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Membrane Operations in the Pulp and Paper Industry for the Recovery of Constituents: A State-of-the-Art Review

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Abstract

The pulp and paper industry is one of the biggest industry sectors worldwide and its market growth is expected to reach 370.12 billion USD by 2028. However, as a water-intensive process, pulp and paper production generates huge volumes of contaminated effluents, some of which contain dissolved high-value chemical compounds, such as lignin, hemicellulose, or carboxylic acids, which can be recovered using membrane operations. Therefore, membrane operations represent a method to valorize effluents and byproducts from this industry sector and could narrow the gap between biorefinery models and pulp and paper production as an integrated biorefinery. The present review discusses the state-of-the-art research and the state-of-the-art applications of membrane operations in the pulp and paper industry for the recovery of constituents.

Keywords

Membrane operations; pulp and paper industry; lignin; hemicelluloses; wood extractives; carboxylic acids; biorefinery; integrated biorefinery

1. Introduction

The advantages of membrane operations (MO) are well described in the literature: they can achieve high selectivity, their energy demand is usually low because they usually do not require a phase change, they are considered easy-operation and low-maintenance processes as they do not have mechanical moving parts, and they are usually better for the environment because of their milder conditions and low chemical demand [1–6]. Membrane technology in the pulp and paper industry (PPI) dates to the 1970s [4–8], but the global applications in this industry represent less than 6% of the global membrane market, which indicates that there is still a considerable area of opportunity for a wider implementation of MO in the PPI (**Figure 1**). However, constraints such as the high costs of industrial scale-up and membrane fouling must be addressed first for such a transition [8].

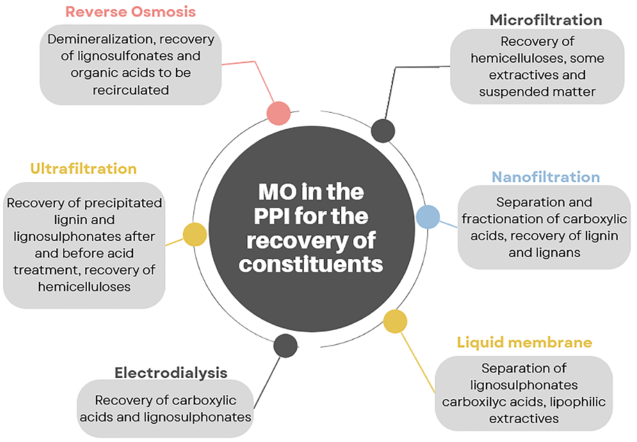

Figure 1: Research of MO applications in the PPI.

In the last decades, research has focused mainly on increasing the technical and economic feasibility and efficiency of MO to promote a shift towards integrated biorefineries to minimize waste production and maximize the value of available biomass and chemicals in the process. Compounds that have been studied for recovery from PPI effluents are described thoroughly in section 2 summarized in **Table 1**.

Much of the literature deals with lignin isolation methods using MO. However, this review presents an overview of other compounds that can also be recovered from the PPI as well and describes their state-of-the-art recovery methods. Process streams in the PPI that are rich in these components and that have been studied for potential recovery processes are outlined as well in section 3. Furthermore, a review of the main constraints and challenges for MO implementation and the reported costs for membrane-based processes for PPI implementation are also presented in section 5. Applications of MO in the wastewater treatment of PPI effluents are beyond the scope of this paper, as this topic is already summarized and discussed in the literature [9,10].

2. Compounds of Interest

2.1. Lignin and Lignosulfonates

Lignin accounts for 20-35% of plant biomass and represents the second most abundant biopolymer of land-based biomass [11], which renders lignin the most important biofuel worldwide. It is built up from monolignols, which are p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [12]. Annually, more than $5 \cdot 10^7$ tons of lignin are dissolved via chemical cooking [13], and around 85% thereof are disintegrated using the kraft process [11]. Normally lignin is used as biofuel in a recovery boiler onsite in the PPI. Lignosulfonates, on the other hand, are byproducts obtained from the production of wood pulp using sulfite pulping. Both lignin and lignosulfonates can be sold as emulsifiers, dispersants, or precursors for the synthesis of electrochemically active substances [11,14,15] UF, MF, NF, supported liquid membranes, electrolysis, diafiltration, or a combination between these operations are commonly used for the isolation of lignin and lignosulfonates [1,13,16–24].

