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Engineering of a Pilot Plant for the Treatment of Effluents from a Mechanical Pulping Line

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Abstract

The mechanical pulping industry faces a lot of challenges today, including economic pressure, a saturated market and competition for biomass from the energy sector. A lot of attention has been attracted by the pulping based “biorefinery concept”, which points out ways towards a more comprehensive, sustainable and efficient utilization of biomass. Its ideas can also be applied to effluent streams from mechanical pulping lines.

The aim of this work was to develop a process concept that can be readily implemented and used on a large scale for the treatment of effluents from mechanical pulping lines. An increase in profits of the stagnant pulping sector, as well as access to new markets should be enabled thereby. The suitability and key features of different unit operations were first studied in a literature survey. Experimental studies using laboratory and pilot scale equipment were used to verify the technical and economic feasibility of the process concept. It was shown that the concentration of the targeted valuable component could be increased by 35 times with a yield of 78%, thereby making the process feasible on industrial scale.

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1

Introduction

Global population growth, increasing energy demand and dwindling fossil fuel resources, as well as the environmental impact of human activities are among the main challenges the international community is facing today. A central task will be the global supply of adequate food, energy and raw materials, while taking care of our planet.

An increased and efficient use of renewable resources, such as lignocellulosic biomass as a feedstock for bio-based materials, may play an important role to meet these targets. Among the main components of lignocellulosic biomass, cellulose is the only one that is already used as an industrial feedstock for a variety of applications. Besides being used for pulp and paper products, it is a raw material in the textile industry and also gaining importance as a feedstock for renewable transportation fuels such as bioethanol [1].

The potential of hemicelluloses and lignin, the two other main components of biomass, is far from being fully utilized, although promising future applications have been identified. Certain properties are attributed to hemicellulose that make it for example suitable for use in biodegradable barrier material and coatings. As the global packaging market is projected to reach a sales volume of nearly $1 trillion by 2020 [2], packaging applications are the key (commercial) motivation to study hemicellulosic materials. The growing number of men, and the increase in living standards in the developing regions, fuels consumption across a wide range of products. Consequently, there is growing demand for the packaging of these goods. In terms of economically developed markets, drivers for the packaging industry include trends towards smaller households and accompanying demand for more, smaller pack sizes. Also, there is an increasing requirement for convenience among consumers [3]. Plastics, which already have the largest market share of over 40%, will experience the highest annual growth according to the market study by Smithers Pira [2]. At the same time, less than 3% of the waste plastic worldwide gets recycled. Furthermore, once discarded, petroleum-derived plastics are non-biodegradable, and accumulated waste generated by the continual disposal of huge volumes of food packaging has raised serious concerns about their detrimental effects on the environment and wildlife [4].

In terms of paper packaging, common barrier materials, used to improve properties of the base material, include aluminium and polyethylene [5]. While the functionality of such barrier materials is without question, their use can complicate or restrict end-of-life treatment options, critically impacting aspects related to sustainability. Innovative new barrier solutions that can address such limitations and contribute to sustainability are increasingly desirable. Hemicelluloses are such organic substances, which can be widely used for these types of applications, especially for the prosperous field of barrier coating. In today's pulp and paper industry, significant amounts of hemicelluloses are dissolved in process waters and become discharged as part of the effluents. With the infrastructure in place, mechanical pulp mills could increase their profits by recovering hemicellulose from the effluent.

Hence, the main objective in this work was to develop a process concept that can be readily implemented and used on a large scale for the separation, concentration and purification of hemicelluloses from mechanical pulping effluents. The concentration, the purity and the yield of hemicelluloses are decisive characteristics of such a process – these parameters should be maximized in order to achieve a competitive product. Yet the recovery/extraction system should be simple, inexpensive, and the energy demand should be kept as low as possible.

This thesis is structured as follows: first, the sources and chemical structure of hemicelluloses, together with properties relevant for their separation are described in **Chapter 2**. Being the industrial source of hemicelluloses in this work, and the targeted customer industry, mechanical pulping and the characteristics of the resulting effluents are discussed in **Chapter 3.** Currently installed wastewater treatment options are illuminated, as well as the opportunities of a hemicellulose recovery system for plant operators and system suppliers (e.g., ANDRITZ' Mechanical Pulping Systems division). While dissolved air flotation was applied specifically for the removal of suspended solids, different types of membrane filtration can be used to fractionate all kind of biomass components. Fundamentals of these separation operations are discussed in **Chapter 4**.

Chapter 5 provides an overview of the processes investigated on lab and pilot plant scale. Effluents were obtained from a mechanical pulp mill, and their composition and characteristics, as a function of the operating conditions during pulping, are displayed in **Chapter 6**. The removal of suspended solids in the effluents was one of the major targets of the current thesis. Investigated processes therefore were dissolved air flotation, microfiltration and separation by a confidential type of separator, and the obtained results are presented in **Chapter 7**. **Chapter 8** deals with the ultrafiltration trials that were performed in order to concentrate and further purify hemicelluloses dissolved in the effluent stream. Inorganics such as salts and other small compounds should be removed by passing the membranes, and the hemicelluloses should be retained by the membranes. Different membranes were tested on lab scale, and the most suitable was employed in pilot plant trials. Finally, concluding remarks and considerations regarding future work are discussed in **Chapter 9**. The used analytical methods, which are required for capturing data and allowing statements about the process performances, can be found in the **Experimental** section. An economic evaluation is subject to non-disclosure.

2

Hemicelluloses

Hemicelluloses are among the most abundant natural and renewable sources of polysaccharides as they constitute a major part of biomass. Thus, they have the potential to become an important resource for various industries, provided that efficient extraction and separation processes as well as promising applications are available.

As the main objective of this work is to find an industrially applicable process for the recovery of hemicelluloses in an effluent from a pulping process, knowledge on hemicelluloses is essential. Fundamentals of their structure, sources and behavior as well as their interaction with the other components of biomass will therefore be discussed in this chapter.

2.1 Sources and structure of lignocellulosic biomass

Hemicelluloses form a major part of lignocellulosic biomass. The latter refers to plant material in which the main components cellulose, hemicellulose and lignin are linked together to obtain structural mechanical strength combined with flexibility. Additionally, biomass contains water and – to a minor extent – pectins, extractives and inorganic compounds. The composition of lignocellulosic material is dependent on the plant species and also on the part of the plant. The pulp mill effluent used in this study contains material originated from aspen wood, while most softwood pulp mills process spruce. The compositions of these woods and other possible sources of hemicelluloses are therefore presented in Table 2.1.

Table 2.1: Composition of relevant sources of lignocellulosic biomass (as % dry weight).

Raw material		Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ref.
Hardwood	Poplar	44–52	18 – 26	20 – 23	[6]
	Silver birch	41.0	29.8[1)]	22.0	[7]
Softwood	Scots pine	40.0	24.9[1)]	27.7	[7]
	Spruce	41.7	24.9[1)]	27.4	[7]
Agricultural waste	Corn stover	35.1–39.5	20.7–24.6	11.0–19.1	[8]
	Rice husks	28.7–35.6	12.0–29.3	15.4–20	[8]
	Wheat straw	30–39	22–50	12–16	[8], [9]
Grasses		25–40	35–50	10–30	[9]
Newspaper		40–55	25–40	18–30	[9]

[1)] consisting of (Galacto-)Glucomannan and (Arabino-)Glucuronoxylan; excluding other polysaccharides.

Cellulose is a long-chain homopolysaccharide composed of β-(1→4) linked D-glucopyranose-units with a typical degree of polymerization (DP) of 10,000 for woody cellulose. By means of strong intra- and intermolecular hydrogen bonds, the linear cellulose molecules are aggregated together to microfibrils. Microfibrils build up fibrils that are finally combined into cellulose fibres, which are responsible for the fibrous nature of lignocellulosic plant cell walls. As a consequence of its fibrous structure, cellulose is insoluble in most solvents. [7] In contrast, hemicelluloses are heteropolysaccharides that contribute to the mechanical properties of the cell wall in serving as an interface between cellulose and lignin [10].

Lignin is a complex macromolecule that provides mechanical support in “gluing” plant fibres together. It is a random, three dimensional aromatic polymer formed from different cross-linked phenyl propane units. So-called “lignin-carbohydrate complexes (LCC)” result from covalent bonds between lignins and carbohydrates, the latter of which are mainly hemicelluloses. The molecular weight of lignin varies among the wood type and the isolation method (i.e., the degree of degradation inherent to the method). Reported values of softwood-lignin are in the order of 10-20 kg/mol. [7]

The structure of lignocellulose and its components is illustrated in Figure 2.1.

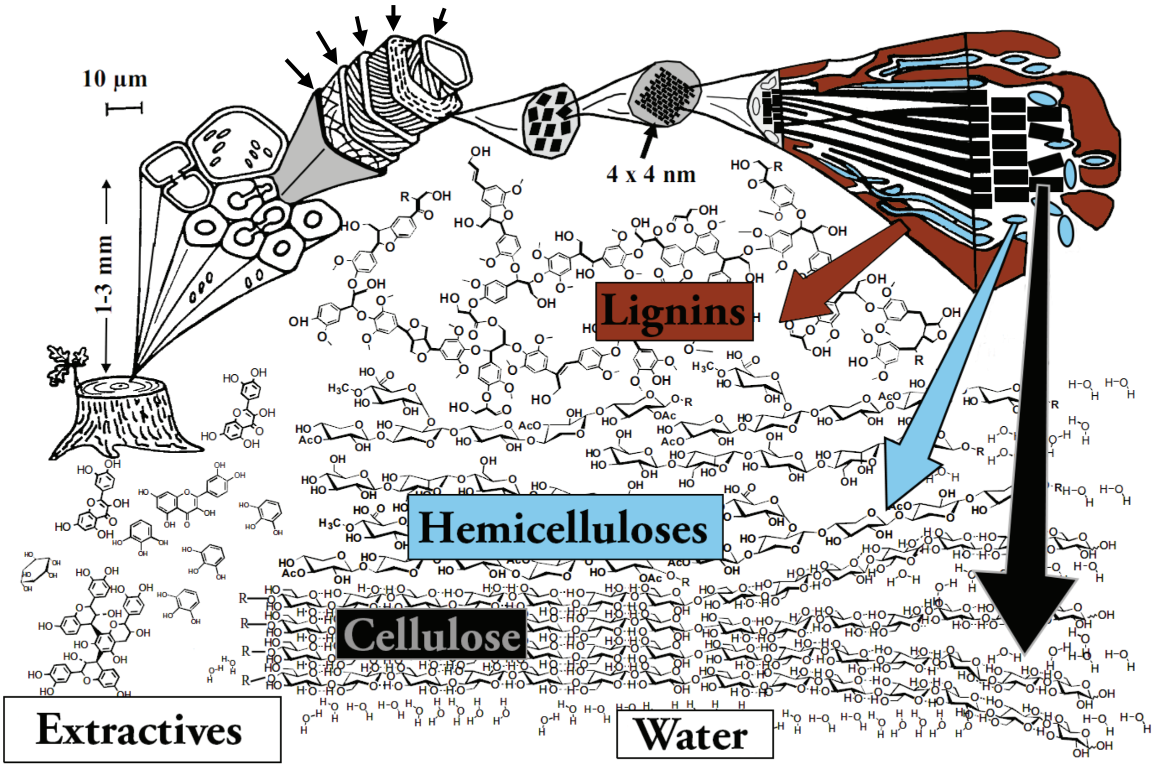


Figure 2.1: Structure of lignocellulosic biomass (illustrated by Per Hoffmann). ML = Middle lamella; P = Primary wall; S = Secondary wall (S1, S2, S3). Adapted from [6]

2.2 Chemical composition and structure

Hemicelluloses are one of the main components in plant fibre materials, comprising usually between 20 and 35% of dry mass of wood (see Table 2.1 and Table 2.2). In contrast to cellulose, hemicelluloses occur generally as branched heteropolymers composed of different quantities of various saccharide molecules. As a consequence of their lower degree of polymerization (typically up to 200), and their higher degree of branching, hemicelluloses show a higher solubility than cellulose in most solvents including water. Also their thermal and chemical stability is usually lower. [7], [10]

The content and structure of hemicelluloses vary among different plants. Their main monomeric building units are pentoses (D-xylose and L-arabinose) and/or hexoses (D-mannose, D-glucose and D-galactose). Certain uronic acids (4-O-methyl-D-glucuronic acid, D-galacturonic acid and D-glucuronic acid) and small quantities of deoxyhexoses (L-rhamnose and L-fucose) are also a part of hemicelluloses. All these components commonly occur as six-membered (pyranose) rings. In addition, hemicelluloses usually contain acetyl groups, which are easily cleaved in an alkalic environment, typically resulting in the formation of acetate in the pulping process. [10]

Table 2.2: Major hemicelluloses in hardwoods and softwoods, adapted from [10].

Occurrence	Hemicellulose	Amount (%)[1]	Units	Molar Ratio[2]	DP
Hardwood	Glucuronoxylan	15-35	β-D-Xyl*p*	10	100-220
			4-OMe-α-D-Glc*p*A	1	
			O-Acetyl	7	
Hardwood	Glucomannan	2-5	β-D-Man*p*	1-2	100-220
			β-D-Glc*p*	1	
			O-Acetyl	1	
Softwood	(Galacto-)	5-8[3]	β-D-Man*p*	3-4	~100
	Glucomannan	10-15[4]	β-D-Glc*p*	1	
			α-D-Gal*p*	1[3] / 0.1[4]	
			O-Acetyl	1	
Softwood	Arabinoglucuronoxylan	7-15	β-D-Xyl*p*	10	~100
			4-OMe-α-D-Glc*p*A	2	
			α-L-Ara*f*	1.3	

[1] by dry weight

[2] approximate values

[3] galactose-rich fraction

[4] fraction with low content of galactosyl units

Hemicelluloses from hardwoods and softwoods differ significantly. Xylans and mannans are the most abundant hemicelluloses. Xylans, the main hemicelluloses in hardwoods, have a backbone of β-(1→4)-D-xylopyranosyl residues and different side groups. In wood xylans 4-O-methyl-D-glucuronic acid in linked to some of the xylopyranosyl units. Hardwood xylans are partly acetylated in their native state, whereas softwood xylans contain L-arabinose side groups. Average DP of 100-220 corresponding to average molar masses of 5,600-40,000 g/mol have been reported for xylans, although these numbers depend on wood species as well as method of isolation and analysis [10].

Glucomannans consist of linear chains of β-D-glucopyranose and β-D-mannopyranose residues connected via β-(1→4)-D-linkages. Galactoglucomannan (GGM), one kind of glucomannans and the predominant hemicellulose in softwoods, constitute about 20% of dry matter. In contrast to hardwood glucomannans, mannosyl residues in GGM partially carry a β-D-galactopyranose unit. Besides, irregularly distributed acetyl groups also occur in the native state of (galacto-)glucomannans, linked to mannosyl residues. [10]

Pectins form another group of polysaccharides present in wood, which make up only a few percent. These irregular, acidic and susceptible compounds consist of a backbone of D-galacturonic acid and D-galactose, L-arabinose and L-rhamnose residues. As they are easily dissolved and degraded by alkali, they can make up a significant amount of dissolved solids in an effluent stream. [10]

2.3 Applications

Hemicelluloses have received considerable attraction as possible renewable resource for numerous applications. This is mainly due to (i) their abundance in biomass, and (ii) their unique nature that makes them extremely versatile. Most important, and in contrast to starch, material based on wood, straw, as well as husks and brans from agricultural crops, have the positive characteristic that they do not interfere with food security. Thus, various applications can be discussed without public outcry.

Upon isolation, hemicelluloses can be present in monomeric, oligomeric or polymeric form, or as a combination of them, which correspond to different products. Various applications have been reviewed in the recent literature [11]–[14]. In this work, polymeric hemicelluloses are of key interest. They can be used as a material for biodegradable packaging films or edible foodstuff coatings. These materials have exceptional grease, oxygen and aroma barrier properties, as well as a satisfactory mechanical strength. Challenges mentioned in literature include their poor stretchability, and the hygroscopic nature of the initial substance resulting in high sensitivity of the properties to moisture. Modification methods help to achieve tailored products and include addition of plasticizer, cross-linking agents and blending polymers, functionalization of the hemicelluloses as well as lamination technique. Further research is needed on their behavior in coating technologies. [14]–[18]

Other prospective applications include foams and gels that could be used, e.g., in cosmetics, tissue-engineering or drug delivery systems [11]. Due to their promising physicochemical properties and biological activity, polymeric hemicelluloses could serve, for example, as environmental-friendly surfactants, or paper additives. Also, these materials could be used in the food, cosmetic, textile and biomedical industry [11]–[14]. Guar gum, a gel-forming galactomannan, exemplifies possible applications of hemicelluloses. It is already commercially employed in the form of guar gum powder as stabilizer, emulsifier, thickener and gelling agent in the food, pharmaceuticals, cosmetics, paper, textile, explosive and oil well drilling industry [19].

Despite the intensive research activities, hemicelluloses are far from being fully utilized as commercial products on an industrial scale. Regarding the pulp and paper industry, there is a general trend towards green chemistry and sustainability, as well as a growing interest for the biorefinery concept. These facts have brought focus on utilizing woody hemicelluloses as a natural resource of value-added chemical products and biofuels in this industry [14]. In this context, the principle of biorefineries, a term that refers to the processing of biomass to produce energy, fuels and chemicals, will be discussed briefly in the next chapter.

2.4 The biorefinery concept

The reliable availability and affordability of energy supply, as well as its impact on environment are some of the most serious challenges the world economy is facing today. Industrial biorefineries have been identified as prospective opportunities for climate protection, value creation and resource efficiency meeting the growing demand for energy, fuels and materials. A biorefinery is defined in the German "Biorefineries Roadmap" as follows:

> "A biorefinery is characterized by an explicitly integrative, multifunctional overall concept that uses biomass as a diverse source of raw materials for the sustainable generation of a spectrum of different intermediates and products (chemicals, materials, bioenergy/biofuels), allowing the fullest possible use of all raw material components. The

> co-products can also be food and/or feed. These objectives necessitate the integration of a range of different methods and technologies." [20]

The biorefinery includes the supply of raw material, the pretreatment/conditioning of biomass and the separation of components (primary refining) and furthermore subsequent conversion and refining steps for the manufacturing of finished products (secondary refining). Various types of biorefineries can be classified based on the aspects of used feedstock, resulting intermediates acting as platforms for secondary refining, employed processes and fabricated products. These central elements of biorefineries are presented in Figure 2.2.

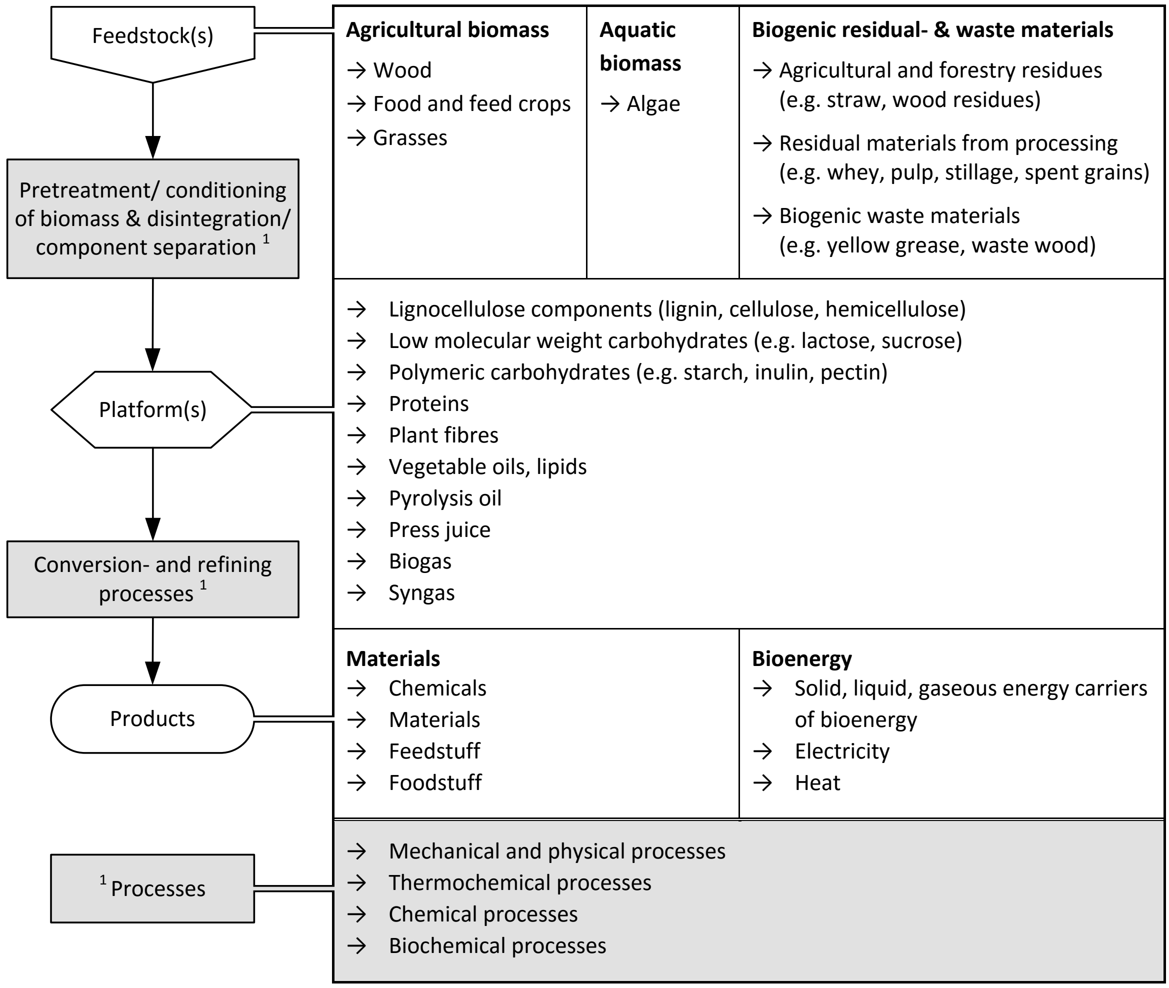


Figure 2.2: Biorefinery process chains and elements used in the classification of biorefineries, adapted from [17].

