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Advanced ultrafiltration technology for lignocelluloses recovery and purification from thermomechanical pulp (TMP) mills process waters

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Advanced Ultrafiltration Technology for Lignocelluloses Recovery and Purification from Thermomechanical Pulp (TMP) Mills Process Waters

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BY

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Abstract

Process waters of thermomechanical pulp (TMP) mills contain a large valuable quantity of lignocellulosic materials that end up in the wastewater for biological treatment. In recent years, interest in utilizing such compounds has increased, and plenty of applications have been proposed. Thus, the recovery of hemicelluloses and lignin from these process waters as value-added chemicals would be beneficial for TMP mills not only to increase their profitability and competitiveness but also to reduce the organic loading to the wastewater treatment facility. However, this implies adoption of different types of appropriate separation technologies. Among the proposed separation methods, membrane technologies have been studied in a wider range of perspectives, and have been shown to play a key role in products recovery and purification in biorefining processes. In this study, the feasibility of the advanced UF technology for hemicellulose recovery and concentration from thermomechanical pulp (TMP) mill process waters was evaluated. In particular, the influence of ultrafiltration membrane cut-offs and volume reduction factors on membrane flux, and recovery and purity of hemicelluloses were investigated.

Based on this study, the three tested membranes had shown different ability to recover hemicelluloses from the TMP process water. 5KDa membranes achieved the highest percent recovery of hemicellulose (95.7%), followed by 10KDa membranes 89.2% for the volume reduction (VR) of 95%. 30KDa membranes had the lowest percent recovery of 52% for VR value of 95%. Compared to 5kDa membranes, a cut-off of 10kDa seems to be feasible for the separation of lignin from hemicelluloses; it retained hemicelluloses while allowing the lignin to pass through it. Retentions of lignin were markedly low with the tested 10kDa membranes, compared with hemicelluloses retention. Volume reduction had a significant influence on the amount of hemicelluloses and lignin held back by the membrane. In this study also the characteristics of permeates and concentrates of UF membrane with different cut-offs were studied.

Keywords: *thermomechanical pulp; hemicelluloses; lignin; ultrafiltration; biorefinery.*

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CHAPTER I

Introduction

1.1. Overview

The forest industry is one of the major industries of Canada. However, more recently has been facing reduced profit margins and a competitive global market. Pulp and Paper companies are examining new ways to diversify revenue streams. This situation led to the study and development of integrated forest biorefinery (IFBR) which utilizes forest-based biomass rather than fossil fuels to produce value-added chemicals and bioenergy (Moshkelani et al. 2013). The biorefinery concept is important because it offers a broad range of economic and environmental benefits. It relies on the products diversification and sustainability perspective.

Products diversification offers interesting economic opportunities for the forest industry to increase its profitability and competitiveness. However, the biorefinery will only ever be truly economically viable if advanced separation technologies that deliver the hemicellulose and lignin fractions in a useable form are developed. In many instances, an effective separation of lignocellulosic materials can be the single biggest factor affecting the overall success and commercialization of biorefineries(Liu et al. 2011; Huang and Ramaswamy, 2013). In the literature, a number of separation and purification approaches have been proposed, to isolate hemicellulose and lignin: the precipitation process (Mussatto et al. 2007) the adsorption process (Olajire, 2010; Liu et al. 2011) and the solid–liquid extraction process (Huang et al. 2012). Among the proposed separation methods, membrane technologies have been studied in a wider range of perspectives, and have been shown to play a key role in products recovery and purification in biorefining processes. Compared with the commonly applied separation methods, membrane technologies offer excellent fractionation, short processing steps, less chemical utilization and considerable energy saving. Also, membrane separation processes can be integrated with the existing operating units, not to mention their easy operation and scale-up. However, the use of membrane filtration in IFBR have some challenges that need be addressed. The biggest problem in membranes biorefining is membrane fouling (Koivula et al. 2011; Koivula et al. 2013) because of the complexity of wood hydrolysates. Due to membrane fouling, the advantages of membrane separations for IFBR have not been fully explored.

In this study, the feasibility of the advanced UF technology for hemicellulose recovery and concentration from thermomechanical pulp (TMP) mill process waters was evaluated.

1.2. Problem statement and justification

In thermomechanical pulping (TMP), wood chips are treated with pressurized steam prior and during the refining process. Through these processes, approximately 2-5% of woody materials, which include hemicelluloses, lignin, and extractives, are dissolved or dispersed as colloidal particles into process waters (Sixta, 2006). It is estimated that 8-40 kg hemicelluloses are dissolved in process waters per ton TMP pulp produced (Sundblom, 1999). Traditionally, the fate of hemicelluloses and other organic molecules in TMP process streams is limited to discharge in wastewater streams for biological treatment (Van Heiningen, 2006), which is costly to the company. Recently, interest in utilizing lignocellulosic materials has increased, and several applications have emerged (Koivula et al. 2011). Hemicelluloses have been found to be an excellent candidate for oxygen barrier materials in food packing, hydrogel, emulsion stabilizers for beverages (Ebringerová 2005), while lignin has found potential applications as carbon fibers, adhesive materials, activated carbon, etc. (Qiu et al. 2005).

Although plenty of applications for lignins and hemicelluloses have been proposed. The lack of effective separation technologies of hemicellulose and lignin with high purity (García et al. 2009) is a major problem with the utilization of hemicellulose and lignins in certain industrial applications. The process water of forest industry is usually a complex mixture of wood components: hemicelluloses, lignin, wood extractives and organic acids. In order to obtain a purified fraction of hemicelluloses and lignin, highly developed separation technologies, that cost efficient and environmentally responsible, are needed (Persson et al. 2010). Thus, value-added chemicals can be economically produced from forest wastewater streams. For the overall biorefinery concept, an effective separation technology of lignocellulosic materials is critical (Liu et al. 2011). Biorefinery concept lies in an economically available processing to achieve a complete utilization of most of the biomass components (Toledano et al. 2010). Also, since each molecular weight of hemicelluloses has a specific application field, fractional separation and structural characterization of the hemicelluloses, are required for effective use of these materials.

1.3. Research objectives

This study aims to evaluate the feasibility of advanced UF technology for hemicellulose recovery and concentration from thermomechanical pulping (TMP) mill process waters. For achieving the overall goal, the following specific objectives were addressed:

1. The performance (membrane flux, hemicellulose recovery, rejection percent of lignin and hemicellulose, and hemicelluloses purity) of UF membranes with different molecular weight cut-offs (5, 10 and 30kDa of a hydrophilic regenerated cellulose membrane) for hemicelluloses recovery and purification from TMP process waters was evaluated.

2. The influence of the volume reduction factors on the membranes performance was assessed.
3. Characterization of the TMP wastewater streams (e.g., hemicelluloses and lignin concentrations, total organic carbon (TOC)) was also performed.
4. The compositions (total organic carbon, total solids, ash content, pH, turbidity, andtotal volatile solids) of concentrates and permeates of the different membrane cut-offs were studied, and also the molecular masses distribution of hemicelluloses and lignin were determined.

1.6. Outline of the thesis

The thesis consists of **IV** chapters. Chapter **I** is an introductory chapter explaining the problem statement and justification and the main objectives. Chapter **II** gives a background of the study, including the pulping processes and the application of separation technologies in integrated forest biorefineries. Chapter **III** describes the applications of ultrafiltration membrane technology for hemicelluloses recovery and purification from thermomechanical pulp (TMP) mill process waters. In this chapter, the use of membrane separation in IFBR is discussed. Finally, the conclusion and future research direction are covered in Chapter **IV**.

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CHAPTER II

Literature review

2.1. Lignocellulosic materials

Lignocellulosic biomass consists of four major components: cellulose, hemicellulose, lignin, and extractives. Table 2.1 summarizes the compositions of woody biomass. Proportions of these components vary depending on the biomass materials (McKendry, 2002). The relative ratio of cellulose and lignin is one of the important factors determining the suitability of plant species for application. Biorefinery takes advantage of these different components and their intermediates, therefore maximizing the values derived from them.

Table 2.1: Typical major components of woody species (%) (Moshkelani et al. 2013).

Component	Softwood	Hardwood
Cellulose	40 – 50	40 – 50
Hemicelluloses	15 – 20	20 – 35
Lignin	23 – 33	16 – 25
Other organics	1 – 5	1 – 2
Inorganic as ash	0.2 – 0.5	0.2 – 0.5

2.1.1. Hemicelluloses

2.1.1.1. Chemical composition

Hemicelluloses represent one of the most abundant renewable resources on the earth. They belong to a group of complex polysaccharides which are formed through biosynthetic paths different from that of cellulose. The composition and structure of hemicellulose vary considerably depending on the plant species. Hemicelluloses are commonly divided into five groups of structurally different oligomer types: xyloglucans, mannans, xylans, glucomannans, and β-(1→3, 1→4)-glucans (Pauly et al. 2013). Xylans are the dominant type of hemicellulose in hardwoods while glucomannans are a major component in softwoods. Table 2.2 shows the components of hemicelluloses in the woody species. Hemicelluloses are not very resistant to chemical attack – many easily break down to monosaccharides: pentoses (xylose, arabinose), hexoses (mannose, glucose, galactose), and sugar acids. Characteristically, softwoods have more mannose and galactose and a reduced amount of xylose and acetyl groups than hardwood. The molecular weight distribution of hemicelluloses varies widely, also depending on the raw materials, and hemicellulose has a far lower molecular weight than cellulose (He et al., 2012). Like cellulose, hemicelluloses function as supporting material in the cell wall.

Table 2.2: The main hemicelluloses in softwood and hardwood (Spiridon et al. 2011)

Component	Hardwood (%)	Softwood (%)
Methylglucuronoxylan	80 – 90	5 – 15
Arabinomethylglucuronoxylan	0.1 – 1	15 – 30
Glucomannan	1 – 5	1 – 5
Galactoglucomannan	0.1 – 1	06 – 70
Arabinogalactan	0.1 – 1	1 –15
Other galactans	0.1 – 1	0.1 – 1
Pectins	1 – 5	1 – 5

2.1.1.2. Major applications

Recently, many applications for hemicellulosic materials have emerged, including the production of hydrogels (Ebringerova, 2005) and the fabrication of oxygen barrier film for food packaging (Willför et al. 2008). Alternatively, it can be fermented to ethanol (Huang et al. 2008) or utilized as an emulsion stabilizer in food and feed (Krawczyk and Jönsson, 2011). Figure 2.1 illustrates some uses of hemicellulose. Moreover, hemicelluloses are used as a raw material for the production of furfural, hydroxymethylfurfural (HMF), and lactic acid (Fatehi and Ni, 2011b). On the other hand, hemicelluloses oligomers are highly bioactive and can be used as growth hormones for trees.

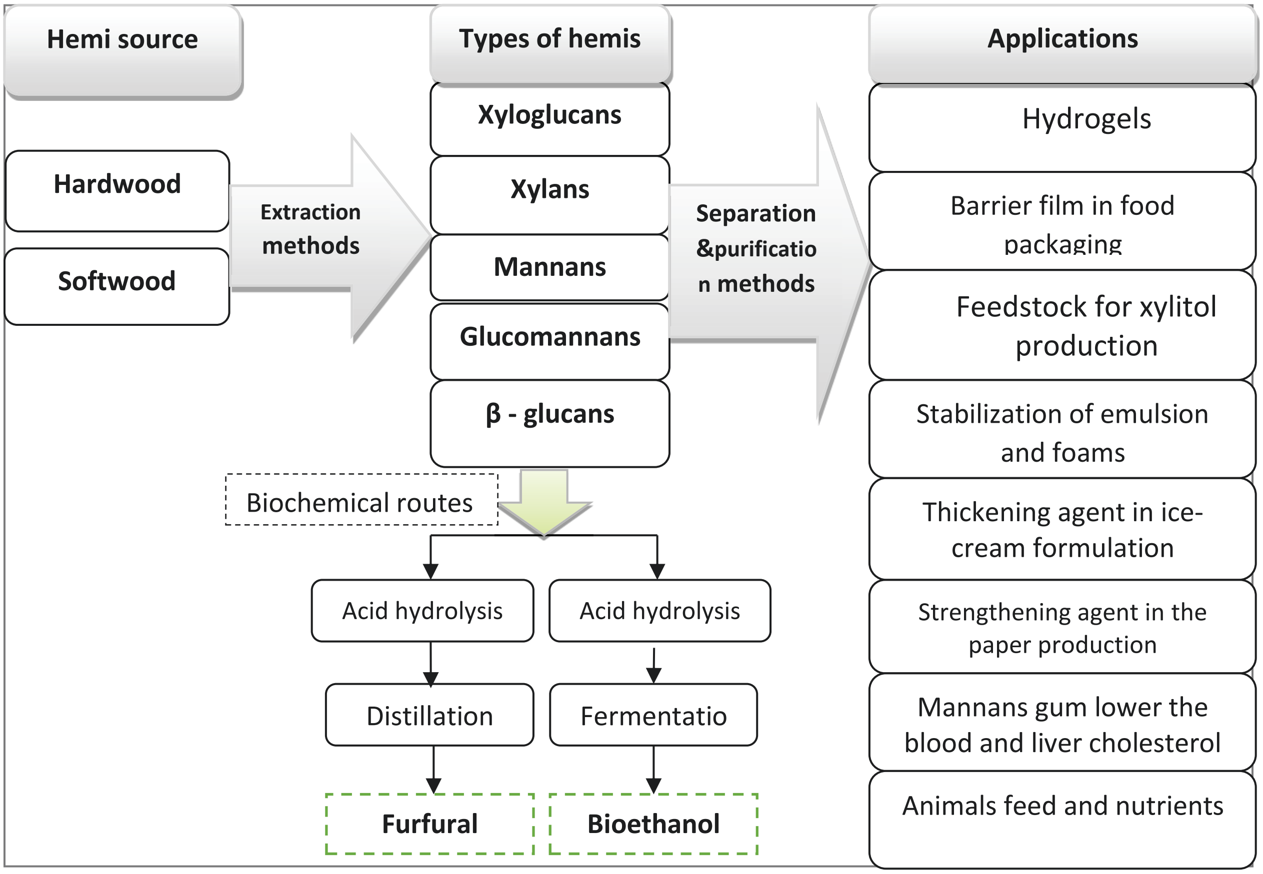

Figure 2.1: Sources and types of hemicelluloses with some of their uses in industry

2.1.2. Lignin

2.1.2.1. Chemical composition

Lignin is a complex natural amorphous polymer. It acts as the essential glue that gives plants their structural integrity and holds the fibers of polysaccharide together. The structure of lignin changes according to the biomass source and the isolation technique. In general, softwoods contain more lignin (25–35%) than hardwoods (20–25%) (Faravelli et al. 2010). Lignin consists of three hydroxycinnamoyl alcohol monomers (C9), differing in their degree of methoxylation: p-coumaryl, coniferyl, and sinapyl alcohols (Boerjan et al. 2003). The molecular weight of kraft lignin extracted from the black liquor range from 1000–2000 Da (Wallberg and Jönsson, 2006).

Today, the main source of lignin available for application on a large scale comes from the pulp and paper industries.

2.1.2.2. Major applications

In the pulping industry, lignin is usually isolated from other components of wood chips (delignification). Several extraction processes have been used, resulting in various types of lignin with different characteristics (spent liquor). Some examples of lignin types and applications in industry are shown in Figure 2.2.

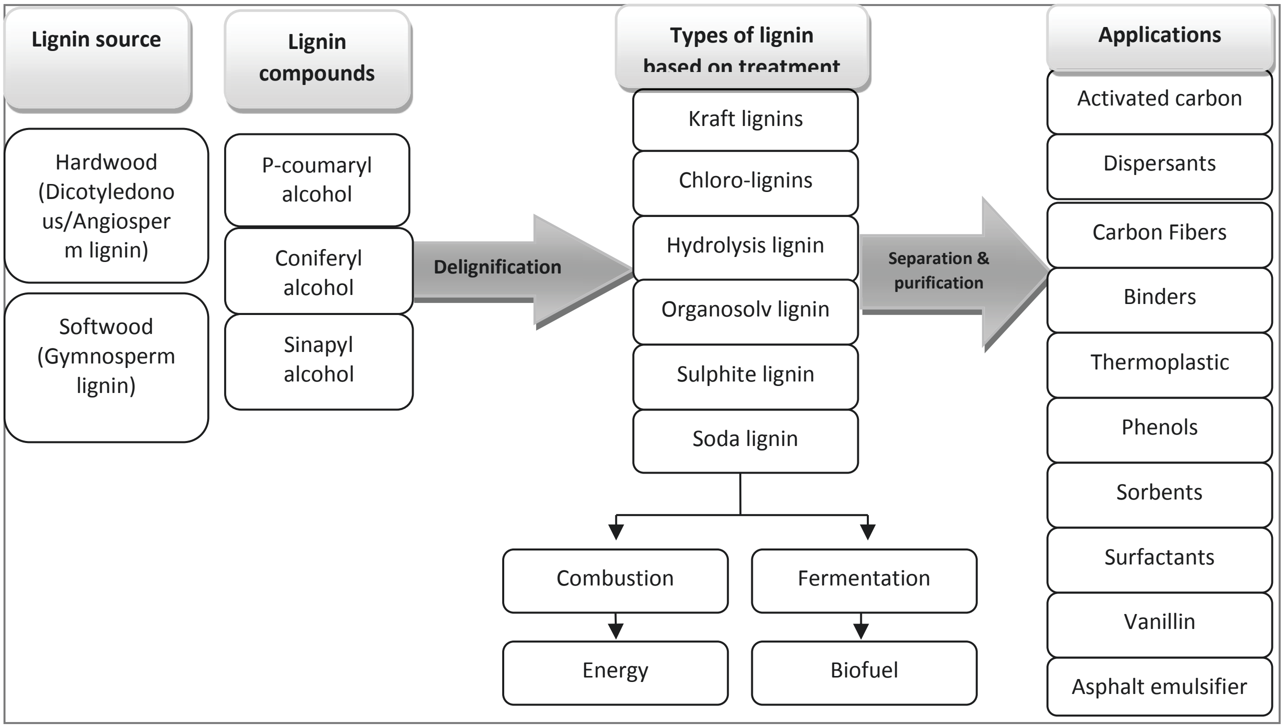

Figure 2.2: Sources and types of lignins with some of their applications in industry.

