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MEMBRANE FILTRATION OF DEBARKING PLANT WASTEWATER

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ABSTRACT

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Membrane filtration of debarking plant wastewater

Master's thesis

2020

105 pages, 53 figures, 23 tables and 2 appendixes

Examiners: Professor Mika Mänttari
Professor Mari Kallioinen

Keywords: nanofiltration, PCD, debarking, high shear rate, NF270, CR-filter

Efficiency of wastewater treatment system in Stora Enso's Anjala mill typically decreases during winter. One possible reason for this problem can come from debarking process where heated water is used to keep debarking process optimal. Higher temperature in the water causes more wood extractives to dissolve from bark to water which increases the load of wastewater coming from debarking plant to the wastewater treatment system.

The goal of the study is to evaluate the possibility of membrane filtration to purify debarking water and reduce the load to wastewater treatment plant. Cross-rotational membrane modules are typically used in treating paper machine circulating waters and concentrating coating effluents. Only one research has been done on their use in the treatment of debarking waters.

Cross-rotational membrane CR-250 module was used to treat debarking wastewater from Anjala mill. Used membranes were ultrafiltration membrane RC70PP and nanofiltration membrane NF270. NF270 reached around 80 % retentions for most of the compounds analysed. Pulsed corona discharge as an oxidation process and adsorption to saw dust, modified saw dust and activated carbon were used as pretreatment methods to increase filtration flux and decrease fouling. All pretreatment methods increased filtration flux, modified saw dust had the greatest effect on the flux. Estimations on investment and operation costs for different process configurations were also made based on the experiments.

TIIVISTELMÄ

Lappeenrannan-Lahden teknillinen yliopisto LUT
LUT School of Engineering Science
Chemical Engineering and Water Treatment

Perttu Salmi

Kuorimon jäteveden membraanisuodatus

Diplomityö

2020

105 sivua, 53 kuvaajaa, 23 taulukkoa ja 2 liitettä

Tarkastajat: Professori Mika Mänttari
Professori Mari Kallioinen

Avainsanat: nanosuodatus, PCD, kuorinta, korkea leikkausvoima, NF270, CR-suodatin

Stora Enson Anjalankosken tehtaan jäteveden puhdistamon toiminta heikentyy yleensä talvella. Yksi mahdollinen syy toiminnan heikkenemiseen voi tulla kuorimolta, jossa talvella käytetty vesi lämmitetään kuorintaprosessin pitämiseksi optimaalisena. Veden korkeampi lämpötila liuottaa puun kuoresta enemmän uuteaineita veteen, mikä lisää jäteveden puhdistamolle kuorimolta kulkeutuvaa kuormitusta.

Tämän työn tarkoituksena on tutkia mahdollisuutta membraanisuodatuksen käyttöön kuoriveden puhdistuksessa sekä jäteveden puhdistamolle kulkeutuvan kuorman pienentämisessä. CR-moduuleita käytetään yleensä paperikoneiden kiertovesien puhdistukseen tai päällystepitoisten jätevesien konsentroimiseen. Näiden käytöstä kuorimon jätevesien puhdistukseen on tehty vain yksi tutkimus.

CR-250 moduulia käytettiin kokeissa Anjalankosken paperitehtaan kuorimon jäteveden puhdistamiseen. Käytetyt membraanit olivat RC70PP ultrasuodatusmembraani ja NF270 nanosuodatusmembraani. NF270 membraanilla päästiin noin 80 % retentioihin useimmilla analysoiduilla yhdisteillä. Pulssitettua koronapurkausta hapetusmenetelmänä sekä adsorptiota sahanpuruun, käsiteltyyn sahanpuruun ja aktiivihiileen käytettiin esikäsittelymenetelminä suodatuksen vuon ja likaantumisen parantamiseksi. Kaikki esikäsittelymenetelmä nostivat suodatuksen vuota, käsitellyn sahanpurun vaikutus vuohon oli suurin. Alustavat investointi- ja käyttökustannusarviot laskettiin eri prosessivaihtoehdoille suoritettujen kokeiden perusteella.

ACKNOWLEDGEMENTS

This master's thesis was done at LUT-university for Stora Enso Anjala paper mill during the challenging first half of 2020. I want to thank Pasi Marin and Heini Kukkonen from Stora Enso Anjala paper mill for interesting topic for my thesis and for their guidance during this thesis.

I would like to thank Professors Mika Mänttari and Mari Kallioinen for their role as examiners and for their feedback in this thesis. I would also like to express my gratitude to Jussi Lahti and Mikko Huhtanen for their help with experiments conducted in this thesis.

Finally, I would like to thank my family, friends and Emma for their support during this thesis and years in LUT.

Lappeenranta, August 2020

Perttu Salmi

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Appendix I

UV-Vis Spectra

Appendix II

PCD treatment analyses

List of symbols

Abs_{280nm}	Absorbance at 280 nm, -
b	Path length in cuvette, cm.
C_{phenol}	Polyphenol concentration, -
C_i^f	Concentration of component i in feed, -
C_i^p	Concentration of component i in permeate, -
DF	Dilution factor, -
$h\nu$	light, -
J	Permeate flux, kg/m ² h
$m\%$	Mass percentage, m-%
m_f	Mass of the feed, kg
m_p	Mass of the permeate, kg
p	Pressure, bar
R	Reacting organic compound, -
R_i	Retention of component i, -
T	Temperature, °C
t	Filtration time, h
$vol\%$	Volume percentage, vol-%

Abbreviations

AC	Activated carbon
AOP	Advance oxidation process
BOD	Biological oxygen demand
BOD₇	Biological oxygen demand, seven days
COD	Chemical oxygen demand
COD_{CR}	Chemical oxygen demand, potassium dichromate
COD_{MN}	Chemical oxygen demand, permanganate
CR	Cross-rotational
DHAA	Dehydroabiatic acid
EC₅₀	Effective concentration, 50-%
ECF	Elemental chlorine free
IC₅₀	Inhibition concentration, 50-%
LC₅₀	Lethal concentration, 50-%
LCFA	Long chain fatty acid
MBR	Membrane bioreactor
MBBR	Moving bed bioreactor
MF	Microfiltration
MWCO	Molecular weight cut-off
NF	Nanofiltration
NTP	Non-thermal plasma
PCD	Pulsed corona discharge
PES	Polyethersulphone
RC	Regenerated cellulose
RET	Reverse electron transport
RO	Reverse osmosis
ROUR	Relative oxygen uptake rate
SS	Suspended solids

TC	Total carbon
TOC	Total organic carbon
TSS	Total suspended solids
UF	Ultrafiltration
VRF	Volume reduction factor
VSEP	Vibratory shear enhanced processing
WF	Water flux

1 Introduction

1.1 Background

In paper and pulp production trees are initially cut to logs and debarked. Debarking is important because bark consists mostly of unwanted compounds that can hinder the processes further in production. Including bark in further processes is not also economically feasible. Water is used in most debarking plants to wash logs and ease the debarking process. Large amounts of wood extractives extract to the used water during debarking, many of these are toxic to the environment such as tannins and resin and fatty acids. (Niiranen 1983) All pulp and paper mill process waters contain these compounds, but from total toxicity of mill wastewater debarking plant wastewater can attribute to more than 50 %. (Savolainen 1992)

Debarking plant wastewaters are usually circulated in debarking due to the high concentration of different compounds. Clarifiers are typically used to treat circulating water. Part of the clarifier effluent is removed to wastewater treatment system of the mill, as new water needs to be added to circulation to prevent concentration of compounds in circulating water.

During winters, there has been challenges with biological wastewater treatment system in Anjala paper mill where the treatment efficiency of the system has decreased. One possible cause for this can come from debarking. In Anjala paper mill water used in debarking is heated during winter to defreeze logs for debarking. Increase in the water temperature leads to more compounds extracting from bark to the water. This raises the measured COD in debarking water, which increases the load coming from debarking to mill wastewater treatment system. Increase of wood extractive concentrations can possibly inhibit biological activity in the wastewater treatment system.

High shear rate membrane modules, such as cross-rotational (CR), have been used in pulp and paper industry for treating circulating water of paper machines or for concentration of coating effluents. One research on the usage of CR module has been previously done (Hakala 2014).

In this thesis Norway spruce bark, debarking and the water used in debarking are discussed. Toxicity of debarking water and individual wood extractives contributing to

toxicity are evaluated. Various water treatment methods are reviewed for the removal of toxicity and different wood extractives from paper and pulp mill effluents. Focus on the literature part is on membrane and advanced oxidation processes.

In experimental part, membrane treatment is used to treat Anjala paper mill debarking water. Ultra- and nanofiltration membranes are used in CR module for purification of debarking water. Smaller scale tests are done in dead-end filtration cell. Activated carbon, saw dust and modified saw dust are used as adsorbents in pretreatment for membrane filtrations. Pulsed corona discharge is used to treat debarking water and nanofiltration permeate. Quality of filtrated debarking waters is evaluated with turbidity, color, pH, conductivity, chemical oxygen demand, total organic carbon, biological oxygen demand and toxicity analyses. Aim is to develop viable membrane process with high permeate flux and sufficient reduction of toxic compounds.