Pulp and paper mills embody several features of a biorefinery [13], which makes them an ideal base to develop an integrated forest biorefinery. Those mills are already focused on the collection and processing of biomass in large quantities with the infrastructure and trained workforce in place. Table 2.3 lists the essential drivers for pulp mill biorefining. A pulp mill fulfils tasks of primary refining including pretreatment, mechanical fractionation, extraction, separation and combustion. Secondary refining is partly done in a paper mill, where final products are manufactured. However, further steps need to be taken to achieve a sustainable "fullest possible use of all raw material components" [20]. Nowadays pulping processes dispose byproducts or thermally convert them to produce heat and power [21]. Additional utilization of byproducts is realized not more than partially in most cases, e.g., in case pulp and paper facilities act as rather rudimentary biorefineries by producing tall oil (kraft process), or cellulose derivatives. Testova [13] provided a list of examples of commercial pulping based biorefineries in Europe. Given the increasing number of biorefineries worldwide [1] and the aspiring technology clusters and funding programs like BBI Joint Undertaking - a €3.7 billion partnership between the EU and the Bio-based Industries Consortium [22], companies will continue to jump on the bandwagon and evaluate their possible contribution to biorefineries.

Table 2.3: Drivers for pulp mill biorefining, from [21].

- Economic pressures of pulp production
- Reduction of dependence on petroleum
- Chance to improved profits of the stagnant paper industry
- Competition for biomass from the energy sector
- Processing of large volumes of biomass
- Available infrastructure
- Global incentives for fuels/chemicals from biomass (incentives, taxes, credits)
- New efficient separation processes are available [23]

3

Mechanical pulping and its effluents

Pulping deals with the liberation of fibres from lignocellulosic plant material, about 90% of global production originating from wood and 10% from annual plants [24]. This is principally achieved by mechanically and/or chemically processes, leading to various pulp grades. Chemical pulping is based on the "cooking" of raw material (mainly wood chips) in chemical solutions at elevated temperature and pressure to soften and dissolve lignin and thus to extract the fibres. Mechanical pulping commonly involves the pretreatment of wood, e.g. with steam, prior to its separation into a fibrous suspension by abrasive grinding or refining.

Pulp can then be converted to a variety of products finding numerous applications including wrapping/packaging, printing/writing, newsprint and tissue.

Efficient, flexible and versatile utilization of all biomass components affords an effective disintegration of the raw material. This is achieved by various methods and processes, pulping being of them. The manufacturing process of pulp, especially refiner mechanical pulp, and characteristics of resulting process streams are discussed in the present chapter.

3.1 Mechanical Pulping Process

Mechanical pulping makes use of most wood material in order to achieve a comparably high yield combined with good strength and acceptable optical properties of the pulp. Whereas 80-95% yield is achieved in mechanical pulping, only approximately half of the wood becomes pulp in chemical pulping as the rest is dissolved [24].

Pulp production based on mechanical defibering can be divided in two categories: groundwood mechanical pulp (GMP) and refiner mechanical pulp (RMP). GMP is produced by pressing wood logs against a rotating grinding stone. New groundwood pulp production lines are no longer starting operations today, only spare parts and services for existing lines are being sold. Refiner mechanical pulp is produced as wood chips are reduced in size and fibrillated, and thus converted to mechanical pulp by means of so-called disc refiners. Pretreated chips are fed between two parallel, patterned refiner discs, at least one of them rotating. There, a substantial part of the mechanical energy is transformed to heat via plastic and visco-elastic work. The induced warming of the wood leads to generation of steam from the moisture in the chips, as well as softening of the lignin. Thereby, the required energy for the liberation of the fibres from the wood matrix is minimized [25]

Several process variants for RMP have been established with the aim of improving pulp quality and reducing energy consumption. They are characterized by applied parameters like (i) temperatures, (ii) pressures, (iii) chemical treatment, as well as (iv) retention times in the course of processing.

Thermomechanical Pulping (TMP) is the most common mechanical pulping process today. In such a process screened and washed chips are preheated and refined under steam-pressurized conditions. This leads to a softening of the lignin, which in turn increases the long-fibre yield, as liberation of the fibres without mechanically damaging them is enhanced. The main raw material for TMP are softwood grades, since hardwood features rather poor pulp strength properties. This is explained by the missing formation of fibrils during refining of hardwood, which is separated into shorter, rigid fragments instead. [26]

Chemi-thermomechanical Pulping (CTMP) combines the TMP process with pre-impregnation of the wood chips with chemicals (e.g., NaOH, Na_2SO_3). By chemically weakening the inter-fibre bonding, fibres can be separated with minimum reduction in fibre length. This treatment allows the production of pulps with higher strength and brightness than that of TMP, even hardwoods can be used. The various operations of a typical CTMP process are shown in Figure 3.1. Bleaching chemicals may be used to achieve certain pulp properties. Addition of hydrogen peroxide for example increases the brightness and the water uptake capacity and improves the strength of the pulp. [24], [25], [27]

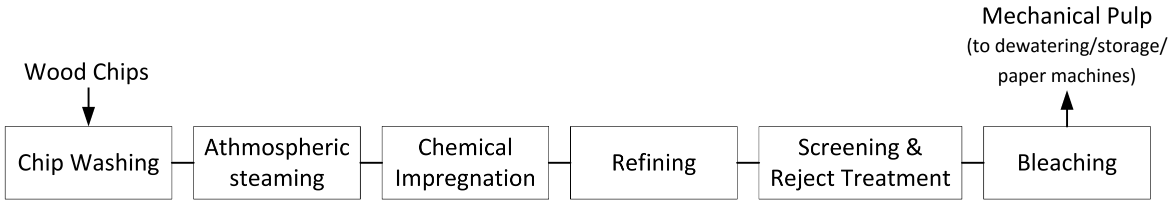


Figure 3.1: Main unit-operations of a typical CTMP process, adapted from [25].

The more recent P-RC-APMP (mild Preconditioning of the chips, Refiner Chemical Alkaline Peroxide Mechanical Pulping) process differs from conventional CTMP as alkaline peroxide solutions are used prior to refining, which enables higher alkali charges before refining. As a result, the energy requirement for subsequent fiberizing and refining is considerably reduced, i.e., from 1350–1500 kWh/ADt to 1050–1200 kWh/ADt. In addition, the use of sodium sulfite can be avoided. [27]

3.2 Dissolution of biomass components during mechanical pulping

As a result of the milder chemical treatment of biomass in mechanical pulping compared to chemical pulping (lower chemical charge, shorter residence time), the covalent linkages between individual biomass compounds are cleaved to a lesser degree. Consequently, most non-cellulosic polymers stay attached to the fibres and contribute to the pulp fraction and the high yield. However, the intensive mechanical work, as well as high temperatures and pressures cause the dissolution of some biomass components in the course of mechanical pulping. Treatment with chemicals in CTMP further enhances the release of wood material into process waters.

Such process waters from mechanical pulping processes typically contain dissolved hemicelluloses, pectic acids, lipophilic wood extractives (e.g. fatty and resin acids), lignin, and low-molecular-weight carboxylic acids, mainly acetic acid. [28]

In the course of thermomechanical pulping of Norway spruce about 10% of galactoglucomannans were found to be released from the wood and dissolved in the process water [29]. Willför et al. [31, 32] found the amount of non-cellulose polysaccharides from various softwood and hardwood species dissolved in water at elevated temperatures to vary between 1.5 and 7%. At the mild conditions applied in this previous study, xylans, the major hemicelluloses in hardwood, were hardly dissolved, probably due to their branched structure.

In CTMP, the alkaline treatment induces deacetylation of hemicelluloses, which leads to (i) the release of substantial amounts of acetic acid, and (ii) a partial re-adsorption of dissolved galactoglucomannans onto fibres. The dissolution of xylans, pectins and lignin on the other hand was found to increase with increasing alkalinity and peroxide bleaching. This was attributed to increased fibre swelling and chemical degradation reactions (also due to the cleavage of lignin-carbohydrate bonds; see [29], [32]–[34]).

3.3 Treatment of effluents from mechanical pulping

Pulping processes utilize considerable amounts of water, which causes significant effluent streams that need to be treated. In addition to dissolved substances from wood, these effluents contain the employed process chemicals. Pokhrel and Viraraghavan [35] performed a review on wastewater characteristics of pulp and paper mills and various treatment options. The following alternatives for the treatment of waste water from CTMP mills are commonly in use [27]:

- The most common method is the activated sludge process (ASP). Sometimes, additional chemical treatment processes are combined with ASP due to the high concentration of nutrients in the wastewater.
- Effluents from CTMP plants are treated together with process streams from adjacent kraft pulp mills, if existing. The mixed effluent from the CTMP process is firstly evaporated to achieve a required minimum consistency. It is then mixed with weak black liquor from the kraft pulping and concentrated to a high dry solids content (69-85%) in a so-called multi-effect-evaporation plant. The concentrates are thermally converted by incineration in a recovery boiler, where also some chemicals are recovered.
- In the P-RC APMP mill from which the effluents were taken for the present thesis, effluents are used for biogas production in an anaerobic stage since 2014. However, according to the mill, the operators are not satisfied with the economical outcome of the biogas production, particularly considering falling oil and gas prices [36].
- The amount of arising effluent is minimized by internal process optimization [35].

3.4 Potential benefits of hemicellulose recovery

Carbohydrates that are dissolved and accumulated in process waters from mechanical pulp production are partly removed with the effluents. On the one hand, this is considered as a drawback, since it is related to a lower pulp yield and a higher load on the environment or wastewater treatment system. If, on the other hand, the waste stream is considered as a feedstock for valuable products, willingness of pulp mill operators to implement a corresponding concept will strongly increase. This especially applies to the concept of recovering hemicelluloses in effluents from mechanical pulp mills, which have not been the primary target of biorefinery concepts so far. This can at least partly be explained by the much higher yields in mechanical pulping compared to those of chemical pulping, resulting in lower amounts of possible raw material for the biorefinery system. [37]

Biomass components in effluents from mechanical pulping are less degraded than those in chemical pulping. Thus, features of their native structure can better be used in value-added products (see Section 2.3) and production costs of such products are potentially decreased.

The development of a system for the recovery of hemicellulose from mechanical pulping effluents offers, inter alia, the following possible benefits to plant operators and system suppliers (e.g., ANDRITZ' Mechanical Pulping Systems division) [21]:

- Increased profitability and competitiveness
- Improved efficiency of raw material utilization
- Existing processes are hardly affected, hence the quality of the main product (i.e., the pulp) is not affected
- Protection and stimulation of traditional product lines (i.e., CTMP systems)
- Generation of know-how on how to steer the mill towards peak performance
- Access to new markets by selling new and or improved products

4

Unit operations for the separation of biomass components

Effluents from mechanical pulping lines have a complex composition. Apart from the targeted hemicelluloses, also other substances like fibres, fines, extractives, lignins and added extraction chemicals are present. Consequently, adequate processes are required to separate the hemicelluloses and unwanted impurities.

4.1 Dissolved air flotation for particle separation

Flotation is an efficient technique to separate light particulates from liquids, especially water. Particulates are attached to gas bubbles and subsequently can be floated from the liquid phase due to the large difference in density between the bubbles and the liquid. The different flotation techniques such as dissolved air flotation (DAF), induced air flotation (IAF) and electroflotation (EF) are used in a variety of applications: (i) municipal wastewater treatment, (ii) minerals processing [38], (iii) the treatment of recycled paper in the pulp and paper industry, (iv) chemical processing plants, or (v) oil refineries [39].

In the first part of this chapter, the fundamentals of flotation technology will be discussed. The key design variables in a flotation system controlling the separation efficiency will be addressed, as well as sample applications of DAF. The second part focuses on an experimental study of a pilot-scale DAF-system. Specifically, the suitability of flotation for the separation of suspended solids from the effluent of a mechanical pulping plant was assessed.

4.1.1 Principles of flotation

A flotation process relies on four fundamental steps [39]:

1. The formation of bubbles in the liquid phase: There are three widely used types of flotation systems, their classification is based on the method of bubble generation:
    a. Dissolved air flotation. Pressurization of air is used for dissolving gas into the suspension to be processed. The subsequent drop of pressure (typically under laminar flow conditions) leads to the generation of extremely fine gas bubbles.
    b. Induced (dispersed) air flotation. This is a process involving the introduction of gas directly into the liquid by means of a revolving impeller, a diffuser, or an ejector at low pressure. This results in the generation of comparably large bubbles under turbulent conditions.
    c. Electroflotation. The dissociation of water causes the formation of oxygen and hydrogen bubbles in the liquid by passing a direct current between two electrodes.

    In this work, the theory of dissolved air flotation (DAF) will be discussed and the other methods will not be further detailed.
2. The contact between a gas bubble and a particle suspended in the liquid phase
3. Particle-bubble coalescence
4. The rise of the gas/solids to the surface of the liquid phase where the floated material can be removed via a skimmer.

Different mechanisms contribute to the formation of bubble/solid agglomerates as shown in Figure 4.1.

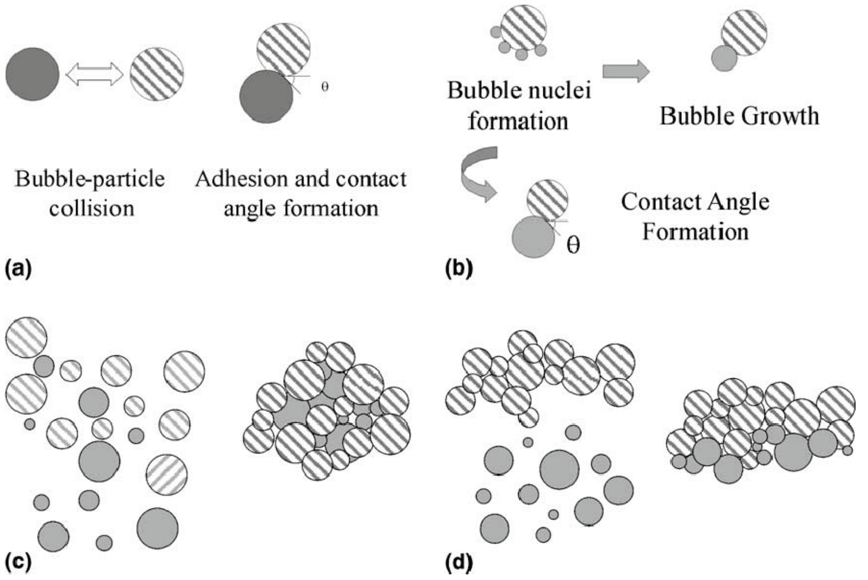


Figure 4.1: Bubble/particle mechanisms in DAF: (a) particle–bubble collision and adhesion; (b) bubble formation at particle surface; (c) micro-bubble entrapment in aggregates; (d) bubbles entrainment by aggregates. [40]

4.1.2 Gas solubility

A key mechanism, but also a process limitation for DAF, is the dissolution of gas (usually air) according to Henry's Law:

$$C_A = H_A \cdot p_A \tag{4.1}$$

Here C_A is the concentration of dissolved gas A in solution, H_A is the Henry constant and p_A is the partial pressure of gas A. Henry's law states that the amount of gas dissolved in the solution, and consequently the amount of gas released upon reduction of the pressure, are both directly proportional to the gas pressure. The solubility of gases is also influenced by temperature and dissolved solids concentration. In general, gas solubilities decrease with (i) increasing dissolved solids concentration (e.g., salinity), and (ii) increasing water temperature [41]. For example, Equation (4.2), proposed by Gameson and Robertson [42], illustrates the effect of high salinity and elevated temperature on the solubility of dissolved oxygen in water:

$$C_{DO} = \frac{475 - 2.65 \cdot S}{33.5 + T} \tag{4.2}$$

Here C_{DO} is the dissolved oxygen concentration in water with air above the water in mg/l; S is the salinity in mg/l and T is the water temperature in °C. According to this equation, approximately 43% less oxygen is dissolved at atmospheric pressure when changing the temperature from 20 to 60°C. However, a temperature change is also accompanied by a 53% decrease in liquid viscosity, which could nullify the net effect on overall process efficiency [43]. Dassey and Theegala [44] even found that the bubble production increased when increasing the temperature, which was explained by the increased gas diffusivity: the reduced air solubility at higher process temperatures was compensated by the increased saturation efficiency due to higher gas diffusion rates in the liquid.

4.1.3 Factors impacting dissolved air flotation

There are many factors that influence a dissolved air flotation system, often with strong interdependencies. Some of these factors have been already mentioned in the previous sections, in the following some will briefly be discussed in the following section ([41], [45]).

1. *Nature and size of the suspended particles*

The specific gravity is a decisive factor of the particle (or liquid) to be separated. While sand, for example, is difficult to flotate, low-density material, or an immiscible liquid like oil, can be often floated in an efficient manner. The surface properties of the suspended matter are also of vital importance: typically only particles with a hydrophobic surface are readily attachable to an air bubble which comes into contact with it [46]. An exception of this rules are moderately concentrated fibre suspensions: in these systems air bubbles become trapped in fibre flocs, leading to a preferred accumulation of fibres in the froth layer [47]. This principle can be even used to fractionate pulps [48].

2. *Bubble-size distribution and number of bubbles per unit volume of liquid*

As the particles to be removed generally need to collide with a bubble or an agglomerate, a large amount of dissolved gas is favourable for the removal efficiency. Other important variables are the number and size of bubbles, being a function of the physical system and the chemical composition of the wastewater. The effect of large air bubbles is (i) a fast, turbulent rise speed, resulting in a smaller air-solids contact time, and (ii) a low specific bubble surface area. More efficient removal of solids is achieved with smaller air bubbles due to an increased contact time and higher specific bubble surface area [49]. Typically, millions of bubbles per m^3 with a size between 30-100 µm are present in a dissolved air flotation system [49], [50].

3. *Design of the flotation unit*

The physical design and hydraulics of the flotation chamber determine the liquid flow profile. Adequate skimming devices are needed to remove the floated material, and to avoid drainage of components from the froth back to the aqueous phase.

4. *Composition and nature of the influent*

The influents' nature and composition are the most important factors. Beside the suspended particles, also the dissolved solids concentration is relevant, as it affects the amount of air dissolved and the size of the bubbles. Additionally, dissolved substances tend to alter the physical properties of the particle surface to be floated. The performance of a flotation system is thereby improved in case a more homogeneous composition and flow distribution can be obtained [45].

5. *Chemicals added*

Most air flotation systems employ the addition of chemicals to obtain optimal separation performance. Different chemicals are used to induce coagulation (i.e., the formation of insoluble flocs), de-stabilize (i.e., "break") an emulsion, and/or aid in the adsorption of air bubbles by the particles (or liquid droplets) to be removed. Also, frothers are essential to generate a stable froth layer for successful skimming.

6. *Temperature*

The temperature has an influence on the amount of gas dissolved (see Chapter 4.1.2) and the bubble size, but also on the influent's properties: some compounds may be dissolved at higher temperatures, but may crystalize at lower temperatures.

7. *Pressurization Mode*

Three configuration can be used, differing by the stream of process suspension that is pressurized [41]:

Full flow: When all of the incoming raw wastewater is pressurized, the most air is dissolved, but also the largest saturation system is required. Moreover, coagulated flocs are subject to the shear stress as a result of the pressurization process, and hence may disintegrate.