This spent liquor is typically concentrated and then fired to a recovery boiler for energy generation and inorganic chemicals production (Sameni et al. 2013). Compared to hemicellulose, lignin can be separated and used as the starting material for a number of useful products. Besides being burned to produce energy in recovery boilers, for example, kraft lignins have been utilized to produce binders, resins, carriers for fertilizers and pesticides, thermoplastic polymers, asphalt, lead storage batteries, and activated carbon (Pye, 2008). Also, it can be used as a chelating agent for the removal of heavy metals from industrial wastewater, as a dispersant in cement and gypsum blends, as emulsifiers, and sequestrates (He et al. 2012). Moreover, it has been proposed that lignin, irrespective of origin, constitutes an attractive feedstock for products, such as carbon fibers, adhesives, and phenol-based polymers (Brodin et al. 2009).

2.1.3. Wood extractives

2.1.3.1. Chemical composition

Extractives substances can be defined as lipophilic compounds that are soluble in various neutral organic solvents (Valto et al. 2012). These substances include simple sugars and high-molecular-weight carbohydrates, fatty acids, waxes, turpentine, resin acids, and complex phenolic compounds, as shown in Table. 2.3. Composition and content of these extractives are quite variable depending on the parts of the tree (e.g., heartwood and sapwood), the wood species, age, growth conditions, site-specific and environmental factors (Valto et al. 2012). Their content is normally less than 5%, and they are found in higher concentrations in the bark of most woods, heartwood, tree branches, roots and wounded wood. In the process waters, the majority of the lipophilic extractives are in the form of colloidal resin particles (Puro et al., 2011). According to Kilulya et al. (2012) sulfite pulps usually contain more extractives than kraft pulps as fatty and resin acids are insoluble in the acid cooking. The majority of the colloidal resin particles have diameters in the range 0.1–2µm and the average are about 0.6 µm (Puro et al. 2011).

2.1.3.2. Major applications

Wood extractives are valuable compounds, which could be utilized as preservatives in food or raw materials in chemical industry (Puro et al., 2011). Another new application for wood extractives is the use as biocides. However, during the pulping processing, the majority of the wood extractives would be dissolved in the BL and either burnt to produce energy or discharged in wastewater.

Table 2.3: Classification of common wood extractives (compiled from Valto et al. 2012 and Amidon et al. 2014)

Types	Components	Types	Components
Lipid extractive components	Aliphatics and alicyclic: Fatty acids	Carbohydrates	Arabinose
	Fats (fatty acid esters of glycerol)		Galactose
	Fatty alcohols		Glucose
	Waxes (esters of other alcohols)		Xylose
	Suberin (polyester)		Raffinose
	Terpenoids: Monoterpenes (turpentine)		Starch
	Diterpenes		Pectic material
	Triterpenes (including resin acids and steroids)		
Phenolic extractive components	Simple Phenolics	Other compounds	Cyclitols
	Stilbenes		Tropolones
	Flavonoids		Amino acids
	Isoflavones		Alkaloids
	Condensed tannins		Coumarins
	Hydrolyzable tannins		Quinones
	Lignans		protein

2.2. Hemicelluloses and lignin extraction and recovery in pulp and paper industry

The pulp and paper industry converts lignocellulosic plant material into pulp, paper, and paperboard. This process can be accomplished mechanically, chemically, or by a combination of both treatments. Based on the treatment method, industrial pulping processes have been divided into mechanical, chemical and semi-chemical. In the most pulp and paper mills, cellulose is devoted to the production of pulp and paper, while the fate of hemicelluloses and lignins are depolymerized, de-branched, and solubilized in the spent liquor.

2.2.1. Mechanical pulping

2.2.1.1.Thermomechanical Pulp (TMP)

In TMP process, wood chips are pre-softened by steam or hot water to make the fiber liberation more easily, followed by a mechanical refining. Currently, mechanical pulp accounts for 20% of all virgin fiber material (Sixta, 2006). The pulp yield is 90-95% (Martin et al. 2000). The rest of woody materials, which include hemicelluloses, lignin, and extractives, are dissolved or dispersed as colloidal particles into process waters (Sixta, 2006). This effluent is currently treated in the wastewater treatment facility of the pulp mill. Thus these valuable lignocellulosic materials are wasted.

2.2.1.2. Chemi-thermomechanical Pulp (CTMP)

In CTMP, the wood chips are impregnated with chemicals (treatment with sodium sulfite) before the refining. Often defibration condition of CTMP begins with the penetration of 1% to 5% of Na_2SO_3 and chelating agents. Then the mixture is preheated for 2 - 5 minutes at 120-135°C and is subsequently refined. The yield is typically between 91–96% (Sixta, 2006). The chemical pretreatment of wood chips during this process dissolves lignin and hemicelluloses in the spent liquor. This spent liquor is biologically treated for pollution control, which is costly to the company.

2.2.2. Chemical pulping

Chemical pulping is the most common pulping technologies. The dominant chemical pulping methods comprise the sulfate or kraft, the acid sulfite, and the soda processes. In 2000, the chemical pulps accounted for more than 77% of all wood-based fiber material worldwide (Sixta, 2006). In chemical pulping, lignin is degraded and dissolved through chemical reactions at elevated temperatures (130–170 °C). The total fiber yield ranges from 45 to 55% (Sixta, 2006).

Although it characterized by low yield, it offers higher strength properties, and the produced fibers are more easily breached (Bajpai, 2011).

2.2.2.1. Kraft pulping process

In Kraft pulping, wood chips are impregnated with the cooking liquors (white liquor: NaOH + Na2S and black liquor: NaOH, Na_2CO_3, H_2S…etc) for delignification. Then the produced brown stock is washed with water to remove cooking (black) liquor for the recovery of chemicals and energy (Bajpai, 2011). This process tolerates a wide range of species and produces high strength pulp. The kraft pulps account for 89% of the chemical pulps and over 62% of all virgin fiber material (Sixta, 2006). Kraft pulping uses less than 50% of the tree. Therefore it characterized by the lower pulp production. The rest ends up as black liquor which is burned in the recovery boiler or biologically treated in wastewater treatment plant.

2.2.2.2. Sulfite pulping

The main Sulfite pulping processes are classified into Acid (bi)sulfite, Bisulfite (Magnefite), Neutral sulfite semichemical (NSSC), and alkaline sulfite (Bajpai, 2011). Sulfite pulping process uses different chemicals as delignifying agent. Today, sulfite pulping accounts for 5.3% of the world chemical pulp production (Sixta, 2006). This process yields bright pulp which is easy to bleach to full brightness. It has been estimated that the pulp yield is generally in the range of 40–50% (Bajpai, 2011). Thus, the spent liquor of sulfite pulping process contains a significant amount of dissolved lignocellulosic materials, which can be converted to various value-added products (Fatehi and Ni 2011a). Area et al. (2000) identified and quantified the organic components in spent liquor of NSSC pulping process using hybrid poplar wood chips. The spent liquor contained 2-24% hemicelluloses, 59-69% lignosulfonates, 12-29% acetic acid, and 1.6-2.4% formic acid (Area et al. 2000).

2.2.3. Dissolving pulp

Dissolving pulping represents specialty pulps within the chemical pulp segment. It has been used to produce a raw material of cellulose derivatives (rayon, cellophane, cellulose acetate, cellulose ether, regenerated fibers, MCC & methylcellulose) and other specialty products. The current technologies of dissolving pulp manufacture are the acid sulfite pulping which produces pulp with a α-cellulose content of 90–92%, and the prehydrolysis kraft pulp process which typically produces pulp with a α -cellulose content of 94–96% (Sixta, 2006). It has been estimated that 60% of dissolving pulps are produced by the sulfite pulping process (Fatehi and Ni, 2011a), while 40% is produced via pre-hydrolysis kraft process (Fatehi and Ni, 2011b). Dissolving pulp accounts for 2.5% of the total pulp production (Fatehi and Ni, 2011b). Based on the total solids analysis studies, the sulfite spent liquor of hardwood of paper-grade pulping contains 15-22% sugars and 50-65% lignosulfonate (Fatehi and Ni, 2011a). While the industrially produced pre-hydrolysis liquor (PHL) contains 1.5-1.7% hemicellulose, 1-1.2% lignin, 1.2% acetic acids, and 1-1.4% ash (Fatehi and Ni, 2011b). However, presently, PHL is combined with black liquor. These amounts of hemicellulose and lignin can be recovered and better used to increase the revenue margin of pulp and paper industry.

2.3. Separation technologies for lignocelluloses isolation from P&P wastewater

In the literature, a number of separation methods have been proposed to isolate hemicelluloses and lignin from black liquor (BL) and prehydrolysis liquor (PHL) of pulp and paper mills. Key separation technologies for lignocelluloses recovery are discussed in this thesis.

2.3.1. Membrane technologies

In the last few years, membrane filtration has been widely considered and implemented because it works simply and efficiently. Membrane separation processes allow the passage of one component more readily than the other because of the differences in physical and/or chemical characteristics of the membrane and the permeating components. Most membranes fall into one of two broad categories: microporous membranes and solution-diffusion membranes (as illustrated in Table 2.4). Membrane processes can be classified further as symmetrical or asymmetrical membranes.

Membrane separation processes, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverses osmosis (RO), pervaporation (PV), membrane distillation (MD), and diafiltration (DF) have special values in bioenergy and biomaterials production (He et al. 2012). MF process is of great interest in the solid particles removal and large molecules separation. It does not develop significant osmotic pressures like the other membrane processes. In the arena of IFBR, UF has been utilized to concentrate and purify hemicellulose solutions with different molecular weight distributions, whereas NF has been used for the lignin recovery from prehydrolysate solutions and black liquor (BL). PV and MD are commonly used for dehydration and separation of organic compounds mixtures, while DF is usually used as downstream processing step for product concentration and purification.

Polymeric membranes, which utilize polysulfone (PS), polyethersulfone (PES), polyvinylidene fluoride (PVDF), regenerated cellulose (RC), polytetrafluoroethylene (PTFE), and fluoropolymers (FP), are the dominant membranes used for hemicellulose recovery. Whereas, ceramic membranes are the primary membranes used for lignin recovery from BL due to BL harsh conditions. Many configurations of membrane modules, such as tubular, flat sheet/plate-and-frame, spiral wound, and hollow fiber, have been used in the forest biorefinery. In IFBR, membrane separation processes are applied as a means of separation, recovery, purification, and dehydration, although they also have many other applications beyond the scope of this area.

Table 2.4: The main membrane separations processes related to IFBR modified from (He et al. 2012).

Membrane	Microfiltration (MF)	Ultrafiltration (UF)	Nanofiltration (NF)	Reverse Osmosis (RO)	Pervaporation (PV)	Membrane Distillation (MD)
Driving force	Pressure < 2 bar	Pressure 1-10 bar	Pressure 5-35 bar	Pressure 15-150 bar	Partial vapor Pressure	Vapor pressure difference
Thickness (µm)	10-150 micron	150-250 micron	150 micron	150 micron	~0.1 to few (Top layer)	20–100
Separation principle	Sieving mechanism	Sieving mechanism	Solution-diffusion	Solution-diffusion	Solution-diffusion	Vapor–liquid equilibrium
Membrane structure	Symmetric porous	Asymmetric porous	Composite	Composite	Homogeneous or composite	Symmetric or asymmetric porous
Pore size (nm)	~50–10,000	~1–100	< 2	0.1-1	Nonporous (dense)	~200–1000
Module Configuration	Flat sheet/plate-and-frame, tubular, hollow fiber	Flat sheet/plate-and-frame, tubular, spiral wound, hollow fiber, capillary	Flat sheet/plate-and-frame, tubular, spiral wound	Flat sheet Tubular Spiral wound Hollow fiber	Flat sheet/plate-and-frame, tubular, hollow fiber	Flat sheet/plate-and-frame, tubular, capillary
Membrane material	Polymeric, ceramic	Polymeric, ceramic	Polymeric	Organic polymers (cellulosic &polyamide derivatives)	Polymeric, ceramic, organic–inorganic	Hydrophobic polymer
Applications	Lignin and hemicelluloses recovery and enzyme recovery	Lignin and hemicelluloses recovery, enzyme recovery	Lignin and hemicelluloses recovery and fermentation inhibitors removal	Lignin and hemicelluloses recovery and fermentation inhibitors removal	Bioethanol recovery	Bioethanol recovery

2.3.1.1. Hemicelluloses recovery

During the pulping, hemicelluloses and lignin are extracted from wood chips and partially end up in the black or prehydrolysis liquor. The fate of the hemicellulose is traditionally, and unfortunately, limited to discharge in wastewater streams for aerobic/anaerobic biological treatment (Persson and Jonsson, 2009). Preferably, it can be burned in the mill’s recovery boiler as BL to regenerate energy. Since the heat value that can be generated of hemicelluloses (13.6 MJ/kg) is nearly half of that of lignin ((26.9 MJ/kg)), using hemicelluloses as a fuel source is unjustifiable (Thorp, 2005).

Hemicelluloses recovery would be beneficial to pulp mills, not only to increase profitability and competitiveness but also to reduce the organic loading to the wastewater treatment facility and minimize overloading to the bottleneck recovery boiler. However, highly developed separation technologies that are cost efficient and environmentally friendly are needed. Isolation of hemicelluloses from different raw materials sources has been studied since the 1950s. However, more ultimate and profitable separation methods, which prevent hemicelluloses degradation and maximize the value derived from hemicellulose, are lacking. Membrane technologies have appeared as a promising separation method for hemicellulose isolation and purification from different raw materials without degradation. This literature review discusses MF, UF, NF, and DF for hemicellulose recovery and purification

2.3.1.1.1. Microfiltration (MF)

MF is a membrane separation process that can be used to separate particles or biological entities in the range of ~ 0.05 µm to 10.0 µm from fluids by passage through a microporous membrane filter. Many studies were conducted to examine the suitability of MF to remove particles and suspended matter from the process water originating from the pulp and paper industry, as summarized in Table 2.5. MF effectively removed all the suspended matter. However, hemicelluloses are partly retained.

Persson et al. (2006) extracted hemicelluloses from process water of the production of Masonite using a method involving three steps: removal of high molecular species by MF, pre-concentration of hemicelluloses by UF, and reduction of the salts concentration and monosaccharides by DF. Their results show that MF could efficiently remove high molar mass compounds. The total dry solid content (TDS) was 0.6 wt% in the primary process water, 0.35 wt% in the permeate, and 5.2 wt% in the retentate. Andersson et al. (2007) confirmed that particles and suspended matters in the process water could be removed by MF. In their study, turbidity decreased from 960 nephelometric turbidity units (NTU) in the process water to 4 NTU in the permeate. Moreover, Hasan et al. (2011) reported that colloidal and particle removal, using MF, is feasible and can significantly reduce turbidity when they examined the separation of sugar maple wood extracts by a ceramic membrane of two different pore sizes: 0.2 µm and 0.01 µm.

Krawczyk and Jönsson, (2011) investigated the influence of membrane pore size (0.2, 0.4 and 0.8µm), cross-flow velocity, and back pulsing on membrane performance during the MF of thermomechanical pulping (TMP) process water. The results revealed the challenges of recovering the pure water flux of the 0.4 and 0.8µm membranes. However, increasing cross-flow velocity and back pulsing had a positive effect on the flux, but only a minor influence on the retention. Also, MF followed by UF was found to be a suitable combination, providing a concentrated and purified hemicellulose fraction (Persson et al. 2007; Krawczyk et al. 2013). MF has shown high capabilities to clarify the process water and successfully remove all suspended matters.

Table 2.5: Summary of MF membrane process for hemicelluloses recovery

Raw material	Characteristics of membrane			Operating conditions						Performance		Reference
	Pore size (µm)	Material	Configuration	Scale	VR	Hemi (g/l)	Temp (C°)	TMP (bar)	Cross flow velocity	Flux (L.M^{-2}.h^{-1})	Hemi rejection (%)	
Spruce wood process water	0.2, 0.4, 0.8	Ceramic	Tubular	Lab scale	–	1.04/0.05 /0.12	80	0.5	4 m/s	60 - 350	>50	Krawczyk and Jönsson (2011)
Sugar maple wood extracts	0.2 /0.01	Ceramic	–[b]	Lab scale	–	–	20	1.5-2	1.3, 2, 2.6 m/s	–	–	Hasan et al. (2011)
Spruce wood process water	0.2	Ceramic	Tubular	Lab scale	~0.98	0.8	60	0.7	5 m/s	60 - 260	80	Krawczyk et al. (2013)
Spruce wood process water	0.2	PTFE[a]	flat sheet/plate-and-frame	Lab scale	–	1-1.5	20 -25	4	8.5 L/min	–	–	Persson et al. (2010)
Spruce wood Process water	0.2	Ceramic	Tubular	Lab scale	0.98	1.16	80	0.7	4 m/s	80-380	55-90	Persson et al. (2010)

[a] PTFE = polytetrafluoroethylene.

[b] –indicates value not reported or not available.

[c] Volume Reduction (VR) is the ratio between the volume of the permeate and the initial volume of the feed.

2.3.1.1.2. Ultrafiltration (UF)

Currently, the UF membrane is widely used for various applications because of its high throughput, low operation cost, excellent selectivity, and requires no chemicals additives, thereby minimizing the extent of denaturation and degradation of biological products. In the pulp and paper industry, UF membrane is an effective method for the treatment of pulp and paper effluent. It removes most of the polluting substances, consisting of high molecular mass compounds, efficiently (Maartens et al. 2002) and recycles valuable materials (Mänttäri et al. 2002; Huang et al. 2008; Persson et al. 2010). Koivula et al. (2011) stated that recovery, purification, concentration, and fractionation of hemicelluloses from wood hydrolysates are most attractive characteristics of UF membrane.