1.2 Anjala paper mill

Stora Enso Anjala paper mill, founded in 1938, is part of Stora Enso Publication Papers Oy Ltd. It produces 435 000 tonnes of book grade paper, magazine paper and improved newsprint from mechanical pulp annually. Currently there are two paper machines running in the mill. Anjala Paper mill is adjacent to Stora Enso Ingerois mill, which produces folding boxboard. Anjala and Ingerois mills share the same raw materials, energy and wastewater treatment. (Stora Enso 2020a, Stora Enso 2020b)

2 Debarking

2.1 Properties of bark

The amount of bark in a tree contributes to 10 – 15 % of the weight of a tree. Conifers consist of 12 – 15 m-% of bark and birch consist 15 m-% of bark. (Seppälä et al. 2005, Sjöström 2013) Composition of wood and bark differ slightly from each other as they both contain different amounts of components like lignin, cellulose and hemicelluloses. Bark contains many compounds not found in wood, such as suberin and condensed tannins. (Fengel & Wegener 1984) There are at least 237 different compounds found in softwood bark that are identified and can be extracted. Many of these compounds can have beneficial effects for e.g. human health. (Jablonsky et al. 2017) Compared to wood, there are greatly increased number of nutrients in the bark; nitrogen content can be 2 – 5 times higher and phosphorus content 5 – 10 times higher (Niiranen 1983).

Krogell et al. (2012) studied the composition of Norway spruce bark. Comprehensive analysis was made with multiple extraction steps from bark powder with hexane, aqueous acetone and water at different temperatures. Inner and outer layers of Norway spruce bark are structurally different and have different compositions. The Norway spruce bark consist mostly of inner bark which also has more moisture than in outer bark. Detailed percentages for dryness and weights are presented in Table I.

Table I Norway spruce bark dry contents and dry bark weight ratio of inner and outer bark (Krogell et al. 2012).

	Dry content, %	% of whole bark
Whole bark	49.5 ± 0.6	100
Inner bark	39.6 ± 0.5	66.3
Outer bark	60.9 ± 0.6	33.7

Chemical composition of inner and outer bark differs significantly. Accurate chemical composition of spruce inner and outer bark is presented in Figure 1. Hydrophilic extractives and cellulose are more common in inner than in outer bark. Structure and composition of lignin in spruce bark is not fully known. Lignin contents of wood can be determined mainly from Klason lignin determined after polysaccharides are removed from wood, and then wood is subjected to acid hydrolysis and insoluble ash is removed.

Acid-soluble lignin can be determined from the used acid. (Sjöström 2013) Klason lignin is found mostly in the outer bark of Norway spruce, where it amounts to one third of the bark (Krogell et al. 2012).

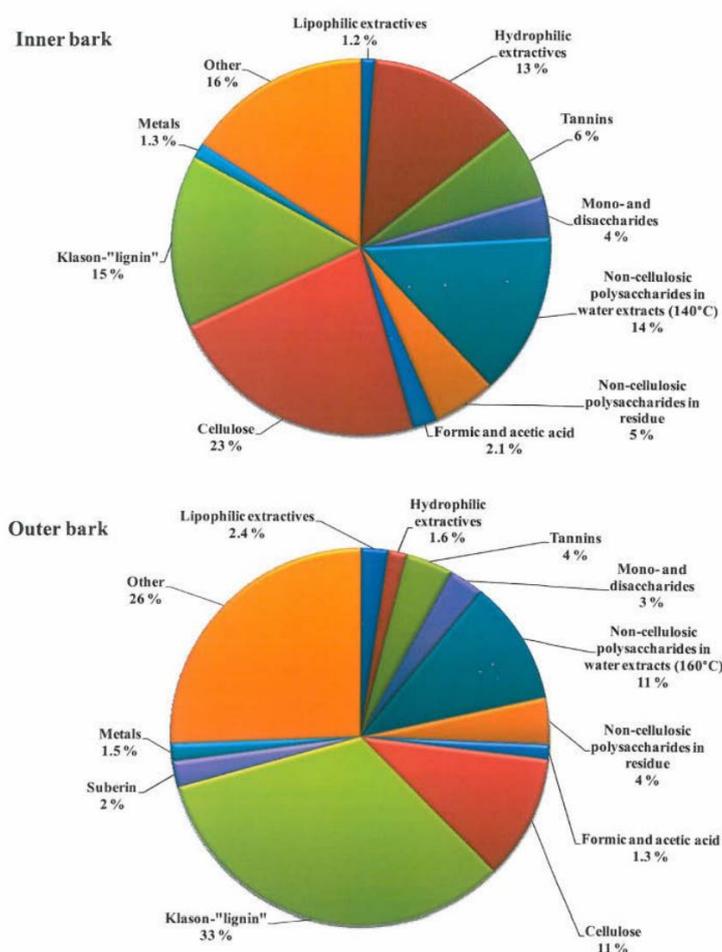


Figure 1 Compositions of Norway spruce bark's inner and outer layers. (Krogell et al. 2012)

External factors can affect the composition of metal ions in the bark. Dominant metal ions in Norway spruce bark are calcium and potassium. They make up to 30 % and 15 % of metal ions found the bark. (Norin & Fremer 1977) Calcium is found more in the outer bark, whereas potassium is more common in inner bark (Krogell et al. 2012). Detailed concentrations of common metal ions found in Norway spruce bark is shown in Table II.

Table II Most common metal ions, and their concentrations, found on inner and outer bark of Norway spruce determined with ICP-AES (Krogell et al. 2012).

	Inner bark g/kg	Outer bark g/kg
Ca	8.10	11.9
K	2.46	1.56
Mg	0.73	0.39
Mn	0.60	0.45
P	0.58	0.34
S	0.24	0.24
Zn	0.20	0.11

2.1.1 Wood extractives

Wood extractives are divided to lipophilic and hydrophilic compounds. Lipophilic extractives are extracted with different non-polar solvents and hydrophilic extractives with polar solvents or water. Wood extractives can make up to 30 – 40 % of bark, whereas in wood they make up to 5 %. (Norin & Fremer 1977) Most common lipophilic extractives are resin and fatty acids, terpenoids and sterols. Hydrophilic extractives are mostly phenolic constituents such as condensed tannins. Many wood extractives have small molecular weight. (Back & Ekman 2000) Composition and occurrence of different extractives depends on the species of wood and its properties, such as age, environment and part of the tree, e.g. pine bark has higher concentration of extractives compared to spruce bark (Ånäs et al. 1983). In Norway spruce wood, dry solids consist of 1.0 – 2.0 % of wood extractives (Stenius et al. 2000).

Detailed composition of lipophilic and hydrophilic extractives found in the inner and outer bark of Norway spruce is shown in Table III. There are almost two times the lipophilic extractives in the outer bark compared to the inner bark. Lipophilic extractives found in the outer bark are for the most part resin acids, triglycerides and diterpenoids, whereas inner bark consists mostly of triglycerides, steryl esters and resin acids. Hydrophilic extractives are considerably more common in inner than in outer bark. More than half of hydrophilic extractives in inner bark are stilbene glucosides, which consists mainly of isorhapontin and astringin. Mono- and disaccharides are the most common hydrophilic extractive in the outer bark. (Krogell et al. 2012)

Table III Concentrations of lipophilic and hydrophilic extractives found in Norway spruce inner and outer bark (Krogell et al. 2012).

	Inner bark		Outer bark	
	Lipophilic, mg/g	Hydrophilic, mg/g	Lipophilic, mg/g	Hydrophilic, mg/g
Fatty acids	0.3	0.7	1.5	0.27
Resin acids	2.8	0.2	10	0.12
Sterols	0.5	0.3	0.4	0.15
Steryl esters	3	-	2.1	-
Triglycerides	4.1	-	3.8	-
Aliphatic alcohols	<0.1	-	0.7	-
Diglycerides	0.6	-	1.9	-
Diterpenoids	0.7	<0.1	3.2	<0.1
Flavonoids	-	-	-	2.8
Stilbenes	-	2.7	-	0.7
Stilbene glucosides	-	106	-	4.8
Mono- and disaccharides	-	35.5	-	29.7
Not identified	-	16.1	-	7.2
Total	12	165.5	23.4	45.7

2.2 Debarking processes

Wood bark contains little useful fibers and it has many compounds detrimental to process condition and equipment. Bark in pulping process decreases brightness of the final pulp and bleaching is inefficient to bark leaving darker impurities in paper and board (AEL 2011). Debarking is one of the first processes in a paper and pulp mill process chain. Before debarking trees are usually cut lengthwise into certain size logs. In debarking, cambium between bark and wood is broken and most of the bark is removed from the log. The aim of debarking is to remove most of the bark in the wood, but in the same time yield minimal wood loss. It is also important that debarked bark is salvaged for further usage and other impurities such as stones and sand are removed and separated from the wood and bark. (Niiranen 1983)

Requirements of bark contents in different pulp mass type processes are shown in Table IV. Mechanical pulp processes generally do not allow much of the bark in the process whereas sulfate pulp can tolerate more bark in the process (Seppälä et al. 2005).