Partial flow: This strategy leads to reduced pumping costs, a better capacity to manage fluctuations in flow. Unfortunately, a lower amount of air can be dissolved when using this strategy.

Recycle flow: By returning a side stream of the clarified effluent to the pressurization system, the disintegration of flocs can be avoided. A disadvantage is the need for a larger flotation chamber.

4.1.4 Design parameters in dissolved air flotation

Based on the affecting parameters described in section 4.1.3, several characteristic numbers are used to control the performance of a DAF system:

Air/Solids Ratio

Widely referred to as the most important parameter in designing an air flotation system is the air/solids ratio. This ratio is defined as the mass of air released from solution (upon pressure change), divided by the unit mass of suspended wastewater solids to be treated [41], [43], [45], [51], [52]. The more air bubbles are interacting with the solids in the flotation basin, the lower the specific gravity of the air/particle agglomerates. The final result is an increased flotation rate, as well as an increased amount of solids collected by the ascending gas bubbles. Less than the optimum amount of air in the flotation chamber leads to a reduction of the removal efficiency, whereas too much air used causes low energy efficiency (i.e., an excessive amount of air needs to be compressed). The air/solids ratio can be estimated for DAF systems using the following equation:

$$\frac{A}{S} = \frac{R \cdot C_S}{Q \cdot X_f}(f \cdot P_a - 1) \tag{4.3}$$

A/S is the air to solids ratio in [mg/mg]; R is the flow rate of the aerated, pressurized stream (which depends on the mode of pressurization) in [l/min]; Q is the flow rate of the suspension to be treated in [l/min]; C_S is the air solubility at 1.0 atm pressure and at the operating temperature and salinity in [mg/l]; X_f is the concentration of suspended solids in the feed in [mg/l]; P_a is the absolute saturation pressure in [atm absolute]; f is the efficiency of air dissolution at the elevated pressure in the saturation chamber (typically f is assumed to be equal to 0.8).

Hydraulic Loading Rate

Another important design parameter that has to be controlled in a flotation system is the hydraulic loading rate. It is defined as the ratio of the total flow rate (i.e., feed flow plus recycle flow through the flotation chamber) and the liquid surface area of the flotation unit. It is typically expressed in [l/min/m^2]. Thus, the hydraulic loading rate has the dimensions of a typical flow speed, and can be interpreted as a superficial velocity. Theoretically, any particles with a rise velocity equal to, or greater than, the hydraulic loading rate will be removed in an ideal flotation unit [45].

Retention time

To obtain satisfactory removal of suspended solids, a suitable retention time of the air-solids mixture in the flotation chamber has to be chosen. The retention time, which is linked to the hydraulic loading rate and the rise velocity of the bubble-particle aggregate, is computed using Equation (4.4).

$$\tau = \frac{V_C}{Q+R} \tag{4.4}$$

Here, τ is the retention time in [min]; Q is the feed flow rate [l/min]; R is the recycle flow rate [l/min]; and V_C is the volume of the flotation chamber [l]. Typical retention times range between 3 and 60 minutes depending on the characteristics of process water, and the performance of a flotation unit. Wang et al. [45] report that the average retention time has significantly decreased in the past 50 years from 30 minutes to 3 minutes in typical applications. Prolonged retention beyond the optimum retention time usually has no substantial effect on effluent quality, as shown by Eckenfelder et al. [53] and Abid Baig et al. [54].

Recycle rate

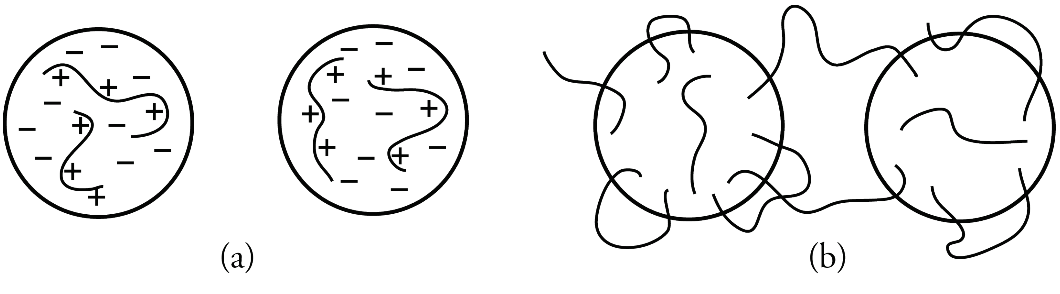
When using the recycle stream pressurization mode, the recycle ratio is another important design variable, which has to be evaluated empirically. It is the ratio of the flow of the recycled effluent to the influent flow. Suggested recycle ratios vary between 10% and 100%. [53]

4.1.5 Coagulation and Flocculation mechanisms

Coagulation and flocculation play an important role in wastewater clarification. Particles in water generally have a net negative charge and repel each other due to predominant electrostatic repulsive forces. Their surface charge can be altered by adding a dissolved substance that carries positive charges, like aluminum salts or polyelectrolytes. This process of charge neutralization and destabilization of the colloidal suspension is called coagulation. A too high dose of coagulant will create oppositely charged components causing redispersion.

Flocculation, induced by polyelectrolytes, typically results in an improved floc quality, i.e. larger and stronger flocs. Patching flocculation (Figure 4.2 a), is created by covering parts of the anionic particle surfaces with a polymer, forming local positively charged regions (i.e., patches). The differently charged parts on particles subsequently cause strong interactions between the particles, thus initiating flocculation. In the mechanism of bridging flocculation (Figure 4.2 b), a long-chain (high molecular weight) polyelectrolyte with usually low charge density is adsorbed on a particle's surface. The tails and loops of the polyelectrolyte are free to attach themselves to the surface of other particles, thereby achieving bridging, resulting in relatively strong flocs.

Apart from these electrostatic interaction mechanisms, flocculation can be induced in case a polyelectrolyte adsorbs via hydrogen bonds or ion bindings. [55], [56]



(a) (b)

Figure 4.2: Patching (a) and bridgding (b) flocculation mechanisms.

Using coagulation and flocculation, the performance of a DAF system can be improvement significantly. Common chemicals for coagulation/flocculation include poly-aluminium chloride (PAC), poly-di-allyl-di-methyl-ammonium chloride (poly-DADMAC), and poly-acrylamide (PAM). Drawbacks are the additional costs and that the further usage of the coagulated and flocculated material is impaired by the added chemicals. Public health concerns are related to the use of alum and PAC regarding disposal problems of sludge and residual aluminium concentration in the treated water [57].

4.1.6 Examples of industrial flotation systems

The first application of air flotation in the field of wastewater-treatment was in the flotation of suspended solids like fibers, and other low-density solids. Nowadays, flotation is also used for the removal of oil and grease from wastewater [58]. Technological and economic advantages have been reported for example by Rubio et al. [40], Wang et al. [45], and Packham and Richards [43], and can be summarized as follows:

- high efficiency to remove contaminants: high capacity, hydraulic loading and low residence time resulting in smaller tank sizes and less space needs;
- higher sludge and scum consistency (i.e., solids content) than in a sedimentation process;
- low investment and operating costs through simple construction;
- hardly consumables (e.g., compared to disc separators)
- relatively easy handling (e.g., compared to disc separators)
- high selectivity to recover valuables with appropriate surface properties (i.e. naturally or by addition of chemicals), e.g. minerals like Au, Pt, Pd.

Shammas and Bennett [41] conclude that it is difficult to compare the efficiency of various air flotation systems due to the high number of differing interdependent operating conditions. However, the ratio of solids concentration in the clarified effluent to solids inflow concentration is a common way to describe a system's performance. Table 4.1 shows typical process efficiency data. Although it should be stated that these values strongly depend on the application and operational parameters, it can be seen, that flotation generally provides high efficiency in the removal of suspended solids.

Table 4.1: Typical removal efficiency of dissolved air flotation systems.

Removal without chemicals (%)	Suspended Solids = 40-80
Removal with chemicals (%)	Suspended Solids = up to 99

4.1.6.1 Coagulation, flocculation and flotation in the pulp and paper industry

Pulp and paper mill industry consumes up to 500 m^3 of water per ton of paper produced [59], [60] and also a large amount of energy. The effluents generated by this industry commonly have a high pollutant load. Considering the environmental impact, as well as the ongoing stringent legal requirements, pulp and paper mills need efficient wastewater treatment methods, flotation being one of them [61].

In their review on the treatment of pulp and paper mill effluent, Thompson et al. [62] name sedimentation and flotation suitable for primary clarification (which refers to physicochemical treatment following pretreatment, mainly to remove suspended solids and colloidal particles). However, sedimentation was the preferred method within the mills in the UK, achieving >80% removal of suspended solids on average.

Lavallèe et al. [63] report that whitewater clarification, deinking washer filtrate clarification, and primary clarification (which can remove up to 98% of the suspended solids) are the most common applications of flotation separation technology within the pulp and paper industry. Moreover, they especially highlight the DAF effectiveness in secondary clarification applications (following primary clarification and biological treatment). They refer to two pulp and paper wastewater treatment systems, in which 97% and 99% removal of mixed liquor suspended solids (MLSS, i.e., a mixture of activated sludge and other wastewater) were achieved using 8.3 ppm and 15-20 ppm of flocculant respectively. Similar values are reported by Métivier et al. [64] with 97%-99.4% TSS removal efficiency in the treatment of up to 10,000 mg/l MLSS in two pulp and paper mills. They used cationic polymers for flocculation.

In most cases, flotation is employed in the treatment of wastewater from recycled wastepaper processing. In this context, high removal rates are reported (e.g., see Wenta and Hartman [65]), with achieved total suspended solids removal (via DAF) in the range of 90% to 95% in paper mills (note, chemicals were used in these studies, but their type is undisclosed).

4.1.6.2 Flotation for de-inking

When flotation is used for removing ink from recovered secondary fibres, it is taken advantage of the hydrophobic nature of the detached ink particles, which can adhere to air bubbles upon colliding with them. Though both mechanisms, i.e., (i) entrainment of fibres in an air/solids network and (ii) adhesion of hydrophobic parts of fibre surfaces to air bubble surfaces, contribute to fibre removal, in dispersed air flotation only about 20% of the fibres are removed by flotation. The surface of fibers and fiber fines, being hydrophilic in nature, can be altered by chemicals and contaminations, making their surface more hydrophobic, which favors their removal [66], [67], [68]. Studies show that in flotation deinking, the removal efficiency of different materials in the paper recycling process descends in the following order: ink, fibre fines, ash, short fibres and finally long fibers [69]. However, more recent studies show that this order is also affected by phenomena taking place in the froth layer, such that in extreme cases long fibers are the primary flotate [48]

Ben et al. [70] demonstrated, that with bentonite/PAM chemistry, DAF units are very effective for removal of suspended solids, increasing it to 98% from 80% without chemical addition, but the flotation of dissolved and colloidal substances (DCS) was negligible. They point out that de-inking process water (which they investigated) differs significantly from TMP process water in which lipophilic substances tend to be present as colloidal solids rather than as dispersed solids. However, adoption of flotation systems seems to be dependent on the employed pulp and paper production process, as well as applied further treatment methods [61].

4.1.6.3 Chemicals as flotation aids in the pulp and paper industry

When speaking of chemical addition in the flotation unit, the most typical mode for pulp and paper mill applications is a dual-component system which uses both the effect of patch and bridging flocculation. Dual-component sysstems are often based on

- a low molecular weight cationic coagulant, which creates positively charged patches on the dispersed particle or neutralizes it's charge, and
- a high molecular weight anionic flocculant, which is added to form bridges between dispersed components.

An alternative to a dual-component system is a single component system at which a high or medium molecular weight cationic flocculant is typically used. It combines the mechanisms of charge-neutralization/patch flocculation and bridging flocculation. The flocculant should have a high molecular weight and a low charge density, as too high charge densities would lead to a flat conformation of the polymer on the surface of the particle [63], [56]. The higher flocculation efficiency of polyelectrolytes of higher molecular weight due to a combination of the charge neutralization effect and bridging mechanism was confirmed by Razali et al. [71]. Long chains (i.e., a high molecular weight flocculant) create loops and tails thereby contributing to the bridging mechanism. Wong et al. [72] studied the flocculation performance of several cationic and anionic polyacrylamides on paper mill wastewater. They concluded that a single-polymer system can be used alone (without combining it with an inorganic coagulant) since the efficiency of the polyacrylamide was remarkable: 98% TSS removal by coagulation-flocculation-sedimentation was achieved with a cationic PAM having a very high molecular weight and a low charge density.

4.1.6.4 Selective removal of DCS by Flotation

A newer application of flotation is in the selective removal of lipophilic extractives and polygalacturonic acids (e.g., pectins) from pulp and paper mill process water. Zasadowski [73] shows that over 90% of lipophilic extractives can be removed from bleached and unbleached softwood TMP process water by addition of a cationic surfactant during flotation. At the same time, the concentration of hemicelluloses (galactoglucomannan) was almost unaffected. He found the flotation to be more efficient at a lower pH than at a higher one. Leiviskä and Rämö [74] achieved effective coagulation of lipophilic wood extractives applying a cationic polyacrylamide with high molecular weight and low charge density on bleaching filtrates from kraft pulp mills. They found the performance of different cationic polyelectrolytes in causing coagulation of various components to be dependent on many parameters including, temperature, pH, and the dosage and charge density of added polyelectrolyte. Aside from the effect of the polyelectrolyte, the effect of temperature was significant, as the concentration of dissolved carbohydrates without addition of chemicals varied between ca. 900 mg/l and 400 mg/l, at 80°C and 18°C respectively (both values were reported for a pH of 5.5). The removal of lipophilic extractives and galacturonic acids from peroxide-bleached, fiber-free TMP water by DAF was investigated by Saarimaa et al. [75], using both inorganic coagulants and organic flocculants. They suggest carrying out at the operation at acidic conditions to increase the aggregation of resin acids (dissolved at pH 8) and to avoid an excessive consumption of chemicals. They used 20-80 mg/l PAM, and additionally 40-70 mg/l bentonite for the flotation of process water with a TOC of about 250 mg/l, achieving a high removal efficiency of lipophilic extractives. Bentonite, a popular natural clay that is widely used as an adsorbent and coagulant for water and wastewater treatment applications, its abundance and low price being beneficial [76], had a substantial effect on the formation of very big flocs. Galacturonic acids were selectively removed (i.e., other carbohydrate groups remained in the water) when inorganic coagulants or PAMs with high charge density were used. This indicates, that aggregation by charge neutralization is a more effective mechanism for galacturonic acids than bridging flocculation.

De Pinho et al. [77] tried to improve an ultrafiltration process for treatment of bleached pulp effluent by integration of upstream dissolved air flotation on a laboratory scale. Indeed, they measured 63% TSS removal, reducing TSS from 397 to 147 mg/l using DAF, but the permeate flux of the dissolved-air/MF/UF sequence showed no improvement relative to the MF/UF sequence. However, an increase of 14% in permeate flux was achieved by the dissolved-CO_2/MF/UF sequence. This fact was explained by a reduction of membrane fouling due to the destabilization of colloidal particles present in the raw effluent, which was induced by the acidification ability of the CO_2 gas.

4.1.7 Preliminary recommendations regarding DAF based on the literature

In summary, the performance of DAF is dependent on a large amount of variables, making it necessary to evaluate its applicability for the specific wastewater to be treated. Usually, a high removal efficiency of suspended solids can be achieved. Most important, also colloids can be removed after an adequate addition of chemicals. Thus, DAF seems to be an ideal pre-treatment method for a subsequent ultrafiltration step. Coagulation and flocculation processes are important, and rely mainly on (i) the adsorption of the coagulant (or flocculant) on the suspended particles, as well as (ii) collisions of the particles. Hence, for the optimum aggregation of more concentrated suspensions, a lower amount of polyelectrolyte is needed resulting in a higher degree of flocculation [78].

4.2 Membrane filtration for the separation of hemicelluloses

Pulp and paper industry processes result in process streams that contain considerable amounts of dissolved biomass components. These substances could principally be used in a variety of high-value applications, e.g. barrier films in food packaging made of hemicelluloses. However, since typical process streams, e.g., process water from APMP-mills, have a complex composition, efficient separation techniques, applicable and economically viable on industrial scale, are required. Membrane filtration processes are widely applied to satisfy the objectives retention, concentration, purification and fractionation in a broad field of applications – also in the field of biomass - and will therefore be discussed in this chapter. [79], [80]

4.2.1 Fundamentals of membrane filtration

Membrane filtration is a physical separation process that employs a semi-permeable membrane. The operation principle of a membrane is similar in the wider sense to that of surface filtration, and schematically presented in Figure 4.3.

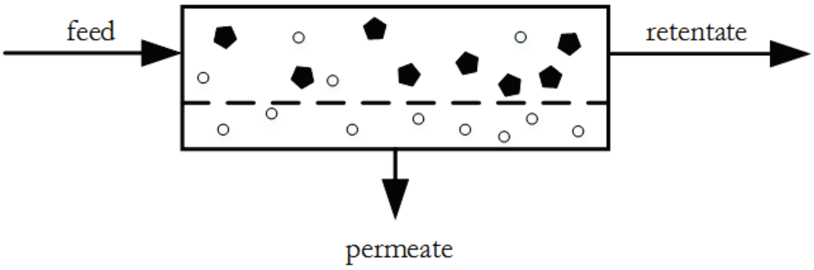


Figure 4.3: Schematic representation of a membrane process.

The mixture to be treated, called feed or raw solution is divided into two streams by the membrane: (i) the permeate or filtrate, containing the substances that are able to pass through the membrane, and (ii) the retentate or concentrate, composed of all substances retained by the membrane. In most cases, the driving force for the separation process is a pressure difference between the feed and permeate side, i.e., the so-called transmembrane pressure (TMPres). This pressure is usually calculated via equation (4.5)

$$TMPress = \frac{p_{in} + p_{out}}{2} - p_p \qquad (4.5),$$

Here p_{in}, p_{out} and p_p denote the pressure at the inlet, the outlet and on the permeate side of the membrane module, respectively. Components are then separated based on their size, or their charge. The process is typically carried out in cross-flow mode, which means that the feed flows across (i.e., tangential to) the membrane surface. This operation mode has the advantage of no (or strongly reduced) cake formation, thus enabling a continuous operation.

Pressure-driven membrane processes are divided into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). The range of molecular weight and size of the particles (or molecules) that can be separated with these processes is indicated in Figure 4.4. The smaller the compounds to be separated, the smaller the pore sizes have to be. This in turn decreases the permeability of the membrane, which means that the applied driving force has to be increased to obtain a certain flux. The retentate can be further purified by diafiltration (DF), which is not another membrane process but just an operation mode. In this operation mode, the retentate is diluted with solvent (e.g., water) such that low molar mass solutes are washed out via the membrane. This work deals with MF and UF and DF. [81], [82]

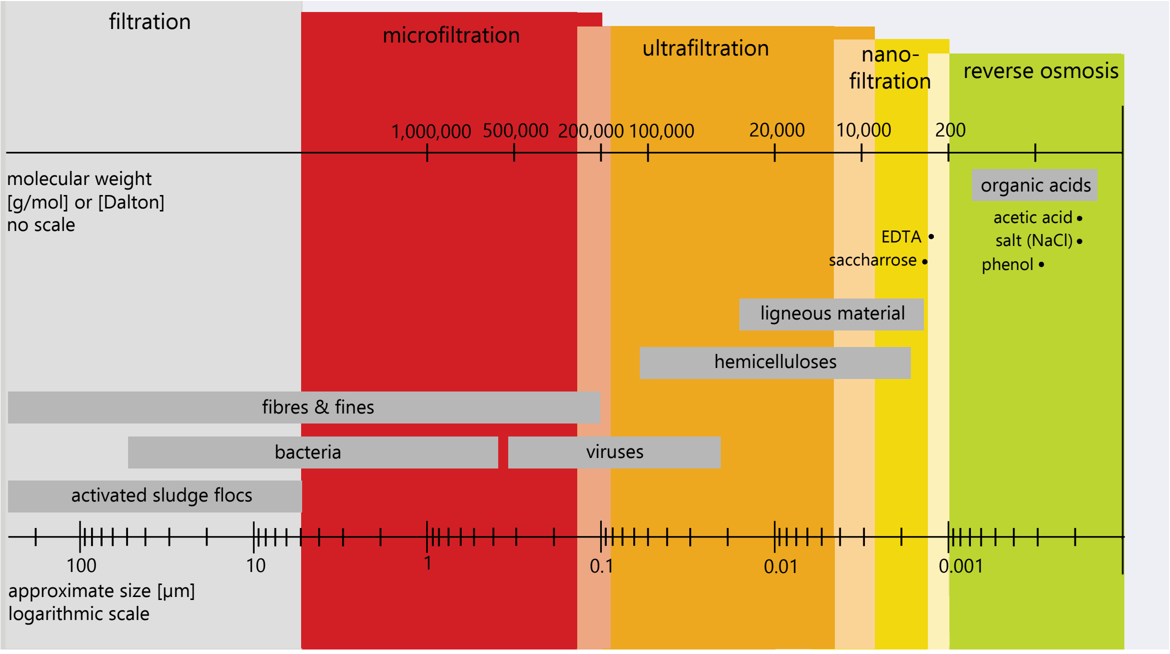


Figure 4.4: Different application areas of pressure driven membrane processes [79].