Hemicellulose isolation from process streams of forest industry using UF membrane has been investigated intensively by many researchers (Persson et al. 2006; Andersson et al. 2007; Persson and Jonsson, 2009). Table 2.6 summarizes the results of recent studies of UF membrane process for hemicelluloses recovery. Persson et al. (2010) investigated four filtrations and membrane filtration process – namely, drum filtration, MF, UF, and NF – to fractionate the process water from a TMP mill. The permeate from the MF stage was ultrafiltered to concentrate and purify the hemicelluloses. They concluded that UF recovered about 95% of the hemicelluloses. Persson and Jönsson, (2010) isolated galactoglucomannan (GGM) from a TMP mill process water using UF membrane. They suggested that to retain the hemicelluloses, a UF membrane with a molecular weight cut-off between 1 and 10kDa should be used.

A comparable study was conducted by Al Manasrah et al. (2012). They recovered GGM from wood hydrolysate using regenerated cellulose UF membranes with different molecular weight cut-off values 5kDa, 10kDa, and 30kDa. 5kDa membrane achieved 88% GGM retention, 63% purity, and 70% recovery rate at a VR of 86%, whereas, cut-off values 10 and 30kDa have partly separated GGM. However, Persson et al. (2006, 2007) achieved 80% purity when separated hemicelluloses TMP process water using hydrophilic UF membranes. Another study on the recovery of hemicellulose was reported by Jun et al. (2012), who extracted hemicellulose from aspen chips before kraft pulping utilizing white kraft liquor by UF. They were able to recover xylan at levels of up to 48 g kg^{-1} of dry chips.

Other studies compared UF with their counterparts. For example, Liu et al. (2014) compared the performance of UF and NF for hemicelluloses concentration. The results of this study showed that NF gave much better rejection rates on organic compounds than UF. In the same way, Ajao et al. (2015a) conducted experiments to screen and select suitable organic membranes among three membranes separation processes – RO, NF, and UF – to concentrate and detoxify Kraft prehydrolysate. The three membranes demonstrated high sugar retentions compared to inhibitor removal. They were, however, not effective for the removal of the phenolic compounds.

During hemicellulose isolation, several studies have proved that a hydrophobic membrane has a higher fouling tendency than a hydrophilic membrane (Persson and Jonsson, 2009; Koivula et al. 2011), while most of the foulants, exhibited in the pulp and paper effluents, are of phenolic and hydrophobic nature. However, pre-treatment methods, such as pH adjustment, ion-exchange resin, use of MF, and activated carbon (AC) adsorption had positive impacts on the filtration capability of UF membrane (Koivula et al. 2011, Liu et al. 2014). From these results, it was demonstrated that effective pretreatment method not only decreases membrane fouling but also enhances the efficiency of membrane cleaning.

Table 2.6: Summary of UF membrane process for hemicelluloses recovery

Raw material	Characteristics of membrane			Operating conditions							Performance		Reference
	MWCO (kDa)	Material[a]	Configuration	Scale	VR[c]	Hemi (g/l)	pH	Temp (C°)	TMP (bar)	Cross flow velocity	Flux ($L.M^{-2}.h^{-1}$)	Hemi rejection (%)	
Spruce wood process water	5/10	PS/PS	Spiral wound	Lab scale	0, 0.7/0.97	14/53.5	–[b]	60	3/5	20/21.6 L/min	32 - 170	70 - 96	Krawczyk et al. (2013)
Spruce wood process water	5	PES	Spiral wound	Lab scale	0.99	0.83	–	80	6	25 L/min	10 -135	93 - 99	Persson et al. (2010)
Birch and Spruce hydrolysate	5/10	PS/RC	–	Lab scale	0.66	–	7 - 8	60/55	3/5.5	1.5 m/s	3 – 55/30 – 179/ 20 – 190	61 - 76	Koivula et al. (2011)
Spruce wood process water	10	PVDF	Spiral wound	Lab scale	0.75 – 0.99	0.5- 0.9	–	60	0.5 – 2.5	20 L/min	20 - 160	72 - 94	Persson and Jönsson et al. (2010)
Spruce wood Process water	1	PVDF	Spiral wound	Lab scale	0 – 0.95	0.5- 0.9	–	60	4 - 10	10 L/min	<105	<90	Persson and Jönsson et al. (2010)
Spruce wood process water	5	PS	Spiral wound	Lab scale	–	0.7	–	75	2 - 6	20 L/min	40 - 90	<90	Persson and Jönsson et al. (2010)
Spruce sawdust extract liquor	30/10/5	RC	flat sheet/plate-and-frame	Lab scale	0.86	4.7	–	65	1/3/3.5	2 m/s	~ 107 - 245	88	Al Manasrah et al. (2012)
Aspen wood chips extracted liquor	10	PS	–	Lab scale	–	–	13.98	70 - 90	3.1 - 3.45	–	–	–	Jun et al. (2012)

[a] RC = regenerated cellulose, PS = polysulfone, PES = polyethersulfone, PVDF = polyvinylidene fluoride.

[b] –indicates value not reported or not available.

[c] Volume Reduction (VR) is the ratio between the volume of the permeate and the initial volume of the feed.

2.3.1.1.3. Nanofiltration (NF)

NF has been implemented effectively in a wide range of applications, such as the removal of organic contaminants from the aqueous solutions (Teella et al. 2011) and partial fractionation and concentration of the sugars (Sjöman et al. 2007). NF has been used widely for a long time, and while its industrial application has been limited to moderate pH for sometimes (Schlesinger et al. 2006). More recently, NF membranes for a broad range of pH have become commercially available.

In the forest industry, NF of effluents, from the alkaline extraction stage, has been investigated extensively using both polymeric and ceramic membranes (Persson et al. 2010; Jönsson et al. 2008; Schlesinger et al. 2006]. Table 2.7 summarizes the results of recent studies of NF membrane process for hemicelluloses recovery. Schlesinger et al. (2006) investigated the performance of five polymeric NF and tight UF membranes during the separation of hemicellulosic materials from process liquors containing 200 g/L sodium hydroxide. The experimental data showed that hemicellulose is almost quantitatively retained at molar masses above 1,000 g/mol. Also, Liu et al. (2014) compared the performance of UF and NF membranes during hemicellulose concentration. Their results indicated that NF gave much better rejection rates on organic compounds than UF. Furthermore, Ajao et al. (2015b) evaluated the performance of six organic NF membranes with different MWCOs and polymer materials to examine their ability to concentrate hemicellulosic sugars from prehydrolysate solution. 200 Da membrane was superior compared with others membranes’ cut-offs and achieved 99% sugars retention. Sjoman et al. (2007) carried out another NF study on hemicelluloses recovery to recover d-xylose in the permeate from a hemicelluloses hydrolyzate stream. According to the results, NF showed a promising ability in recovering xylose from hemicellulose hydrolyzate permeate.

Other reported applications include the effects of fouling on the performance of NF membrane separation process. Shen et al. (2013) used a combined process, involving activated carbon adsorption, ion exchange resin treatment, and membrane concentration, to concentrate dissolved organic compounds from prehydrolysis liquor (PHL). Similarly, Ahsan et al. (2014) also employed activated carbon to reduce the fouling of NF and RO during the recovery and concentration of sugar and acetic acid from PHL. Pretreatment of pulp and paper wastewater, prior to filtration, could efficiently reduce the membrane fouling. Also, membranes with a high contact angle were found to have worse fouling during filtrations of paper mill process water at constant pressure compared with membranes with a low contact angle. High fouling was also observed in the filtrations made at an acidic pH solution, as compared to a neutral pH. Additionally, the retention of organic substances was significantly better at a neutral pH, and the hydrophilicity of the membrane increased with the increase in pH.

NF has been used in a wide range of prehydrolysate solutions. It showed good performance regarding pure permeate product and low energy consumption. However, the fouling phenomenon is one of the main shortcomings facing NF’s commercialization. Therefore, treatment of PHL, prior to the NF step, might be an effective way to improve filterability of the NF membrane process. Also, future research should include pilot scale experiments to enable a detailed economic analysis of the membrane system in a biorefinery process as few studies have examined the feasibility of using NF membranes for the filtration of paper mill process water.

Table 2.7: Summary of NF membrane process for hemicelluloses recovery

Raw material	**Characteristics of membrane**			**Operating conditions**							**Performance**		**Reference**
	MWCO (kDa)	Material[a]	Configuration	Scale	VR[b]	Hemi (g/l)	pH	Temp. (C°)	TMP (bar)	Cross flow velocity	Flux (L.M^{-2}.h^{-1})	Hemi rejection (%)	
Spruce wood Process water	1	–[a]	Spiral wound	Lab scale	0.5-0.76	0.07	–	50	20	18L/min	63/27	100	Persson et al. (2010)
Hardwood black liquor	1	–	Tubular	Lab scale	0.7	2.5	–	60	25	4 m/s	110	–	Jönsson et al. (2008)
Aspen/ Maple wood prehydrolysate	0.2	Polyamide/ CelluloSe acetate	flat sheet/plate-and-frame	Lab scale	–	–	–	40	21/35	0.45/0.66 m/s	12	99	Ajao et al. (2015a)
Hemicellulose hydrolysates	0.15/0.3	Polysulfone	–	Lab scale	–	–	–	40/50 /60	20/25/ 30/35	–	36.4 – 180.6	78-82/ 86-88	Sjöman et al. (2007)
Aspen/ Maple wood prehydrolysate	0.15/3.5	polyamide	flat sheet/plate-and-frame	Lab scale	–	–	2.8/3.5	30/40	5.5/21	0.4/0.5 m/s	14	84 -92	Ajao et al. (2015b)
Maple, Poplar and Birch prehydrolysis liquor	0.15/0.3	polyamide	–	Lab scale	0.5	31/196	4.3	–	34.5	–	–	74/99	Ahsan et al. (2014)
Maple, Poplar and Birch prehydrolysis	–	polysulfone	–	Lab scale	0.3	172	–	–	34.5	–	190 – 31.6	–	Wang et al. (2015)

[a] –indicates value not reported or not available.

[b] Volume Reduction (VR) is the ratio between the volume of the permeate and the initial volume of the feed.

2.3.1.1.4. Diafiltration (DF)

DF is a technique that selectively utilizes permeable (porous) materials to separate the components of solutions and suspensions based on their molecular size. Recent technological advances in membrane technologies and system design have created a new opportunity for efficient DF of various organic polymers and inorganic chemicals. However, the success of a DF for performing fractionation and concentration processes is largely associated with the selection of an appropriate membrane.

In general, DF is commonly used as downstream processing steps for product concentration and purification. For example, Andersson et al. (2007) used DF to recover hemicelluloses from process water of a TMP mill using spruce. They found that the purity of hemicellulose was increased from 57 to 77% after DF when they compared the UF retentate before and after DF. Also, González-Muñoz et al. (2011) assessed the performance of DF as a method for purification of oligosaccharides obtained by auto-hydrolysis of Pinus pinaster wood. Continuous DF has been observed to result in an increased weight percent of substituted oligosaccharides, from 79.2% up to 94.7%. Further, the selective removal of monosaccharides rose from 4.3 up to 17.8 as a substituted oligosaccharides to monosaccharides ratio.

Al Manasrah et al. (2012) also reported that DF could achieve a partial removal of xylan and a complete removal of monosaccharides from the GGM rich concentrate. González-Muñoz et al. (2013) studied the fractionation of extracted hemicellulosic saccharides from Pinus pinaster wood by a multistep membrane process. The solution from the hydrothermal process was subjected to consecutive steps of DF using membranes of 0.3, 1, 3, 5, and 10kDa. This work resulted in streams containing poly- and oligosaccharides (POHS) of different molecular mass distribution with decreased contents of monosaccharides. The DF approach is suitable for obtaining a product with a high purity, depending on the molecules of interest and process conditions. Thus, selecting the most compatible membrane processes for overall effectiveness is important.

2.3.1.2. Lignin recovery

Several possible techniques for the removal of lignin from the industrial residue stream have been tested. The most common applied methods for the extraction of lignin are precipitation and filtration (Arkell et al. 2014). However, the differential precipitation of the liquor gradually decreases the pH of the solution, which is a clear disadvantage for this method. Also, colloids formation during the precipitation process complicates subsequent filtration and separation steps, resulting in a relatively low purity of the lignin obtained. As effective separation technologies, membrane filtration can be tailored to the required degree of purification compared to traditional separation methods.

Membrane processes have been applied since the late sixties, but most of the applications have focused on the treatment of bleach plant effluent and fractionation of spent sulfite liquor (Jönsson et al. 2008). More recently, much effort has been spent, and many in-depth investigations have been carried out, to reduce the organic load to the recovery boiler. Consequently, a wide range of pressure-driven liquid phase membrane separation processes, including MF, UF, NF, RO, or a combination of them, has been studied. UF and NF membranes were the most common types among them. This can be attributed to the size of the lignin molecules. UF and NF have been applied at both lab- and pilot-scale studies.

Many studies investigated the applications of ceramic UF membranes to isolate lignin from cooking liquors (Wallberg and Jonsson 2003; Jönsson et al. 2008; Toledano et al. 2010). Table 2.8 summarizes the results of recent studies. Wallberg and Jonsson, (2003) and Toledano et al. (2010) investigated the performance of UF membranes for lignin isolation from black liquor (BL) solutions. It was found that UF membranes were an effective method to fractionate lignin. However, Holmqvist et al. (2005) found that membrane flux for treating hardwood cooking liquor was much higher, and the retention was much lower compared to that for treating softwood liquor.

Likewise, some studies examined the use of polymeric UF membranes for lignin recovery (Wallberg and Jönsson 2006; Jönsson et al. 2008). The results of these studies indicated that the extraction of lignin from kraft cooking liquor, taken directly from a continuous digester without adjustment of pH and temperature, is possible. On the other hand, NF membranes were also applied to separate the dissolved lignin from pulp and paper mills BL. As shown in Table 2.8, both ceramic and polymeric NF membranes were studied. Arkell et al. (2014) reported that polymeric NF membranes with a MWCO of 1kDa had the best performance when compared to the other membranes.

Alternatively, several studies investigated hybrid membrane systems that apply combinations of UF with NF to treat BLs. Keyoumu et al. (2004) and Dafinov et al. (2005) reported that NF and UF were technically feasible ways to remove the organic materials from kraft pulping BLs and could achieve a higher flux in a batch process. Furthermore, Jonsson et al. (2008) studied the performance of hybrid UF/NF and evaporation/UF processes for lignin extraction from BLs and cooking liquor. UF/NF process achieved a higher product concentration and purity compared to evaporation/UF process. Most of these studies have reported that there are certain ranges of the molecular masses that have a negative impact on filtration capacity. It is recommended that to decrease membrane fouling, the focus should be not only on the highest removal of lignin and hemicellulose but also on the sizes of hemicelluloses and lignin molecules.

Polymeric and Ceramic membranes for lignin recovery and purification were the focus of the majority of the reported studies. Ceramic membranes have been shown to possess better performance over polymeric membranes (Arkell et al. 2014). Compared to polymeric membranes, ceramic membranes can withstand BLs without pH and temperature adjustment because of their high thermal and chemical stability. Moreover, ceramic membranes are slower to foul and can be recovered utilizing more extreme membrane performance recovery systems that polymeric membranes are not able to handle. Although the ceramic membranes exhibit a higher capital cost compared to polymeric membranes, they are capable of achieving a high productivity as a result of their inherent hydrophilicity, which leads to reduced organic fouling.

The performance of membrane technologies also depends on the application of appropriate module design and configurations. There are two main types of modules used in BL treatment: plate and frame module and tubular module. The plate and frame module is the simplest configuration, comprising two end plates, a flat sheet membrane, and spacers; whereas in the tubular module configuration, the membrane is often cast on the inside of a tubular support, the feed will be pumped through the tube, and the permeate will be collected on the outer surface of the tube into a shell which could hold one or many tubes packed in a bundle. The feasibility of membrane technology for lignin recovery from BL has been widely studied. Jonsson et al. (2008) studied UF and a hybrid UF/NF process of cooking liquor and BL. The production cost of

UF of extracted BL and the hybrid UF/NF process was € 33 per ton of lignin produced. Holmqvist et al. (2005) conducted a cost estimate of lignin fuel extraction from BL. The cost was approximately € 20 per MWh of the calorific value of the lignin fuel. Also, Jönsson and Wallberg (2009) estimated recovery costs of hardwood lignin by a ceramic UF membrane with a MWCO of 15kDa from two process streams in a Kraft pulp mill processing 200 m^3/h pulping liquor. Lignin was concentrated to 100 g/L, and the estimated cost was about € 60 per ton of lignin. This cost could be further reduced if high membrane fluxes could be achieved.

Both UF and NF showed a high performance in the removal of hemicelluloses and lignin from BLs. However, some issues need further investigation. Since each molecular weight of the lignin has designated applications, the remaining question is whether the quality of purified lignin fulfills the demands for high-value-added products. Also, to date, most of the studies have been conducted on a lab-scale, with a few pilot- and full-scale applications. Long-term feasibility studies at pilot-scale and full-scale applications are needed to offer a starting point for further optimization of separation processes in lignin recovery. Figure 2.3 shows a proposed technical path for hemicelluloses and lignin recovery and purification from pulp and paper effluents.