Table IV Allowed amounts of bark in different pulp mass types (Seppälä et al. 2005).

Pulp mass type	Allowed bark content, %
Mechanical	0.2 – 0.5
Thermomechanical	0.2 – 1.0
Chemi-thermomechanical	0.2 – 2.0
Unbleached sulfate	1.0 – 1.5
Bleached softwood sulfate	1.0 – 2.0
Birch sulfate	~ 0.5

The amount of force required to remove bark from the tree is dependent on the species of the wood, the time of the year and in so on the dryness and temperature of the wood. For example, birch bark is harder to debark than pine bark which breaks easier. Water is usually used in debarking processes to ease the separation of bark from wood. When tree freezes, the force needed to debark the tree increases significantly. In winter, hot water or steam is used to defreeze trees before debarking to reduce the force binding bark to the wood. Finnish paper and pulp mills use mostly hot water for defreezing. (AEL 2011) In large scale debarking processes wood loss during debarking increases as debarking efficiency is improved. Because of the additional wood loss, logs are not usually

debarked completely, and small amounts of bark is left on the logs. Selective recycling of wood back to debarking can be used to improve debarking efficiency when as little amount as possible of bark in wood after debarking is crucial. (Niiranen 1983)

There are various types of debarking processes used worldwide. Single wood debarking can be done with, e.g. rotor or hydraulic debarking. In rotor debarking single tree is placed in the debarker, where blades spin around the tree and scrape the bark from the tree. Rotor debarking is used mostly in sawmills and plywood mills. The maximum capacity of the process is around 40 m³/h. Advantages of rotor debarking are that no water is used, and wood losses are minimal. Principle figure of rotor debarking is presented in Figure 2. In hydraulic debarking the wood is debarked with water jets with pressures up to 10 MPa. Hydraulic debarking can have high capacity, but it uses vast amounts of water. These type of debarkers are mainly used in North America. (Niiranen 1983)

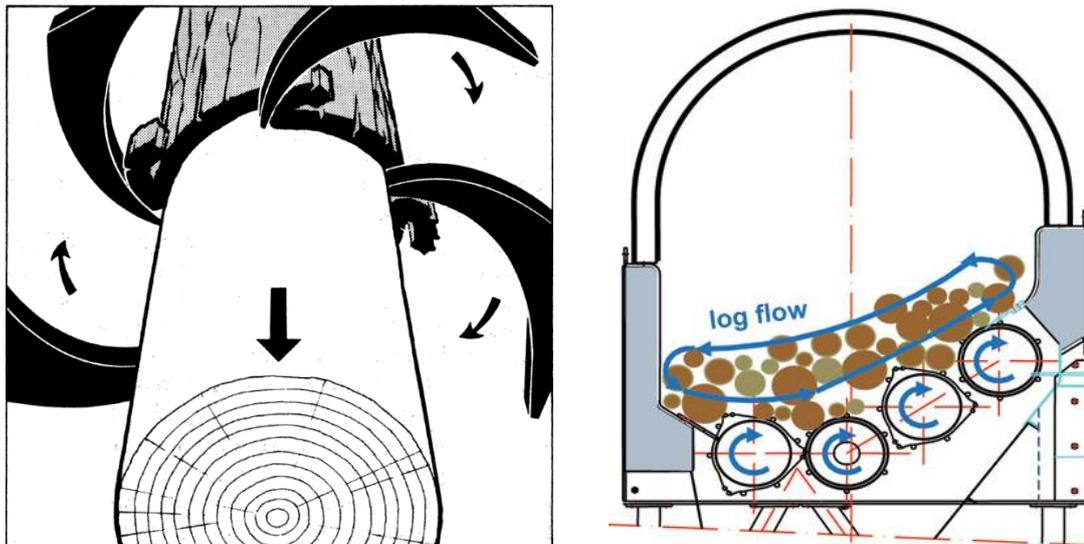


Figure 2 Principles of rotor debarking (left) and rotary debarking (right) (Niiranen 1983, AEL 2011)

Large scale debarking of wood is usually done with drum debarking or rotary debarking. In rotary debarking there are spinning rotor discs at the bottom slope of a drum (Figure 2). Spinning rotors have teeth in them which scrape the bark from the logs. Bark falls down from gaps between rotor discs. Like rotor debarking, rotary debarking does not need

water and it has lower energy requirement compared to drum debarking. (AEL, 2011)
Drum debarking is discussed in detail in Chapter 2.3.

2.3 Drum debarking

Drum debarking is efficient mass debarking process. Debarking is based on horizontal rotating drum to which logs are fed continuously. Forces that separate wood and bark during drum debarking are friction and impacts to trees from other trees as they travel through the drum. Drum debarking can be done with dry or wet debarking depending on the amount of water used in the process. Half-wet debarking processes are also used when little water is needed and in these processes water is only added at the front of the drum. Dry drum debarking is used whenever possible.

There are two different types of drum debarking processes based on the length of logs used in debarking. In tumble debarking length of the logs is maximum of 0.7 times the diameter of the drum and move freely during debarking. In parallel debarking the logs are longer than the drum diameter and move lengthwise during debarking. In drum debarking logs form two layers in the drum. Logs in upper layer are exposed to more forces as they roll over other logs. In lower layer the logs do not move as much and therefore debarking happens in the upper layer. (Niiranen 1983, Seppälä et al. 2005)

Typical debarking drum is shown in Figure 3. Debarking drum has bark slots from which bark and water can fall through during debarking. These slots are usually around 40 – 45 mm in width and length is 500 – 600 mm. Larger slots often lead to increase in wood loss. The drum is also often equipped with metal bars, called log lifters, which raise and drop the logs as the drum rotates and therefor increase debarking performance. Log lifters are usually made from steel, rubber lining can be used to reduce wear of the lifters. Rotation of drum is provided by steel or rubber tires under the drum, hydrostatically where the drum rests on waterbed or by a roller system. Not all the bark is extracted through the holes in the drum, some of it flows out with the trees at the end of the drum. Under the debarking drum there is a bark conveyor which transports bark and other substances, that have fallen through the bark slots, into further separation. (Niiranen 1983, AEL 2011)

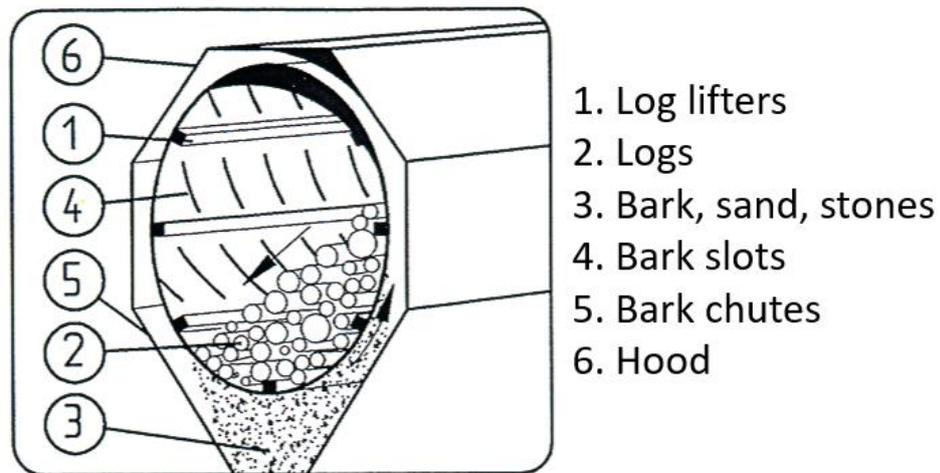


Figure 3 Schematic of typical debarking drum (AEL 2011, modified).

Many different variables affect the debarking performance in drum debarking. These are mostly the same as in other debarking processes, like wood species and dryness. Additionally, the parameters of the debarking drum have an effect. The dimensions and rotation speed of the drum as well as the residence time of the wood inside the drum are important. (Seppälä et al. 2005) Optimal rotation speed depends on the type of wood used, but usually it is around 4 – 7 rpm. Optimal filling degree for short logs is around 45 – 55 % and when debarking logs with random length optimal filling degree is 25 – 30 %. (AEL 2011)

In dry drum debarking no water is used or all the water is circulated within the process. Dry debarking drum system is shown in Figure 4. Water can be used before debarking drum to defreeze logs when necessary or after the drum to wash the logs. It is often necessary to use water in dry debarking to remove sand and stones from bark. There is no water added in the debarking drum, so debarking happens solely based on the moisture in the bark. Totally dry barking is not possible in Nordic countries due to the need of defreezing logs in winter. (Niiranen 1983)

Dry debarking drum has bark slots throughout the whole drum which provides maximum bark extraction in every part of the drum. Fallen bark is transported with conveyor to bark shredders. Bark shredders make bark pieces smaller to increase the efficiency of bark presses and available burning area. Dry content of bark must be above 35 % for it to be efficiently used as a fuel. Bark presses can achieve up to 50 % dry content of the bark. (Seppälä et al. 2005)