2.2. Lignans

Lignans, such as matairesinol or pinoresinol, are low molecular weight polyphenols [25] that are - like lignin - responsible for the structural integrity of plant cell walls. They are built from the same monomers as lignin, but they are dimeric instead of polymeric and, in contrast to lignin, are optically active. Due to their associated anticancer and antioxidant activity, lignans are commonly used for pharmaceutical applications and as nutritional supplements. The market for lignans was valued at USD 420.55 million in 2021, and it is expected to reach USD 745.6 million by 2029 [26]. For instance, the price for the lignan hydroxymataurestinol, which is used as a nutritional supplement, is reported at 1 €$\cdot$mg^{-1} [1]. Even when high prices are attributable to this compound, the concentration of lignans in wood sources is smaller as compared to lignin, and their isolation requires a series of more complex processes, for example, a cascade of liquid extractions using polar and nonpolar solvents [1,27,28].

Table 1: Membrane operations were studied for added value production in the PPI.

Compound	Reported characteristics	MO	Applications
Lignin[*]	molecular weight willed wood lignin: 5,900-23,500 g·mol^{-1} molecular weight hardwood kraft lignin: 3,300-3,900 g·mol^{-1} molecular weight softwood kraft lignin: 6,500-8,000 g·mol^{-1}	UF, MF, NF, UF-NF, Diafiltration [13,16–19]	Biofuel, emulsifiers, dispersants, precursors for some chemical synthesis
Lignan	< 0.1 µm	NF	Pharmaceutical applications and nutritional supplement
Lignosulfonates	anionically charged. water-soluble particle size > 2 µm molecular weight: 1,000-140,000 g·mol^{-1}	UF, liquid-membrane [20–23]	Biofuel, emulsifiers, dispersants, precursors for some chemical synthesis
Hemicelluloses	particle size > 2 µm molecular weight (from sulfite pulping): 18,900 and 30,000 g·mol^{-1}	UF-NF, MF, MF-UF [18]	Oxygen barrier films for packaging, paper additives, food ingredients, or coatings
Extractives and acids	colloidal < 3 kDa particles	MF, NF-UF, UF, liquid-membrane, pervaporation [18,23]	Production of biodegradable polymers and plastics, cosmetics, and heavy metal chelating agents, solvents, for some organic synthesis

[*] The size of lignin agglomerates varies greatly after acid precipitation.

2.3. Hemicelluloses

Hemicelluloses are heterogeneous, amorphous, polymeric carbohydrates composed of pentoses, like arabinose and xylose, and hexoses, such as mannose, glucose, or galactose [14]. Depending on the wood source the proportion of the sugars changes, but their main constituents are xylan, arabinan, and galactan [24,29]. In process streams of chemical pulping, they are present in the form of galactoglucomannan, glucomannan arabinoglucuronoxylan, and glucuronoxylan. Some applications of hemicelluloses include oxygen barrier films for packaging, paper additives, food ingredients, or coatings [30–34]. Many laboratory products based on hemicelluloses have not been scaled up yet due to their low availability [35], but there is a well-known potential for this compound as raw material.

Hemicelluloses could be recovered from almost any chemical pulping process, but their isolation is complex and not yet state-of-the-art for kraft and sulfite pulping [24,27]. Nevertheless, hemicelluloses from the process water of thermomechanical pulping (TMP) are already recovered today [31], although hemicellulose concentration is smaller in this process stream. UF and MF are the most common membrane operations studied for the isolation of hemicelluloses [18,30,35].

2.4. Hydroxy Carboxylic Acids

During kraft or alkaline pulping, a substantial part of hemicelluloses is converted to hydroxycarboxylic acids [29]. The dry solids content of kraft black liquor (BL) is typically 12-18%, from which 10% are hydroxycarboxylic acids [36]. Compared to lignin, organic acids have a lower heating value when burned on-site in the chemical recovery cycle of a pulp mill but could have greater value for other purposes and new products [36]. For instance, hydroxycarboxylic acids can be used to produce biodegradable polymers and plastics, cosmetics, and heavy metal chelating agents [29]. It has been suggested that size exclusion and electrostatic repulsion may affect the separation of hydroxy acids via MO, but just a few papers have addressed the issue [36–38]. NF, UF, liquid-membrane, electrodialysis, and pervaporation are some MO studied for the isolation of carboxylic acids [6,18,23].

2.5. Extractives, Turpentine, Tall Oil

Wood extractives are lipophilic compounds such as fatty acids, resin acids, sterols, steryl esters, and triglycerides [39]. They are present in pulping liquors either in their original forms or in a variation after undergoing hydrolysis or other transformation reactions [29]. Depending on the wood source, these extractives can account for up to 10 wt.% of the wood dry matter [39] and when not removed, can cause toxic and hormonal effects in the aquatic environment already at low concentrations [18]. MF, UF, and liquid-membrane are some MO studied for the isolation of carboxylic acids [18,23].