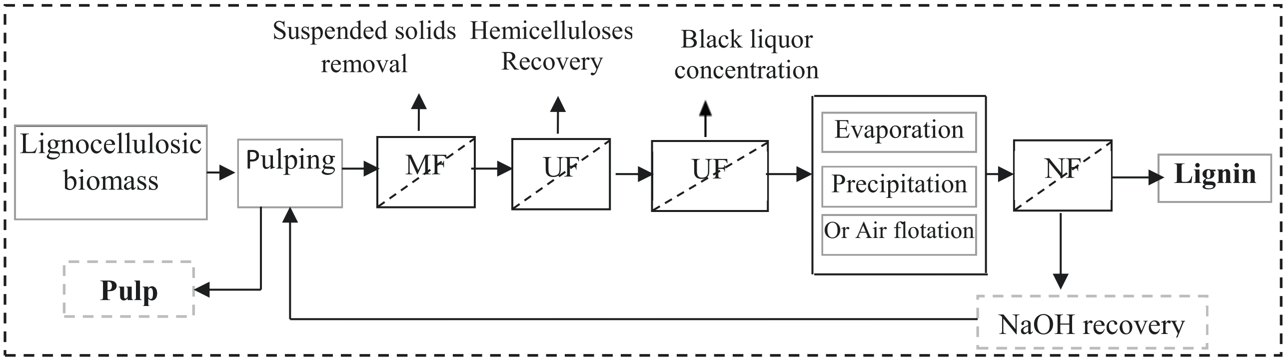

Figure 2.3: Separation and recovery of hemicelluloses and lignins from product stream

Table 2.8: Summary of UF & NF membrane processes for lignin recovery

Raw material	Class	Characteristics of membrane			Operating conditions							Performance		Reference
		MWCO (kDa)	Material[a]	Configuration	Scale	VR[b]	Lignin (g/l)	pH	Temp (C°)	TMP (bar)	Cross flow velocity	Flux (L.M^{-2}.h^{-1})	Lignin rejection (%)	
Hardwood kraft black liquor (permeate of UF)	NF	1	–[a]	Tubular	Lab	0.7	54	–	60	25	4 m/s	110	80	Jönsson et al. (2008)
Softwood Kraft black liquor	UF	20	Al_2O_3/TiO_2	Tubular	–	–	57.6	13	90	2	5 m/s	–	–	Arkell et al. (2014)
Softwood Kraft black liquor	NF	1	TiO_2	Tubular	–	0.85	252	13	90	2 - 20	4 -2 m/s	159	~78	Arkell et al. (2014)
Softwood Kraft black liquor	NF	0.2//0.6 /1	–	Tubular	–	0.70	282	13	70	5 - 35	4 -2 m/s	81	~90	Arkell et al. (2014)
Spruce wood Process water	NF	1	ZrO_2	–	Lab	–	48.8	–	25	2 - 6	1.5 m/s	1-5	67.4	Keyoumu et al. (2004)
Black liquor	NF	1	TiO_2	Tubular	Lab	–	–	12	30	3 - 7	2.1 m/s	12-22	–	Dafinov et al. (2005)
Birchwood chips extract	UF	5	Polysulphone	Flat sheet	Lab	0.66	2.2 – 4.4	–	60	5.5	1.5 m/s	`5-120	–	Strand et al. (2015)
Woody spent liquor	NF/UF	1/4	TiO_2 and ZrO_2	Flat sheet /Tubular	Lab	–	16 - 24	–	25	5	2 m/s	30-139	75-94	Servaes et al. (2016)
Spruce wood extract	UF	5/1	TiO_2 and ZrO_3	–	Pilot	–	–	–	40	2.6//2.2	1.7 m/s	–	–	Westerberg et al. (2012)
Olive Tree Black liquor	UF	300/150 /15/5	Ceramic	Tubular	Lab	–	–	–	–	–	–	–	–	Toledano et al. (2013)
Spent sulfite liquors	UF	1/5/15	Ceramic TiO_2	–	Pilot	0.78/0.5 /0.15	44.25 / 39.57/ 40.67	3.3	20	1.8 - 2	8 m/s	55.45/ 5.77/ 6.00	45.67/65.38 / 41.69	Fernández et al. (2015)

[a] –indicates value not reported or not available.

[b] Volume Reduction (VR) is the ratio between the volume of the permeate and the initial volume of the feed.

2.3.1.3. Wood extractives recovery

Different methods have been investigated to separate wood extractives from BL. One of the possible alternatives for separation of wood extractives is membrane separation processes (Valto et al. 2012). Membrane-based techniques are known to offer a high level of purification coupled with a relatively low level of energy consumption. However, only a few studies were conducted for the use of the membrane technology in the removal of wood extractives, because membrane fouling hinders the wide adoption of this technology.

Leiviskä et al. (2009) characterized wastewater (influent and effluent) from integrated kraft pulp and paper mill by MF (8, 3, 0.45 and 0.22 µm) and UF (100, 50, 30 and 3kDa) membranes, based on different size fractions. It was found that the sieved influent contained about 14.3 mg/L of wood extractives, of which 12.8 mg/L were resin and fatty acids and 1.5 mg/L sterols. The sieved effluent contained 1.7 mg/L of wood extractives, of which 1.45 mg/L were resin and fatty acids and 0.26 mg/L sterols. Leiviskä et al. (2009) also reported that MF with a large pore size (8 µm) was able to remove 30–50% of wood extractives.

In another study, Puro et al. (2011) achieved 90% extractives retention from two chemo thermomechanical (CTMP) pulp mill process waters using one regenerated cellulose (RC) UF membrane and two polyethersulphones (PES) UF membranes. Kilulya et al. (2012) revealed that the utilization of an ionic liquid, in the extraction of lipophilic wood extractives, coupled with liquid membrane extraction systems, offered a possible separation method. Pinto (2014) tested different NF membranes and UF membranes with a lower molecular weight cut-off for the concentration of polyphenolic compounds (gallic, tannic acids and maltose) and carbohydrate from an ethanolic extract of *Eucalyptus globulus* bark. All the tested membranes exhibited selective retention of polyphenolic compounds.

2.3.1.4. Black liquor concentration

Kraft pulp mills have utilized BLs as an energy source since the 1930s. Weak black liquor (WBL) is typically 15% dry solids and 85% water. It is usually concentrated to 65 - 80% by multi-effect evaporators and burned in a recovery boiler for the energy production. This technique consumes much energy during the evaporation of the water in the large steam-heated multiple-effect evaporators. Membrane filtration has been proposed as possible techniques to reduce this amount of water prior to evaporation. Pre-concentration of BL streams by membrane processes reduces power consumption rate in the evaporation stages.

However, unlike conventional membrane separation processes for water purification/desalination applications – the membranes required for concentrating BL must withstand the high pH (>12), high temperature (80-90°C), and different fouling species in BL. Technically, ceramic membranes appear to be an appropriate choice for this task. Liu et al. (2011) studied BL concentration conditions using UF ceramic membrane technology. They concluded that BL could be concentrated up to 4-6 times by UF membrane. However, ceramic membranes are characterized by higher capital costs. In contrast, polymeric membranes are available at reasonable prices, but without pretreatment, are not withstand the harsh natures of the BL. To overcome these problem, the U.S. Department of Energy developed sacrificial protective coating materials that can be regenerated in-situ to enable high-performance membranes. They believe that this layer will prevent foulants in the WBL from adhering to the membranes, while also giving protection from BL harsh conditions (Peter et al. 2015). Also, New Logic International developed

“Vibratory Shear Enhanced Process” (VSEP™) for the treatment of BL streams without causing the fouling problems exhibited by conventional membrane systems. VSEP can be used with polymer MC, UF, NF and RO membranes (Adnan et al. 2010).This technology applies vibration technique to reduce fouling, and it has been studied in the pulp and paper industry for applications in black liquor concentration, paper mill effluent, paper coating effluent, white-water treatment, and paperboard mill effluent (Adnan et al. 2010).

2.3.1.1. Fouling phenomenon and control

In recent years, membrane separation processes have received much attention from lab-scale studies to wide applications in industrial operations. However, in the pulp and paper industry, fouling is the most determining factor affecting the broad applications of membrane filtration because of the complexity and high fouling tendency of wood hydrolysates (Koivula et al. 2011; Gönder et al. 2012). The wood hydrolysate effluents contain various substances such as carbohydrates, extractives, and lignins. Based on particle sizes, the pulp and paper mill effluents categorized into three groups: suspended solids (size > 2 µm), colloidal substances (0.1-2 µm) and dissolved substances (< 0.1 µm) (Puro et al. 2002). The main difference between the types of membrane fouling is the nature of the particles that cause the fouling. During pulp and paper process wastewater filtration, organic and inorganic were the most dominant mechanisms of membrane fouling.

The constituents that cause membrane fouling during the filtration of pulp and paper process water were investigated by relatively few studies. Weis et al. (2005) reported that resin, fatty acids and to some extent lignans were the main wood extractives that caused membrane fouling during the filtration of pulp and paper mill wastewaters. Also, Maartens et al. (2002) treated pulp and paper effluent by UF and observed that foulants present in the effluent were of a phenolic nature. Puro et al. (2011) studied the fouling of extractives of two process wastewater originated from a pulping process using a mixture of hardwood and softwood and softwood alone by UF. They found that fatty and resin acids were the most abundant foulant materials in the membranes; however, they also noticed that sterols contributed remarkably to the fouling of RC membrane although their amount in the process wastewaters was low. In general, detailed information about the nature of foulants is lack, due to the complexity of constitutes in pulp and paper wastewaters and limited studies of membrane fouling in IFBR.

Based on the attachment of particles to the membrane surface, membrane fouling can be classified into reversible and irreversible fouling. Chen et al. (2015) characterized membrane foulants in a fine paper mill effluent filtration by a polyethersulfone (PES) UF membrane. Their results indicated that the reversible membrane foulants accounted for 85.52% of the total foulants and mainly came from retention aids, drainage aids, and wet strength resins, whereas the irreversible adsorptive foulants accounted for 14.48% and mostly originated from sizing agents and coating chemicals.

In biorefining and bioenergy production, great progress has been made in understanding the connections between the membrane types, foulants, and the operating conditions (Maartens et al. 2002; Puro et al. 2011). Puro et al. (2011) reported that polyethersulfone (PES) has greater fouling tendency than regenerated cellulose (RC) membranes. According to Puro et al. (2010), surface roughness has a positive effect on membrane fouling in pulp and paper mill applications. It was also found that a membrane with a rougher surface has more fouling tendency than a membrane with a smoother surface. Also, compared to tighter membranes, looser membranes are more sensitive to fouling during pulp mills effluent filtration. On the other hand, Maartens et al. (2002) and Weis et al. (2005) indicated that the hydrophilicity of the membranes has a major role in the membrane fouling reduction during pulp and paper effluents filtration.

However, membrane fouling characterization in pulp and paper mill effluents filtration using analytical methods, such as atennual total reflectance Fourier transform infrared spectroscopy (ATRFTIR), scanning electron microscope (SEM), energy dispersive spectrometry (EDS), and contact angle and zeta potential measurements, are very limited (Carlsson et al. 1998; Kallioinen et al. 2003). Carlsson et al. (1998) used a surface spectroscopic method for membranes fouling study in pulp mill effluent treatment. They noticed that fatty acids were the dominant foulant materials in the membranes rather than resin acids. Kallioinen et al. (2003) analyzed organic foulants by ATR-FTIR during the filtration of ground wood water. Fatty and resin acids and cellulosic species were the major foulant materials. Puro et al. (2002) studied organic foulants in membranes fouled by pulp and paper mill effluent using solid-liquid extraction and further identified foulants with gas chromatography (GC). They found that fatty and resin acids and some traces of lignans fouled the membranes in the filtration of ground wood water. However, the hydrophobic membranes were more severely affected by these acids and lignans than the hydrophilic membranes.

Many strategies have been developed to mitigate membrane fouling, including physical or chemical cleaning, membrane surface modification, optimization of membrane and biomass characteristics. Pretreatment methods gained increasing popularity in membrane technology. Effects of the pretreatment methods on membrane fouling are briefly described in Table 2.9. Ko and Fan (2010) added laccase, prior to filtration of pulp and paper wastewater, and concluded that a laccase pretreatment and membrane process is a good combination for treating the pulp and paper effluents. However, inactivated laccase addition caused further flux reduction. Persson and Jönsson (2009) reported that pretreatment of forest industry effluents by activated carbon before filtration had positive impacts on permeate flux improvement and membrane fouling reduction. However, pretreatment methods have to be tailored separately, because each pulp and paper effluent has different characteristics, depending on the pulping process such as thermomechanical (TMP) or chemithermomechanical pulp (CTMP) or the raw material used in the pulp manufacturing. Membrane fouling could be reduced if the process operating conditions could be optimized.

Among fouling control and prevention strategies, chemical cleaning remains the favored method for real industrial applications. Cleaning agents such as detergents, acids or alkalis are often used to clean fouled membranes. However, the chemical cleaning sometimes damages the membrane materials and causes secondary pollution. Another problem associated with chemical cleaning is that cleaning often modifies membrane characteristics that are critical to filtration such as membrane hydrophobicity and charge. Alternatively, ultrasound has also been used as a method for cleaning, but studies on ultrasonic membrane cleaning are limited. Also, the enhancement of membrane shear-rates has been considered one of the most efficient ways for fouling control.

Fouling phenomena during the application of membrane technology in IFBR represents a significant impediment to the adoption of this technology on a large scale. Fouling leads to a decrease in filtration capacity, an increase in the number of membrane cleanings required, and a reduction in membrane lifetime, consequently leading to higher operating and membrane replacement cost. Therefore, for the vast implementation of membrane technology in IFBR, much research and development effort are needed for the development of effective membrane fouling control strategies.

Table 2.9: Effects of the pretreatment methods on membrane fouling control

Raw material	Pretreatment Method	Results
Masonite process stream/Birch and spruce sawdust hydrolysate	pH adjustment	Lowering the pH from 4.5 to 3 led to less fouling of RC membrane, but a lower flux of the composite fluoropolymer membrane (Persson and Jönsson, 2009). pH (7–8) had a minor influence on the filtration capacity of RC UF membrane (Koivula et al. 2011). pH adjustment to 10 significantly reduced UF membrane fouling (Gönder et al. 2012). Filtration at neutral pH associated with reduced fouling (Chen et al. 2016).
Birch and spruce sawdust hydrolysate	Centrifugation at room temperature	No significant influence on the filtration capacity was noticed (Koivula et al. 2011).
PHL	Ion exchange resin	Ti resulted in significant removal of acetic acid (Shen et al. 2013). Increased oligosaccharides purity (Ko and Fan, 2010).
Masonite process stream/Birch and spruce hydrolysate/PHL	Activated carbon adsorption	Resulted in higher flux and less fouling of both hydrophilic and hydrophobic membranes (Persson and Jönsson 2009). Membrane filterability improved (Koivula et al. 2011; Shen et al. 2013).
Spruce hydrolysate	Hemp adsorption	No significant influence on the foulants adsorption (Koivula et al. 2011).
Birch and spruce sawdust hydrolysate/ Wood auto-hydrolyzate	Oxidation by pulsed corona discharge (PCD)	Significant improvement in the filtration capacity (Koivula et al. 2011). Its effect on the fouling of the cellulose-based UF membranes was low (Mänttäri et al. 2015).
PHL/Kraft pulp and paper mill effluent	Laccase addition	Membrane filterability increased (Wang et al. 2015) Polymerized pollutants removed without significant fouling (Ko and Fan 2010).
Kraft pulp and paper mill effluent	Inactivated laccase addition	Caused further flux reduction (Ko and Fan 2010).
Hemicelluloses hydrolysate from TMP mill	MF	MF with a pore size of 0.1 µm removed colloidal extractives while a high amount of high molecular mass hemicelluloses passed to permeate (Thuvander and Jönsson, 2016).

2.3.2. Liquid-Liquid extraction (LLE)

The use of liquid-liquid extraction has been deemed as a potentially feasible technique in numerous industrial processes for valuable materials recovery or undesirable impurities removal.

Namely, in the forest biorefinery, LLE has been used in the separation of biofuels from dilute mixtures, extraction of acetic acid from biomass hydrolysates, and removing of inhibitors from biomass hydrolysates. Solvent extraction is a simple, clean, and fast process (Mussatto et al. 2005). Also, used solvents can be recovered (Cruz et al. 1999), and high purity can be achieved (Hassan et al. 2013). Besides, extraction reduces the need to evaporate huge amounts of water, which is very energy demanding (Kiss et al. 2016). Nevertheless, the extraction of carbohydrates from an aqueous media into an immiscible organic solution using such technique is still lacking in the literature (John Griffin and Shu, 2004). Sparse studies have been investigated the extraction of lignocellulosic materials from aqueous feeds. Table 2.10 shows the results of hemicelluloses extraction from aqueous solutions.

Several solvents have been tested for the extraction of lignocellulosic materials from aqueous solutions. For example, ethyl acetate and diethyl ether have been used for lignin-derived compounds removal from *Eucalyptus* hydrolysates (Cruz et al. 1999), whereas boronic acid extractants have been used for purifying and concentrating the sugars present in hemicellulose hydrolysates. Also, the use of butanol, methyl tertiary-butyl ether (MTBE), and n-hexane for the recovery of mono- and disaccharides have been demonstrated (Hameister and Kragl, 2006). Dichloromethane showed high efficiency in the extraction of a wide range of non-polar to polar compounds. However, dichloromethane is carcinogenic, and the recent trends have been to refrain from the use of this solvent in liquid-liquid extraction. Organic solvents and amines have shown high extraction efficiency for lignosulfonates (Kontturi and Sundholm, 1986). The main issues of extraction with amine based solvents are complete removal of the amine, foam formation and emulsion problems (Ringena et al. 2005).

Many factors should be considered in evaluating the use of potential solvents for specific extraction processes such as the capacity for partitioning of product, affinity or selectivity for desired product over other components, and miscibility with the aqueous phase (McPartland et al. 2012) as well as they should be environmentally-friendly. Generally, the more polar the solvent, the higher is the degree of extraction (Kontturi and Sundholm, 1986). Also, the capacity of the solvent can be enhanced by adding one or more extractants to the solvent phase. However, the high cost and toxicity of organic solvents hinder their broad applications (Ramaswamy et al. 2013). Also, it must be stated that LLE is a time-consuming process.