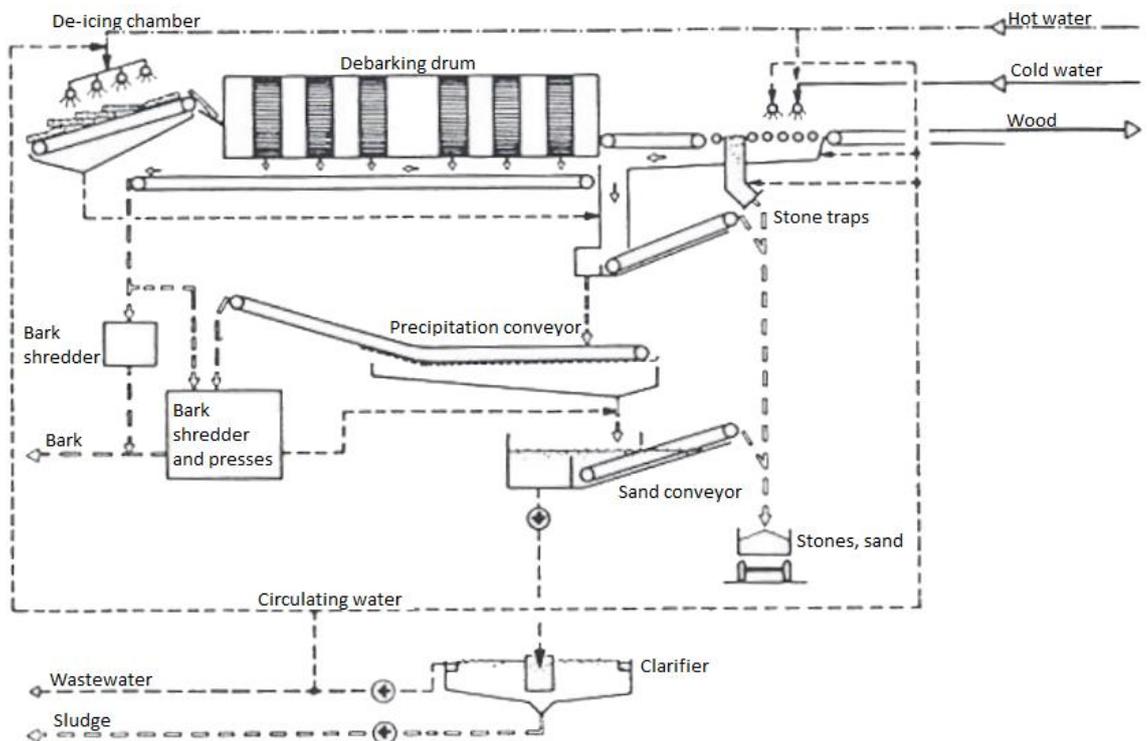


Figure 4 Schematic of dry debarking drum system (Niiranen 1983, modified).

In wet debarking amount of water used is significantly higher compared to dry debarking. Wet debarking drum has holes only at the end of drum to keep water inside during first part of debarking (Niiranen 1983). Water usage in wet debarking is discussed in Chapter 3.1.

2.4 Debarking in Anjala paper mill

In Anjala paper mill debarking is done with drum debarking. Typical load of the debarking process is 3 300 m³/d with potential capacity of 4 000 m³/d. In 2009 amount of wood debarked was 1 150 000 m³. Before debarking, wood is cut in two different cutting lines with widths of 4.5 m and 9 m. In these lines wood is cut to 1.5 m long logs.

Debarking is done in two debarking drums. Drum 1 has diameter of 3.9 m and it is 24 m long, capacity of the drum is 1 750 m³/d of wood. The drum is dry debarking drum, but it is used as wet debarking drum. Drum 2 has diameter of 5 m and is 26 m long with capacity of 3 750 m³/d of wood. Like drum 1, drum 2 is also a dry debarking drum which is used as wet debarking drum. The optimal filling degree of the drums is 40 – 50 % wood. After leaving debarking drum bark and other solids go through many separation steps such as precipitation. Separated bark goes through a bark shredder and then removed bark is dried to around 40 – 50 % dry content in two bark presses. Dried bark is used as a fuel in power plant located inside the mill grounds.

3 Debarking water

3.1 Use of water in debarking

Water is used in many parts of debarking process. In debarking, logs are defrosted with water and they can be additionally washed before and after the debarking to reduce the amount of unwanted substances like sand and metals advancing to further process sections. Water is also used to reduce dust, transport bark and other materials. Additional water can come to debarking from ice and snow attached to the logs during winter. (Niiranen 1983, Seppälä et al. 2005)

Debarking water consists of bark, water, sand and other solids which are separated from wood during debarking. Water and bark are separated from other substances in the debarking water. Schematic presenting process flows in wet debarking drum process is presented in Figure 5. When debarking water leaves debarking drum there is a primary bark precipitation conveyor which is usually a gutter with around 8 mm holes. Water and solids smaller than the holes are separated again with precipitation conveyor with smaller holes around 2 -3 mm wide (Niiranen 1983). Bark separated from the water is made finer with bark shredders and further dried in bark presses. Sand still present after two separations is removed from water with sand conveyer. Stones, too large to fall through bark slots, are separated after the debarking drum with larger holes in a conveyer in which logs are transported. Stones and sand are usually transported to a landfill. (AEL 2011, Seppälä et al. 2005)

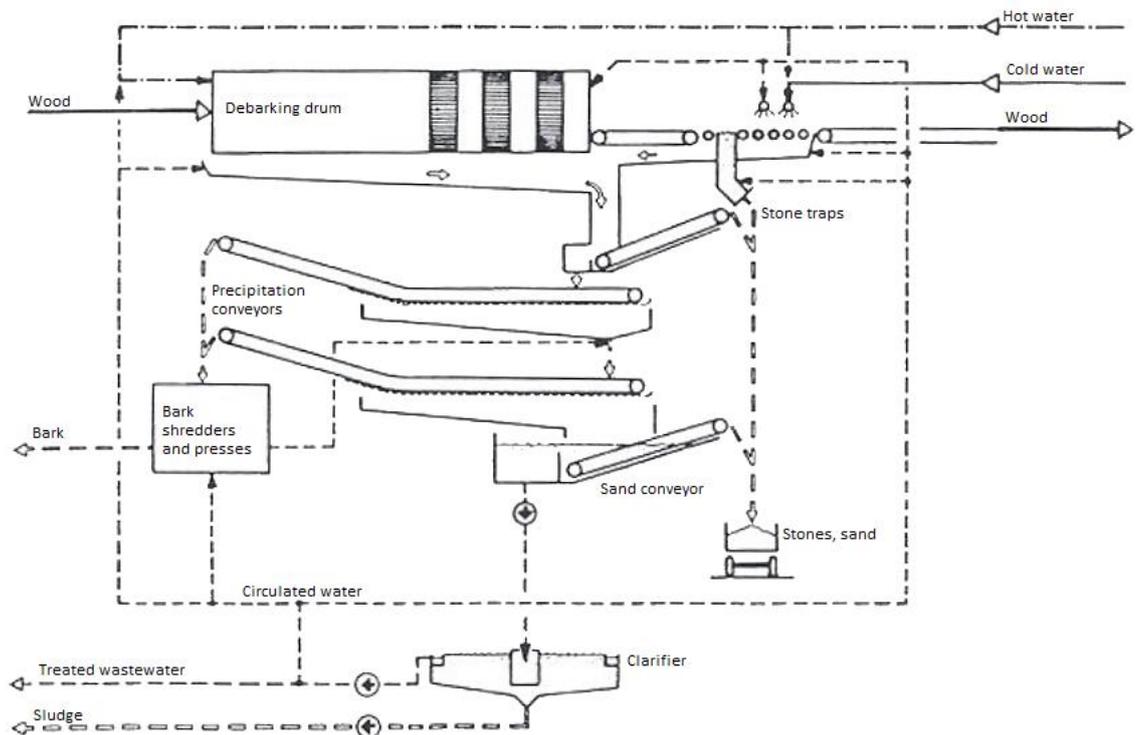


Figure 5 Schematic of a wet debarking drum system (Niiranen 1983, modified).

Due to the concentrated amounts of compounds in debarking water, it is mostly circulated back to the debarking process. Circulating water tanks are used to provide steady flow of water. In order to reduce load of debarking water to process equipment, the water is usually treated before going back to circulation. Treatment of debarking water is often done with mechanical separation or clarification. In clarification large clarifier is used to settle solids and other material from debarking water. Effluent of the clarifier is fed back to circulation and small portion is pumped to external wastewater treatment. Sludge produced during clarification is taken to sludge processing. Dry drum debarking produces around 0.5 ds/m^3 of wood and wet debarking produces $2 - 8 \text{ ds/m}^3$ of wood (Frantzen et al. 1997). Fully closed circulation is not feasible in all situations so clean water is added to the debarking process. Closing the water circulation is known to increase odor and slime formation on wet surfaces and decrease pH of the circulating water (Niiranen 1983).