Turpentine, a fluid obtained from the resin of trees made up of terpenes, is a by-product of the kraft process and can be removed via MF, steam stripping, or air stripping. Removal of turpentine before further processing is beneficial because it has been identified as a primary foulant in later MO [35,40]. Its primary uses are as a solvent and as a source of materials for organic synthesis. Besides turpentine, also tall oil is obtained during the pulping process. After BL is concentrated, it is left to settle where a top layer builds up, which is known as "tall oil soap." Tall oil can be sold as a feedstock for special chemical production [41].

3. Streams Studied for Compound Recovery and Treatment

3.1. Black Liquor

The composition of BL, a byproduct of kraft pulping, varies considerably with the digestion process and the raw material used (for example, the type of wood being processed). Typically, lignin accounts for approximately one-third of the mass of BL; the remaining part consists of hemicelluloses, organic acids, wood extractives, and various inorganic and organic compounds. Kraft lignin from BL accounts for nearly 85% of the total amount of industrial lignin in the world [19].

The isolation of valuable compounds from BL is already state-of-the-art. For instance, it is well known that lignin can be separated from BL by acid precipitation, which is used by the state-of-the-art processes LignoBoost, LignoForce, Sequential Liquid-Lignin Recovery and Purification (SLRP), and WestVaco processes, with the WestVaco being the oldest process of them all [15,42,43]. As a first step of these processes, carbon dioxide is used as the acidifying agent to prevent changes in the matrix of BL. Kraft lignin is soluble at pH>10, and when lowered to a pH between 8 and 10, it precipitates into colloidal forms with a molecular weight of around 1,700-4,500 $g \cdot mol^{-1}$ [30,36,44]. In the LignoBoost, LignoForce, and SLRP process, a second acidification step follows. H_2SO_4 is added to exchange sodium atoms bound to the lignin by hydrogen resulting in a high sodium recovery and lowered ash content of lignin, which facilitates the following filtration step. In the WestWaco process, LignoForce process, and LignoBoost process, the maturing of precipitated lignin before washing and filtering is included to improve the filterability of the lignin [30,36,44]. The SLRP process has high operating temperatures and pressures to increase the absorption of CO_2 [30] and as a result, the final product is lignin in the liquid state. In all four processes, the cost-driving factor is CO_2 pumping [43]; the CO_2 demand for the LignoBoost process is 150-300 kg CO_2 per ton of isolated lignin, while the CO_2 demand for LignoForce System^{TM} is reported to be 300-400 kg CO_2 per ton isolated lignin. In the SLRP process, the demand for CO_2 is 170 kg of CO_2 per ton of lignin, which is comparably low due to the high temperatures and pressures in the system.

These lignin recovery processes have been implemented by different companies. West Fraser Company in Canada uses the LignoForce technology; the West Virginia Pulp and Paper Company patented and currently uses the WestVaco process, whereas Domtar Corporation and the Stora Enso Sunila mill in Finland have been using the LignoBoost technology to produce roughly 25,000 tons and 50,000 tons of isolated lignin per year, respectively. More recently, SunCarbon AB, founded in 2014 in Sweden [45], runs a pilot plant with an integrated three-step process: membrane separation, hydrothermal treatment and purification, and process integration to recover lignin from BL [46,47]. The membrane pilot plant with a production capacity of 1.5 kg $lignin \cdot h^{-1}$ was built to scale up the patented SunCarbon process and has been in operation at the kraft mill since 2016 [47].

For the extraction of organic acids from BL, studies have mainly focused on multistep processes combined with MO to increase the separation efficiency. Mänttäri *et al.* [36] employed UF and NF membranes combined with acid precipitation and cooling crystallization for the simultaneous recovery of lignin and organic acids **(Figure 2)**. The UF step aimed at separating lignin from the organic acid fraction. The NF membrane was used to separate molecules in the molar range of 150-1000 kDa and could therefore retain and even fractionate acids present in the BL. Acid precipitation and cooling crystallization were employed to further purify the hydroxy acid fraction obtained from the UF permeate. The UF membrane with a molecular weight cut-off (MWCO) of 1 kDa increased lignin concentration from 40 $g \cdot L^{-1}$ to 100 $g \cdot L^{-1}$ showing faster acid retention in the membrane than water molecules, which probably can be attributed to the Donnan exclusion and electroneutrality principles. NF was carried out in diafiltration mode to further purify the organic acids after acidification and crystallization took place. Thereby, 70-80% of sulfate ions, UV-absorbing compounds, and other inorganic compounds were removed. However, it was concluded that UF had a detrimental effect on the flux of the NF membrane and did not help to increase the acid purity after NF. The reason was that the UF removes about 75% of the lignin and, therefore, the cake thickness after the precipitation step was significantly lower than when the precipitation was done with the original black liquor. In contrast, when a larger amount of high molar mass precipitated lignin is formed, it facilitates the removal of smaller molar mass compounds, and thus, the removal of the UV-absorbing compounds is better. However, adsorption is suggested to possibly further purify the NF permeate.