4.2.2 Membrane design

Membranes can be classified according to different characteristics:

- Origin
- Material
- Morphology and structure
- Membrane geometry and configuration

Membranes can be of synthetic or biological origin, differing in structure, function and material transport. While biological membranes like cell membranes are essential to human and animal life, in this thesis only synthetic, solid membranes are of key importance. Therefore, different organic (e.g., cellulose, polymer) and inorganic (e.g., ceramic) membrane materials are applicable, depending on the characteristics of the process stream in question and the requirements in terms of operating conditions.

Synthetic polymer membranes are the predominantly used membranes today, as it is possible to choose a polymer suitable for the specific separation task from the huge number of existing synthetic polymers. In addition, polymer membranes often are easier to process and less expensive than other membrane materials.

Inorganic membranes are gaining more importance because of their higher chemical and thermal stability, combined with a high regeneration capacity, as well as reduced aging and long service intervals. The downside of using inorganic materials is the higher investment cost due to the more expensive membrane material and module constructions.

The structure of membranes can be symmetric or asymmetric. Symmetric membranes have an almost homogeneous structure over the thickness of the membrane. In contrast, asymmetric membranes consist of two layers: (i) a so-called active layer on the feed side which determines the separation characteristics of the membrane, and (ii) a supporting layer providing the mechanical stability of the membrane. In this way, the active layer may be kept as thin as possible, thereby minimizing the flow resistance of the membrane.

The configuration of the membranes, i.e., their design and the way they are mounted and oriented in relation to the flow of the process stream, is decisive for the overall process performance [83]. In order to apply separation by membrane technology on industrial scale, a large membrane surface area is usually required. The design of the membrane module - the unit in which the membrane elements are packed – is important to achieve the highest packing density whilst ensuring effective filtration. The modules are based on two main types of design [81]:

i. Flat – utilized in the construction of spiral wound, cushion, plate, and disc-tube modules
ii. Tubular – utilized for tube, capillary and hollow-fiber modules

4.2.3 Process design

The decisive characteristics in membrane processes sealing their economic efficiency are purity, recovery and capacity. Optimizing the membrane process is typically a trade-off between these parameters, as high recovery and high purity are often incompatible process parameters [84]. To ensure a cost-efficient process, the longest possible operational lifetime of the membrane should be targeted, as membrane replacement costs can account for a significant part of the total operating costs of the process [85].

4.2.3.1 Flux

The capacity determines the required size of the membrane plant and is defined via the flux, which is the volumetric flow of permeate per unit surface area (in $l/m^2 \cdot h$). The higher the flux, the lower is the capital cost.

4.2.3.2 Volume reduction

The degree of concentration is often indicated by the volume reduction (VR), or the volume concentration factor (VCF). VR defines how much of the initial feed Volume, V_0, has been withdrawn as permeate, V_p, and VCF expresses how many times the initial feed volume has been concentrated by dividing it by the remaining retentate volume, V_r.

$$VR = \frac{V_p}{V_0} \tag{4.6}$$

$$VCF = \frac{V_0}{V_r} = \frac{1}{(1 - VR)} \tag{4.7}$$

As VCF increases during concentration, the flux usually decreases.

4.2.3.3 Retention

The separation characteristics of the process are assessed by the retention of individual components. The observed retention R is defined by the following equation:

$$R = 1 - \frac{C_p}{C_r} \tag{4.8}$$

where C_p and C_r denote the concentrations in the permeate and in the retentate respectively.

In UF, the membranes are usually characterized by their “molecular weight cut-off” (MWCO), which, by definition, is equal to the molecular weight of globular proteins which are 90% retained by the membrane [86]. Typically, the retention of a certain component (e.g., hemicelluloses) increases during concentration, partly explained by an increase in molecular weight. It is important to bear in mind that the actual retention depends on the operating conditions, as well as the suspension (or solution) to be treated [84].

4.2.3.4 <fPurity and recovery

The retention and VR govern the purity and the recovery of the product. The purity is the concentration of the product considered, divided by the sum of the concentration of all compounds in a certain process stream. The purity in the course of the membrane process depends on the difference in retention of the feed components.

The recovery, or yield, is the fraction of the targeted component in the feed that is obtained as a useful product in the retentate. Retention smaller than 100% is synonymous to the loss of product with the permeate during filtration, which diminishes the recovery. If the retentate is the product and the retention is constant during concentration, recovery can be calculated by:

$$\text{recovery} = \frac{m_r}{m_0} = (1 - VR)^{1-R} \tag{4.9}$$

where m_r and m_0 are the amounts of substance in the retentate and feed respectively. As VR increases during concentration of the product in the retentate, the purity increases at the expense of recovery in case $R < 100\%$. [84]

4.2.3.5 Operating parameters

Several operating parameters affect the membrane performance and costs. The following parameters need to be optimized in each specific application and are commonly studied in pilot-scale investigations:

- TMPress
- cross-flow velocity
- temperature
- pH

Although their influence depends on the specific situation, some general trends in MF and UF can be recognized:

- For low pressure differences, the flux increases almost linearly with increasing TMPress. In most practical applications this linear behavior levels off until no more increase of the flux can be observed when the so-called limiting flux is reached.
- When the cross-flow velocity (i.e. the turbulence) is increased, the flux also increases.
- An increase in temperature causes a decrease in the viscosity and consequently an increase in the flux.
- Flux decreases with increasing solute concentration. [84]

4.2.4 Polarization phenomena and membrane fouling

When employing a real-world suspension (or solution), the system performance often changes with time during the separation process. Typically, the flux decreases over time, mainly due to two phenomena: (i) concentration polarization, and (ii) fouling.

ad (i): In consequence of the selectivity of a membrane, at least one component is (partly) retained. To meet mass conversation, it has to be transported back into the bulk of the feed by diffusion in steady-state operation. This requires the formation of a concentration gradient from the membrane surface to the bulk solution, which is called concentration polarization. This phenomenon causes a deterioration of the purity of the permeate and is the reason why the observed retention (which is used in this work) is often lower than the real retention.

ad (ii) In addition to concentration polarization, the performance of a MF- or UF-module can be impaired by fouling, which can be defined as the (ir)reversible deposition and accumulation of feed components, e.g., suspended particles, colloids and macromolecular material on (a) the membrane surface, and/or (b) within the pores of the membrane. Figure 4.5 provides a schematic representation of the different mechanisms of fouling, which can be classified into covering gel layers, pore narrowing by internal adsorption, pore plugging, and biofouling.

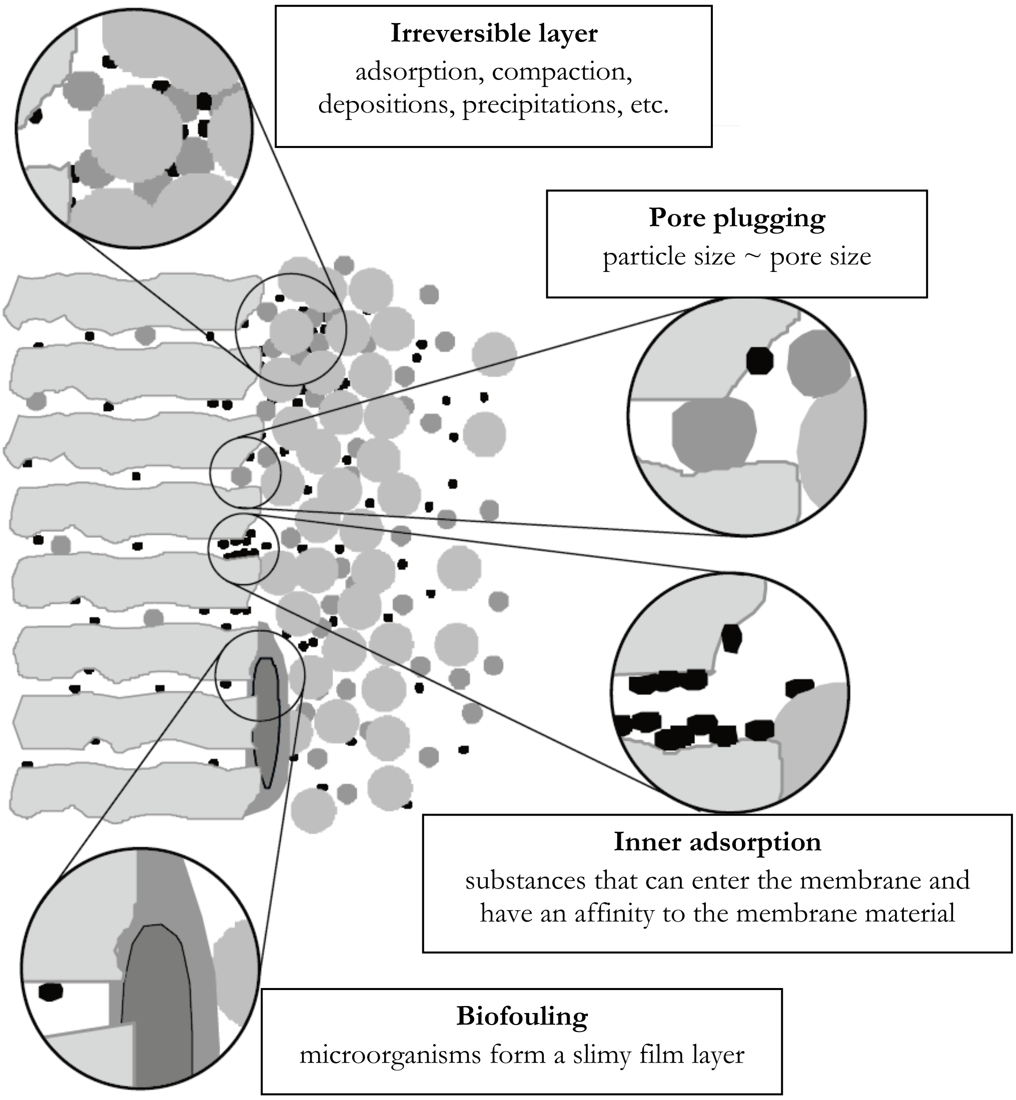


Figure 4.5: Fouling mechanisms in filtration with porous membranes [87].

The pure water flux (PWF) is defined as the flux of deionized water. It is used to characterize the extent of fouling and to control the efficiency of cleaning, by comparing PWF at different points during operation.

4.2.5 Methods to maintain filtration performance

The time frame for the change of the performance is determined by the employed membrane module, as well as the operating and feed conditions (see Figure 4.6).

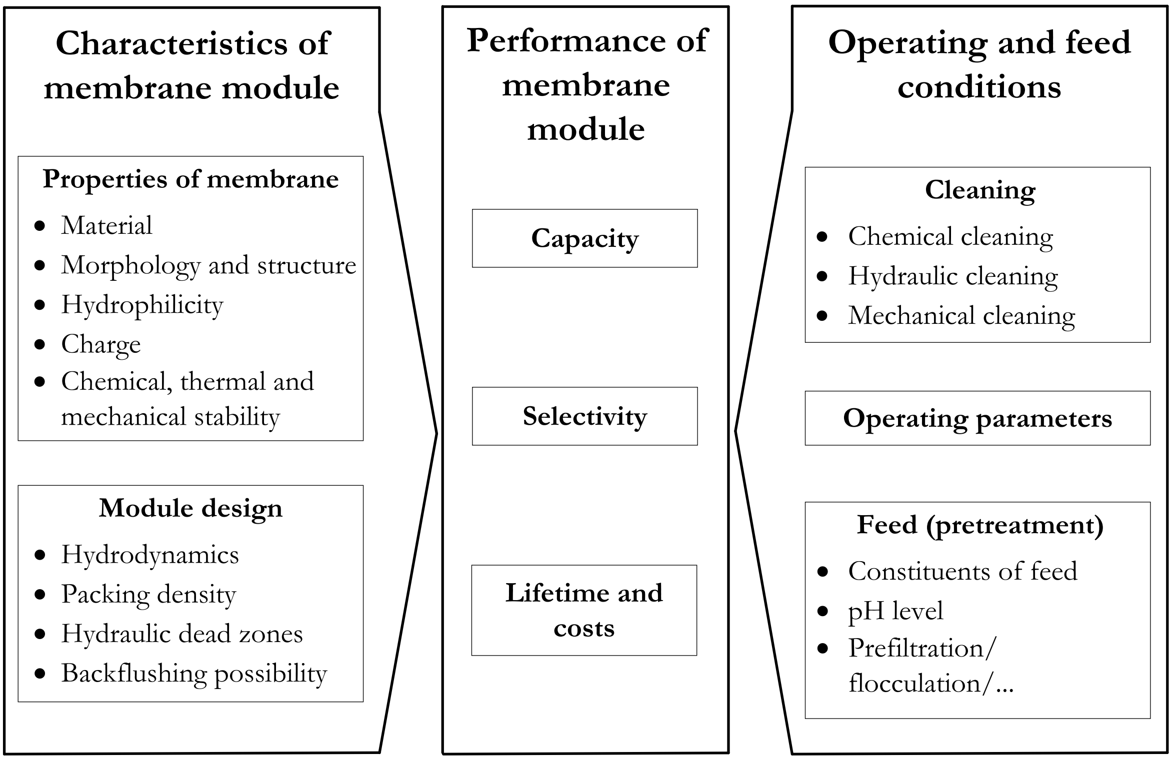


Figure 4.6: Factors influencing the performance of a membrane module [87].

As process streams can be huge, especially in the pulp and paper industry, a high and stable filtration capacity is required. Therefore, fouling control is a main aspect in membrane processes. Due to the complexity of the phenomenon, many factors are involved and the appropriate measures depend on the nature of the actual fouling phenomenon. [81],[84]

4.2.5.1 Membrane properties

Surface morphology (i), hydrophilicity (ii) and charge (iii) have all been found to be key membrane properties regarding fouling tendency:

ad (i): Beside the pore size itself, also the pore size distribution has an effect, with a narrow one usually reducing fouling.

ad (ii): Hydrophilic membranes are generally less prone to fouling: Hydrophobic substances like fats adsorb more strongly on hydrophobic surfaces, and are hence less easy to remove compared to hydrophilic surfaces [81]. Kallioinen et al. [85] named several cases from pulp and paper industry where hydrophilicity was shown to decrease fouling, as major foulants like fatty and resin acids are of hydrophobic character.

ad (iii): Many natural substances and colloids, e.g., compounds dissolved from wood, dissociate in the process streams, yielding negatively charged particles or ions. In case the membrane has the same charge as the compounds in the treated water, electrostatic forces lead to repulsion. Thereby, flux and retention is improved while fouling is diminished. [85], [87]

4.2.5.2 Cleaning

In practical, cleaning is an integral part to reduce fouling and to maintain filtration performance. Three cleaning methods can be roughly distinguished:

- Hydraulic cleaning: This method includes alternate pressurizing and depressurizing, changing of the flow direction and back-flushing, where the feed pressure is released and the direction of the permeate flow reversed from the permeate side to the feed side.
- Mechanical cleaning can be applied in tubular modules using oversized sponge balls.
- Chemical cleaning: Chemical agents are used, whereby concentration of the chemical, cleaning time, temperature and hydrodynamics also being of importance. The efficiency of chemical cleaning can be decisive for the overall performance and efficiency.

Periodic cleaning of fouled membranes not only causes operational breaks, but also might shorten the lifetime of membranes, which increases the operating costs.

4.2.6 Pros & cons of microfiltration and ultrafiltration

The following lists provide a quick overview of what should be taken into consideration when employing membranes, founded on the previous discussed principles of membrane filtration. [79],[82],[80],[85]

Major benefits of membrane technology are:

- separated materials are neither thermally nor chemically or biologically modified;
- the process is relatively easy and efficient to carry out in continuous mode;
- simple scale up principles can be used, i.e., the processes can be easily scaled;
- relatively low energy consumption;

- high selectivity;
- process can be tailored by appropriate membrane choice to meet requirements set by a certain application
- operating conditions (e.g., pressure, temperature, pH) are easy to adjust

Drawbacks:

- flux decline due to fouling and concentration polarization phenomena;
- relatively short lifetime of some membranes;
- occasionally insufficient selectivity and flux problems.

4.2.7 Previous studies in the field of hemicellulose recovery with membranes

The application of membranes for the separation of biomass components has first been studied in the 1930s. Actually, the recovery of sodium hydroxide from large volumes of hemicelluloses/sodium hydroxide streams in the production of rayon from cellulose was the first membrane process to be used on an industrial scale [88]. However, interest in hemicellulose as the targeted compound has evolved quite recently with its possible utilization for bio-based high-value products.

Membrane filtration of biomass-containing process streams, including wood hydrolysate, bleach plant effluents and solutions obtained from agricultural residues have been studied following similar objectives in most cases: purification or concentration of process streams, and recovery of hemicelluloses or lignin (also lignosulfonates) for further usage.

In this work, membrane filtration processes were applied to recover hemicelluloses, especially xylan, from APMP effluents by concentrating and purifying them.

One of the first studies on the recovery of hemicelluloses from process water was presented by Willför et al. [89], who proposed a targeted use of the hemicelluloses in the wet-end of the paper machine. Their procedure consisted of coagulation/filtration to remove colloidal wood resin and adsorption to remove dissolved aromatic substances from the TMP process water. Further purification was accomplished by ultrafiltration using a 20 kDa filter, giving hemicelluloses at a yield of 5 kg/ton pulp and at high purity. Many researchers apply a combination of microfiltration for the removal of suspended solids and colloidal matter followed by ultrafiltration for the concentration and purification of hemicelluloses [80], [82], [90], [91]. Persson et al. [90] showed the economic feasibility of such a process on full scale (i.e., to recover hemicelluloses from TMP process water), producing a solution that contained 30 g hemicelluloses per liter with a purity of 80%. Diafiltration of the UF concentrates was suggested to further purify the hemicelluloses fraction. It was found to probably be the most cost-efficient method to separate hemicelluloses from smaller components such as small oligosaccharides, monosaccharides, and especially salts, whereas purification from lignin fragments was only partial accomplished [90], [92], [93].

The majority of existing studies concur that a membrane cut-off of 5 to 10 kDa is optimal with respect to flux and selectivity [80], [82], [94], [95], [96], [97]. Also, hydrophilic membranes made of polysulfone showed the best applicability in the field of hemicellulose recovery. These membranes provided a high flux, a high retention of hemicelluloses, and lower retention of lignin in addition to their relatively high thermal resistance and low price. [80],[94] [96]

One of the key challenges faced when treating lignocellulosic process streams by membrane filtration is the reduction of capacity as a consequence of fouling. That's why various pretreatment methods (e.g. adsorption, flocculation, oxidative degradation, microfiltration, pH adjustment) are being investigated. It was found that in addition to the total concentration of organic components in the treated streams, also their size has a significant effect on filtration capacity: generally, less detrimental components are small compounds that can easily permeate the membrane without blocking it, and large compounds which cannot penetrate the membrane. On the one hand, the membrane flux substantially increased and fouling could be reduced by appropriate pretreatment of the process streams. On the other hand, those effects are accompanied by a loss of hemicelluloses. [80], [91], [97]–[99]

Most of the investigations are based on solutions obtained upon processing of softwood, whose main hemicelluloses are glucomannans. Although hardwood hemicelluloses (i.e., mainly xylan) have similar molecular weight and structure, their behavior during membrane filtration can differ. This could partly be explained with different lignin contents, linkages and molar mass distributions. Further research on the process streams in question is therefore needed. [97]

4.2.8 Preliminary recommendations regarding membrane filtration based on the literature

Design variables that influence the performance of membrane filtration include the membrane itself, module configuration, and operational modes. Membranes made of polysulfone with pore sizes of 5 to 10 kDa and have been found to be most suitable for the selective separation of hemicelluloses from pulping process streams [80]. The flux through the membrane is typically increased by a high turbulence in the modules. Hence, a high crossflow velocity and spiral wound modules, which also provide a high packing density (i.e., membrane area per volume of module), are suggested. A multistage recirculation design of the membrane filtration plant is the most common design and will further help to make the process feasible [90].