3.2 Properties of debarking water

In debarking, many different substances extract from the bark into the water used. Debarking water has high amounts of dissolved and extracted wood compounds. Dark color of the debarking water comes mostly from excessive amount of tannins in the water. pH of typical debarking water is ~5 due to the wood extractives. Constant circulation of water used in debarking causes an increase of compound concentrations in debarking water. (Frantzen et al. 1997)

Wet debarking processes have much higher pollution loads than dry debarking processes. Increased amount of water used has direct correlation on how much compounds are extracted from the bark to the water used during debarking. (Frantzen et al. 1997) As Table V shows, BOD₇, COD and total phosphorus loads are more than two times greater in wet debarking compared to dry debarking.

Table V Pollution load of wet and dry wet debarking processes (Frantzen et al. 1997).

Debarking technique	Effluent, m ³ / m ³ wood	BOD ₇ , kg/ m ³ wood	COD, kg/ m ³ wood	P _{Tot} , g/ m ³ wood
Wet debarking	0.6 – 2	1 – 3	4 – 6	5 – 7
Dry debarking	0.1 – 0.5	0.1 – 0.5	0.2 – 2	2 – 4

Table VI shows the debarking pollution loads of some Finnish paper and pulp mills. Effluent flows are similar in all the mills, but the pollution loads differ significantly. Paper mills using spruce have COD_{CR} loads of up to 9 times higher than in pulp mill using pine and birch. Paper and pulp mill using combination of softwood and birch has BOD₇ load more than two times lower compared to paper mill using spruce. When comparing pollution loads based on the used wood, pulp mills have lower oxygen consuming pollution levels, but higher phosphorus loads.

Table VI Typical debarking effluent flows and pollution discharges for different paper and pulp mills in Finland in 1995 (Frantzen et al. 1997).

Plant type	Wood used	Effluent flow, m ³ /m ³ wood	COD _{Cr} , kg/m ³ wood	BOD ₇ , kg/m ³ wood	TSS, kg/m ³ wood	P, g/m ³ wood
Paper	Spruce	0.4 – 0.6	2.5 – 4.0	-	-	-
Paper	Spruce	0.54 – 0.68	1.23 – 5.48	0.58 – 2.6	0.31 – 0.79	-
Pulp	Pine, Birch	0.5 – 0.8	0.5 – 0.6	-	-	3 – 5
Paper and pulp	Softwood, Birch	0.2 – 0.6	-	0.2 – 0.5	-	1

Wastewater volumetric load of debarking process is small in whole mill scale, but as there are concentrated amount of pollutants in the water, the effect of debarking water is significant (Table VII). In paper mills, debarking water attributes to at least one fourth in most of the measured wastewater pollutants, COD_{MN} percentage being the highest in at roughly on third of the overall mill. In pulp mills, the oxygen demands from debarking water compared to the whole mill are significantly lower than in paper mills.

Table VII Contribution of debarking wastewater to the cumulative wastewater load of paper and pulp mills (Mattinen 1974).

Factory	Wastewater, %	BOD ₇ , %	N, %	P, %	COD _{MN} , %	SS, %
Paper	5.5	25	23	18	32	28
Pulp	3.1	4.7	20	22	5	16

COD values differ significantly based on the used wood, used process and the part of the debarking process where sampling is done. Table VIII shows different COD values of wet and half-wet debarking processes. COD of debarking press effluent can be as high as 80 000 mg/L (Saunamäki & Savolainen 1999).

Table VIII COD values of different wet and half-wet debarking process wastewaters, [1] Wirkkala 1984; [2] Virkola & Honkanen 1985; [3] Hakala 2014; [4] Saunamäki & Savolainen 1999.

Process	COD, mg/L
Wet debarking	4 111 ^[1]
	1 333 ^[1]
	1 034 ^[1]
	940 ^[2]
	1 825 ^[3]
Half-wet debarking	2 000 ^[1]
	889 ^[1]
	500 ^[2]
	4 000 – 7 000 ^[4]

Kylliäinen & Holmbom (2004) studied the composition of spruce bark water and spruce debarking waters analytically. Amount of components was determined with TOC and GC analyses. TOC of extracted bark water was 4 200 mg/L, debarking process water 1 930 mg/L and bark press water 16 100 mg/L. They were able to identify roughly 75 % of organic components in bark water and 50 % of organic components in process wastewaters.

Determined tannin type polyphenols amount was approximately 50 % of TOC in bark water and around 30 % in process waters. In general, reduced amounts of almost each component was found in debarking water, possibly because bark water came from finely crushed bark and bark in debarking water was in larger chunks. Only resin acids were found considerably more in debarking water. (Kylliäinen & Holmbom 2004) Detailed concentrations of different components are presented in Table IX.

Table IX Concentrations of components in water from crushed spruce bark, industrial spruce log debarking process and industrial bark press. Total calculated TOCs were 4 200 mg/L for spruce bark water, 1 930 mg/L for debarking water and 16 100 for bark press water. (Kylliäinen & Holmbom 2004).

	Spruce bark water		Debarking water		Bark press water	
	Amount, mg/L	Calc. TOC, mg/L	Amount, mg/L	Calc. TOC, mg/L	Amount, mg/L	Calc. TOC, mg/L
Fructose	504	200	255	100	1 007	400
Glucose	623	270	189	85	1 978	870
Sucrose	394	160	414	170	2 250	990
Oligosaccharides	421	170	233	90	1 349	540
Polysaccharides	280	110	-	-	-	-
Isoharpentin- and astringinglucoside	2 140	1 280	460	280	4 405	2 640
Catechin	42	26	7.2	5	74	45
Isorhapontigenin, Astringenin	11	8	11.8	5	56	20
Resin acids	1.7	1.3	10.6	8	52	40
Polyphenols	-	920	-	240	-	2 470
Total		3 150		980		8 020

Seasonal variances of debarking water concentrations are high. As mentioned in the Chapter 2.2, in winter trees used in debarking are frozen which makes debarking more difficult. Hot water is used to defreeze the logs. Using hot water causes more compounds to extract from the wood to the process water. This increases the concentration of pollutants flowing to wastewater treatment. Figure 6 shows amounts of different pollutants from debarking plants during summer and winter. In paper mill COD of the debarking water was more than two times higher in winter compared to summer. (Saunamäki & Savolainen 1999)

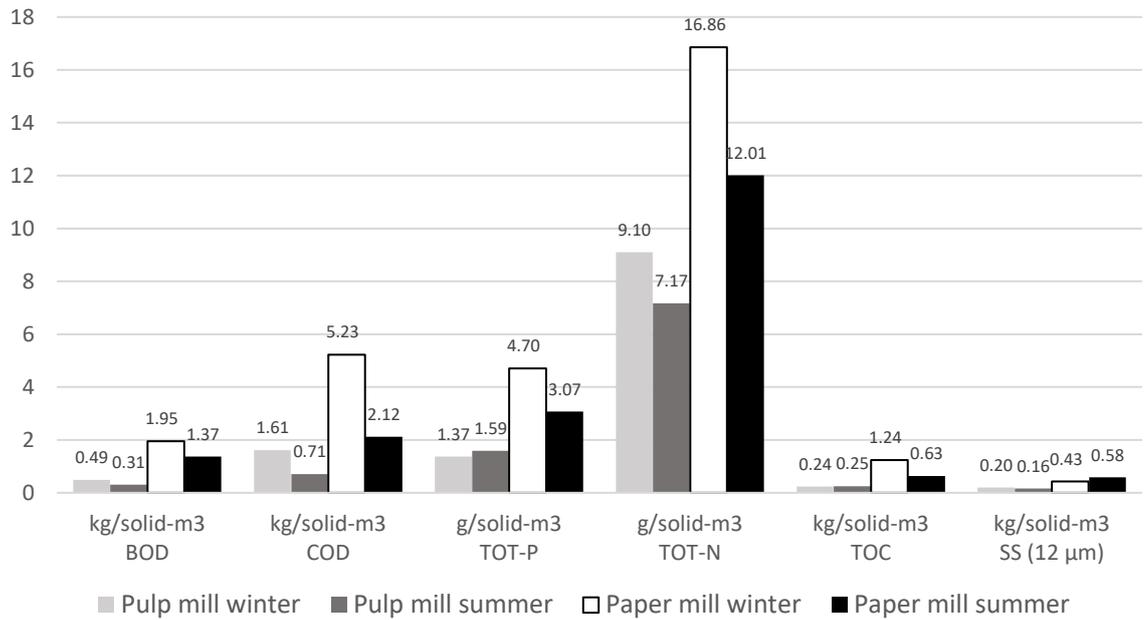


Figure 6 Seasonal variation of different pollutant discharges from paper and pulp mill debarking plants in Finland (Saunamäki & Savolainen 1999, modified).

3.3 Toxic compounds in debarking water

Toxicity is usually presented as lethal concentration, 50 % -value (LC_{50}). This means the minimum concentration of a substance that will kill 50 % of tested organisms with given exposure time. Other value used is EC_{50} which means that used substance concentration has an effect on half of the test subjects. Usually the concentration unit used is mg/L and the exposure time is 24, 48 or 96 hours. (Ali & Sreekrishnan 2001) In bacteria, same indication can be used, and it is called inhibition concentration IC_{50} , which indicates the concentration where 50 % inhibition is observed in the bacteria (Field et al. 1988).