The recent work of Maitz *et al.* [38] achieved the simultaneous recovery of carboxylic acids and NaOH by using a sequence of NF and bipolar membrane electrodialysis units. NF retained the majority of lignin, resulting in a concentration increase of more than 120% of low-molecular-weight carboxylic acids in the permeate. Subsequent treatment with bipolar membrane electrodialysis recovered carboxylic acids in the acid compartment and NaOH in the base compartment. The final recovery of 17% of the acids was achieved in the acid compartment of the electrodialysis unit. Rowe and Gregor [37] patented a process that combines UF, electrodialysis, and reverse osmosis (RO) to separate aliphatic organic acids from BL. A simplified diagram of the process is shown in **Figure 3**. Recirculations to the pulping process are omitted for simplification purposes.

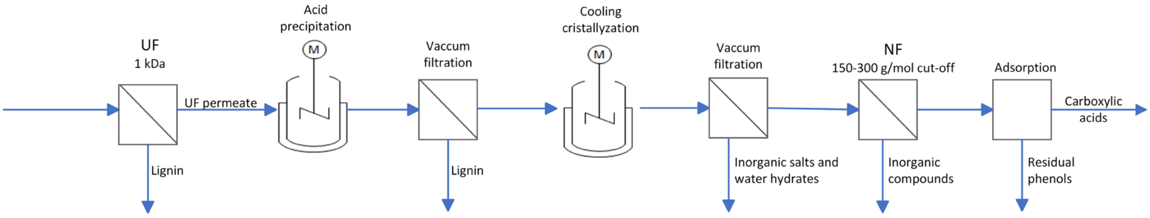

Figure 2: Schematic drawing of simultaneous recovery lignin and carboxylic acids from BL using UF and NF. Based on [36].

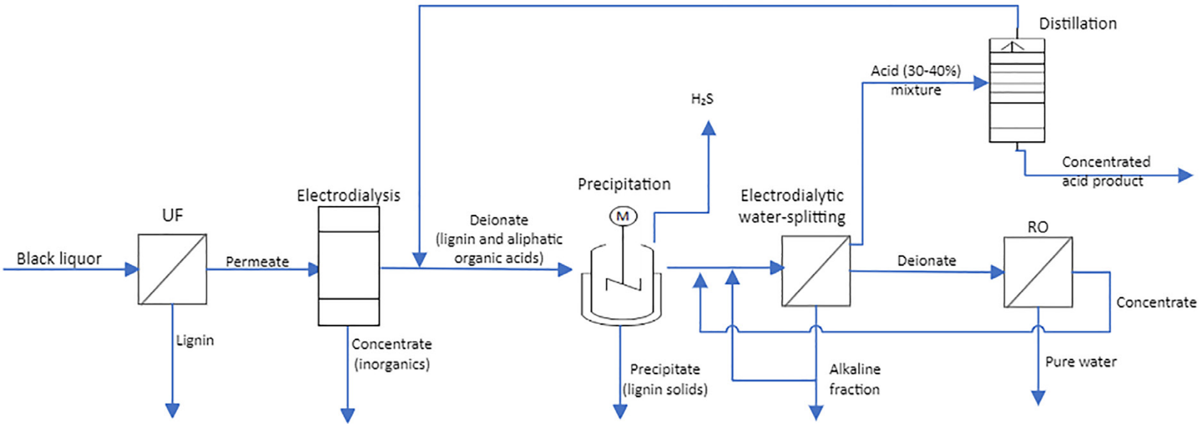

Figure 3: Schematic drawing of the recovery of carboxylic acids from BL. Based on [38].

3.2. Sulfite Spent Liquor (SSL)

Chemical cooking using the sulfite process is operated at neutral to acidic pH values, typical pH values range from 1 to 5 [42]. Thereby, lignin is disintegrated forming lignosulfonates that are, in contrast to kraft lignin, water-soluble over the whole pH range. After sulfite pulping, hemicelluloses can be removed via filtration as their molecular weight is higher than that of other components in spent liquors [42]. Since lignosulfonates are water-soluble, they cannot be precipitated by acidifying the spent liquor, and thus, other methods have been extensively studied.