Experimental Work

5

Investigated process design

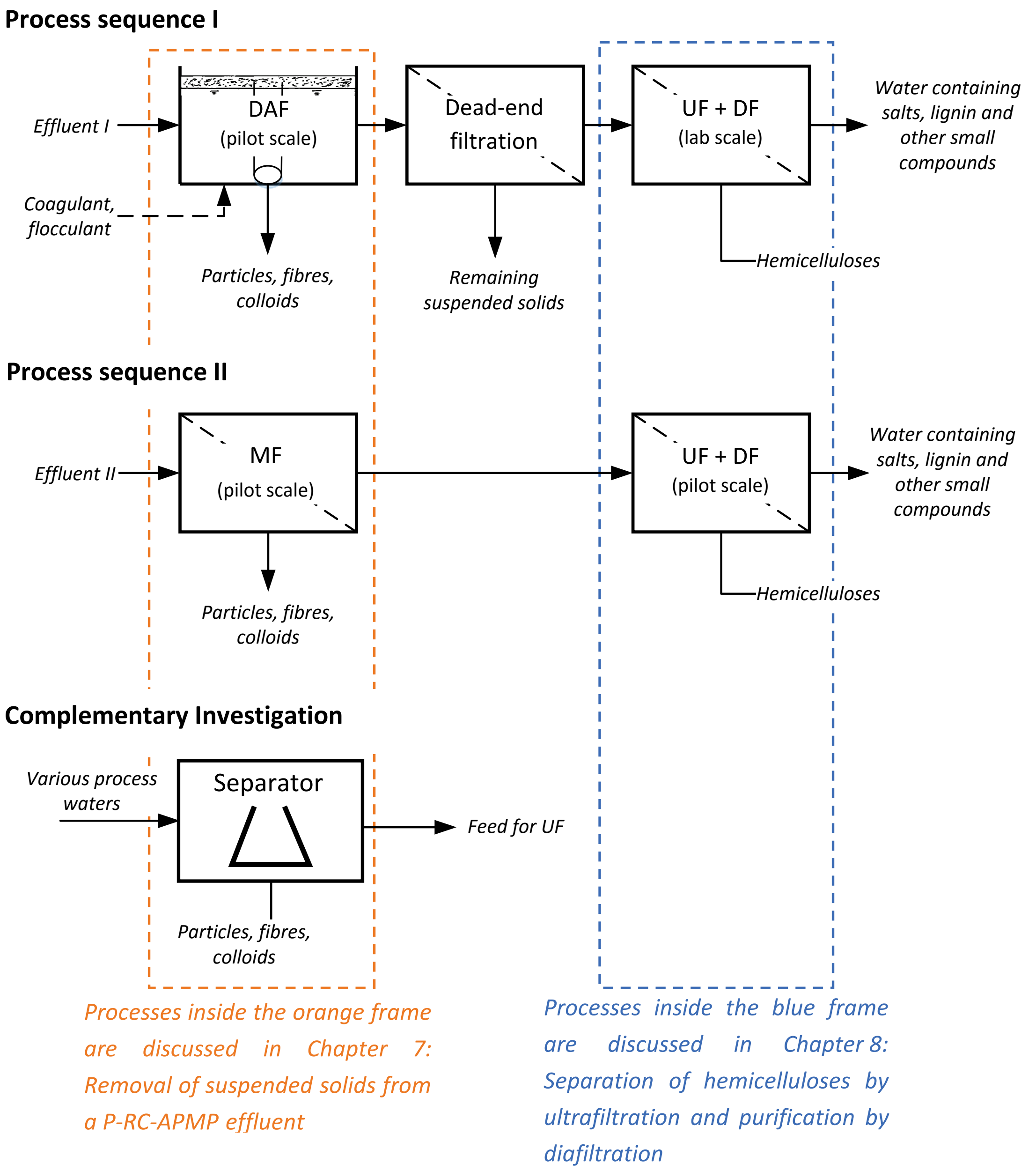
The overarching goal of the present study was to develop and test a process for the recovery of hemicelluloses from effluents discharged from mechanical pulping lines that can be readily implemented into existing mills. Due to the nature of the effluent and the envisaged separation methods, it became apparent that two research objectives should be pursued:

i. Screening of pretreatment methods for the separation of suspended solids to enable a subsequent ultrafiltration

ii. Investigation of the performance of ultrafiltration and diafiltration with the objective of concentrating and purifying a hemicellulose-rich product

The investigated processes are schematically shown in Figure 5.1. The initially goal was to use dissolved air flotation (DAF) to remove most of the suspended solids and some colloids, and then separate the hemicelluloses by ultrafiltration (UF) in a second stage. As DAF did not provide the expected and required separation efficiency, leaving too much suspended solids in the process water, an additional process step was necessary prior to UF. Therefore, dead-end filtration was performed (using a 5 µm bag filter) before different membranes were screened on laboratory scale (see process sequence I). Process sequence II started with microfiltration as a possible alternative to DAF, or as an intermediate step to remove suspended matter and colloids. The hemicelluloses were subsequently separated by UF on a pilot plant scale, employing a membrane that had been proven suitable in the membrane screening from process sequence I. UF was in both sequences paired with diafiltration (DF) to wash out smaller components like salts.

The initially feed stream was in both sequences effluent from a pulp mill employing a P-RC APMP (Pre-conditioning Refiner Chemical Alkaline Peroxide Mechanical Pulp) process. The NaOH charges in the pulping process were about 39 kg and 60 kg per ton of pulp for sequence I, and sequence II respectively. Consequently, the initial concentration of hemicelluloses in the feed solution was higher for process sequence II.



Processes inside the orange frame are discussed in Chapter 7: Removal of suspended solids from a P-RC-APMP effluent

Processes inside the blue frame are discussed in Chapter 8: Separation of hemicelluloses by ultrafiltration and purification by diafiltration

Figure 5.1: Overview of the investigated process sequences.

6

Process Water

The process waters used for the investigations in this work was an effluent from a mechanical pulping mill producing P-RC APMP from aspen wood. That mill is thus a potential industrial user of the investigated process. The sampled effluent originated from the first screw press, following the first refiner stage and the first bleaching tower. The sampling point was upstream of the fibre recovery process (i.e., a disc filter). This is motivated by the fact that the effluent becomes diluted in the fibre recovery process, which had to be avoided to obtain a more concentrated effluent with a higher purity.

The effluent was withdrawn from the mill on two different occasions, corresponding to two different NaOH charges. About 24 m^3 of effluent were withdrawn from mechanical pulping mill, when a process was run where 39 kg NaOH charge per ton of pulp produced in the pulping process were applied. It was filled directly into 24 intermediate bulk containers (IBC), with a filling capacity of 1 m^3 each over the period of about 3 hours. It was then immediately transported to the ANDRITZ site. The temperature of the effluent at the time of exiting the mill is 80°C and the pH was about 6.2. As soon as the effluent had arrived at ANDRITZ, 100ml of biocide ("polycide", Polypharm Private Limited., India [100]) were added to each 1 m^3 IBC in order to prevent microbial deterioration of the effluent. This effluent (named "effluent I" further on) was used for dissolved air flotation (DAF) trials and lab scale ultrafiltration trials. About 3 litres of effluent were drawn from each IBC after thoroughly mixing. Three of these IBC samples were then blended to yield one sample for analysis. Eight samples with a volume of 9 litres each were obtained this way and used for analysis of solids content (TS, DS, SS). As the DAF pilot plant was not available for tests until three weeks after the effluent had been withdrawn from the pulping process, measurement of solids was repeated at the time of the

DAF experiments. This time, two of the initial 9 litre samples were analysed. Measurement of hemicelluloses was also performed three weeks after sampling.

A second batch of effluent was withdrawn from the pulp mill at a higher NaOH charge (60 kg NaOH/ t of pulp) and directly transported to the site where the microfiltration and ultrafiltration pilot plant tests were conducted. About 5 m^3 of this effluent (named “effluent II” further on) were used in those trials, where one sample (2 litres) of the “original” effluent was drawn after completely mixing. Its pH was significantly higher, namely 7.4.

As the main interest was the performance of the processes, the following values refer to the composition the effluents had right before these separation processes were performed. The characteristics of the two effluents are shown in Table 6.1.

Table 6.1: Characteristics of the effluents used in the investigations.

	Unit	Effluent I	Effluent II
NaOH applied in the pulping process	kg/ ton of pulp	39	60
Total volume withdrawn	m^3	24	5
Temperature when exiting mill	°C	80	80
pH	-	6.2	7.4
Total solids content	g/kg	27	35
Suspended solids content	g/l	2.1	0.93
Used for	-	DAF, UF lab test	MF & UF pilot test

The total solids contents of the process waters were rather high, 2.7 wt% and 3.5 wt%, for effluent I and effluent II respectively. Figure 6.1 illustrates their compositions. As the process stream was withdrawn from the pulping process before entering the fibre recovery process (i.e., a disc filter), effluent I contained a relatively high amount of 2.1 g/l of suspended solids (a 0.6 µm filter was used for this analysis). The amount of hemicelluloses (and pectins) was relatively low, accounting for about 9% of the total solids. When the effluent was taken at the higher NaOH charge (effluent II), the amount of suspended solids was reduced to 0.93 g/l while the portion of hemicelluloses was increased to 15% at the same time. The major constituents of the dissolved hemicelluloses are xylan (with its building units xylose and 4-O-methyl-D-glucuronic acid) and pectin (with its main build unit galacturonic acid). Besides, also glucomannan is present (i.e., glucose and mannose unit). A peculiar feature of the xylan composition in the effluent is that the molar ratio of xylose to 4-O-Methylglucoronic acid is 2.1, whereas it is about 10 in native hardwood xylan (see section 2.2).

The amount of suspended solids in effluent I obviously decreased over time, as it was 4.2±1.2 g/l in the first measurements (immediately after arrival). The amount of dissolved solids on the other hand increased over storage time. This can be explained by two effects: (i) microbial degradation, and (ii) the effect of chemicals originating from the pulping process.

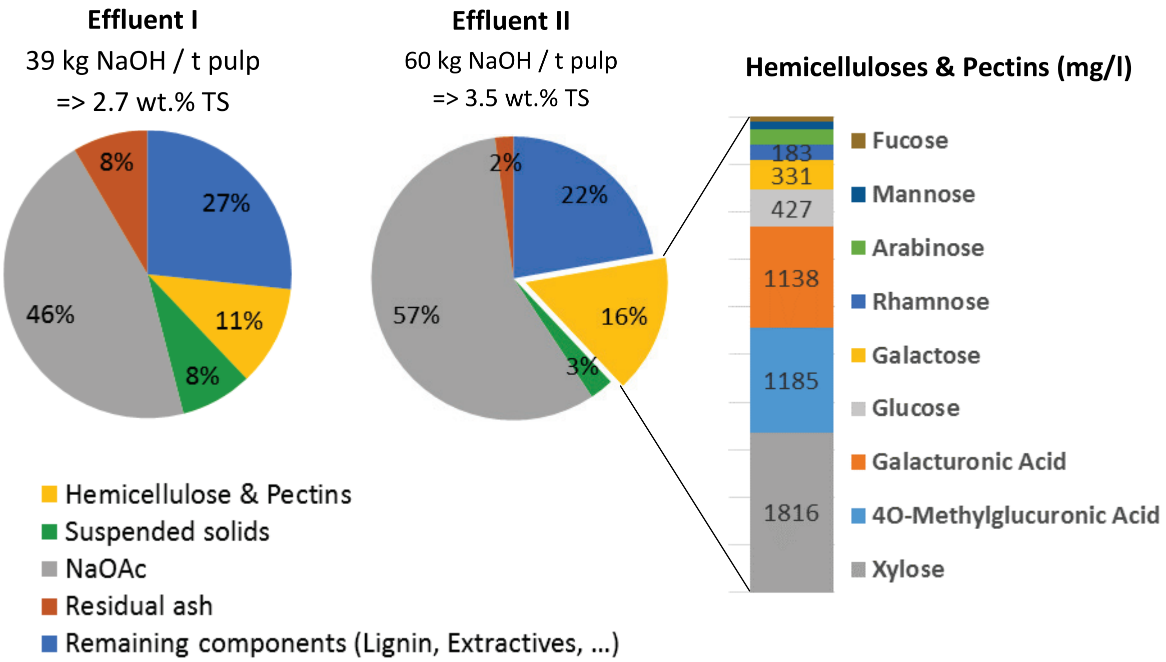


Figure 6.1: Composition of total solids content in the effluents used as feeds in the investigations, and composition of hemicelluloses and pectins in case of effluent II.

The particle size distribution (PSD) of the suspended particles, shown in Figure 6.2 and Figure 6.3, obtained by laser diffraction (LD) analysis, was broad with particle diameters ranging between 0.25 µm and 800 µm. The density distribution showed peaks at 2 µm and 75 µm, meaning the probability of particles having such a diameter is relatively high. However, laser diffraction analysis has to be treated with care, since the particle's shape is not directly measured. Thus, a strongly non-spherical particle can appear as particles of widely different size in an LD analysis since light is scattered differently from different edges of such a particle. Unfortunately, a more detailed particle size and shape analysis (e.g., with an automated light or electron microscope) could not be performed.

The PSD can be used to determine the portion of suspended solids that would be removed with a certain cut-off. The amount of SS would for example decrease by about 90%, if all particles >1 µm would be removed. The broad PSD definitely requires a carefully chosen method for the removal of these particles.

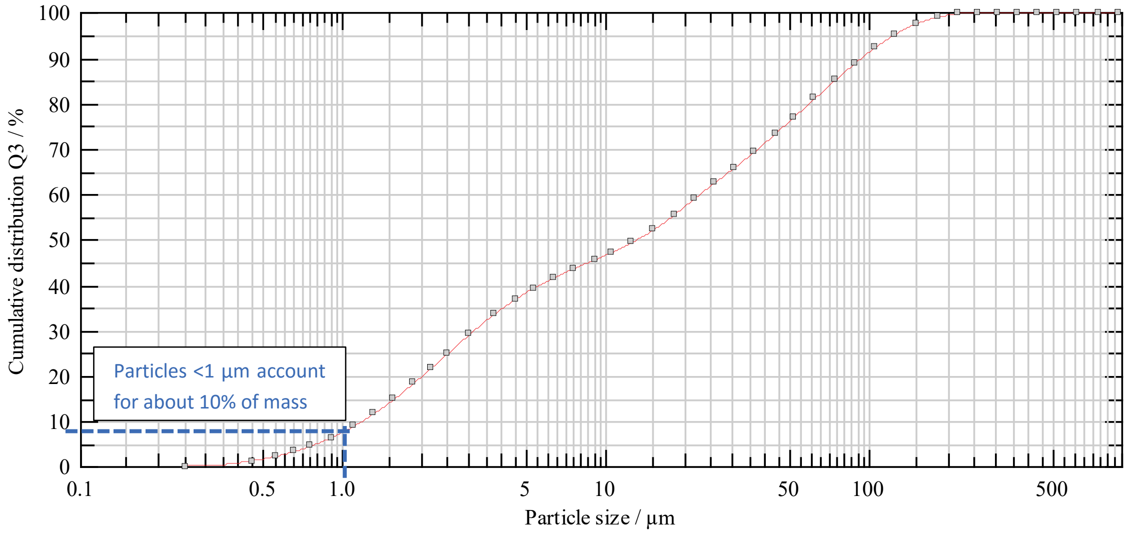


Figure 6.2: Cumulative PSD of effluent I [101].

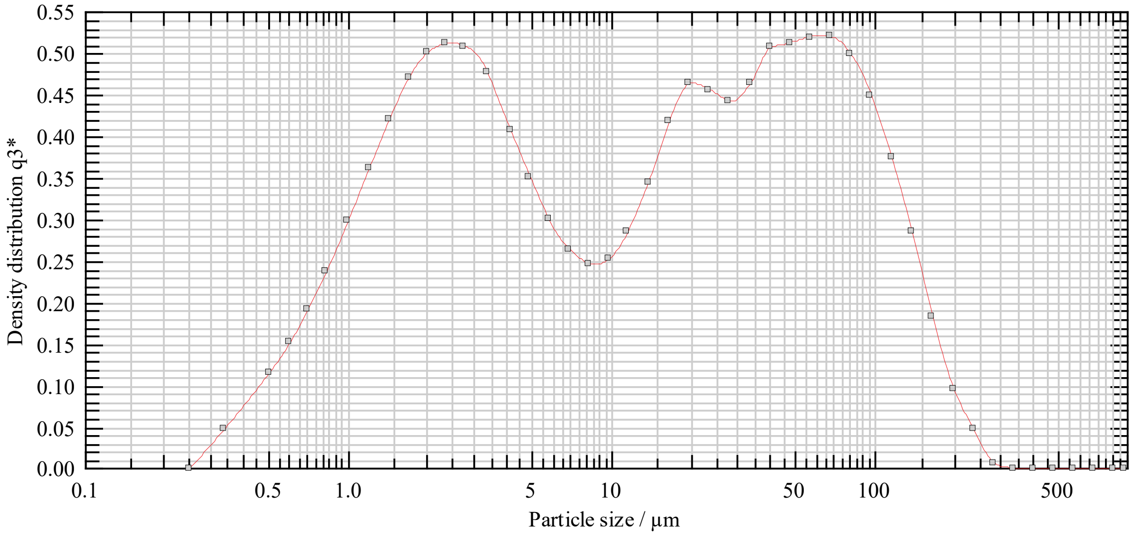


Figure 6.3: Density PSD of effluent I [101].

Observations made by optical microscopy and additional investigations of the influence of pH on the amount of suspended and dissolved solids and the particle size distribution are undisclosed [102].

7

Removal of suspended solids from a P-RC-APMP effluent

Various pretreatment methods, i.e., dissolved air flotation, microfiltration and separation of confidential type, to efficiently remove suspended solids from the effluent leaving the P-RC APMP process were investigated. This effluent contained over 2 g/l of suspended solids, which need to be removed prior to ultrafiltration for three reasons: first, remaining particles would block the membrane modules and make the operation impossible. Second, suspended matter would reduce the purity of the hemicellulose in the ultrafiltration retentate. Third, the removed fibres and fines could be recycled into the mechanical pulping process and enhance the yield.

While the suspended solids should be removed to the greatest possible extent, hemicelluloses should be retained in the process stream to maximize the hemicellulose yield.

7.1 Dissolved Air Flotation (DAF) for the removal of suspended solids

One part of this study was the evaluation of dissolved air flotation as a pretreatment method to efficiently remove suspended solids from the effluent leaving the P-RC APMP process. The achievable removal of suspended solids, as well as the influence of several key design variables were investigated on a DAF-pilot-plant (see Figure 7.1). This plant is routinely used for the clarification of mixed wastewater from a test hall from Andritz AG, following a disc filter.

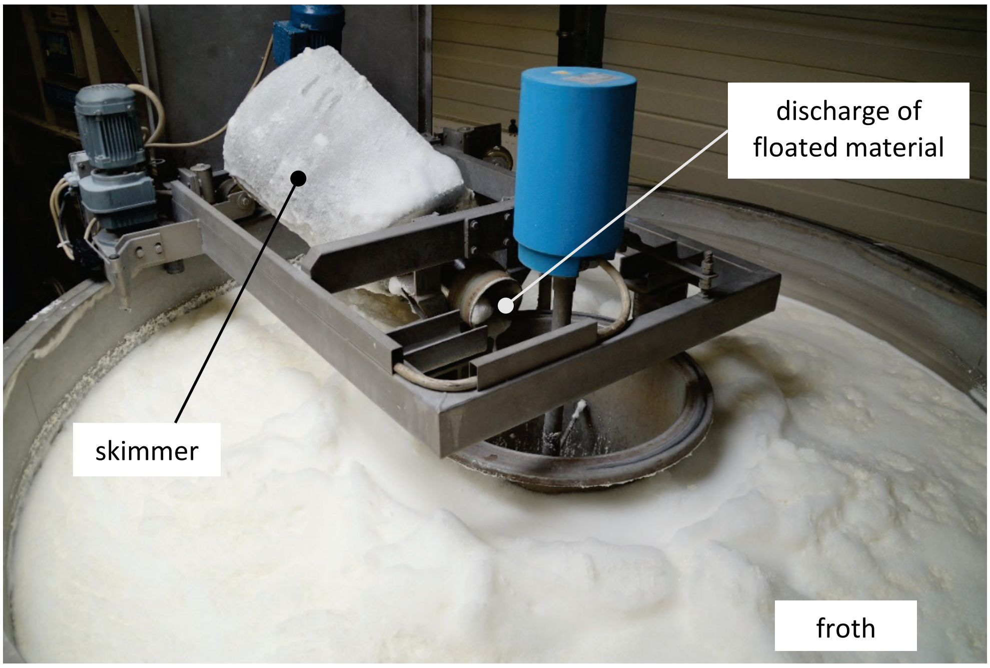


Figure 7.1: The used DAF plant in operation.