There are many toxic compounds in paper and pulp mill wastewaters that are harmful not only for the environment but also for biological wastewater treatment methods. Paper and pulp mill effluents are known to cause mutagenic and genotoxic effects. (Ali & Sreekrishnan 2001) Debarking wastewaters are significantly more toxic than other effluents in paper and pulp mill, they can attribute more than 50 % of paper and pulp mills total wastewater toxicity. (Savolainen 1992) Study by Nikunen (1983) analysed the toxicity of different paper and pulp mill effluents. LC_{50} 96 h toxicity for rainbow trout in debarking wastewater was found to be 2.0 vol-% for bleached kraft pulp mill and 1.3 vol-% for mechanical softwood mill. For same mills, the total effluent LC_{50} 96 h toxicity was 15 vol-% and 9.0 vol-%. Different wood extractives are the probable main cause of toxicity in paper and pulp mill wastewaters (Ali & Sreekrishnan 2001). Most common toxic extractives are resin and fatty acids, phenolic substances and terpenes. (Ekman & Holmbom 1989) Debarking effluents have high concentration of resin and fatty acids. Debarking water from Finnish paper mill studied by Saunamäki & Savolainen (1999) had 110 mg/L resin acid and 125 mg/L fatty acid concentrations.

The toxicity of various wood extractives found in debarking water to different organisms and biological water treatment is discussed in the next chapters.

3.3.1 Tannins

Tannins are polyphenolic compounds which can be divided into condensed tannins and hydrolysable tannins. Typical molar mass of tannin is 500 – 3 000 g/mol. In trees tannins are found in the bark and they are classified as wood extractives. COD of debarking water can consist up to 50 % of tannins. (Field et al. 1988) Monomeric tannins have limited

ability to form hydrogen bonds to proteins due to their phenyl groups and as they polymerize their bonding ability increases. Oligomeric tannins can form multiple hydrogen bonds with proteins. Toxicity of tannins is related to their ability to form hydrogen bonds with proteins and in so their degree of polymerization (Field et al. 1988). Research has shown that tannins inhibit enzymes and bacteria due to the hydrogen-bonding reactions and the ability of penetrating bacteria due to their low molecular weight (Tamir & Alumot 1969), and they have methanogenic toxicity when they are present in paper mill wastewaters (Field et al. 1988). The basis of tannin size affecting its properties and effects of tannins is known as tannin theory. Concept of the tannin theory is shown in Figure 7. Even though higher molecular weight tannins can form multiple hydrogen bonds, they are not toxic to bacteria because they cannot penetrate the bacterial barrier and bond with bacterial proteins. (Field et al. 1989)

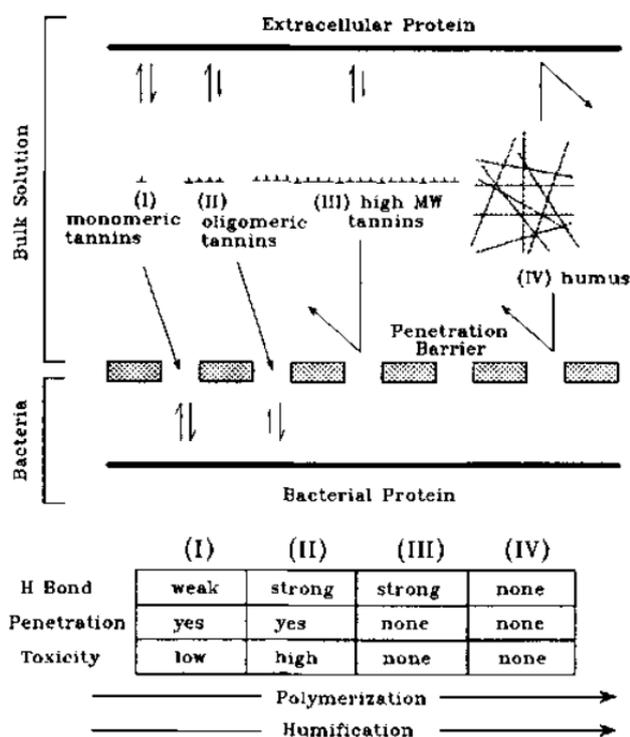


Figure 7 Concept of tannin theory (Field et al. 1989).

Temmink et al. (1989) showed with carps that tannins from Norway spruce bark are toxic to aquatic organisms. LC₅₀ concentrations of Norway spruce bark extract for *Cyprinus carpio L.* was found to be 65 mg/L COD for 24 h exposure and 50 mg/L COD for 96 h

exposure. Inhibition effects of bark water for methanogenic bacteria is mainly based on tannins. Field et al. (1988) studied methanogenic toxicity of tannins from bark and discovered that IC_{50} value of tannins was 410 mg/L for pine, 510 g/l for spruce and 845 mg/L for birch. In the same study resin acids only achieved 15 % inhibition.

Phenolic compounds have inhibiting effect on activated sludge systems at 50 – 200 mg/L concentrations and they also inhibit nitrification at 4 – 10 mg/L concentrations (EPA 2004) Du et al. (2019) studied the effect of phenol addition to relative oxygen uptake rate (ROUR) of activated sludge microbes. Relative oxygen uptake rate describes the metabolic activities of activated sludge. They found that adding only 10 mg/L phenol to the activated sludge reduced the ROUR around 50 %. Phenols also affect the COD removal of activated sludge systems. Elbarki et al. (2006) added 100 mg/L phenol to activated sludge system and COD removal was around 75 %. When phenol concentration was increased to 300 mg/L, the COD removal efficiency decreased to around 60 %. In the same study increase in phenol concentration also reduced the maximum specific growth rate of heterotrophs in the biomass from 3.20 L/d at 0 mg/L phenols to 1.21 L/d at 300 mg/L phenols.

3.3.2 Resin acids

Resin acids are weak hydrophobic acids. Resin acids are believed to be one of the main reasons for toxicity of wastewater in softwood pulping wastewaters (Peng & Roberts 2000). When resin acids and unsaturated fatty acids are present in a solution, chronic toxicity occurs to aqueous organisms at 20 μ g/L concentration (Oikari et al. 1983). Most common resin acids in paper and pulp mill effluents are dehydroabietic acid (DHAA), isoprimeric acid and abietic acid. Structures for these and other common resin acids found in wood bark are shown in Figure 8. (Peng & Roberts 2000)

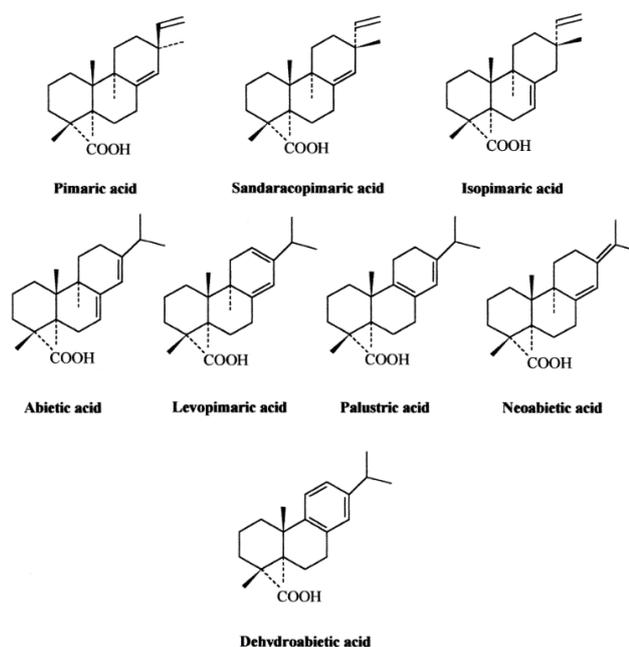


Figure 8 Chemical structures of common resin acids (Peng & Roberts 2000).

Different resin acids are found in high concentrations in pulp mill, which use softwood, debarking effluents. Table X shows that there can be up to 86 mg/L of resin acids in debarking wastewater. Isopimaric, DHAA and abietic are the most common resin acids found.

Table X Concentrations of different resin acids found in debarking effluents of 10 Canadian pulp mills using softwood (Leach & Thakore 1978)

Resin acid	Concentration, mg/L
Dehydroabietic	3.4 – 22.9
Abietic	2.0 – 22.1
Primaric	0.8 – 7.6
Isopimaric	2.4 – 33.4
Total	8.6 - 86

Peng & Roberts (2000) studied the solubility and toxicity of different resin acids. Using data from literature on the toxicity of resin acids to rainbow trout (*Salmo gairdneri*) and own experiments with *Daphnia magna*, they found a correlation between the solubility and toxicity of resin acids. Acute lethal concentrations of different resin acids to rainbow trout are between 0.4 and 1.1 mg/L and to *D. magna* 0.26 – 1.89 mg/L (Figure 9). Figure 10

presents the correlation between resin acid solubility and lethal concentration. More soluble abietic type resin acids are also least toxic. Inversed correlation is seen in other resin acids, most toxic pimaric type resin acids are also the least soluble.