A commercial method for the recovery of lignosulfonates is the patented Howard process (**Figure 4**). This process is commercially operated at Borregaard Industries Ltd located in Sarpsborg, Norway [42] and essentially consists of sequential precipitation of the spent liquor with the addition of lime to form colloidal particles and a calcium sulfite precipitate. The colloidal calcium lignosulfonate phase is low in ash and free of carbohydrates and can be further treated to obtain vanillin [48,49]. The first precipitation step occurs at a pH of 8.5, followed by a filtration step using a UF membrane with a MWCO of 20 kDa and a second precipitation step with a pH higher than 12 [42,50–52]. The concentrated stream can be used to convert lignosulfonates at least partially to vanillin. This can be accomplished by ion exchange to obtain sodium lignosulfonate, followed by an oxidation and acidification step [42]. The recovery of lignosulfonates through the Howard method can be as high as 90-95%. However, the main drawback of this method is the high consumption of chemicals required for the precipitation of $CaSO_3$ before membrane filtration.

Electrolysis, the Pekilo process, and RO are other membrane separation techniques suggested for separating lignosulfonates from SSL. In electrolysis, magnesium sulfite from the spent liquor is desalinized and demineralized to produce lignosulfonates. In the Pekilo process, hemicelluloses are fermented and ultra-filtered to obtain lignosulfonates. UF of 20,000 kDa has been commercially applied in a calcium bisulfite pulping mill in Norway since 1982, resulting in concentrations of 12 to 22 wt% based on dry matter [42].

Kilulya *et al.* [53] demonstrated the technical feasibility of the isolation of lipophilic extractives from the sulfite pulping process after the oxygen bleaching stage by performing a liquid-liquid extraction followed by a hollow fiber-supported liquid membrane (HFSLM). Liquid-liquid extraction was carried out using hexane and hexane-ethyl acetate as solvents. The extract was dried, weighted, and afterward dissolved with acetone for derivatization with methanolic HCl addition. After pH adjustment, a two-phase HFSLM extraction was performed using propylene hollow fibers impregnated with a mixture of 1-octanol and undecane. The lipophilic extractives obtained were mainly fatty acids, identified as their methyl esters, sterols, and steroid hydrocarbons.

3.3. Thermomechanical Pulping Water

Process water from TMP contains low concentrations of hemicelluloses, lignin, lignin carbohydrate complexes, and lipophilic and phenolic extractives [1,35]; their concentrations are in the range of 1-3 $g \cdot L^{-1}$ altogether [1] and of approximately 2 $g \cdot L^{-1}$ of hemicelluloses alone [1,35]. However, the potential for TMP process water valorization is high given the high flow rate of several hundred cubic meters per hour [1]. Additionally, the mild conditions of TMP maintain the native structure of the wood components, such as lignin, which suggests them as suitable candidates for other fine processes, such as depolymerization into bulk and fine aromatic and phenolic chemicals [1]. Studies of MO for the isolation of compounds present in the TMP process water include the recovery of hemicelluloses [35,54–56], lignin, extractives [1,40,54], and lignans [1,40].

Thuvander *et al.* [35] studied the recovery of hemicelluloses from TMP process water (**Figure 5**). They pre-filtered TMP process water with a 100 µm membrane for the removal of fibers and particles. The mother liquor was further filtered with a SiC MF membrane with 3 mm flow channels and a crossflow velocity of 3 $m \cdot s^{-1}$ to remove suspended and colloidal material (extractives). The permeate was then concentrated and purified using regenerated cellulose on a polyester support UF membrane with a MWCO of 10 kDa to remove hemicelluloses and a smaller proportion of lignin [35]. The cost estimate of this continuous, multistage membrane process for galactoglucomannan (GGM) recovery was 1,160 € per ton of hemicelluloses produced [35]. Reported market prices of GGM are around 800 USD per ton, hence, the process remains unfeasible to date.

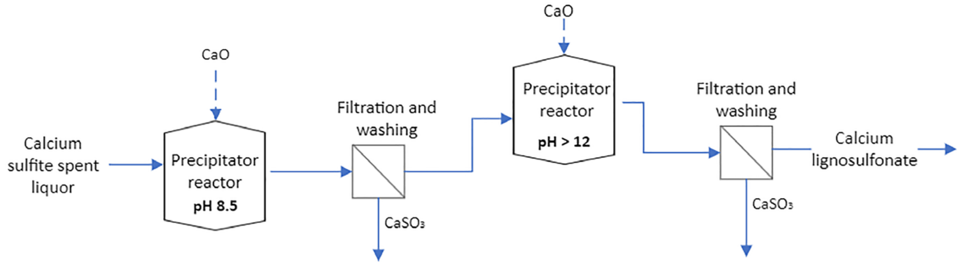

Figure 4: Schematic drawing for the recovery of lignosulfonates from SSL (Howard process). Based on [42].