7.1.1 Process Description

Figure 7.1 shows the principle of the dissolved air flotation (DAF) system, on which the pilot-plant experiments were carried out. As the aim is to simulate the industrial-scale process as accurately as possible, the temperature of the effluent should be close to 80°C (this is the temperature of the effluent from the mechanical pulping process when entering the flotation system). Unfortunately, the flotation experiments could be only performed at 60°C, which is the highest temperature realizable with the applied heating steam. In addition, due to condensation of the heating steam, the raw water becomes diluted, by 20% (on a volume basis) on average.

The DAF test series was divided into four separate experiments, each consuming 6 m^3 of raw effluent. At first, the raw wastewater was transferred from the IBCs into a reservoir tank having a capacity of 3 m^3 to enable the heating and ensure a continuous processing of a greater amount of effluent. When the maximum steady-state temperature in the reservoir was reached, the feed pump started filling raw process water into the flotation chamber. At the same time, additional raw effluent was pumped from IBCs into the reservoir tank, till the designated 6 m^3 where consumed. When the liquid level in the flotation chamber had reached a certain height, pressurization started. The selected operation mode was a recycle-flow pressure flotation, which means that a portion of the treated wastewater is recycled to the pressurization system. There, air is dissolved in the wastewater under elevated pressure. Subsequently, the stream passes through a pressure-reducing valve and is mixed into the originally feed before the stream enters the flotation basin. As a result of the sudden reduction in pressure, small bubbles are generated. Solid particles get attached to these bubbles and are carried towards the surface of the water, where they are skimmed off by a skimming device. The skimming mechanism consists of two rotating scoops mounted on a circulating bridge. The filling level is controlled via a valve that determines the flow of clarified effluent withdrawn from the flotation chamber. Chemicals can be added to the feed just before the intake of the pressurized recycle stream. Samples were drawn from the samples points (SP) 0-3. Samples from Sample Point 0 were taken to secure, that no separation takes place in the reservoir tank.

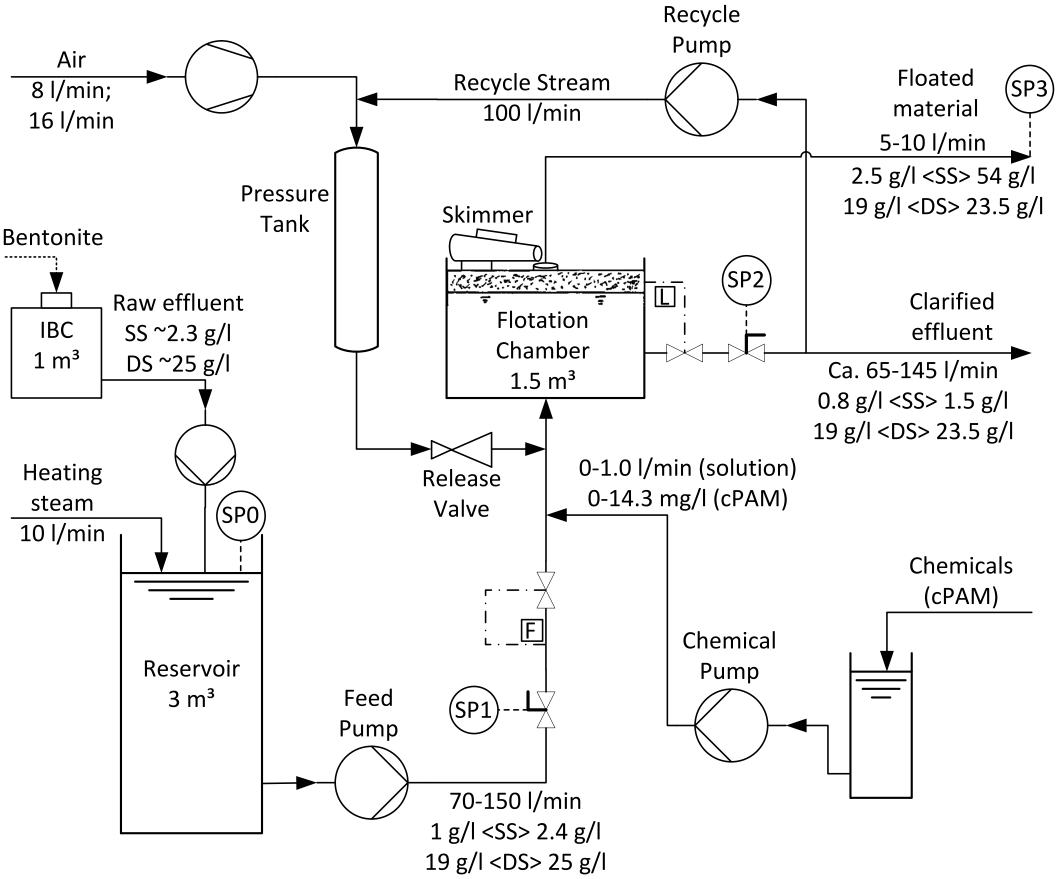


Figure 7.2: Schematic diagram of used DAF-system.

7.1.2 Determination of flocculant and coagulant dosage

As there does not exist an analytical way to predict the applicability or interaction of a particular polymer with a specific wastewater at the present time, the behavior has to be evaluated in laboratory experiments. Thus, the ability of different chemicals to cause flocculation and coagulation and their respective optimum dosage were investigated in preliminary laboratory experiments in a Standard Jar Test Apparatus [103] by optically rating the flocculation behavior (Figure 7.3).

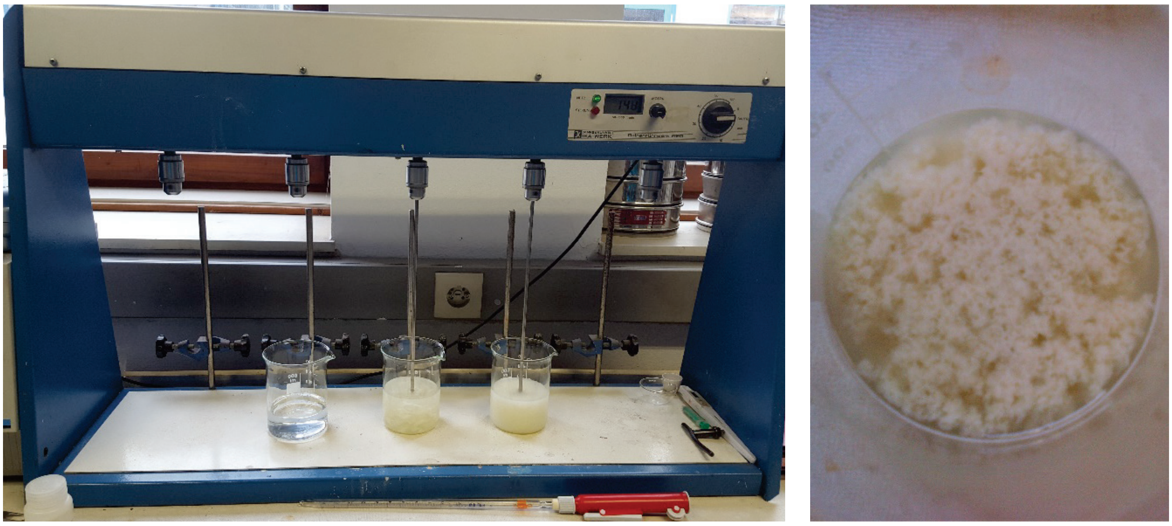


Figure 7.3: Flocculation tests on Standard Test Jar Apparatus (left) and flocculated effluent (right).

The cationic polyacrylamide FlocStar 262® (named cPAM from now on) was chosen as flocculant motivated by the following arguments:

- it is a high molecular weight cationic PAM, which is a recommended type of polyelectrolyte for similar applications usually inducing coagulation, as well as patching and bridging flocculation (see sections 4.1.5 and 4.1.6.1);
- satisfying flocculation could be observed when testing in preliminary flocculation experiments;
- it has been shown that 99% of the added PAM is carried out with the rejects of DAF-systems [104], which means that the final (liquid) product containing the hemicelluloses will not be significantly contaminated.

The optimum dosage of cPAM was determined by optically rating the flocculation behavior. It was found to be in the range between 2 mg/l, where the coagulation/flocculation process started, and 15 mg/l, where maximum flocculation was observed.

The effect of additional usage of bentonite as coagulant was also investigated, as it is a cheap, but still effective coagulant. Adsorption on bentonite is even considered a pretreatment for the ultrafiltration based hemicellulose recovery process [98]. Suggested ratios of polyelectrolyte to bentonite [105] were checked in the standard test apparatus again, and the amount of 75 mg bentonite per liter of effluent was found to be adequate.

7.1.3 Design Variables

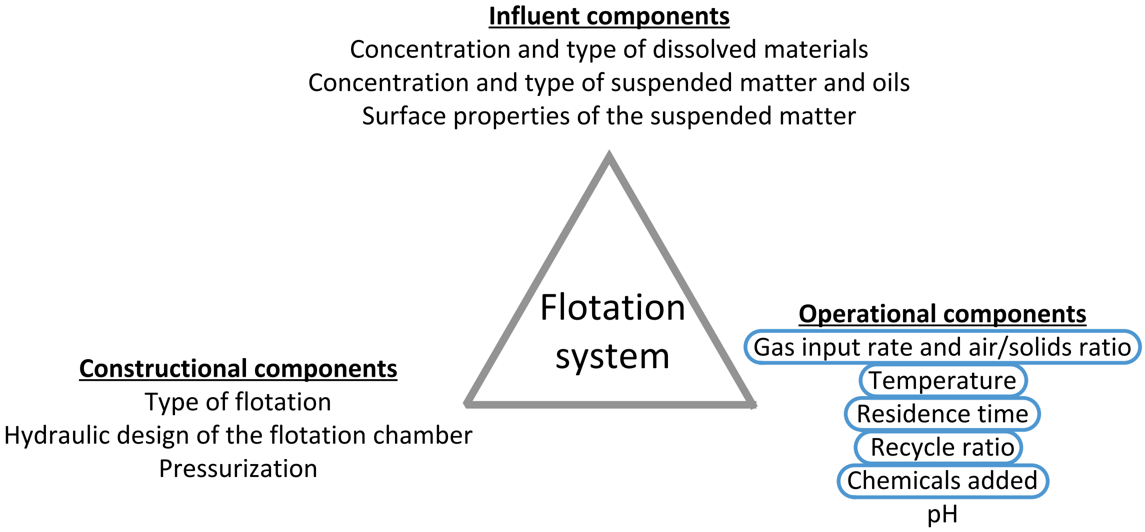


Figure 7.4: Design variables to be considered for a flotation system.

Flotation systems offer a large number of design variables. Figure 7.4 gives an overview and highlights the parameters that have been varied in this study. In Table 7.1, the different operating conditions and characteristic numbers are presented. The first trial was used to identify the primal performance of the DAF-system for the purpose of preparing the effluent for the recovering of hemicellulose by ultrafiltration. No chemicals were added. Two different feed flows and consequently retention times (see Equation (4.4)) were tested.

In the second trial, again the feed flow was varied. Moreover, the flocculant cPAM was applied in different concentrations. As the variation in feed flow did not induce any significant changes in the performance, the feed flow was held constant in trials #3-#4 at the lowest possible value (since the feed pump has a minimum flow rate) to keep the hydraulic loading low, the retention time high, and to enable a handle the experiments with ease. Lower flocculant concentrations were investigated in DAF-experiment #3 as it was assumed that its concentration could have been two high in test #2, resulting in a reversal of the flocculating effect The fourth experiment was subject to the influence of the supplementary application of the inorganic coagulant bentonite. Also the flotation system's performance at two different temperatures were compared.

An abundant amount of recommended design values for flotation systems can be found in the literature. Wang et al. [39] collected and complemented them. Typical values from his compilations have been added to Table 7.1 for completeness.

Table 7.1: Operating conditions and characteristic numbers of the DAF-experiments.

Nr. of DAF-experiment	#	1	2	3	4	Values from literature
Air flow	l/min	16	16	8 & 16	16	-
Feed flow	l/min	70 & 100	70 & 150	70	70	-
Recycle flow	l/min	100	100	100	100	-
Air pressure	bar	6.0	6.0	6.0	6.0	1.7-6.0
Temperature	°C	60	60	60	23 & 60	-
Flocculant	ppm	0	6.6-14.3	1.8 & 3.6	8.6	-
Coagulant	ppm	0	0	0	75	-
Retention time in flotation tank	min	8-10	6-10	10	10	3-60
Recycle ratio	%	100 & 143	67 & 143	143	143	10-60
Hydraulic loading	$l/min/m^2$	65 & 77	65 & 96	65	65	40-200
Air-to-solids ratio	g/g	0.075-0.12	0.018-0.041	0.043-0.063	0.031 & 0.037	0.03
Retention time in pressure tank	min	2.6	2.6	2.6	2.6	0.5-3.0
Air hold up	%	0.16 & 0.23	0.11 & 0.23	0.11 & 0.23	0.16	0.02-0.37

As can be seen from Table 7.1, all operating figures are perfectly in the recommended range. Only the recycle ratio is far higher, based on the system's dimensioning that (unfortunately) cannot be changed. As it causes an increase of the air/solids ratio, a recycle ratio above average should positively influence process performance, as long as it does not cause undue hydraulic loading.

The air/solids ratio, one of the most important characteristic numbers in flotation technology, is influenced by many parameters, see Equation (4.3). These are the feed flow rate, recycle flow rate, air pressure, temperature and solids concentration in the feed. That is why it is difficult to compare the different air/solids ratios.

It can be stated that the experiments' results did not show any significant correlation of the air-solids ratio and the solids removal efficiency. It is speculated that the former is always in the optimal range, and lowering the air/solids ratios resulted in higher removal of suspended solids because of the use of chemicals in these experiments.

The reduction of the retention time in the flotation tank had no noticeable influence on the removal of suspended solids. This indicates that the optimum retention time, speaking in terms of throughput and economy, is not longer than 6 minutes.

Also the retention time in the pressure tank and the air flow are sufficient, as a reduction of the latter by half did not impair process performance.

7.1.4 Effect of chemicals

The employment of chemicals addition had a remarkable influence on the removal of suspended matter. It was the only design variable that had a clear impact on the performance of the flotation process. This fact was already substantiated by a qualitative assessment of process performance (i.e., an observation of the froth layer), and was quantified via a detailed analysis of the removal efficiency of suspended solids upon addition of chemicals in different concentrations. As soon as a sufficient amount of flocculants was added to the system, the formation of a relatively stable layer of floated material on the surface was noticed. The froth layer did not develop in case too little or no flocculant was added.

Figure 7.5: Photo of floated material, dewatered with the bare hand.

As the foam fraction contained significant amounts of fibers and fines, as well as other suspended matter (see Figure 7.5), it was concluded that the removal of suspended solids was better when using chemicals. Although the amount of suspended solids removed as floated material increased dramatically upon the dosage of chemicals, the content of suspended material in the clarified effluent after the flotation treatment was only marginally lower (or even higher) than in the feed. This increase in the total amount of suspended solids can be explained by, on the one hand, the reduction in solubility of originally dissolved substances and, on the other hand, the entrapment of colloidal substances in larger flocs.

Complementary investigations on the chemical's influence on the agglomeration/precipitation of dissolved solids and the initiated removal of hemicelluloses from the solution were performed using the Standard Jar Test Apparatus. More than 8% of dissolved solids became insoluble upon addition of 8.6 mg/l of cPAM to the raw wastewater. Whereas the carbohydrates (i) uronic acids and (ii) mannoses were the substances that agglomerated the most (i.e., up to 16% removal), the decrease of dissolved xylose is rather small with approximately 5%. The subsequent addition of 75 mg/l of bentonite at a concentration of 8.6 mg/l cPAM decreased the observed reduction of dissolved solids from 8.4% to 5.7% without significantly changing the amount of dissolved carbohydrates. This indicates that bentonite adsorbs other dissolved solids than carbohydrates.

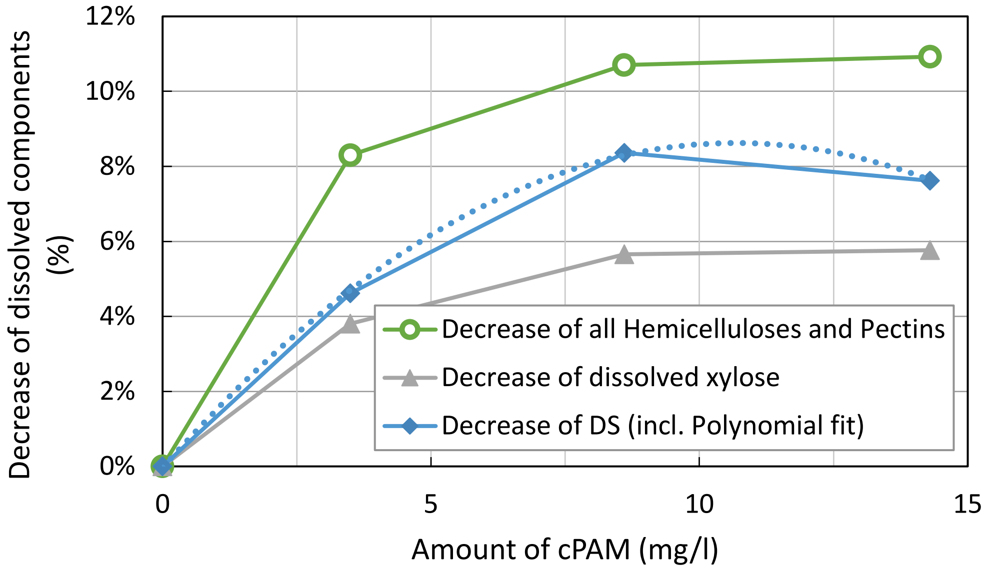


Figure 7.6: Precipitation of dissolved components upon addition of cPAM to the raw effluent.

7.1.5 Calculation of SS removal efficiency

As significant amounts of suspended solids are "generated" from dissolved solids upon addition of chemicals, the removal efficiency cannot be calculated using Equation (7.1), because this would lead to a negative removal rate.

$$Removal_{SS}\,(\%) = \frac{SS_{influent} - SS_{clarified}}{SS_{influent}} \cdot 100 \tag{7.1}$$

Instead, "total concentrations" (i.e., accounting for the effect of flocculant and coagulant) of the different matters (TS, SS, DS) are obtained by calculating mass balances for SS, DS and TS via two methods:

1. Using the concentrations measured in the filtrate and froth together with the respective volumina;
2. Using the concentrations measured in the feed and the amount of precipitation of dissolved solids ("Amount $_{DS \rightarrow SS}$") obtained upon the flocculation tests on the Standard Jar Test Apparatus.

The individual equations therefore are presented in Table 7.2, where C_i is the concentration of matter i; V_j is the volume of phase j; $Amount_{DS \rightarrow SS}$ is the rate of DS precipitating upon addition of the respective amount of chemicals (obtained from the polynomial fit in Figure 7.6); *TS*, *SS* and *DS* being the individual matters and *feed*, *clarified* (effluent) and *froth* being the individual phases.

Table 7.2: Equations for obtaining "total concentrations" in the DAF chamber.

Calculation method	#1: Concentrations measured in filtrate and froth	#2: Concentrations in feed and amount of precipitation of dissolved solids
$C_{SS,Total} =$	$= \frac{(C_{SS,Clarified} \cdot V_{Clarified} + C_{SS,Froth} \cdot V_{Froth})}{V_{Clarified} + V_{Froth}}$	$= (C_{SS,Feed} + C_{DS,Feed} \cdot Amount_{DS \to SS})$
$C_{DS,Total} =$	$= \frac{(C_{DS,Clarified} \cdot V_{Clarified} + C_{DS,Froth} \cdot V_{Froth})}{V_{Clarified} + V_{Froth}}$	$= (C_{DS,Feed} - C_{DS,Feed} \cdot Amount_{DS \to SS})$
$C_{TS,Total} =$	$= \frac{(C_{TS,Clarified} \cdot V_{Clarified} + C_{TS,Froth} \cdot V_{Froth})}{V_{Clarified} + V_{Froth}}$	$= C_{TS,Feed}$
$C_{TS,Total} =$	$= (C_{SS,Total,\#1} + C_{DS,Total,\#1})$	$= (C_{SS,Total,\#2} + C_{DS,Total,\#2})$

The volumes of the different phases, measured in the collection containers after the trials, were inaccurate. This is why they were edited by minimizing the sum of squares of the errors between method #1 and method #2 using the excel-solver with the volumes as variable. As a final point, the average “total concentrations” of two methods is the final values for the total concentrations which can be further used for calculating the removal efficiency by Equation (7.2).

$$Removal_{SS}\,(\%) = \frac{SS_{total} - SS_{clarified}}{SS_{total}} \cdot 100 \qquad (7.2)$$

A main objective is to remove as much suspended solids as possible and as little xylan as possible at the same time. This goal is represented by the length of the arrows in Figure 7.7. In this diagram, the remarkable influence of flocculant on the removal efficiency is also illustrated. The highest removal of SS that was reached is about 60%, when employing approximately 8 mg/l of optimal concentration of cPAM. Supplementary bentonite addition improves the removal of SS only to a small extent. The addition of bentonite at 60°C seems to be adverse for the dissolution of xylan, because over 50% of it is removed with the froth. At 23°C on the other hand, this phenomenon did not appear. When using the residual SS concentration as the critical factor, the percentage of “total suspended solids” removed may be misleading, as the residual SS concentration in the clarified effluent is hardly lower or even higher than the concentration of SS in the influent.