Table 2.10: The applications of liquid-liquid extraction in lignocellulosic materials isolation from aqueous feeds.

Raw material	Solvent	Carrier	Result	Ref.
Eucalyptus wood hydrolysates	Ethyl acetate and diethyl ether	–	84% of lignin-derived compounds were extracted.	Cruz et al. (1999)
Lignosulfonates	-1-butanol - 1-pentanol - methyl isobutyl ketone	Aliphatic amines	The degrees of extraction were close to 100%.	Kontturi, and Sundholm (1986)
Sugar model solution and hydrolysates of bagasse	Aliquat 336	Boronic acid	Xylose concentration had been increased over seven times that of the original hydrolysate while reducing the concentration of the acid-soluble lignin by over 90%.	John Griffin and Shu, (2004)
Xylitol from fermented hemicellulosic hydrolyzate	Either ethyl acetate, chloroform or dichloromethane	–	Ethyl acetate clarified the broth without xylitol loss.	Mussatto et al. (2005)
Mono- and disaccharides from aqueous media	butanol, (MTBE), n-hexane or toluene	Primary amines	Recovery rates of carbohydrate were up to 40 %	Hameister and Kragl (2006)
lignin from an aqueous composition	Methyl isobutyl ketone	–	The degree of extraction was 99%	Matala et al. (1982)
Acetic acid from pre-pulping extracts	Trioctylphosphine oxide (TOPO) and	Alkane	The acetic acid extraction efficiency of TAPO was 83.1%	Kim et al. (2015)

	trialkylphosphine oxide (TAPO)			
Spent sulfite liquor	Complexation dicyclohexylamine	–	81% of the sample material used could be recovered	Ringena et al. (2005)

2.3.3. Precipitation

Precipitation by acidification using carbon dioxide, sulfuric acid, or hydrochloric acid has been used for lignin isolation from kraft black liquor (BL) (Olivares et al. 1988) and pre-hydrolysis liquors (PHL) (Liu et al. 2011a). Mussatto et al. (2007) achieved 81.43 % removal of soluble lignin from black liquor by decreasing the pH from 12.56 to 2.15, using sulfuric acid. Liu et al. (2011a) studied lignin recovery from PHL. PHL was acidified to a pH of 2 for lignin separation. They reported 47% lignin precipitation, and they also indicated that lignin precipitation could be further improved by adding polyethylene oxide and poly aluminum chloride, or ethyl acetate. Ethanol precipitation has also been used for hemicellulose recovery from PHL (Liu et al. 2011b). The advantage of this process is the molecular mass of precipitated hemicelluloses can be controlled by adjusting the amount of ethanol (Swennen et al. 2005). However, this process requires additional ethanol recovery system. Globally, the potential of precipitated lignin was assessed to be about 1 million tons each year and around 1.5 Mt/year in North America (Mahmood et al. 2016). However, regarding the content and properties of obtained lignin, there are clear differences between the precipitates obtained at the different pH intervals (García et al. 2009). Acid precipitation is cost-effective method once implemented on a large scale. The main drawback of this process is the use of corrosive acids.

2.3.4. Adsorption

In biorefineries, adsorption has been used for the efficient removal of inhibitors from biomass hydrolysate, removal of impurities, separation and purification of biofuels and chemicals (Kiss et al. 2016). Adsorption concept was also used for separating lignocellulosic materials from various spent liquors. Liu et al. (2011a) reported that activated carbon (AC) is an efficient adsorbent for the organic materials of PHL. Activated carbons have characterized by relatively large surface area and high charge density, as well as highly porous structure (Liu et al. 2011b). Also, AC can be recycled and reused. However, not only absorbent characteristics influence the adsorptive capacity, but also the properties of adsorbate such as molecular structure, solubility, and ionization. Both modified and unmodified ACs has been investigated. It has been stated that the higher adsorption of hemicelluloses on unmodified AC was achieved at neutral pH than acidic one (Liu et al. 2011b). It was also reported that P-DADMAC or chitosan could be used to improve the adsorption capacity of lignocelluloses on AC Liu et al. (2011a). Also, oxidized AC was proven to be a capable adsorbent for isolating the organic materials of PHL than untreated AC (Liu et al. 2011b). However, after the adsorption, a desorption process is required for removing the lignocellulosic materials from AC (Liu et al. 2011a).

On the other hand, precipitated calcium carbonate (PCC) and calcium oxide has been tested as adsorbents for lignocellulosic materials separation. Fatehi et al. (2013) used porous, and nano-sized precipitated calcium carbonate (PCC) for adsorbing the oligo-sugars. In this study, the adsorptions of oligo-sugars, lignin and furfural were better on porous PCC than on nano-sized PCC. Shen et al. (2011) treated industrially produced PHL with lime for acetic acid, furfural, UV lignin, and hemicelluloses concentrations. This treatment resulted in increased acetic acid concentration due to the degradation of sugars under the alkaline condition. Due to the smaller surface area and charge density, these adsorbents showed lower adsorption capacity for lignocellulosic materials than that of activated carbons (Oveissi, 2014). Adsorption process has the flexibility of having certain selectivity towards the adsorption of a desired lignocellulosic material of the PHL.

2.3.5. Chromatographic separation

The chromatographic technique has been used to separate hemicellulose in aqueous solutions (Heinonen and Sainio, 2012). It has been employed widely on an analytical scale, but it is not extensively used in biorefinery for full-scale purposes (Westerberg, 2014). Due to the solvent addition requirement for elution, and great feed volumes that need to be separated. Saari et al. (2010) studied chromatographic separation of galactose, and they reported that large-scale liquid chromatography could be used effectively for galactose separation from carbohydrate mixture. Andersson et al. (2007) studied size-exclusion chromatography (SEC) for hemicellulose recovery and purification from thermomechanical pulping of spruce, and the purity of hemicelluloses after SEC was approx. 82%. Chromatographic separation of sugars using ion exchange (IEX) was also studied (Saari and Hurme, 2011).

2.3.6. The lignoBoost Process

The lignoBoost process has been developed to extract lignin efficiently from Kraft black liquor, and the full-scale plant has been built. In this process, BL is taken from the evaporation plant; then lignin is precipitated by acidification utilizing CO_2, followed by dewatering using a chamber press filter. Instead of using conventional filtering in this system, the filter cake is redispersed in spent wash water and acid. After that, the resulting slurry is filtered and washed by displacement washing method for pure lignin production (Tomani, 2010). Compared to the previous technology, the benefits of this system are displacement washing of lignin without plugging the filter cake and mineral loss; the produced lignin has higher solids and lowers carbohydrate contents (Tomani, 2010).

2.3.7. The lignoForce System

The LignoForce process has been developed for the recovery of high-quality lignin from black Liquor, and a pilot plant facility was built. This process tends to reduce CO_2 usage and improve filtration rates (Kouisni et al. 2012). To improve the lignin filtration rates, the BL was oxidized (O_2) under controlled conditions. The oxidized BL was then acidified by adding carbon dioxide and coagulated and then followed by filtration by a filter press, washing with sulphuric acid and water and lastly air drying (Kouisni et al. 2012).

2.3.8. Flocculation

More recently, flocculation concept was applied to isolate the organic materials of various hydrolysis liquors. In the flocculation process, flocculating agents (electrolytes and polymers) flocculate lignocellulosic materials through the mechanisms of charge neutralization, patching, and bridging, followed by precipitation. Yasarla and Ramarao, (2012) investigated the dynamics of flocculation of sugar maple hydrolyzates using alum and cationic polymers. They concluded that the separation of lignin and its derivatives could be achieved by low molecular weight high charge density polymers. Shi et al. (2012) used overliming and cationic surfactants to separate the lignin of PHL. Overliming followed by the dodecyl trimethyl ammonium chloride (DTAC) achieved 43.6% lignin and 27% hemicellulose removal. Also, chitosan was used for treating lignocellulosic materials of the PHL, oligomeric sugars recovery was 20%, and lignin recovery was 40% (Saeed et al. 2011). Poly ethylene oxide (PEO) flocculation can improve the lignin removal from PHL of the kraft-based dissolving pulp production process (Shi et al. 2011). Duarte et al.

(2010) treated the extracts of sugar maple hardwood with a cationic flocculating agent poly diallyl dimethyl-ammonium chloride, and they reached 36% lignin reduction. Flocculation can reduce the toxicity of the hydrolysates to fermentation micro-organisms and flocculants can easily be handled. However, it is removal capacity of the lignocellulosic materials was limited; Thus further treatment is required.

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CHAPTER III

Ultrafiltration membrane technology for hemicelluloses recovery and purification from thermomechanical pulp (TMP) mill process waters

3.1. Abstract

Process waters of thermomechanical pulp (TMP) mills contain a large valuable quantity of lignocellulosic materials that end up in the wastewater for biological treatment. The recovery of hemicelluloses and lignin from these process waters as value-added chemicals would be beneficial for TMP mills not only to increase their profitability and competitiveness but also to reduce the organic loading to the wastewater treatment facility. In this study, a lab-scale experimental setup, utilizing dead-end stirred cell filtration unit was implemented. The feasibility of three hydrophilic UF membranes made of regenerated cellulose with different molecular weight cut-offs (5, 10, and 30kDa) for hemicelluloses recovery from TMP process waters was evaluated. The results showed that 5 and 10kDa membranes gave much better recovery efficiency on hemicelluloses than 30kDa membranes. The recovery of the hemicelluloses was above 95% for 5kDa and around 89% for 10kDa, with hemicellulose purity of approx. 75 and 80%, respectively. Cut-offs of 5 and 10kDa seem to be feasible for the separation of lignin and hemicelluloses. While a cut-off of 30kDa membrane was found to be unsuitable for hemicellulose isolation from TMP process water since both hemicellulose and lignin passed through the membrane to the permeate side. An optimal MWCO of 10kDa membrane gave the highest purity of hemicelluloses.

3.2. Introduction

Decreasing competitiveness of the forest products industries and the growing environmental concerns have motivated the research to focus on exploitation of the different wood components in an efficient way. This situation led to the study and development of integrated forest biorefinery (IFBR) which utilizes forest-based biomass rather than fossil fuels to produce value-added chemicals and bioenergy (Moshkelani et al. 2013). This new business paradigm offers a broad spectrum of potentially attractive bioproducts. These compounds can be economically recovered from IFBR either after hydrolysis of carbohydrates or from pretreatment process if effective separation technologies are developed.

In thermomechanical pulping (TMP), wood chips are treated with pressurized steam. During this process approximately 5-10% of woody materials, which include hemicelluloses, lignin, and extractives, are dispersed as colloidal particles into process waters for biological treatment (Persson and Jonsson, 2009; Koivula et al. 2011). These compounds can be recovered for their better applications. Recently, isolation of hemicelluloses and lignin from wood have gained increasing interest, and several applications have emerged. Hemicelluloses have been found to be an excellent candidate for the production of hydrogels, oxygen barrier film in packaging materials, emulsion stabilizer in food and feed, and surfactants, as well as a source of sugars that can be fermented to ethanol, (Krawczyk and Jönsson, 2011; He et al. 2012; Lemaire et al. 2016). lignin has used as carbon fibers, adhesive materials, activated carbon, asphalt, lead storage batteries, phenolic and resins (Khan et al. 2004; Pye et al. 2005; Mahmood et al. 2016). Thus, the recovery of hemicelluloses and lignin from TMP process streams as value-added chemicals would be beneficial to TMP mills not only to increase their profitability and competitiveness but also to reduce the organic loading to the wastewater treatment plant, as well minimizing overloading to bottleneck recovery boilers.

Although plenty of applications for lignocellulosic materials have been proposed, the lack of effective separation methods of hemicellulose and lignin with high purity (García et al. 2009) is a major problem with the utilization of hemicellulose and lignins in certain industrial applications. Usually, the process water of forest industry is a complex mixture of wood components: hemicelluloses, lignin, wood extractives and organic acids. In order to obtain a purified fraction of hemicelluloses and lignin, highly developed separation technologies that are cost effective and environmentally responsible are needed (García et al. 2009). Also, since each molecular weight of hemicelluloses has a specific application field, fractional separation and structural characterization of the hemicelluloses are required for the effective use of these materials.

Membrane technology has been proposed as a possible separation technique for IFBR because of its capacities to offer fractionation and separation. Also, it is characterized by the short processing steps, less chemical utilization, and considerable energy saving, as well as can be easy integrated with existing operating units (He et al. 2012, Chen et al. 2016). Recent advances in membrane technology and system design have created a new opportunity for effective UF of several organic polymers and inorganic chemicals. In forest biorefinery, UF membrane is found to be an effective method for the treatment of pulp and paper effluent not only to purify the process water for reuse but also to recover and fractionate dissolved lignocellulosic materials for industrial applications (Persson et al. 2010; Al Manasrah et al. 2012; Ajao et al. 2015; Mänttäri et al. 2015; Wang et al. 2015; Thuvander and Jönsson 2016).

The use of membrane filtration in IFBR has some challenges that need be addressed before commercially feasible membrane concentration of process waters can be carried out due to the complexity of wood hydrolysates. The biggest problem for membrane separation of hemicelluloses and lignin recovery is membrane fouling (Koivula et al. 2011). So far, significant progress has been made in understanding the interactions between the foulants, the membrane nature, and the operating conditions. Also, it has been found that pretreatment methods such as pH adjustment, or using ion-exchange resin, pulsed corona discharge, and activated carbon (AC) adsorption significantly improve membranes filterability (Koivula et al. 2011; Liu et al. 2014). Koivula et al. (2011) indicated that pretreatment processes have to be tailored separately for different hydrolysates due to their different characteristics. Persson and Jonsson (2009) reported that a hydrophobic membrane has high fouling tendency than a hydrophilic membrane. Gonder et al. (2012) stated that membrane fouling could be reduced by optimizing membrane operating conditions.

Usually, the successful application of a UF, for performing separation and purification processes, is associated with the selection of appropriate membrane molecular weight cut-offs, average permeate flux, and volume reduction factor. Although some studies reported in the literature, the optimal membrane cut-off for the isolation of hemicelluloses and lignin is not obvious (Jönsson et al. 2008). Also, the membrane geometry can play a major role in the hemicelluloses retention rates and membrane flux because it impacts the membrane fouling and concentration polarization. In this study, a lab-scale experimental setup, utilizing dead-end stirred cell filtration unit was implemented. The performance (membrane flux, recovery, and purity of hemicelluloses) of UF membranes with different molecular weight cut-off (5, 10 and 30kDa of a hydrophilic regenerated cellulose membrane) for hemicelluloses recovery and purification from TMP process waters was evaluated.

3.3. Materials and methods

3.3.1. Process water

The raw material used in this study was process water from a Canadian thermomechanical pulp mill. The wastewater stored in a cold room at 4 C° to prevent hemicelluloses degradation. Table 3.1 summarizes characteristics of the tested process water. The content of total solids, TDS, lignin (UV absorbance at 205nm), hemicelluloses, ash content, COD, turbidity, and total organic carbon (TOC) of the samples was analyzed. The content of total solids was determined by drying measured samples for 24 h in an oven at 105 °C, and then weighing the residue after it is has been cooled to room temperature in a desiccator. The dry sample was further burned to 575°C in a furnace, and this temperature was maintained for three hours. The ash content was determined from the weight of the residue after cooling to room temperature in a desiccator. The total dissolved solids (TDS) were measured by filtering the samples through a filter paper, and then drying the sample which passes through in the oven at 105 °C using a standardized method. The turbidity was determined at room temperature using a turbidity meter (2100AN Turbidimeter, HACH Co., USA) to detect the presence of suspended solids and possible extractives in the process water and retentates and permeates. Total carbon (TC) and total inorganic carbon (TIC) were measured by TOC analyzer (Vario TOC select, Elementar). In addition, pH was measured by Oakton pH/Ion 700 (Cole-Parmer, Canada) at room temperature to determine the ionic content of the samples. Total suspended solids were calculated from the difference between total solids and dissolved solids. The compositions of the process water are listed in Table 3.1. It was found that the concentration of the hemicellulose around 0.72±0.135.

Accordingly, a high volume reduction factor is needed for its recovery and concentration. All tests were made in triplicate, and results were presented as mean value ± SD.

Table 3.1. Composition and properties of TMP mill process water used in this study (average value ± SD)

Analyzed parameters	Average values
Ash content (g/l)	0.9±0.2
Chemical oxygen demand (COD) (mg/l)	3862±99
Total solids concentration (g/l)	3.3±0.14
The total dissolved solids (TDS) (g/l)	2.3±0.2
Suspended solids concentration (mg/l)	0.9±0.2
pH	4.2±0.15
Total organic carbon (TOC) (g/l)	1.4±0.06
Turbidity	1115±5.29
Lignin concentration (g/L)	1.94±0.21
Total hemicelluloses (g/L)	0.72±0.135
▪ Arabinose (g/L)	0.075±0.019
▪ Galactose (g/L)	0.516±0.095
▪ Raminose (g/L)	0.001±0.001
▪ Glucose (g/L)	0.046±0.007
▪ Xylose (g/L)	0.013±0.002
▪ Mannose (g/L)	0.070±0.015

3.3.2. Membrane

The performance of three UF membranes with different molecular weight cut-offs (5, 10 and 30kDa) was investigated in this study. Table 3.2 displays characteristics of the tested membranes. Hydrophilic, regenerated cellulose (RC) UF flat sheet membranes from EMD Millipore Corporation, Billerica, MA 01821USA with a filter diameter of 63.5 mm and active membrane area 0.00287m^2 were used. Hydrophilic UF membrane has previously shown low fouling tendency during the filtration of pulp and paper effluent. Maartens et al. (2002) reported that foulants present in the effluent of pulp and paper mills are of phenolic and hydrophobic nature and increasing the hydrophilic characteristics of the membranes have been found to reduce the amount of organic foulants that adsorbed onto the membranes. Weis et al. (2005) stated that the hydrophilicity of the membranes has a significant role in reducing fouling of UF fouled with spent sulfite liquor when they studied fouling mechanisms of polysulfone (PS), regenerated cellulose (RC) and polyethersulfone (PES) UF membranes. Puro et al. (2010) compared fouling of PES and RC membranes during the treatment of (softwood and hardwood) pulp mill process waters by UF. The results of this study showed that the fouling of PES was greater than that of RC with both types of process waters, regarding their flux recovery and membrane nature and morphology.