Another study by Villain-Gambier *et al.* **[1]** used an NF membrane to retain lignin and lignans from TMP process water in a pilot plant study **(Figure 6)**. The TMP process water was pre-treated with a flotation step to remove lipophilic matter, followed by a clarification step with a 150 kDa UF membrane to remove suspended matter. After these pre-treatment steps, an NF membrane of 1 kDa was used to retain lignin, followed by a membrane with a MWCO of 300 Da to retain lignans. By this treatment, 39% of the initial lignin was retained by the 1 kDa membrane, whereas, the retention of lignin and lignan by the 300 Da membrane was 29% of the remaining lignin and 70% of lignans, respectively. The permeate from this membrane was re-introduced into the process, consequently saving freshwater consumption. The concentrations of lignin and lignan extracts that can be achieved with a plant capacity of 10 $m^3 \cdot h^{-1}$ are 27.4 $g \cdot L^{-1}$ and 7.4 $g \cdot L^{-1}$, respectively. The techno-economic evaluation showed that a selling price - including production costs – equal to or below 10 € per kg of extract was acceptable for a plant with this capacity or higher. For instance, a pilot plant with a capacity of 60 $m^3 \cdot h^{-1}$ was able to produce up to 12 tons of lignin and 825 kg of lignans per month **[1]**.

In another study, the fractionation of TMP process water into lignin, hemicellulose, extractives, suspended matter, and water was performed using a cascade of MF, UF, and NF membranes. Each ton of produced pulp resulted in about 10 kg of suspended matter, more than 0.3 kg of extractives, 11 kg of hemicelluloses, and 8 kg of lignin in the retentate of a drum filtration. Besides the recovery of valuable compounds, it was determined that approximately 40% of the filtered process water had the conditions to be recovered as freshwater **[54]**.

4. Liquid Membranes and Permeation

The viability of other non-commercially scaled-up MO such as supported liquid membrane extraction and permeation is still under investigation. Liquid membrane permeation with supported membranes has been demonstrated to be a potential future isolation technology for the treatment of process streams from the PPI, particularly for the extraction of lignosulfonates **[18]**. As support layers, cellulose **[18]** and polyvinylidene fluoride have been studied **[13]** with tri-*n*-octylamine (TOA) used as the reactive extraction agent **[13,19]**. The extraction efficiency of lignosulfonate isolation was reported between 85 and 92% **[19]**. Ke Xian *et al.* **[21]** extracted lignosulfonates from an aqueous solution using a polycylidene membrane of 0.45 μm, kerosene as the solvent, and NaOH as the stripping agent. Patil *et al.* **[6]** performed a scale-up study of an HFSLM for a generic extraction of carboxylic acids and developed a mathematical model for their transport behavior. They compared the extraction performance using tri-*n*-butyl phosphate (TBP), TOA, and tri-*n*-octyl phosphine oxide (TOPO) as extractants and concluded that almost 99% of the carboxylic acids can be extracted using 1% TOPO as an extractant; this proposes a generalized methodology for the HFSLM extraction of carboxylic acids and could serve as a future reference for scale-up calculations.

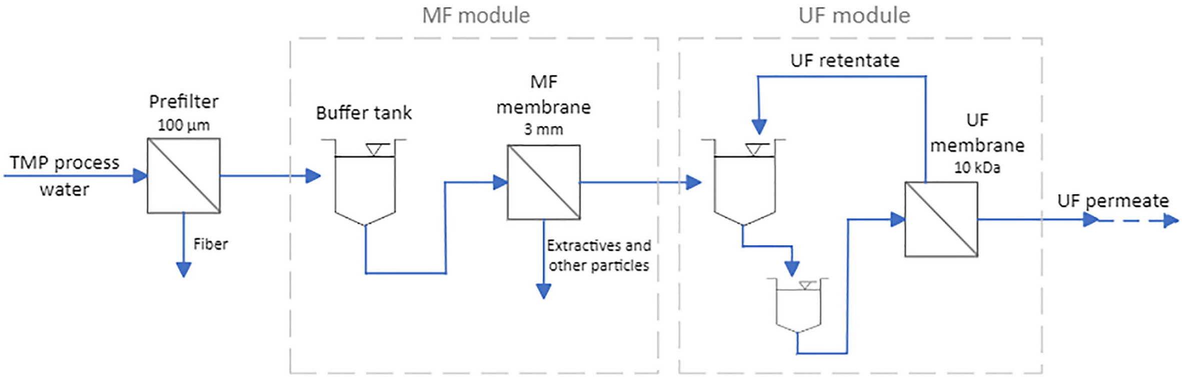

Figure 5: Schematic drawing of the recovery of hemicelluloses from TMP process water using MF and UF. Based on **[42,56]**.