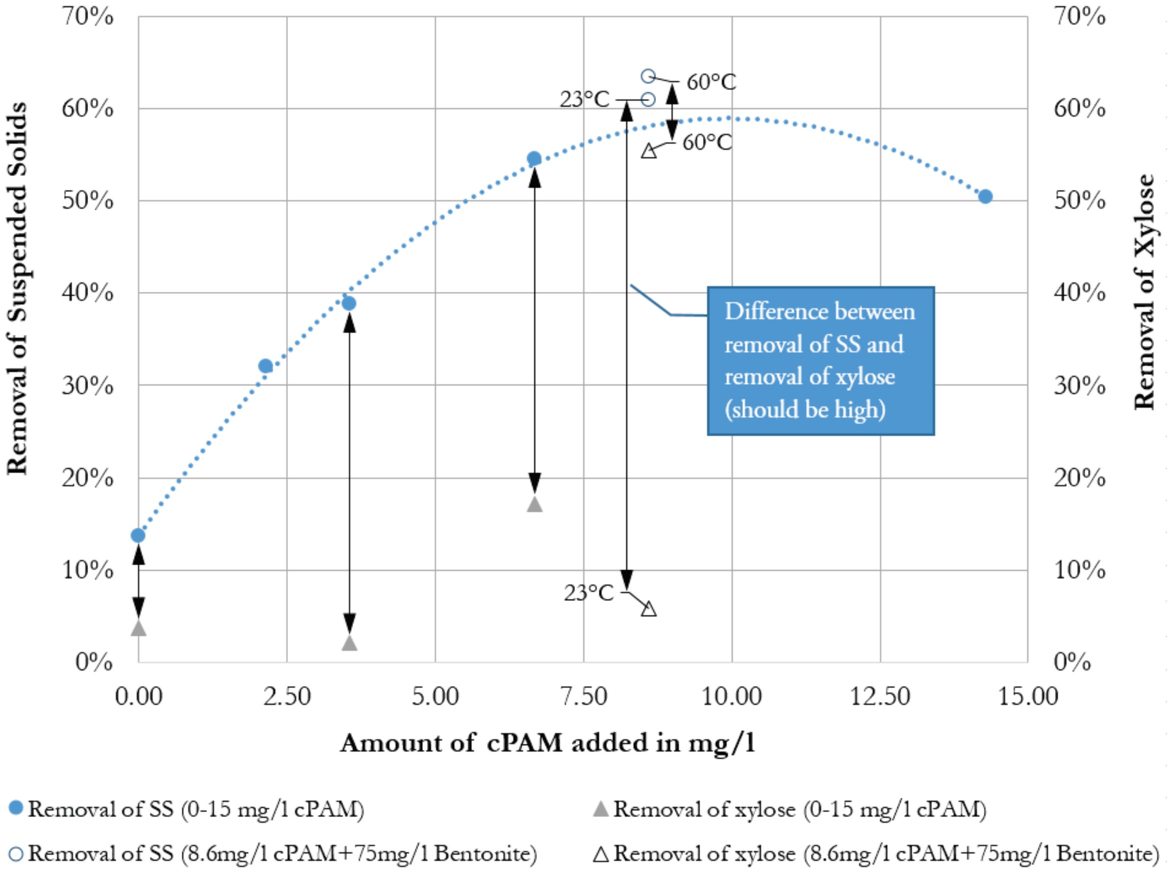


Figure 7.7: Removal of "total" suspended solids.

7.1.6 Conclusions from DAF pilot plant trials

The DAF system was not able to remove the desired amount of suspended solids. Only approximately 14% removal was achieved without addition of chemicals (i.e., cPAM and bentonite). This suggests that the nature of the raw suspension to be treated is not suitable for flotation as a separation technology.

The problem of an insufficient fibre recovery in the DAF process was also reported by the operators of the TMP-line at Braviken Paper Mill [106]. Although good results were achieved there in a laboratory scale process, only 19% removal was measured at the full scale DAF system. Neither temperature, nor the particle size distribution, or water quality had an influence on the efficiency.

Although in our case the removal efficiency was quadruplicated using 8.6 mg/l of a high molecular weight cationic PAM and 75 mg/l of bentonite, the resulting 60% removal of suspended solids is still too low. This makes an additional pretreatment step necessary, before the process water can be used for ultrafiltration. Such a pretreatment step could be, for example, microfiltration. Although the performance of microfiltration and ultrafiltration would probably be improved when implementing an upstream DAF system, the installation of a dissolved air flotation process cannot be recommended from the results obtained in this study. Nevertheless, the exploration of a better suited coagulant and flocculant, as well as screening the influence of pH on DAF performance are possible keys for a (future) successful integration of a DAF.

7.2 Microfiltration (MF) for the removal of suspended solids

Microfiltration is the most common method to remove suspended solids and colloids in the fractionation of biorefinery process streams [84] and was also the recommended pretreatment step in the ultrafiltration pilot trials by the industrial partner. This is because MF ensures an almost complete removal of suspended solids. Thus, microfiltration was investigated, and the results are summarized in the corresponding confidential report [107]

7.3 Removal of suspended solids by a separator

As neither DAF nor MF yielded useful results, trials using a separator (of confidential type) were performed by ANDRITZ to evaluate its suitability as an alternative for the removal of suspended solids. Details of the trials (i.e., the equipment and the operating parameters) are confidential.

Three different feed solutions were tested. The amount of remaining SS in the clarified effluent were hardly dependent on the initial SS in the feed. These results (see Table 7.3 for a summary) pointed out, that the suspended solids are removed to a specific, "fixed" extent. ANDRITZ provided the information that particles with > 2-3 µm are removed, which is in accordance with evaluation using the particle density distribution (cf. Figure 7.9). 85% removal of SS indicates for example a removal of all particles >1.5µm. This cut-off would be adequate for ensuing ultrafiltration, as shown in the ultrafiltration membrane screening (see Section 8), where a bag filter with a pore size of 5 µm was a sufficient pretreatment. Microfiltration cut-off sizes also are typically in the range of 0,1 - 1,5 µm, when applied prior to ultrafiltration of hemicellulose containing process streams [80], [108].

In addition, the concentration of total dissolved solids – and consequently of dissolved hemicelluloses – were not affected upon treatment with the separator. The only dissolved hemicelluloses lost are those discharged with the suspended solids. 20 volume% of suspended solids at the time of discharge result in about 1% of total volume lost, when assuming a SS concentration of 2 g/l in the feed and a density of 1 kg/l for the suspended solids.

Table 7.3: Removal of SS by separator.

Feed solution	SS in feed (mg/l)	SS in clarified effluent (mg/l)	Removal of SS (%)
Effluent I	2570	320	88
Clarified effluent from DAF-trials with pH changed to 9.1	1270	220	83
Clarified effluent from DAF-trials, Bentonite added	1270	430	66

As plugging issues can also occur in the separator with too coarse particles, an equipment for the removal of these particles, e.g., a disc filter, is necessary within the recovery process. Either the disc filter is already available in the existing pulping line, or needs to be additionally installed. Figure 7.9 provides an insight in the cut-offs (i.e. the minimum size of a particle that can be removed by this method) of the various discussed equipment.

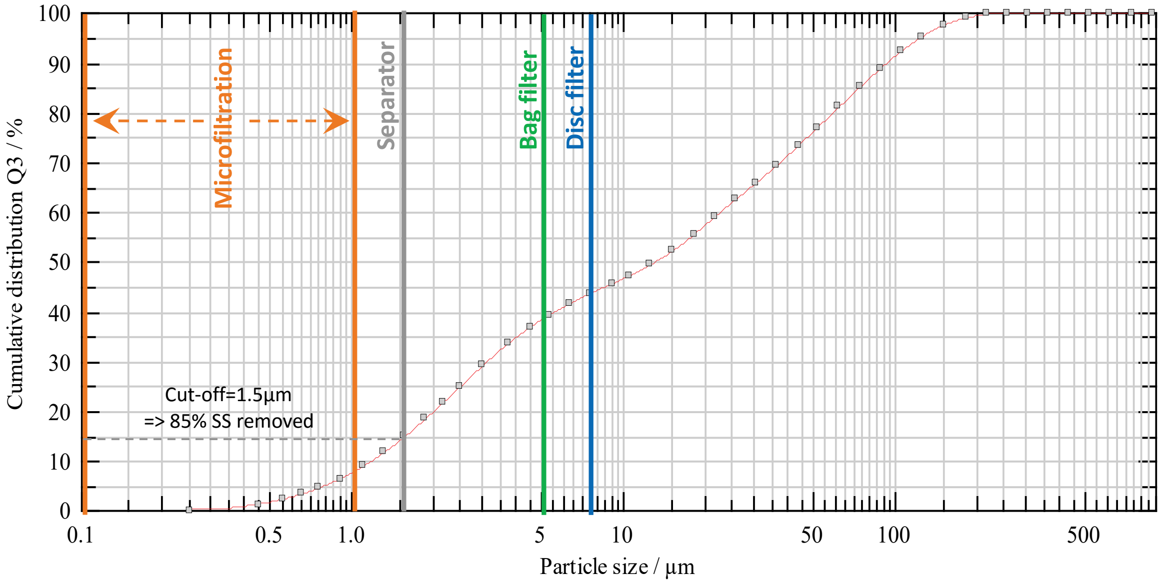


Figure 7.8: SS distribution curve to specify separation characteristics: Vertical lines show the cut-off of different equipment that can be used for solids separation (underlying PSD measurement from [101]).

7.4 Summary of results for the removal of SS

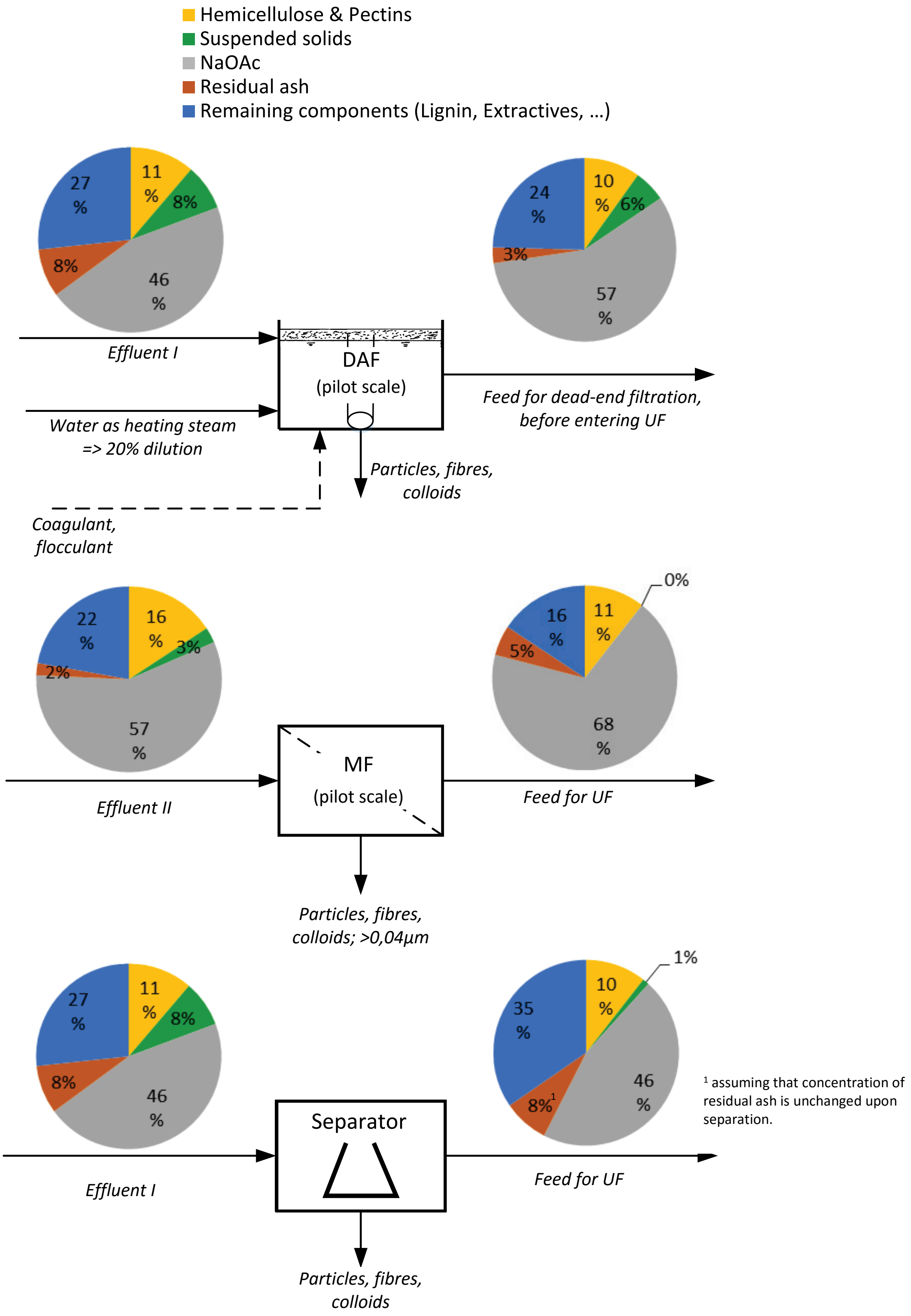


Figure 7.9: Composition of process water for different scenarios with respect to the removal of suspended solids.

8

Separation of hemicelluloses by ultrafiltration and purification by diafiltration

After the removal of suspended solids, ultrafiltration paired with diafiltration can be applied to concentrate the hemicelluloses and separate them from smaller compounds, e.g. salts, which pass through the membrane. The decisive characteristics to ensure an economic operation of the membrane process are (i) a high retention of the hemicelluloses, and (ii) a low retention of the impurities. Thereby, high yield, purity and concentration of the hemicelluloses can be achieved. Moreover, a high flux is desired to maximize the capacity of the process.

To find the best membrane for the pilot trials, three membranes were investigated on lab scale regarding flux and retention performance. The next step was the investigation of the separation of hemicelluloses by UF on a pilot plant scale, employing a membrane that had been proven suitable in the membrane screening from process sequence I. UF was in both sequences paired with diafiltration (DF) to wash out smaller components like salts.

Membrane filtration trials were performed at the test site of an industrial partner. Consequently, the details of these trials, particularly the set-up and operating parameters, are subject to non-disclosure and therefore discussed in a confidential evaluation. Apart from that, findings regarding separation performance are discussed in the present chapter.

8.1 Screening of UF membranes

For the comparison of three different membranes on laboratory scale, the cleared effluent from the dissolved air flotation of P-RC APMP process water was used as the feed solution. The characteristics of the studied ultrafiltration membranes are given in Table 8.1.

Table 8.1: Characteristics of the investigated UF-Membranes.

Membrane	Material	Cut-off (kDa)
A – 5kDa	A	10
A – 10kDa	A	5
B – 5kDa	B	5

Retention characteristics, presented in Figure 8.1, were similar for both "A" membranes, regardless of their different molecular weight cut-off (MWCO), which can be explained by immediate blocking of pores in case "A - 10kDa". Initial retention of sodium (Na) was almost zero, meaning it can pass freely through the pores. The concentration and purification of hemicelluloses is possible, as their initial retention was sufficient with 85%, while total solids were retained by only 35%. As xylan retention was generally a little higher than overall hemicellulose retention (~5%), it becomes also purified from other hemicelluloses and pectins.

The "B - 5kDa" membrane generally provided higher retention, but lower flux. Therefore, "A - 5kDa" should have been chosen for further investigation on larger scale, which was also suggested by the industrial partner.

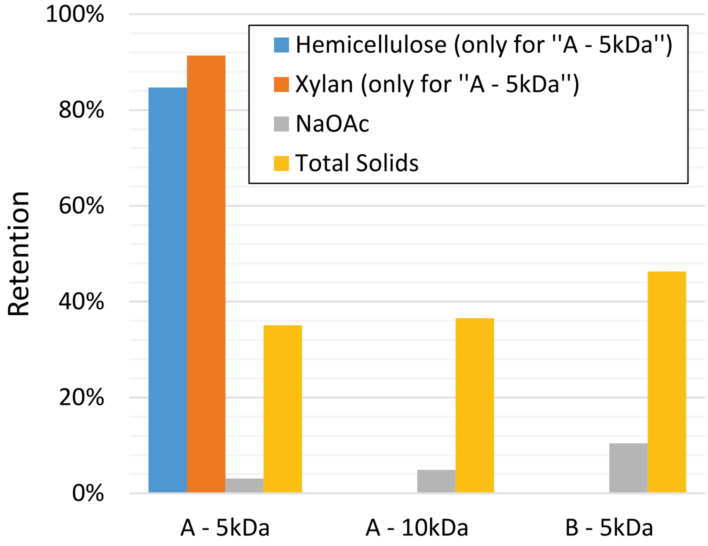


Figure 8.1: Retention of different components for membranes tested. Hemicelluloses were only measured for Membrane "A - 5kDa".

8.2 UF performance on pilot-plant scale

The process water was concentrated to a total final VCF of 45.8 (which stands for a reduction in volume of 97.8%). Industrially relevant fluxes were achieved throughout the processing of the solution. The concentration of hemicellulose could be increased from 3.3 g/l to over 100 g/l, which is higher than reported by others, mainly due to the high VCF.

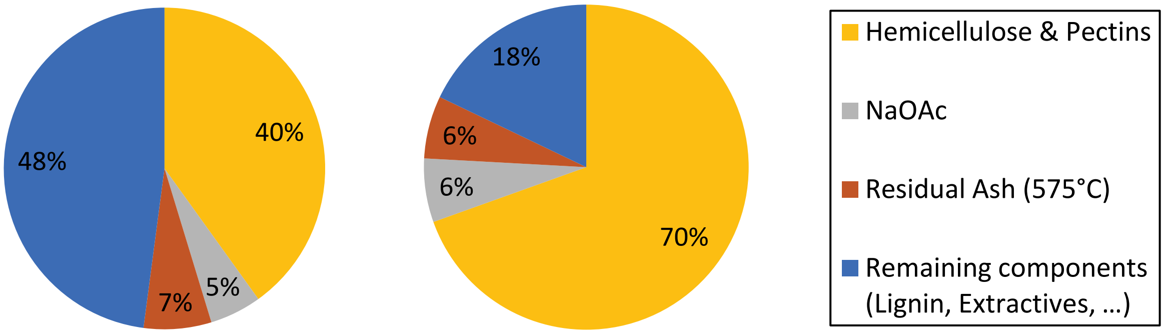


Figure 8.2: Composition of final products of UF lab trials (left; TS = 66.7 g/l; VCF = 18.9) and UF pilot trials (right; TS = 148.6 g/l; VCF = 45.8).

Diafiltration served its purpose, as it not only reduced the fraction of sodium from 13% to 6%, but also lead to a significant increase of the hemicellulose concentration in the retentate. The latter indicates that a layer of solutes (including hemicellulose) had formed on the membranes and was washed into the retentate by diafiltration. At an average retention of xylan of 94%, the yield over the UF process was 78% (Figure 8.3), which can be calculated via Equation (4.9). The upper temperature limit of the system, which is determined by the membrane stability, was not pushed to the limits. Thus, further potentials for improvement regarding the flux are possible.