Table 3.2: Characteristics of ultrafiltration membranes used in this study and their pure water fluxes (PWF) before and after filtration

Membrane (MWCO)	Module type	Maxi. Press. (bar)	Max. Temp. (C°)	Membrane material[b]	PWF before, kg/(m^{2}h)[c]	PWF after, kg/(m^{2}h)[c]	Percentage change, %
5 KDa[a]	Flat sheet	4.8	121	RC	10.45	9.22	11.77
10 KDa[a]	Flat sheet	4.8	121	RC	75.26	67.53	10.27
30 KDa[a]	Flat sheet	4.8	121	RC	491.29	468.29	4.68

[a] EMD Millipore Corporation, USA
[b] Regenerated cellulose
[c] Test conditions: 1 bar, 22°C, cimarec™ magnetic stirring at 300 RPM (Thermo Scientific™).

3.3.3. Equipment and filtration experiments

A lab-scale experimental setup, utilizing dead-end stirred cell filtration unit, purchased from EMD Millipore Corporation, was employed for measuring the performance of UF membranes with different molecular weight cut-offs (MWCO) for hemicelluloses and lignin separation. A schematic diagram of the process used in this investigation is shown in Fig. 3.1. In each run, the filtration cell was fed with 150ml of the process water. The experiments were conducted in concentration mode of filtration (CMF), where three samples were collected from each filtration: feed, permeate and concentrate in separate containers. Since the feed solution was reduced gradually, the feed quality continuously concentrated until the desired volume reduction (VR) was achieved.

During the filtration experiments, a magnetic stirrer device was used to decrease the concentration polarization effect, which declines the permeate flux (J) during the filtration process because of the resistance of transport across the membrane increase. In contrast to membrane fouling, concentration polarization is a reversible phenomenon that occurs during filtration when the concentration of solutes on the membrane surface. Before the use, the membranes were pretreated by soaking in distilled water for one hour. The bright skin side down as recommended by the manufacturer. The water was changed three times during the soaking process. Membranes are soaked to prevent the membranes from absorbing any of the filtration water and removing any materials that may have been attached to the membranes during packaging and shipment such as glycerin which is used to prevent drying and sodium azide as a preservative.

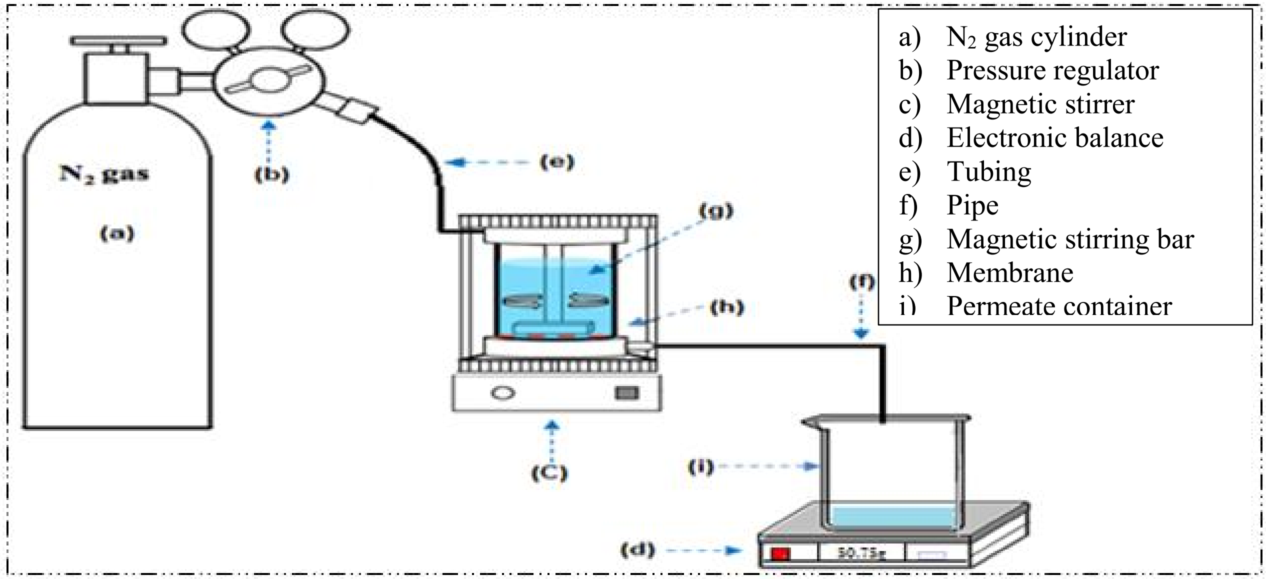

Fig. 3.1. Diagram illustrating ultrafiltration cell used in this study

3.3.4. Analytical methods

3.3.4.1. Hemicelluloses

Hemicelluloses quantification was measured by Dionex ICS-5000 Ion Chromatography System equipped with CarboPac™ PA1 column (Dionex-300, Dionex Corporation, Canada) and a pulsed amperometric detector (PAD) after diluting acid hydrolysis of the samples using a standardized method for acid hydrolysis. The settings of PAD were E1 = 0.1 V, E2 = 0.6 V, and E3 = -0.8 V. The deionized water was used as eluant with a flow rate of 1 ml/min, and a NaOH solution with the concentrations of 0.2 M was used as the supporting electrolyte with 1 ml/min flow rate (Shi et al. 2011). Hemicelluloses were hydrolyzed by adding 5ml of 4% (w/w) H_2SO_4 at 121 °C to the sample for converting the polysaccharide to monomeric sugars. The acid hydrolysate was oil bathed at 121°C for bath for 1 h (Neslab Instruments Inc., Portsmouth, NH, USA) (Liu et al. 2011). Then the monomeric sugars were analyzed via ion chromatography system, and the concentration of hemicellulose was obtained as the sum of the monomeric sugars as showed in Table 3.1. The concentration of hemicelluloses in the process water was determined before and after ultrafiltration with different membrane cut-offs.

3.3.4.2. Lignin

For lignin content determination, photometric measurements were carried out using a GENESYS™ 10S UV-Vis Spectrophotometer at a wavelength of 205 nm according to Tappi UM 250 (Liu et al. 2011; Shen et al. 2011). Before the measurement of the light absorption, the samples were diluted with DI water, and the dilution factor included in the final calculations. Also, the pH of each sample (feed, concentrate and permeate) was adjusted (between 7 -8) from an original pH value of about 4.2, with 0.025 M sodium hydroxide as required before the measurements for stabilizing lignin network. Then lignin content of the concentrates and permeates was measured after each experimental run.

3.3.4.3. Molecular mass distribution of hemicelluloses and lignin

The molecular weight distribution of hemicelluloses and lignin of concentrates and permeates were determined by a size exclusion chromatography (SEC) system, equipped with a refractive index (RI) detector and a UV detector (Malvern, Worcestershire, UK). The lignin and hemicelluloses samples were determined as a weight average (Mw) and a number average molecular (Mn) weight. Also, the particle size distributions (PSDs) of concentrates were measured using Malvern Mastersizer 2000 instrument (Worcestershire, UK) which has a detection range of 0.02 -2000 µm. The instrument detects the scattered light using a detector that converts the signal to size distribution based on volume or number. Each sample was automatically measured three times with a standard deviation of 0.1-4.5%.

3.3.4.5. Calculation

In each run, the filtrations were interrupted at different volume reduction (VR).VR was defined as the ratio between the volume of the permeate and the initial volume of the feed and was calculated using Eq. (1):

$$\mathrm{VRF} = \frac{V_p}{V_f}\mathrm{x}100 \qquad (1)$$

Where V_p is the permeate volume, and V_f is the initial volume of the feed.

In each separation process, mass fluxes were measured. Mass flux is the rate of permeate mass flow obtained during the process per area of membrane (m^2) as a function of time (h). In this study, it was calculated as mass flux at a specific VRF (Kg/m^2h) by Eq. (2):

$$\mathbf{J_m} = \frac{\boldsymbol{m_f}}{\boldsymbol{A_m}} \qquad (2)$$

Where J_m is the mass flux ($kg/(m^2h)$), m_f is the mass flow rate (kg/h), and A_m is the membrane surface area (m^2).

Membrane fouling was calculated by comparing the difference between the pure water flux before and after the filtration, Eq. (4):

$$\text{Fouling (\%)} = \frac{\mathrm{PWF_b} - \mathrm{PWF_a}}{\mathrm{PWF_b}}\mathrm{x}100\% \qquad (3)$$

Where PWFa is the pure water flux after filtration ($kg/(m^2h)$) and PWF_b is the pure water flux prior filtration ($kg/(m^2h)$).

The recovery of hemicelluloses during filtration was calculated by, Eq. (5):

$$\text{Recovery (\%)} = \frac{\mathrm{m_{hemi(c)}}}{\mathrm{m_{hemi(f)}}}\mathrm{x}100\% \qquad (4)$$

Where $m_{hemi\ (c)}$ is the mass of hemicelluloses in the concentrate and $m_{hemi\ (f)}$ is the mass of hemicelluloses in the feed.

The separation performance of the different membranes was assessed by using the percent rejection (R) or retention of feed components. This measurement calculated based on the following equation:

$$\text{Retention } (\%) = \left(1 - \frac{\text{Cp}}{\text{Cf}}\right) \text{x}100\% \qquad (5)$$

Where C_p represents the concentration of hemicelluloses in the permeate at the end of the separation and C_f is its initial feed concentration.

The following equation measures the purity of hemicelluloses recovered by different membranes. The purity of hemicelluloses is defined as the ratio between the carbon content in the hemicelluloses, which accounts for about 40% of the hemicellulose molecular mass, and the total organic carbon (TOC) concentration in the final concentrate (Mänttäri et al. 2015).

$$\text{Purity } (\%) = \frac{\text{C.hemi(c)}*0.4}{\text{TOC(c)}} \text{ x}100\% \qquad (6)$$

Where $C_{hemi(C)}$ is the concentration of the hemicelluloses and $TOC_{(C)}$ is the total organic carbon in the final concentrate.

3.4. Results and discussion

3.4.1. **Permeate flux and fouling**

Before each run, a new membrane was first stabilized with distilled water under the conditions of 1 and 2 bar, room temperature, and zero rpm until its pure water flux remained stable. Meanwhile, the pure water flux (permeate flow) was also measured gravimetrically with a digital balance. During the membrane filtration process, the concentrate remained in the dead-end cell, and the permeate was collected from the outside in the permeate container, as shown in Fig. 3.1. The endpoint of every filtration experiment was determined by the volume reduction factor, which is the ratio between the permeate volume and the initial feed volume as indicated in Eq. (1) above. Permeate flux decreased with increasing VR for all experiments. However, an initial rapid decline in flux was more seen at 30kDa membrane compared to 10kDa membranes, while the permeate flux of 5kDa was to some extent stable as shown in Fig. 3.2.

The time evolution of the permeate flux for the different MWCOs is characterized by an initial decline of the permeate flux due to the deposition and growth of a polarized layer, as can be seen in Fig. 3.5 below. The filtration processes were conducted under a pressure of 100kPa. Average permeate fluxes data for all the three membranes used in our study are shown in Fig. 3.3 and 3.4. The average fluxes of the 30kDa membranes were 46.38, 50.43, 54.80 and 56.29 Kg/m$^{2\cdot}$h for 95%, 90%, 80%, and 75% VR, respectively. Whereas, the average fluxes of the 10kDa membranes were 45.26, 46.39, 47.57 and 49.12 Kg/m^{2}h to 95%, 90%, 80%, and 75% VR, respectively. For 5kDa membranes, average fluxes were 6.8, 7.5, 8.5, and 9.22 Kg/m$^{2\cdot}$h for 95%, 90%, 80%, and 75% VR, respectively.

The ratio of the pure water flux (PWF) of the membrane prior to concentration to the flux after process water concentration is used as an indicator of flux decline. The pure water flux before and after the filtration measurements showed that a slight fouling during the filtration has occurred as specified in Table 3.2, which may be partly explained by the most hydrophilic character of the RC membranes (Koivula et al. 2011). However, the concentration polarization layer effect at the surface of the membrane was observed more, which resulted in a decline of the membranes fluxes.

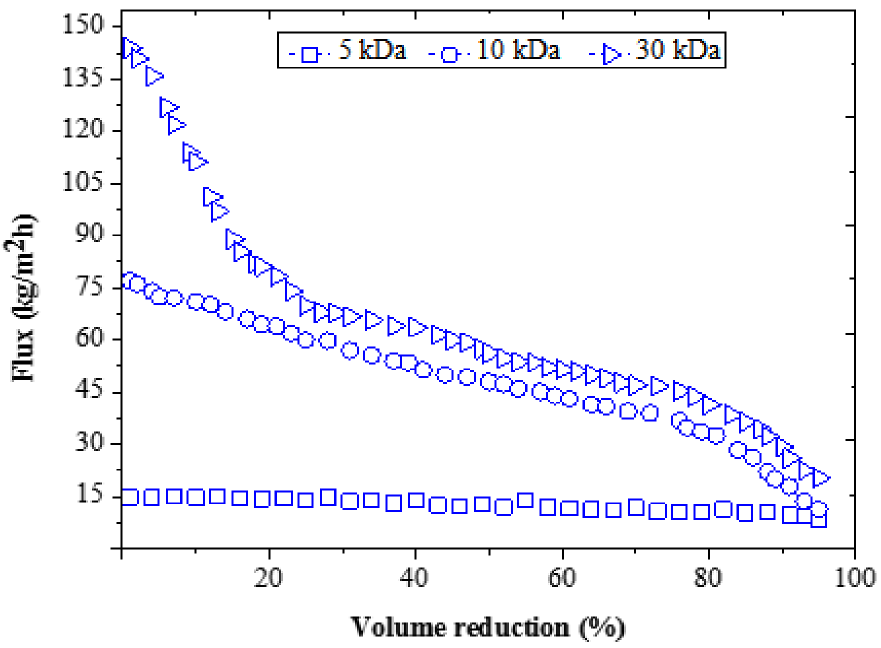

Fig. 3.2. Permeate fluxes of 5, 10, and 30kDa membranes versus volume reduction values. Ultrafiltration was carried out at 1 bar, 22°C, and magnetic stirring plate 300 RPM for 10 and 30kDa, while at 1.5 bar for 5kDa.

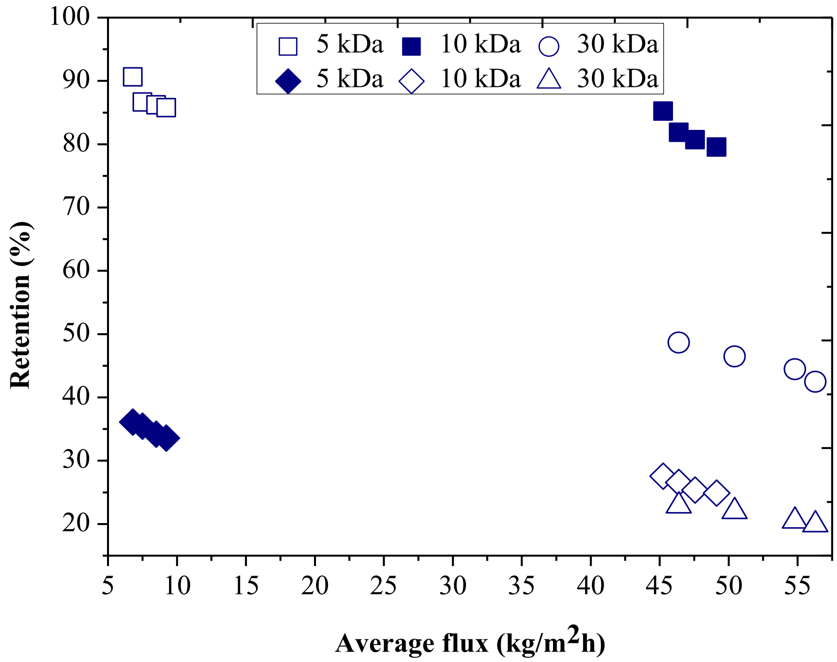

Fig. 3.3. Evaluation of membranes (5, 10, and 30kDa) retention of hemicelluloses (□, ■, and O) and lignin (♦, ◊, and Δ) and average permeate flux data. Ultrafiltration was carried out at 1 bar, 22°C, and magnetic stirring plate 300 RPM.