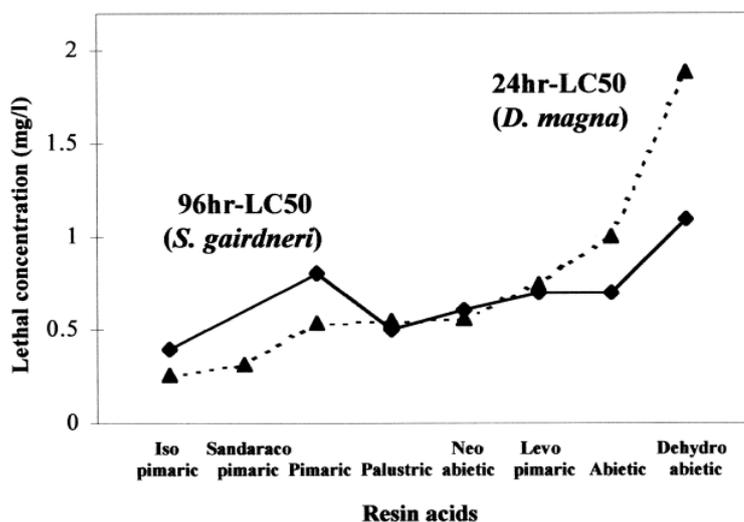


Figure 9 Lethal concentrations of different resin acids to rainbow trout (*S. gairdneri*) and *D. magna* (Peng & Roberts 2000).

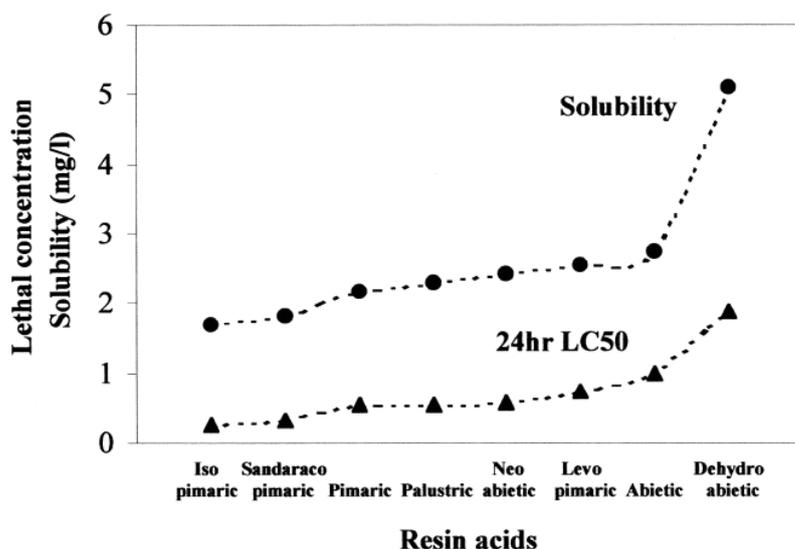


Figure 10 Solubility and lethal concentration to *D. magna* of different resin acids (Peng & Roberts 2000).

Abietic resin acids are known to transform anaerobically to retene (7-isopropyl-1-methylphenanthrene), which is toxic to aqueous organisms. Although DHAA has high

solubility and in so low toxicity, it can easily reduce to retene. In activated sludge systems, there can be anaerobic zones where anaerobic bacteria can transform resin acids to retene. (Mohn et al. 1999) In natural waters retene can be found in sediments downstream of paper and pulp mills. Transformation reaction rate is slow in lower temperatures in the sediments, which means accumulated resin acids continue to transform to retene for extended period after initial exposure (Leppänen & Oikari 1999). Retene is known to cause teratogenicity in fish larvae, which means that it can disturb the development of an embryo. (Oikari et al. 2002) Neobatic acid has different kind of toxicity as it is the only resin acid that is mutagenic to bacteria (Nestmann et al. 1980).

The toxicity of resin acids is dependable on the pH of the solution. Zanella (1983) studied the effect of pH on the toxicity of DHAA on *Daphnia magna* and Fathead minnow. Toxicities were measured in pH 6.5 – 10.0. With *D. magna*, the LC₅₀ value increased from lowest to highest pH by 31 times and with Fathead minnow the toxicity increased by 30 times from pH 6.5 to 9.0. This means that toxicity of resin acids has inverse correlation with pH, increasing pH decreases toxicity. (Zanella 1983) LC₅₀ values are shown in Table XI.

Table XI Effect of pH to the LC₅₀ toxicity of DHAA on *Daphnia magna* and Fathead minnow (Zanella 1983).

	pH 6.5	pH 7.0	pH 7.5	pH 8.0	pH 8.5	pH 9.0	pH 10.0
	mean LC ₅₀ , mg/L						
<i>Daphnia magna</i>	2.47	6.35	10.8	21.7	-	38.3	76.9
Fathead minnow	1.5	3.2	-	9.9	-	45.5	-

During normal mill operations there can be sudden increased pollution load, called shock load, that is released to the wastewater treatment system. Shock loads containing large amounts of resin acids can inhibit the resin acid removal efficiency of activated sludge system (Werker & Hall 1999, Werker & Hall 2000). Cumulation of resin acids onto biomass can increase the total toxicity of activated sludge system effluent (Makris & Banerjee 2001).

3.3.3 Other compounds

Long chain fatty acids inhibit gram-positive microorganisms, but not gram-negative microorganisms. Gram-negative organisms have more complex cell wall, which LCFAs cannot penetrate. (Kabara et al. 1977) Like tannins, long chain fatty acids are known to inhibit methanogenic bacteria. Inhibition happens when LCFA encapsulate biomass in the sludge and that blocks substrate and product transport in and from the biomass. (Pereira et al. 2005) Fatty acids are also thought to be toxic to activated sludge system (Hynninen 2008).

There are phytosterols (plant sterols) present in paper and pulp mill wastewaters. Phytosterols can transform inside aquatic organisms to estrogens or androgens and disrupt biochemical or hormonal systems. Lehtinen et al. (1999) discovered that exposing brown trout to 10 and 20 µg/L phytosterols leads to increased mortality of their eggs and affected their maturation harmfully. Same kind of relation of phytosterols affecting offspring of fishes was discovered in viviparous blenny, where fishes were exposed to 10 – 30 µg/L concentrations of phytosterols (Mattsson et al. 2001). Phytosterols are also known to biotransform by bacteria in biological wastewater treatment rather than degrade (Tana & Lehtinen 1996). Biotransformation can lead to androgenic effects in phytosterol β-sitosterol found in paper mill wastewaters (Stahlschmidt-Allner et al. 1997).

Lignin has also been noted to be one possible compound which can cause toxicity in paper and pulp wastewaters. Pessala et al. (2004) discovered that lignin in kraft pulp mill effluent has EC₅₀ values of 34 mg/L in reverse electron transport (RET) test, which measures the inhibition of substance on enzymes. The effluent was also highly toxic to *D. magna* and *V. fischeri*. Lignin concentration correlated highly with the toxicity of the whole effluent.

3.4 Anjala paper mill debarking water

Debarking in Anjala paper mill is wet debarking. The water flow and process equipment, other than using dry debarking drum, are similar to wet debarking schematic presented in Chapter 3.1. Raw water is used in debarking drum, in bark presses and washing logs before and after debarking. Circulating water is used in other parts of the process such as forming water flow in stone traps and to transport bark and other materials in the process. There is a 90 m³ circulating water tank where all the water in debarking flow. All other process waters except bark press waters are directed to circulation tank. Flow to the circulating water tank is after secondary precipitation conveyor which means that also solids flow to the tank. At the bottom of the circulating water tank there is a sand conveyor which removes sand and other fine solids from circulating water.

Circulating water from debarking is pumped to 1 720 m³ clarifier. At January 2020 flow to debarking clarifier was around 3 974 m³/d or 46 l/s. As previously mentioned, fully closed circulation is not feasible, so small amount of effluent from the clarifier is lead to external wastewater treatment. Effluent flow from the clarifier to wastewater treatment is set to 519 m³/d or 6 l/s. Rest of the effluent flow goes back to debarking and it goes through grinding plant where its pH is adjusted with NaOH from around 5.3 to optimal 6.2 – 6.3. Properties of the circulating water used are not extensively monitored. Before clarification there are high amounts of suspended solids. Suspended solids are effectively removed in the clarifier. COD of circulating water from clarifier is around 5 000 – 20 000 mg/L depending on the time of the year. Effect of seasonal changes on the COD concentration of debarking water is shown in Figure 11. In summer COD values are around 5 000 – 12 000 mg/L, but in the winter it stays above 12 000 mg/L when heated water is used in debarking.