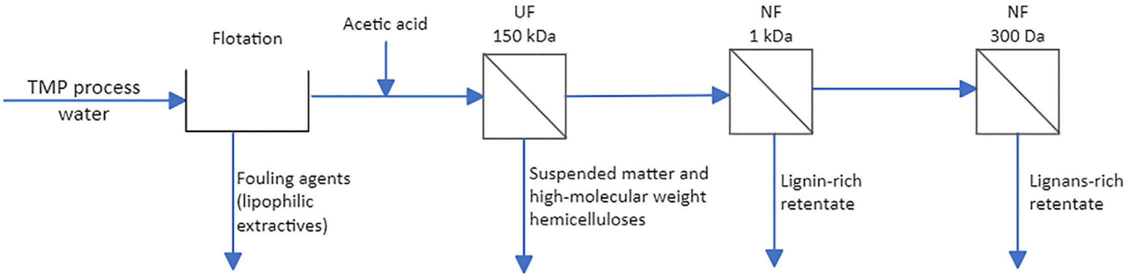

Figure 6: Schematic drawing of the simultaneous recovery of lignin and lignans from TMP process water. Based on **[1]**.

5. Challenges for MO Industrial Scale-Up

The main challenges for the implementation of MO at an industrial scale are membrane fouling and the high costs of making the recovery of compounds economically feasible in industrial scale-up. For such, suitable membrane materials and MCWO, an understanding of fouling mechanisms, and economy of scale must be considered.

5.1. Membrane Selection

The selection of the appropriate membrane material should make use of some considerations regarding selectivity, performance, and fouling. For instance, inorganic membranes have high mechanical, chemical, and thermal stability, a long service life, a comparatively low membrane resistance, and a high filtration performance compared to organic membranes [57]. Among inorganic membranes, polymeric membranes such as polyacrylonitrile, polysulfones, polyethersulfone, polyamide-imide, and polyether-imide membranes, are the more economical ones and provide higher retention of lignin (and hemicelluloses) than ceramic membranes [15,19,27,41], although they have poor chemical stability and display higher fouling due to its hydrophobicity. However, organic membranes usually have easier processability, and hydrophilic membranes in particular, such as regenerated cellulose membranes, and thin film composite membranes exhibit a low fouling potential [51,58]. Lignin is a hydrophobic molecule; therefore, it generally adsorbs to hydrophobic membranes and thus causes blocking and non-reversible fouling. In contrast, hydrophilic membranes exhibit lower lignin retention but they have shown higher hemicellulose retention [51].

5.2. Fouling

Fouling types, fouling mechanisms, and main foulants in membrane processes applied to process streams in the PPI are presented in **Table 2**. Membrane fouling refers to the accumulation of undesirable material on the surface and in the pores of the membrane and is usually accompanied by a loss of membrane performance in terms of flux and retention properties [39,59,60].

Characterizing membrane fouling caused by PPI effluents is complicated, as the complexity and inherent seasonal compositional variation of forest-based streams involve a variety of different foulants and fouling mechanisms in the membrane filtration processes such as pore blocking, cake or gel layer formation, and adsorption [59,60] derived from three different scenarios:

1. The size of foulants is smaller than the pore size of the membrane, allowing foulants to enter the membrane pores, adsorb on the pore walls, shrink the pore diameter, or block the pores. When this occurs, the volume of the pores decreases proportionally with the volume of solution filtered, and the cross-sectional area of the membrane pores thus decreases with time.

2. The size of the foulants is significantly bigger than the pore size, thus, the pore size remains unchanged but the accumulation of foulants on the surface starts a formation of gel or cake layer. The voids between the foulant layer increase when the foulant size increases.

3. The size of the foulant is similar to the membrane pores, resulting in intermediate blocking. In intermediate blocking, membrane pores are blocked by a foulant while other foulants can settle on top; in other words, not every foulant compound that arrives at the membrane blocks a pore. Hence, the probability of a foulant blocking a pore decreases continuously with time.

The studies of Rudolph [39] give insight into the fouling mechanisms that occur during membrane filtration of TMP water. They observed that fouling was caused mainly by both adsorption and pore blocking in the following mechanism: GGM and hemicelluloses are immediately adsorbed on the membrane surface, creating a thin, rigid layer of fouling. Over time, a thicker and softer layer on top is formed with colloidal droplets of extractives in the form of a multilayer.

With fouling caused by organic molecules in PPI effluents, it is reasonable that alkaline cleaning has been demonstrated to be a suitable cleaning strategy, particularly when it contains NaOH, surfactants, and chelating agents as well. In contrast, acidic cleaning has been found not to improve the membrane permeability significantly, as inorganic fouling is likely not significant. Enzymatic cleaning, an environmentally friendlier alternative, does not improve membrane permeation by itself either, but it does when combined with alkaline cleaning [36,39,59–61]. It should also be noted that loose fibers in PPI effluents also cause pore blocking in membranes, thus their removal before membrane separation could increase separation efficiency [35,62].

