreatment, improved operational conditions, membrane modification, and physical/ chemical membrane cleaning have already been applied. There remains a great deal to learn about membrane fouling in the PPI due to the complexity of these wastes. Therefore, myriad issues require further study, and the following section presents challenges that need further research.

- The reviewed studies indicated that the pretreatment of feed-water prior to filtration has an important effect on the minimization of membrane fouling. However, the development of tailored and cost-effective pretreatment protocols for alleviating the fouling problem in pulp and paper waste streams is still needed. This may be achieved through the appropriate selection of pretreatment agents (e.g., coagulants, adsorbents, oxidants, etc.), which are characterized by high performance, low cost, and reduced hemicellulose degradation.
- Major advancement is anticipated in the control of membrane fouling through new membrane configurations and fabrication. The development of antifouling membranes for specific purposes could ensure a high level of membrane

performance. Also, membrane configurations that strike a balance between high membrane performance and the control of fouling would be of great benefit.

- It has been intensively discussed that fouling is the result of the interactions between membrane materials, process conditions, and treated feed. Thus, further research is required to identify the optimal operating conditions (e.g., optimization of hydrodynamics, feed environment, and membrane characteristics) that reduce the membrane fouling problem.
- Membrane cleaning protocols still appear practically insufficient, where the costs of the chemicals required to clean membranes still represent a heavy burden on the economic feasibility of membrane technologies aside from environmental issues. Thus, the development of an effective combined physical/chemical cleaning process, which reduces membrane fouling and is environmentally compatible calls for further investigations.

- Fouling characterization is essential for the adoption of membrane technologies in the PPI; however, although some progress was made in the characterization of fouling, additional data are required for the identification of the major foulants due to the complexity and high fouling propensity of pulping effluents. This might be accomplished through the adoption of the advanced membrane autopsy and characterization techniques.

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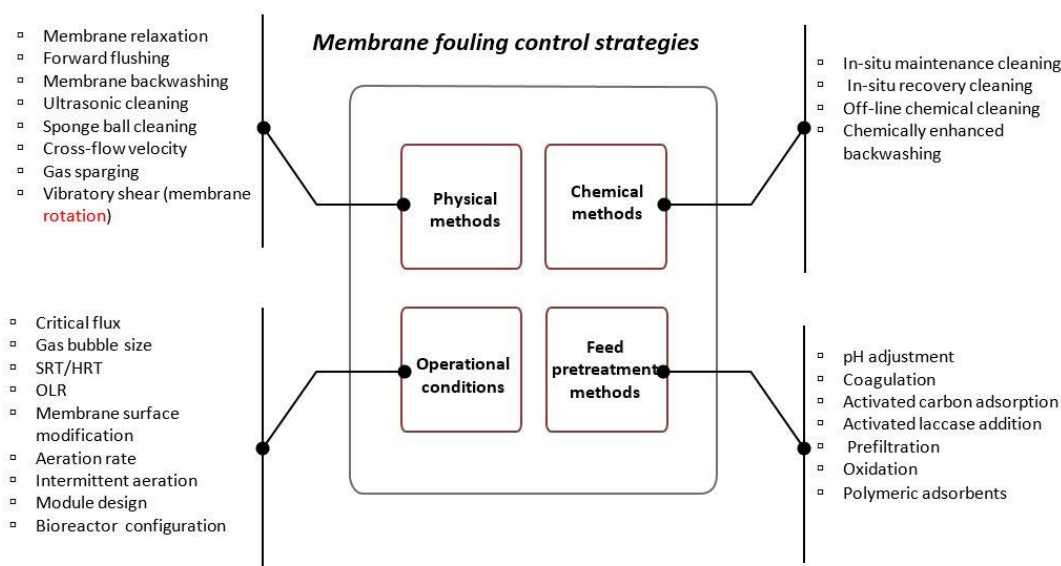


Fig. 3. Summary of membrane fouling control strategies.

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