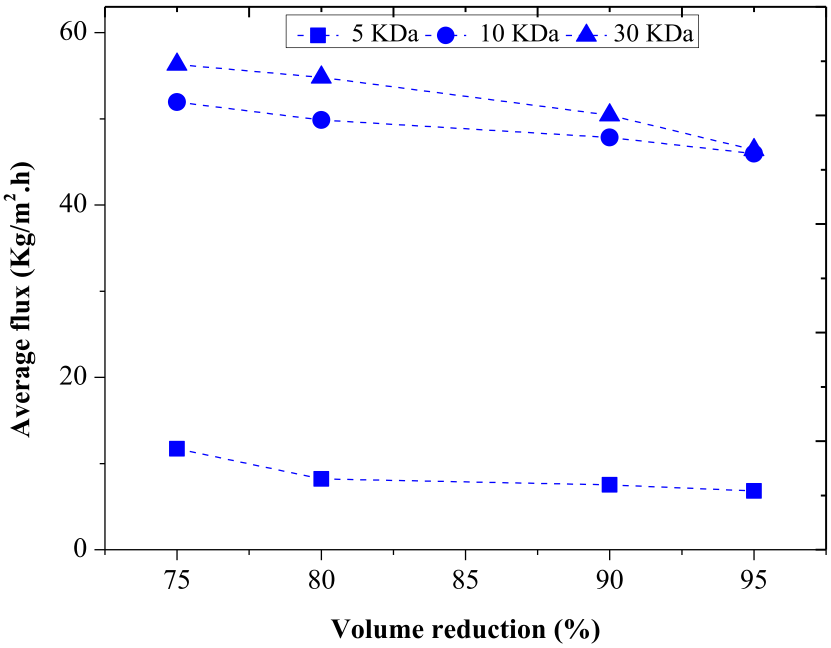

Fig. 3.4. Average fluxes of 5, 10, and 30kDa membranes versus volume reduction values. Ultrafiltration was carried out at 1 bar, 22°C, and magnetic stirring plate 300 RPM for 10 and 30kDa, while at 1.5 bar for 5kDa.

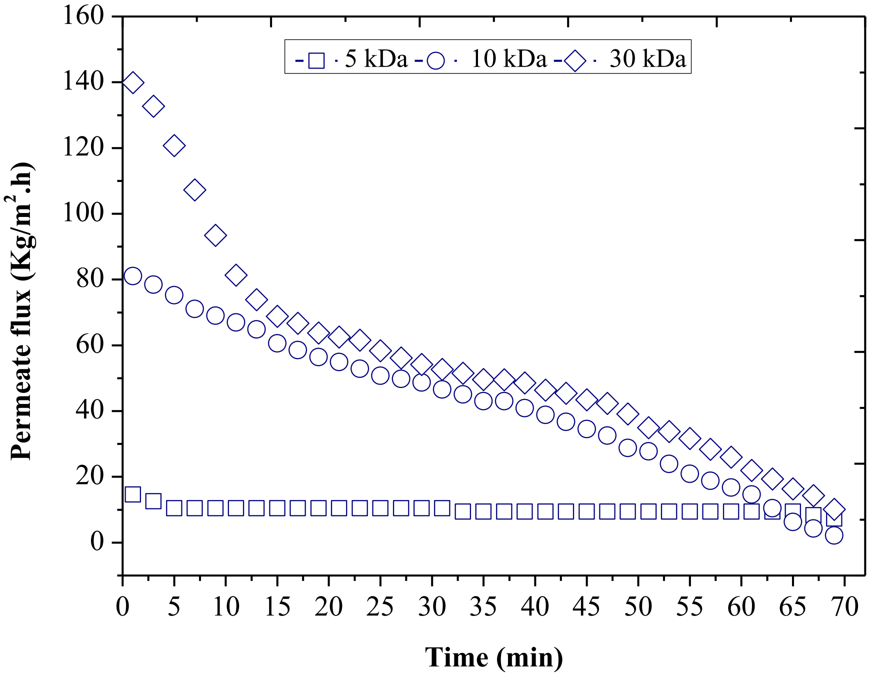

Fig. 3.5. Permeate fluxes of 5, 10, and 30kDa membranes versus operating time. Ultrafiltration was carried out at 1 bar, 22°C, and magnetic stirring plate 300 RPM for 10 and 30kDa, while at 1.5 bar for 5kDa.

3.4.2. Hemicelluloses recovery

Before the beginning of each separation, all samples were pre-filtered through a 0.177 mm wire screen strainer to remove large particles (standard sieve series 80, The W.S. Tyler Company, Canada). Then the concentration of hemicelluloses in the process water was measured, and it was about 0.75±0.2g/l. Hemicelluloses consisted of the monosaccharides arabinose, galactose, raminose, glucose, xylose, and mannose, as showed in Table 3.1. Subsequently, these samples were concentrated using a Millipore Stirred Ultrafiltration Cell, Model 8200, regenerated cellulose (RC) membrane with MWCO of 5, 10 and 30KDa and pressure of 100kPa. Concentration was interrupted at VR of 75, 80, 90, and 95%.

The three tested membranes have shown different ability to recover hemicellulose from the feed water, as can be seen in Fig. 3.6. 5KDa membranes achieved the highest recovery percent of hemicellulose 95.7, 91.5 and 85.8 %, followed by 10KDa membranes 85.2, 80.1 and 64.9 % for VR value of 95%, 90%, and 80%, respectively. Whereas, 30KDa membranes had the lowest recovery percent 52, 43.7 and 32.5 % for VR value of 95%, 90%, and 80%, respectively. Fig. 3.7 shows the concentration of hemicelluloses in permeates for the different membrane cut-offs. Hemicelluloses concentration after ultrafiltration varied between 2.87 and 12.139 g/l depending on volume reduction factors and the membrane cut-off. The concentrations of hemicelluloses in retentates increase steeply from VR value of 80 to 95%, as can be seen in Fig 3.12. Due to the low concentration of hemicelluloses in the feed, a high volume reduction (95%) is required for obtaining high concentered retentate.

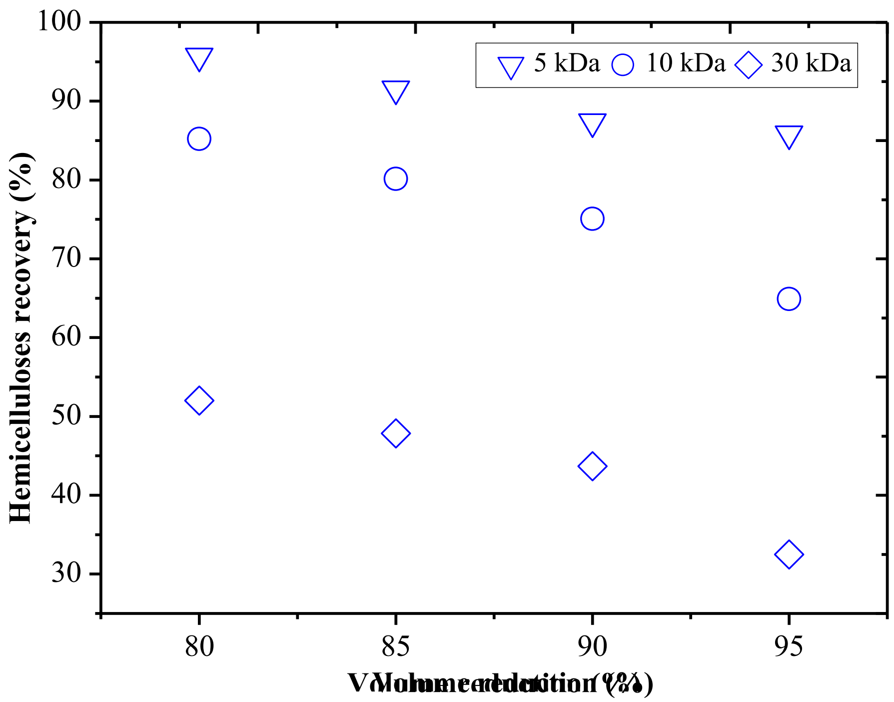

Fig. 3.6. Recovery (%) of hemicelluloses during ultrafiltration process using different membranes cut-offs and VR%. Ultrafiltration was carried out at 1 bar, 22°C, and magnetic stirring plate 300 RPM.

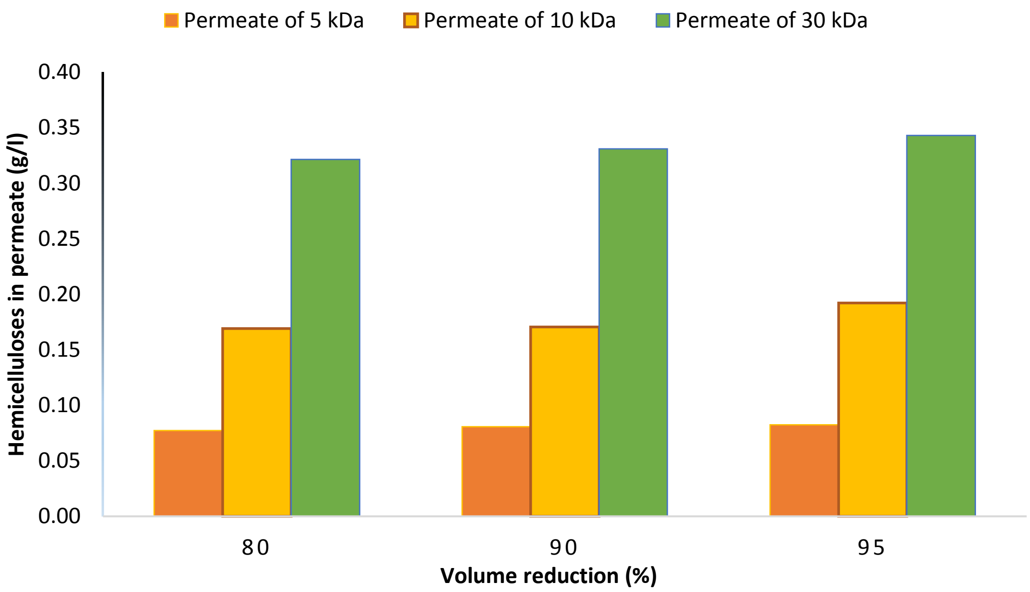

Fig. 3.7. The concentration of hemicelluloses in permeates during the ultrafiltration experiment with different MWCO, as a function of volume reduction.

3.4.3. Retention of hemicelluloses and lignin

Volume reduction has a significant influence on the amount of hemicelluloses and lignin retendered by the membrane. In order to predict the purity and yield of these compounds, the correlations between the concentrations in the retentate and permeate and volume reduction are required. In this experiment, it was found that both 5 and 10kDa membranes exhibited excellent overall hemicellulose retention, while retention of hemicellulose was noticeably lower for 30 kDa membrane. Figs. 3.8 – 3.10 show the retention of hemicelluloses and lignin, during concentration using 5, 10 and 30kDa membranes. The retention of hemicelluloses was found to increase with increasing volume reduction.

Retentions of lignin were markedly low with the tested 10kDa membranes, compared with hemicelluloses retention. Hemicelluloses retention was in the range of 79–85%, whereas lignin retention was between 23.6 and 27.5. For 5kDa membrane, hemicellulose retention was between 85 and 90.5%, while lignin retention was between 33.8% and 36%. Consequently, hemicelluloses concentrated from 0.75 to 12.0 g/l, for the highest VR factor 95%. Hemicellulose retention of the 30kDa membrane was markedly lower (between 42 - 48%) compared to that of the other membranes, but lignin also passed through the membrane and the retention of lignin was only 15%.

The lignin retention can be attributed to lignin-hemicellulose complexes (covalent linkages) and molar masses overlapping (Al Manasrah et al. 2012; Krawczyk et al. 2013). Also, the formation of a concentration polarization layer on the membrane surface reduces the transmission of lignin (Jönsson et al. 2008). For overall effectiveness, a membrane with a nominal MWCO of 5kDa was the best choice for a high hemicellulose yield from TMP process water. While for higher hemicellulose purity and lower lignin rejection 10kDa membrane is more appropriate. Both 5kDa and 10kDa membranes retained hemicelluloses better than they retained lignin and that can be used for effective removal of hemicellulose from process waters.

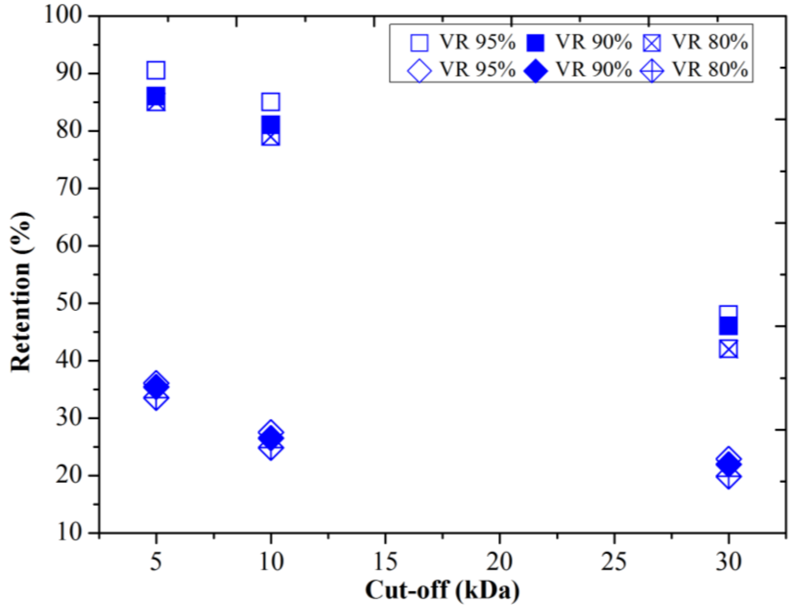

Fig. 3.8. Retention of hemicelluloses (□, ■) and lignin (◊, ♦) during ultrafiltration of TMP process waters at 22°C, 100kPa.

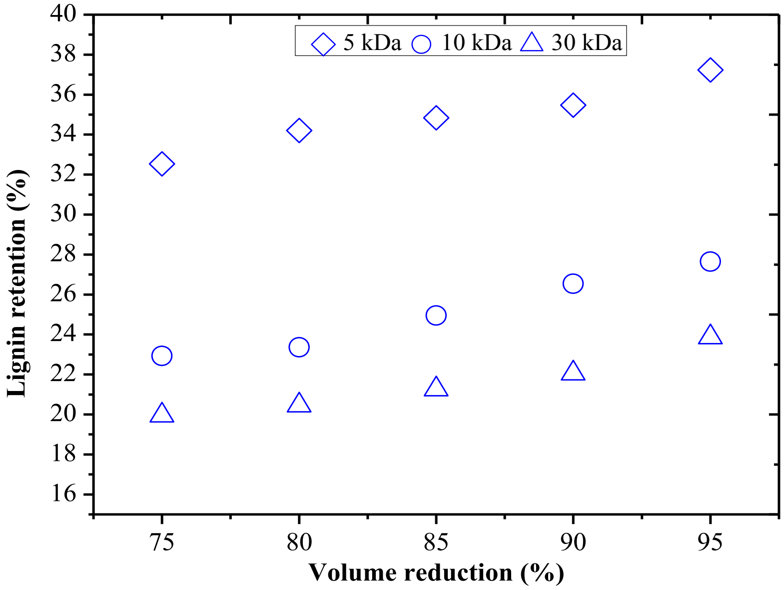

Fig. 3.9. The percent rejection rate of lignin for the different membrane cut-offs, as a function of volume reduction.

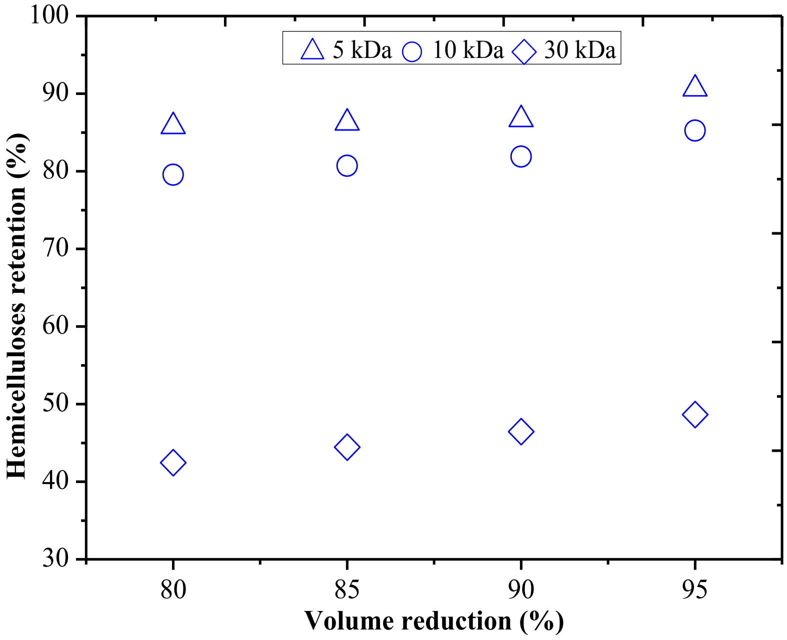

Fig. 3.10. The rejection rate of hemicellulose for the various membrane cut-offs and corresponding VR factor.

3.4.4. Hemicellulose purity

In order to make hemicellulose as a suitable raw material for the manufacturing of high-value-added products, a higher hemicellulose purity is required. The yield of hemicellulose and lignin/hemicellulose ratio rely on the volume reduction applied during ultrafiltration process. Thus, to predict hemicellulose purity and yield, correlations between the concentration in the retentate and permeate and volume reduction are needed (Jönsson et al. 2008). Fig. 3.11 shows the purity of hemicellulose for the three tested membranes and corresponding VR%. Based on the results of this study, it was found that a hydrophilic membrane with a cut-off of 10kDa had better hemicellulose purity than a hydrophilic membrane with a cut-off of 5 and 30kDa. The purities of hemicellulose after ultrafiltration were between 75 and 80%. For further hemicellulose purity, it can be recommended subsequent purification steps such as diafiltration or SEC. Diafiltration probably provides a less expensive alternative in this application (Andersson et al. 2007). Hartman et al. (Hartman et al. 2006) obtained a purity of GGM of about 90% after diafiltration of the 1kDa UF retentate. Willför et al. (2003) achieved purity of 95 mole% when they recovered Acetyl-GGM from the mechanical pulp using ethanol precipitation and polymeric adsorbents techniques. For a separation process to be successful, not only a high concentration and a high yield, but also a high purity is required.