Some strategies to prevent or reduce fouling include selecting an appropriate membrane material (thus reducing the frequency of cleaning), using pretreatment steps such as flotation [1,40], cell geometry [17], optimizing operation parameters such as temperature, and crossflow velocity [63], or chemically modifying of membranes, such as the addition hydrophilizing agents to reduce hydrophobic interactions [64], activated carbon nanoparticles [19], titanium dioxide, or the addition of a graphene oxide composite layer [65].

5.3. Costs

Cost estimates for membrane plants in pulp and paper mills are rare in scientific journals [35], but **Table 3** summarizes the literature dealing with cost estimation for MO in the PPI. NF and UF are the most widely studied membranes for pilot plants and economic analysis, mainly for lignin and hemicellulose recovery. Sharma *et al.* [19] suggested the preparation of mixed matrix membranes to save costs instead of purchasing commercial UF and NF membranes, with an estimated cost of 3.5-37 $€·m^{-2}$ and 4-58 $€·ton^{-1}$, respectively including reagents and utilities; however, the cost of the product extraction still needs to be improved to be an attractive investment.

Table 2: Fouling types, fouling mechanisms, and main foulants in membrane processes for compound valorization. Based on [39,59,60].

Process	Membrane type	Fouling type	Mechanism	Main foulant
Lignin recovery	MF, UF, NF	Organic	Cake/gel layer, pore blocking, adsorption	Lignin, extractives
Hemicelluloses recovery	MF, UF, NF	Organic	Cake/gel layer	Hemicelluloses, extractives
Extractives recovery	UF	Organic	Adsorption	Dissolved and colloidal lipophilic extractives, sterols

Table 3: Reported costs for different stream applications and membrane types.

Process	Application	OPEX k€·year^{-1}	Production rate	Cost/product	Ref.
NF ceramic 1 kDa	Lignin from TMC process water	92.8	1.049 ton retentate·year^{-1} (23% lignin); capacity: 8 m^3·year^{-1}	17,000 €·ton^{-1}	[1]
NF polymeric 300 Da	Lignan from TMC process water		0.697 ton retentate·year^{-1} (2% lignan)	17,000 €·ton^{-1}	
UF (ceramic) NF (ceramic)	Lignin from BL	2.8	8,300 ton lignin solution·year^{-1}	430 €·ton^{-1}	[27]
UF (ceramic) NF (polymeric)		3.0	30,000 ton lignin solution·year^{-1}	130 €·ton^{-1}	
NF (ceramic)		3.6	41,000 ton lignin solution·year^{-1}	68 €·ton^{-1}	
NF (polymeric)		2.8	68,000 ton lignin solution·year^{-1}	46 €·ton^{-1} lignin in solution (230 g·L^{-1})	
UF-RO 80% water recovery	Lignin from spent liquor (AlkOx process; reuse of purified water)	51	10,000 m^3 treated liquor·year^{-1}	521-1,175 €·ton^{-1}	[50]
UF-RO, without water recovery		55	10,000 m^3 treated liquor·year^{-1}	521-616 €·ton^{-1}	
UF	GGM from spent sulfite liquor	1.06	2.75 kg GGM·h^{-1}	48.23 €·ton^{-1}	[59]
MF-UF	GGM from TMC process water	713 €·ton^{-1}	180 m^3 of process TMC water·h^{-1*}	1,160 €·ton^{-1} GGM in solution (47 g·L^{-1})	[35]

*TMC water with a concentration of 2.35 g·L^{-1} hemicelluloses.

6. Conclusions

Membrane operations can be used to extract high-value products, such as lignin, hemicelluloses, and extractives from process streams of the pulp and paper industry. Of main interest are black liquor, sulfite spent liquor, and thermomechanical pulping water. A combination of more than one membrane technique is usually necessary to obtain a purified or concentrated fraction of interest. The main challenges for industrial implementation of membrane operations are fouling, selectivity, and costs, but some industries have already overcome these challenges by combining other separation technologies, such as flotation, precipitation, or alike. By that, a high potential in scaling MO to industrial applications with economic feasibility is demonstrated, but yet to be validated for commercial scale.

Authors' Contributions

Daniela Silva Benavidez: Conceptualization, Investigation, Writing-Original Draft, Visualization. Marlene Kienberger: Conceptualization, Validation, Writing-Review & Editing, Funding acquisition, Supervision, Project Administration. Paul Demmelmayer: Validation, Supervision, Project Administration, Editing. All authors have read and agreed to the published version of the manuscript.

Data Availability

The data supporting the findings of this study are available in the patents, articles, and books cited in the references section.

Conflicts of Interest

The authors declare no conflict of interest.

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Ethical Approval

The study has been approved by the ethical national committee. The authors declare that the study has followed the guidelines of the Declaration of Helsinki.

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