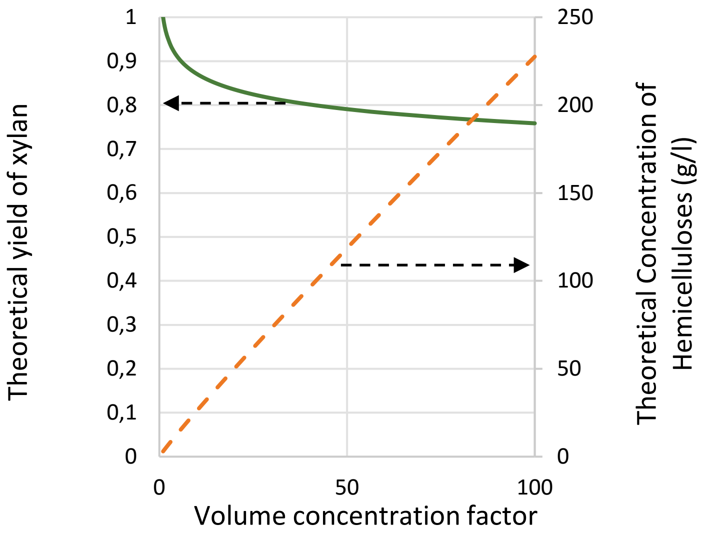


Figure 8.3: Theoretical yield during concentration (retention = 94%), (cf. Equation 4.9).

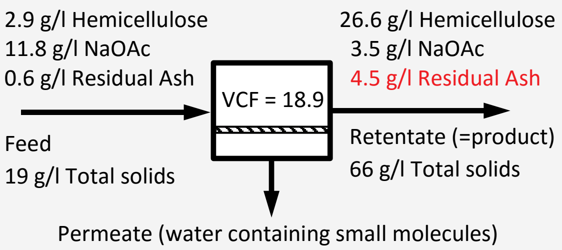
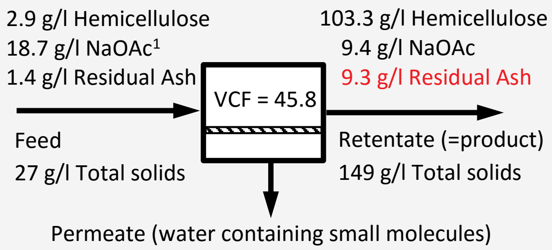
The amount of residual organics (i.e., lignin, extractives, and others) was highly reduced in the UF pilot trials, compared to the final retentate from the membrane screening. Figure 8.2 shows that residual organics account for only 18% of solids in the final retentate of the pilot trials. This was probably due to the higher alkalinity and peroxide charge in the pulping process, which caused a more severe degradation of those organic constituents. As a consequence, their molar mass is reduced and they can pass the membrane to a greater extent. [33]

Moreover, the COD in the average permeate (i.e. permeate withdrawn at constant time intervals) was reduced by 48%, from 26,060 to 13,650 mg/l.

8.3 Challenge of reducing ash content in the hemicellulose product

The content of sodium, measured by the conductivity, could be highly reduced by ultra- and diafiltration, e.g., compared to concentration by evaporation, where all inorganics would remain in the product as impurities (see Table 8.2). However, the amount of residual metal ions (e.g. Ca, Si) increased with increasing concentration, which is in accordance with results from direct measurement performed with ICP-MS.

Table 8.2: Comparison of UF lab and UF pilot trials.

UF lab trials (membrane screening, chapter 8.1) *pH = 6.2*	*UF pilot trials (chapter 8.2)* *pH = 7.4*
	
98.5% of NaOAc removed => NaOAc makes up 5.2 % of solids in retentate	98.9 % of NaOAc removed => NaOAc makes up 6.3 % of solids in retentate
60.2 % of residual ash removed => residual ash makes up 6.8 % of solids in product	85.9 % of residual ash removed => residual ash makes up 6.2 % of solids in product

Possible reason for the retention of "inorganics" are:

- Negatively charged uronic acid groups (MeGlcA as side-groups of xylan as well as GalA as main component of pectin), which consequently might bind more metal ions, are dissolved with the hemicelluloses and pectins. Bound metal ions are consequently retained by the membrane with the xylan and pectin. As uronic acid groups account for a much larger proportion in hardwood than in softwood – especially in the dissolved state – these issues with significant retention of ash are less pronounced in previous studies which are usually based on spruce as raw material [80], [108]. It is reported that galacturonan (GalA) residues have a strong tendency to form complex with Ca^{2+} [10].

- Chelating agents from the pulping process form linkages with metal ions.
- Lignin and related complexes might also bind metal ions.

Possible methods for further reducing ash content in UF product are:

- As the ability of uronic acids to bind metal ions increases with increasing pH (as described by [10]), lowering the pH prior to UF (after effluent is withdrawn from the pulping process and SS are removed) could reduce the ash content in the product. Thus, we expect a further decrease in the sodium and calcium content in the UF retentate following such a pH adjustment.
- A higher alkalinity in the pulping process should also help to remove “residual ash”, as metal ions like Ca^{2+} are bound to lignin and other complexes. Consequently, reducing the average degree of polymerization of lignin should help to reduce their retention by the UF membranes, and hence the inorganics should be removed with them.

9

Conclusions and future work

Significant amounts of hemicelluloses are dissolved in the process waters during mechanical pulping and subsequently lost in the effluents. Plant operators and system suppliers could benefit in case these biopolymers are recovered and used as a resource for bio-based value-added products. The present work was concerned with the separation of hemicelluloses from other components in the effluents from a P-RC APMP mill, thereby producing a concentrated and purified hemicellulose solution suitable for further investigations in product tests.

9.1 Conclusions

First, the separation of suspended solids was focused on, and a number of processes where considered: literature data indicated that dissolved air flotation achieves a typical removal of suspended solids of 40-80% without addition of chemical aids, and up to 99% with usage of adequate coagulants and flocculants [39]. Unfortunately, only ~10% and ~60% where achieved in the pilot trials in the present study for operation without chemicals and the optimum dosage of cPAM respectively. In fact, addition of coagulants was the only operating parameter that had a remarkable influence on the separation efficiency. Microfiltration (MF) removed all suspended solids, but at the same time reduced the amount of hemicelluloses by 46%, which is coinciding with previous findings from literature (cf. [80], [108]). Unfortunately, this loss of material appears to be too significant, and hence lowers the chances of an industrial application of this technology. In contrast to DAF and MF, a separator provided satisfactory results. With 88% removal of suspended solids, it was found the most suitable operation for the removal of SS, whilst ensuring a minimum removal of hemicelluloses. Nevertheless, the advantages of the separator (i.e., a higher yield of hemicelluloses) must be weighed against its higher power consumption compared to MF in the design of future plants. The MF and separation trials also revealed that an additional coarse separation, for example a disc filter, is most probably necessary to remove coarse particles. These particles could cause plugging in a subsequent separator or microfiltration unit, leading to a catastrophic interruption of the process.

Second, the isolation of hemicelluloses from other dissolved solids was pursued. The screening of UF membranes demonstrated the suitability of the "A" membranes with cut-offs between 5 and 10 kDa. In the UF pilot trials, the effluent could be concentrated to a volume concentration factor of 45.8 (= reduction of volume of 97.8%) at a satisfying flux. At a hemicellulose concentration of over 100 g/l, a final permeate flux of 33 $m^3/m^2/h$ was achieved, which is high compared to literature (cf. [80]). The fraction of sodium in the product could be reduced from 13 to 6% by diafiltration. Nevertheless, the final hemicellulose purity of 68%, as well as the remaining ash content (i.e., 11%) are the most critical product attributes regarding the desired application as barrier material.

A higher NaOH charge in the pulping process reduces the amount of residual organics in the UF product as their degradation is accelerated. This leads to smaller molecules that can pass the membrane. Furthermore, a higher alkalinity enhances the removal of inorganics during UF, as larger organics to which they are bound, are degraded and reduced. Whereas the amount of sodium decreases with increasing concentration by UF, the amount of residual metal ions (e.g. Ca, Si) was found to increase.

9.2 Future Work

This work focused primarily on the development of a hemicellulose recovery process that can be implemented into a mechanical pulp mill without significantly affecting the pulping process itself. However, far less work has been carried out on determining and investigating the most suitable application for the obtained concentrated and purified hemicellulose solutions. Studies of the properties and behaviour of potential high-value products and possible refining methods to manufacture these end products should be carried out. Initially, this work had an industrial customer of the produced hemicelluloses, who conducted application tests. In the field of barrier coatings, patents already exist [109], that need to be considered. Industrial customers are also necessary to convince mill operators of implementing a hemicellulose recovery system.

The next step towards industrial realisation are long-term tests on a larger scale. Preferably, these investigations are carried out as on-site tests at mechanical pulp mills. Beside the long-term performance of the recovery system, also the possible alteration of pulping process streams could be studied. For example, the permeate stream from the ultrafiltration could be directly reused in the pulping process.

To summarise, future work has to target and collaborate with industrial customers of the recovery system (i.e., pulp mill operators) on the one hand, and target the final application of the hemicellulose on the other hand.

Abbreviations

ADt	air-dry tonne (typically defined as 10% moisture and 90% oven-dry pulp)
Ara*f*	arabinofuranosyl
BOKU	University of Natural Resources and Life Sciences
CIP	membrane cleaning procedure ("cleaning in place")
COD	chemical oxygen demand
cPAM	cationic polyacrylamide
CTMP	chemi-thermomechanical pulping
DAF	dissolved air flotation
DCS	dissolved and colloidal substances
DF	diafiltration
DP	degree of polymerization
DS	dissolved solids
Gal*p*	galactopyranosyl
GC-MS	gas chromatography - mass spectrometry
Glc*p*	glucocopyranosyl
Glc*p*A	glucopyranosyl uronic acid
GMP	groundwood mechanical pulping
HPTLC	high performance thin layer chromatography
IAF	induced air flotation
ICP-MS	inductively coupled plasma mass spectrometry
LD	laser diffraction
LCC	lignin-carbohydrate complexes

Man*p*	mannopyranosyl
MF	microfiltration
MLSS	mixed liquor suspended solids
MWCO	molecular weight cut-off
NaOAc	sodium acetate
PAC	polyaluminium chloride
Poly-DADMAC	polydiallyldimethylammonium chloride
PSD	particle size distribution
P-RC-APMP	mild preconditioning of the chips, refiner chemical alkaline peroxide mechanical pulping
PWF	pure water flux
RO	reverse osmosis
SS	suspended solids
TMP	thermomechanical pulping
TMPress	Transmembrane Pressure
TS	total solids
TSS	total suspended solids
UF	ultrafiltration
VCF	volume concentration factor
Xyl*p*	xylopyranosyl

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Experimental

All concentrations refer to 80°C, which is the temperature of the effluent when leaving the pulping process. Total solids, suspended and dissolved solids, as well as ash content were determined according to the procedures developed by the U.S. National Renewable Energy Laboratory (NREL) [110], [111]. Samples were dried in pre-weighed aluminium dishes at 105°C to constant weight in an oven. The total solids (TS) content was then calculated by weighing of the residue after cooling to room temperature in a desiccator.

Samples were filtered through a glass fibre filter (Macherey-Nagel MN 85/70) with a pore size of 0.6 µm. The filtrate and the filter were dried at 105°C to constant weight. The content of suspended solids (SS) was then calculated after weighing the matter on the filter. The content of dissolved solids (DS) was calculated after weighing the filtrate. Thus, the suspended matter is defined as the solid material retained by a filter with 0.6 µm pores and the dissolved matter as compounds that pass through the filter throughout this work.

Oven-dried samples were further heated to 575°C, and this temperature was maintained for 24 ± 6 h to reach constant weight. The samples were then cooled down cautiously. The ash content was determined by weighing the residual sample.

Sodium concentration can be measured via the conductivity as there is a linear correlation, which was quantified in advance by direct measurement of sodium using ICP-MS (for the corresponding report see “Measurement of Na, Si and Ca at different stages of xylan-recovery process by ICP-MS and correlation between Na-Conc. and conductivity”). Thus, the concentration of sodium, C_{Na} in [mg/l], in the effluent was calculated using Equation (A.1), where σ denotes the electrical conductivity at 20 ± 2°C in µS/cm.

$$C_{Na} = 0.328 \cdot \sigma \tag{A.1}$$

Beside sodium, also the amount of silicate and calcium was determined by ICP-MS analysis. As the different inorganics (i.e., Na, Si, Ca) behaved different during ultrafiltration, with only sodium showing a reliable linear dependence on conductivity, sodium acetate (NaOAc) and residual inorganics were treated as different fractions in the course of the component analysis. Consequently, the concentration of NaOAc, i.e., c_{NaOAc}, was calculated from the Na concentration via the molar masses of Na and NaOAc via Equation (A.2).

$$c_{NaOAc} = \frac{82.034}{22.990} \cdot c_{Na} \tag{A.2}$$

Since upon incineration, sodium acetate decomposes to sodium carbonate (Na_2CO_3) [112], the mass originated from NaOAc in a sample decreases during ash analysis. The resulting amount of Na_2CO_3 was calculated by taking the corresponding molar masses and stoichiometry of the chemical reaction into account. Consequently, the amount of "residual ash" (as a measure of "residual inorganics") was calculated by subtracting the amount of ash that belongs to Na_2CO_3 from the total ash content. This way of calculating the content of inorganics is just an estimation, as the occurrence of ions is complex. Sodium for example is present mainly as sodium acetate [113], but also as sodium silicate, sodium carbonate et cetera. Besides, bound sodium is attached to carboxylic groups originating from hemicelluloses, lignin and pectin.

Analysis of the hemicelluloses and pectins was done at the University of Natural Resources and Life Sciences (BOKU), Department of Chemistry, using methanolysis – GC-MS based on the method developed by Bertaud et al. [114]. Dissolved, non-crystalline polysaccharides are determined as the sum of monosaccharides they are composed of. Taking into account the difference to their native form in the polysaccharides, anhydro correction factors were used. Methanolysis has the advantage over hydrolysis that the degradation of released monosaccharides is lower. Furthermore, also uronic acids, part of hemicelluloses and pectins, can be determined quantitatively. However, the polysaccharides quantified by this analyses are simply called "hemicelluloses". This method is subject to measurement errors of ±15% according to BOKU [115]. To prove that the determined monosaccharides are completely part of oligo- and polysaccharides, the initial amount of monosaccharides in the raw effluent was measured using HPTLC. Only negligible amounts of monosaccharides were present in the effluent (~50 mg/l).

The concentration of the "remaining components", which includes lignin, acetic acid, extractives and others, was calculated by subtracting the concentrations of suspended solids, NaOAc, residual ash and hemicelluloses from the concentration of total solids (acc. to equation (A.3)).

$$C_{others} = C_{DS} - \left(C_{NaOAc} + C_{Residual\,Ash} + C_{Hemicelluloses}\right) \quad \text{(A.3)}$$

For measurements of solids (i.e. TS, DS, SS) and ash, all samples were analysed in duplicate and the displayed value is their average. The same applies to measurement of hemicelluloses. For temperature, pH and conductivity, single measurements were performed.

Densities of the process waters of 0.97 kg/l at 80°C and 1.00 kg/l at 20°C were used in the calculations, which is in accordance to the density of water and was validated by own measurements of the solutions' density.

Measurement of Na, Si and Ca at different stages of xylan-recovery process by ICP-MS and correlation between Na-Concentration and conductivity

A direct measurement of the concentration of three inorganic elements in the original pulp mill effluent (i.e., "effluent I"), the feed, different permeates and retentates of the ultrafiltration, was conducted at the University of Graz, using inductively coupled plasma mass spectrometry (ICP-MS). The aim was to get a clear and accurate correlation between the concentration of these inorganics (present as salts) and conductivity, which can be measured easily. This is necessary to make material balances and evaluate the efficiency of the ultrafiltration to remove the salts. The details of the materials and methods are given in Table A.1

Table A.1: Facility, materials and methods of ICP-MS analysis.

Facility of execution	KFU Institute of Chemistry
Executing Research Group	Analytical Chemistry for Health and Environment (ACHE)
ICP-MS System	Agilant 7700x ICP-MS

Material of vessels	Quartz Glass, Polysterol
Method of digestion	5ml HNO_3 per 3ml effluent, kept for 30min at 250°C & 40 bar
Digestion System	Ultraclave IV, MLS GmbH (microwave-heated)
Calibration Standards	ICP-Standard-Solutions from Carl Roth GmbH+Co. KG
Dilution Water	Ultrapure Water (18.2 MΩ*cm)
Calibration Solution	Calibration Standards + Nitric Acid + Ultrapure Water to final acidity of 10%

With the exception of the retentates, all samples were analysed four times: two times undigested and two times digested. The retentates were analysed three times, always digested because they were not transparent enough for untreated use in ICP-MS.

Table A.1 shows the obtained data and the fitted correlation curves. Different conductivity measurements were used: Once the values from the industrial partner (which conducted the ultrafiltration tests) at unknown temperature (coloured blue), and once the values obtained at ACHE at temperatures of 21 and 18°C for permeates and retentates respectively (coloured red). The calibration of the conductivity measuring instrument at ACHE was maybe incorrect, that's why the correlation with the conductivities from the industrial partner is more reliable. The industrial partner measured similar conductivity values at lower Na-concentrations and lower conductivities at higher Na-concentrations compared to the measurements at ACHE, which reinforces the assumption that the industrial partner carried out the conductivity measurements at ambient temperature.

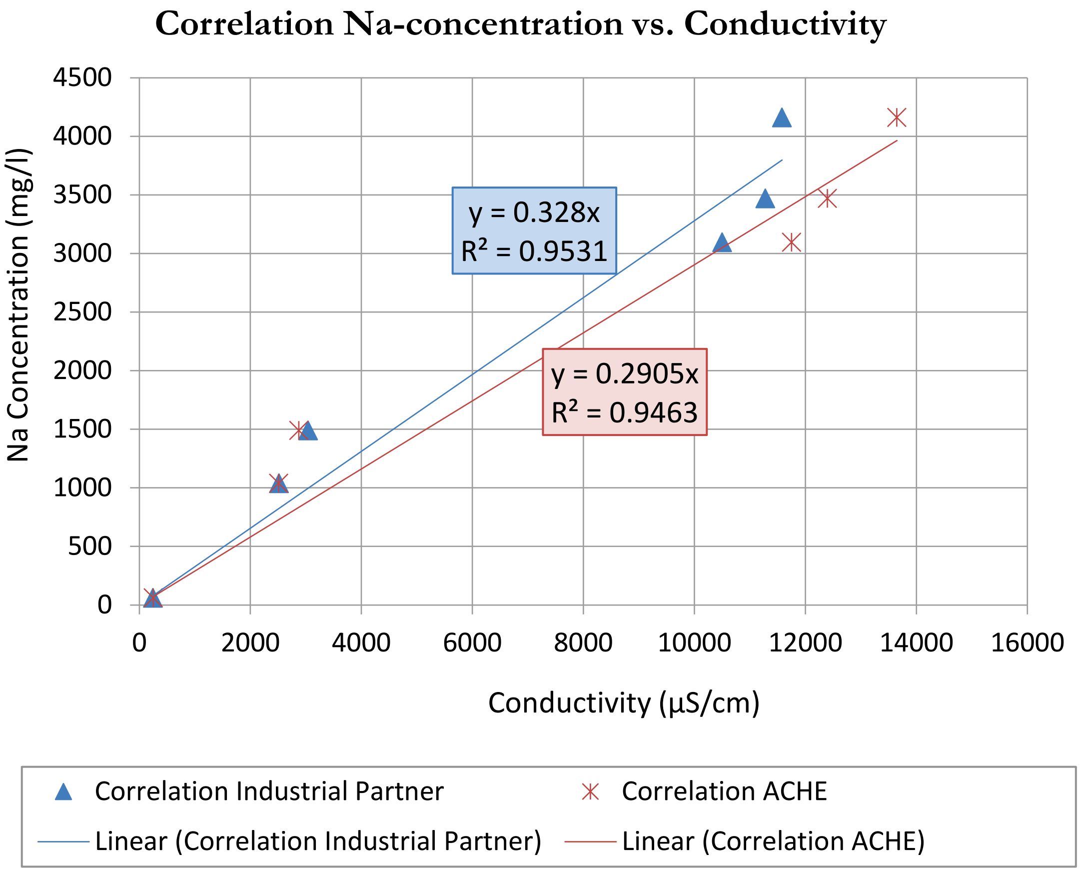

Figure A.1: Correlation between Na and Conductivity

It must be mentioned, that the ICP-MS determination exhibits relative standard deviations between 3% and 16% for sodium measurement. As the coefficient of determination (R^2) is about 0.95, it can be stated that there is a good linear correlation between conductivity and concentration of sodium. Measurement of conductivity could further be used as an indirect measure of salts.

The original mill effluent (pre-filtered through 0.6µm filter) had a concentration of about 4700 mg/l of sodium, but its conductivity showed deviation from the linear correlation, indicating an interference in the conductivity measurement. The concentration of silicon (measured as isotope 29) ranged from 78±10 mg/l in a permeate sample to 216±84 mg/l in a sample of a highly concentrated retentate and the concentration of calcium ranged from 31±4 mg/l in a permeate sample to 886±131 mg/l in the highly concentrated retentate.