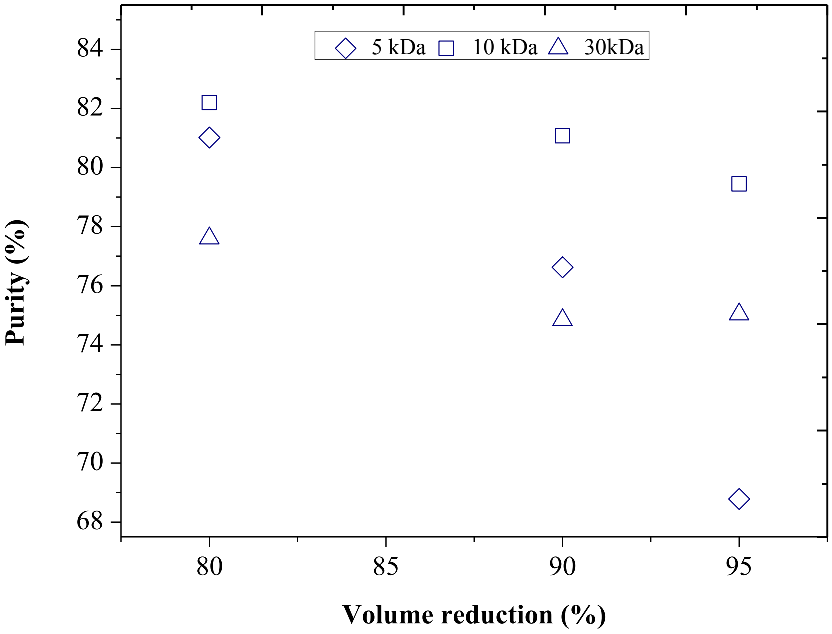

Fig. 3.11. Hemicelluloses purity of the different MWCOs, as a function of volume reduction.

3.4.5. Concentrate and permeate composition

The characteristics of retentate and permeate of UF membrane with different cut-offs are given in Table 3.3. For 95% volume reduction, samples of the permeate and retentate were analyzed to obtain the values of total solids, ash content, COD, pH, turbidity, lignin, and hemicelluloses. The pH of 5kDa permeates was higher than 10 and 30kDa, respectively. That can be attributed to most the materials were recovered on the retentate side, (Table 3.3). The turbidity of 5 and 10kDa membranes permeates was much lower than that of 30kDa membranes, (Table 3.3).

It is also seen that the concentration of lignin in the permeates increased with increasing membrane cut-offs and volume reduction. They were 1.2±0.02, 1.5±0.22, and 1.7±0.06 g/l for 5, 10, and 30kDa, respectively. While the concentration of hemicelluloses in the permeates followed the same trend, but it was very low compared to lignin concentration. The average concentration of hemicelluloses in 5, 10, and 30kDa permeates was about 0.07, 0.15, and 0.30 g/L, respectively as can be seen from Fig. 3.7. The concentration of hemicellulose in the retentate was about 13 g/l (5kDa), 10g/l (10kDa), and 4g/l (30kDa) for 95% volume reduction, can be seen from Fig. 3.12. According to Thuvander and Jönsson (2016), hemicellulose could be concentrated more if the UF concentration followed by ethanol precipitation or film model. Fig. 3.13 shows the lignin concentration in the retentates of the different membrane cut-offs.

On the other hand, the concentration of total solids, total organic carbon, and ash content increased with decreasing membrane cut-offs. Total solids concentration were 18.3±0.03, 17.6±0.15, and 14.7±0.7 g/l in 5, 10, and 30kDa retentates, respectively. Whereas, total organic carbon was 6.9±0.69, 5.1±0.39, and 1.9±0.02 g/l as showed in Table 3.3.

Table 3.3: Physico-chemical analyses of permeate and concentrate of UF membrane with different cut-offs (average value ± SD) at VR 95%.

Analyzed parameters	5kDa		10kDa		30kDa	
	Perm.[a]	**Conc.**[b]	**Perm.**	**Conc.**	**Perm.**	**Conc.**
Total solids (TS) (g/L)	0.34±0.01	18.3±0.03	0.5±0.04	17.6±0.15	0.87±0.01	14.7±0.7
Total organic carbon (TOC) (g/l)	–	6.9±0.69	–	5.1±0.39	–	1.9±0.02
Ash content (g/l)	–	2.2±0.07	–	1.5±0.2	–	0.61±0.03
Total volatile solids (TVS)(g/l)	–	16.4±0.05	–	16.2±0.13	–	14.1±0.4
Chemical oxygen demand (mg/l)	908±52	–	1418±32	–	1521±91	–
pH	5.2±0.03	–	4.8±0.01	–	4.4±0.04	–
Turbidity	1.9±0.2	–	3.2±0.33	–	6.2±0.32	–
Lignin concentration (g/L)	1.2±0.02	12.5±0.04	1.5±0.22	6.9±1.5	1.7±0.06	6.4±0.55
Total hemicelluloses (g/L)	0.10	12.14	0.15	8.82	0.34	4.61
Arabinose (g/L)	0.01	1.24	0.02	1.03	0.04	0.53
Galactose (g/L)	0.04	9.13	0.05	7.11	0.22	3.72
Raminose (g/L)	0.00	0.04	0.00	0.00	0.00	0.00
Glucose (g/L)	0.02	0.67	0.03	0.28	0.03	0.17
Xylose (g/L)	0.00	0.25	0.01	0.12	0.01	0.05
Mannose (g/L)	0.03	0.82	0.05	0.28	0.05	0.14

[a] Perm. = permeate

[b] Conc. = concentrate

[c] – Indicates value not measured

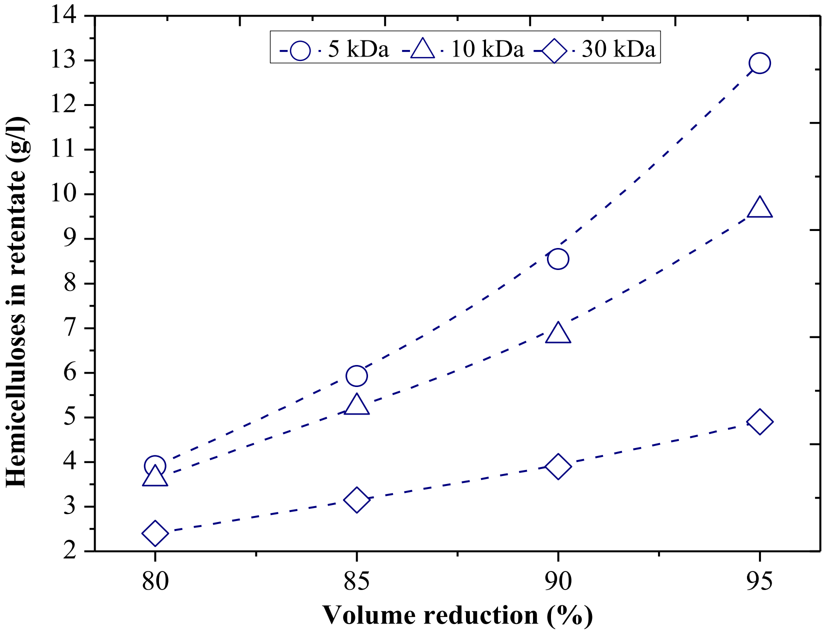

Fig. 3.12. Concentration of hemicelluloses in retentate during the ultrafiltration experiment with different MWCO, as a function of volume reduction.

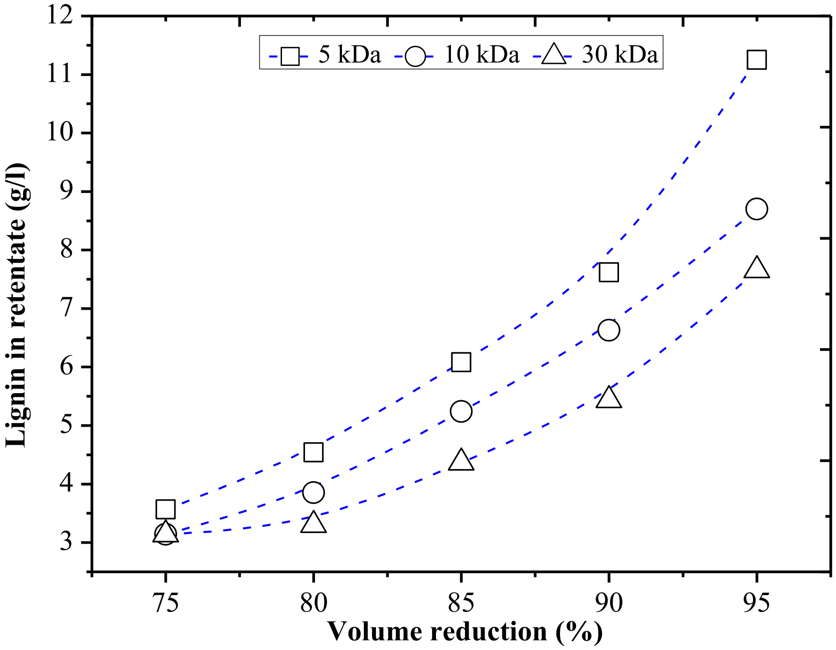

Fig. 3.13. Concentration of lignin in retentate during the ultrafiltration experiment with different MWCO, as a function of volume reduction.

3.4.6. Molecular mass and distribution of concentrate and permeates

Each molecular weight of hemicelluloses has a specific industrial application. In some applications high-molecular-mass hemicelluloses are favorable (Rissanen et al. 2014). According to Kisonen et al., (2014) high molecular mass of GGM is desirable because it improves the properties of GGM films. In the case of biofuel production, hemicelluloses need to be hydrolyzed into sugar monomers and then fermented, and for this purpose, low molecular mass extracts are required (Rissanen et al. 2014). Therefore, determination of hemicelluloses molecular weight is useful for directing the properties of concentrated hemicelluloses stream towards suitable processing step. Fig. 3.14 illustrates the particle size distribution of all components in the concentrate. This result indicated that the molecular weight of all the elements in the concentrate fell in the range of lower than 1000 µm. Table 3.4 shows the molar mass obtained by size exclusion chromatography (SEC); number-average molecular weight (Mn), and a weight average molecular weight (Mw). The GPC results showed two main peaks corresponding to two different molecular weights of hemicelluloses in the retentate. From Table 3.4, it can be concluded that the molecular weight of hemicellulose appears in the 5kDa concentrate have a molecular weight (Mw) of 22310, whereas the molecular weight of the hemicelluloses for both 10 and 30kDa concentrates was Mw of 33002 and 54052 Da, respectively. All three permeates of 5, 10, and 30kDa had RI peaks at about 741 and 776 Da, this corresponded well with molecular weight distributions in TMP mill process water reported by Thuvander and Jönsson (2016).

From Table 3.4, also it could be observed that the molecules of hemicellulose present in the 5kDa permeate have a molecular weight (Mw) of 1108, while the molecular weight of the 10 and 30kDa permeates were Mw of 2827 and 6805 Da, respectively. In contrary, the molecules (Mw) of lignin of 5, 10, and 30kDa permeates were 2096, 2365, and 2281 Da, respectively. However, M_n molecular weight of molecules in these permeates were varying from 741 to776. Based on these results, the molecular mass of the hemicelluloses and the lignin (Table 3.4) suggests that an ultrafiltration membrane with a cut-off between 1 and 15kDa should be used to retain the hemicelluloses and allow at least part of the lignin to pass through. Since each molecular mass and purity of hemicelluloses has a specific industrial application, it is important to select the most compatible membrane (type, cut-off, area, and materials) for overall effectiveness.

Table 3.4. Analysis of GPC results of the molecular mass distribution of (a) sugars (measured as refractive index) and (b) lignin (measured as UV absorbance) in the retentate of UF.

	Hemicellulose						**Lignin**					
	Concentrate			Permeate			Concentrate			Permeate		
MWCO (kDa)	M_n [a] (Da)	M_w [b] (Da)	IP [c]	M_n (Da)	M_w (Da)	IP	M_n (Da)	M_w (Da)	IP	M_n (Da)	M_w (Da)	IP
5	12018	22310	1.858	747	1108	1.483	1405	3669	2.611	776	2096	2.701
	1192	1474	1.237									
10	13742	33002	2.402	1018	2827	2.777	2348	4429	1.886	741	2365	3.192
	1167	1467	1.257									
30	14798	54052	3.653	1427	6805	4.769	990	2676	2.704	755	2281	3.021
	1261	1623	1.287									

[a] M_n, number-average molecular weight. [b] M_w, weight-average molecular weight. [c] IP, polydispersity. Samples were diluted 13 and 9 times of 5 and 10kDa retentate before the analysis.

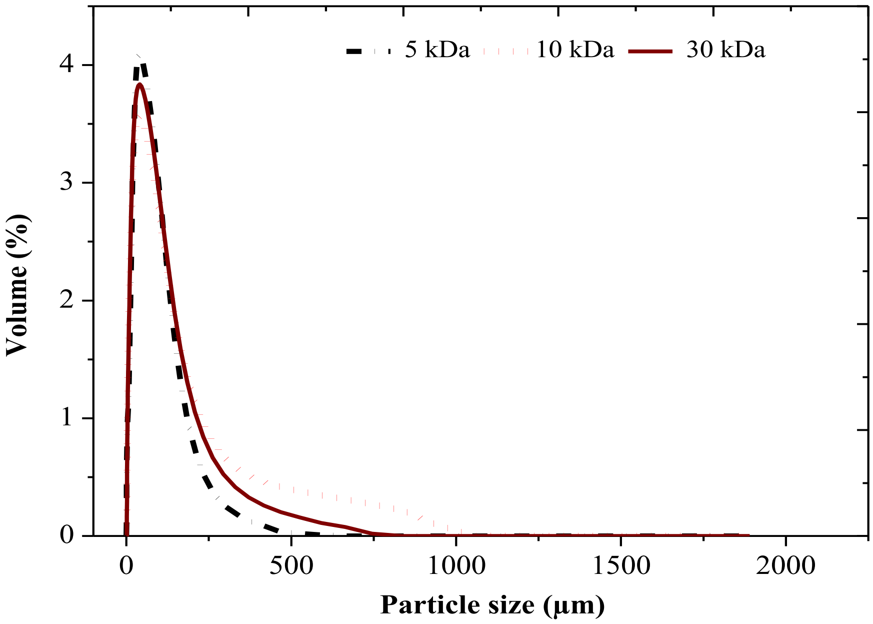

Fig. 3.14. Particle size distribution of the retentate components of 5, 10 and 30kDa membranes

3.4.7. Conclusions

Hemicelluloses and lignin recovery and purification from thermomechanical pulp (TMP) mills process waters were studied in this investigation using three hydrophilic UF membranes made of regenerated cellulose with different molecular weight cut-offs (5, 10, and 30kDa). After UF of the process waters, 5 and 10kDa membranes showed high hemicellulose recovery rates compared to 30kDa membranes. The recovery of the hemicelluloses was above 95% for 5kDa membranes and around 89% for 10kDa membranes, and the purity was approx. 75% for 5kDa and 80% for 10kDa membranes. Hemicellulose recovery of 30kDa was only around 52%. Compared to 5kDa membranes, a cut-off of 10kDa seems to be feasible for the separation of lignin from hemicelluloses; it retained hemicelluloses better than it retained lignin. While a cut-off of 30kDa membrane was found to be unsuitable for this application since both the recovery and the retention were too low. In summary, ultrafiltration appears to be a feasible method for hemicelluloses separation and concentration from TMP process waters.

3.4.8. References

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CHAPTER IV

Conclusion and Future Research Directions

4.1. Conclusion

Although hemicelluloses are potential raw material for the production of various bioproducts. However, the fate of hemicelluloses and other organic molecules in TMP process streams is limited to discharge in wastewater streams for biological treatment. In this study, the feasibility of advanced ultrafiltration technology for hemicelluloses recovery from TMP wastewaters was investigated. Particularly, the influence of ultrafiltration membrane cut-offs and volume reduction factors on membrane flux, recovery and purity of hemicelluloses were evaluated. Ultrafiltration of TMP process water using three hydrophilic regenerated cellulose membranes with cut-offs of 5, 10 and 30kDa shown higher retention of hemicelluloses and lower retention of lignin in the all tested conditions. However, 5 and 10kDa membranes gave much better recovery rates on hemicelluloses than 30kDa membranes. Hemicelluloses concentration in retentates after ultrafiltration varied widely depending on volume reduction factors and the membrane cut-off. Thus, to predict the purity and yield of hemicellulose and lignin, not only the correlations between the concentrations in the retentate and permeate are required, but the volume reduction as well. Based on these results, the molecular mass of the hemicelluloses and the lignin suggests that an ultrafiltration membrane with a cut-off between 10kDa should be used to retain the hemicelluloses and allow at least part of the lignin to pass through. UF membrane process is capable method for hemicelluloses recovery from TMP side stream, however, further investigations are needed on a larger scale to study the process feasibility, meanwhile to optimize its performances.

4.2. Future Research Directions

Despite the success of UF membrane process in hemicelluloses recovery, some challenges persist and need to be further addressed. Some future research opportunities include:

- *Concentration polarization control:* During the process water filtration, concentration polarization is causing a permeate flux (J) decline. Thus, further studies to find an optimum way of decreasing the concentration polarization effect are needed to reduce the deposition that takes place on top of the membrane.

-*Feasibility and reliability:* We thought that further investigations should be conducted on the larger scale to study the process feasibility and reliability because the transition from lab scale- and pilot-scale studies to industrial operations is still a remaining challenge in IFBR. Also, further researches should focus on the fabricating of novel membrane materials to meet the requirements in pulp and paper industry.

- *Membrane fouling control*: Because of the composition of forest industry process streams and effluents. Membrane fouling is the most important issue affecting the broad applications of membrane separation technology in this area. Therefore, strategies for applying appropriate pre-treatment methods to the feed stream, employing appropriate physical or chemical cleaning protocols, and chemically or biochemically modifying the mixed liquor are called for further studies to control membrane fouling and clogging.