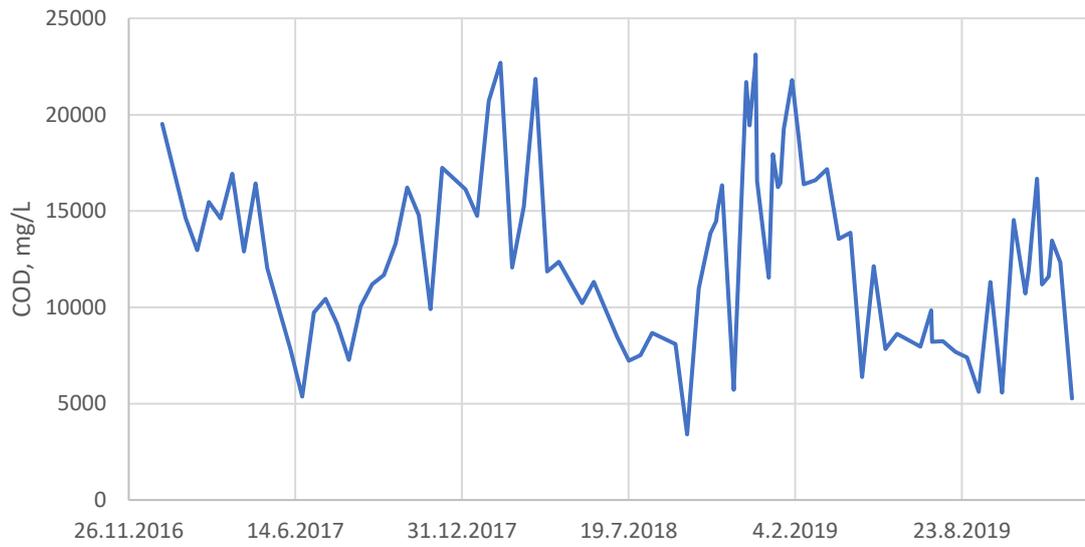


Figure 11 COD concentration levels of debarking water in Anjala paper mill during a two-year period.

3.5 Treatment processes for pulp and paper mill wastewaters

3.5.1 Aerobic treatment

Junna et al. (1982) studied the performance of activated sludge treatment on the removal of pollutants found on debarking and kraft pulp bleaching effluents. Before aeration basin the effluents were mixed, neutralized, and nutrients were added. Activated sludge treatment was able to remove total of 79 % of all resin acids in the effluents, most common resin acid DHAA was also removed with best efficiency. Detailed reduction efficiencies are shown in Table XII. Reduction of fatty acids and sterols was lower in the treatment with 53 % reduction of fatty acids and 54 % reduction of sterols. The activated sludge treatment process also reduced the Acute toxicity LC_{50} 96 h to trout by 70 %. Adding aluminium sulphate in the treatment process to reduce color in the effluent caused the sludge settling to reduce which in turn reduced the performance of the treatment. (Junna et al. 1982)

Table XII Average resin acid concentrations before activated sludge treatment and their reduction in the treatment (Junna et al. 1982).

	Average concentration, mg/L	Reduction, %
Dehydroabietic	1.24	81
Abietic	0.49	75
Neoabietic	0.25	74
Palustric	0.13	63
Pimaric	0.28	72
Isopimaric	0.30	77
Other	0.15	-
Total	2.84	79

Saunamäki & Savolainen (1999) treated debarking water from paper mill and plywood mill. Debarking waters had COD of 4 000 – 7 000 mg/L and high toxicity, around 3 % LC_{50} to *D.magnia*. Figure 12 shows the BOD and COD removal efficiencies of laboratory scale activated sludge method for paper mill and pulp mill debarking waters and full scale activated sludge method for plywood mill debarking water. Almost 100 % BOD removal

and up to 85 % COD removal was achieved with low sludge load. BOD and COD removal efficiencies decreased as the sludge BOD load increased.

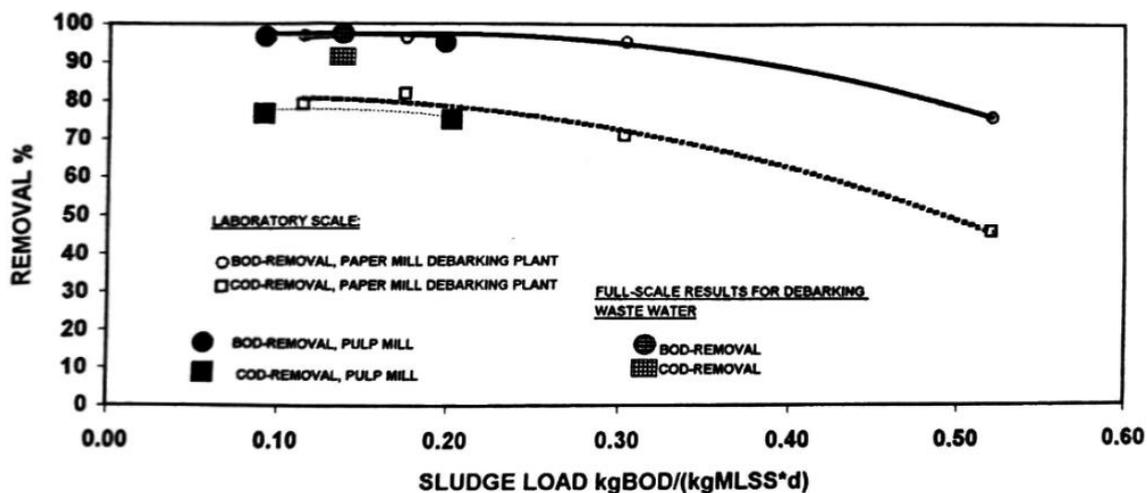


Figure 12 BOD and COD removal percentages from debarking water from paper mill, pulp mill and plywood mill by activated sludge system and the effect of BOD sludge load on the removal percentages (Saunamäki & Savolainen 1999).

Kostamo & Kukkonen (2003) also studied the removal of resin acids and sterols in activated sludge treatment. The treatment was able to remove 94 % of resin acids and 41 % of sterols from total effluent of elemental chlorine free (ECF) pulp mill. In the study there was sampling points in different parts of the treatment system, also sampling was done before and after debarking water was introduced to the effluent. It was noticed that concentrations of resin acids and sterols of the total effluent increased after the debarking water addition. Toxicity increased as well after the addition of debarking water, which directly correlates that debarking waters are highly toxic (Savolainen 1992). Method of reduction for resin acids and sterols was additionally studied. 93 % of resin acids were degraded or transformed during the treatment and 4 % was removed with sludge. Sterols degraded and transformed in lesser quantities (55 %) than resin acids, removal with the sludge was greater at 43 %.

Another study on the fate of lipophilic extractives on aerobic wastewater treatment system found that total reduction of 82 % was achieved with two MBBRs and activated sludge process (Pärttö 2009). MBBRs are able to reduce around 40 % of the lipophilic extractives, mainly triglycerides and steryl esters, and final reduction happens in the activated sludge.

Sterols are the only lipophilic extractives that were reduced fully in the treatment, most of the extractives found on the effluent of the treatment are triglycerides and fatty acids. For COD reductions, MBBRs were able to reduce 48 % of COD and the total COD reduction of the whole treatment was 87 %.

There are conflicting reports on how shock loads of resin acids affect the activated sludge system. According to Werker & Hall (1999) the accumulation of resin acids can have long lasting effects on the metabolic activity of the biomass due to long lag time. However, Saunamäki & Savolainen (1999) reported that activated sludge method was able to recover quickly from a shock load caused by bark press filtrate with high amounts of organic compounds and toxicity. Excess amounts of resin acids are reported to be harmful for activated sludge systems (Makris & Banerjee 2002, Ledakowicz 2006) Biomass in activated sludge is system specific and build upon existing effluent concentrations. This means that how activated sludge system reacts to different pollutants is very subjective.

3.5.2 Anaerobic treatment

Anaerobic treatment is a good option for the treatment of paper and pulp mill wastewaters. Anaerobic treatment has its advantages compared to aerobic treatment, as it requires less energy, it generates energy and it is applicable to higher amounts of organic loads. However, debarking waters have shown strong toxicity to methanogenic bacteria. Especially resin acids and tannins are the main inhibitors and make the usage of anaerobic treatment not suitable for concentrated debarking waters without proper pretreatment. (Field et al. 1988) Studies have shown that polymerizing phenolic compounds in debarking water with phenol oxidases and flocculation (Savolainen 1992) or oxidation (Field et al. 1990) can reduce methanogenic toxicity of debarking water to anaerobic bacteria.

Savolainen (1992) added an enzymatic pretreatment to anaerobic treatment of debarking waters. Used debarking waters were from debarking process waters and bark press wastewaters with COD_{CR} of 5 500 – 11 500 mg/L. Laccase was used as a catalyst to oxidative polymerization and aluminium sulphate and waste fiber as flocculants. 3 h of laccase treatment and flocculation was able to remove 43 % of COD_{CR} and 39 % of BOD₇ from the bark press water with 11 200 mg/L COD_{CR}. The treatment also completely

removed toxicity of bark press water. Using the laccase and flocculation pretreatment with spruce debarking water with 11 500 mg/L COD_{CR} reduction of COD_{CR} and BOD₇ were only 23 % and 15 %, but the treatment removed 75 % phenolic compounds and color and removed all toxicity of the water.

Table XIII shows how the decrease of chemical oxygen demand in debarking water increases the removal efficiency of anaerobic treatment with laccase and flocculation pretreatment. Reducing the COD_{CR} of debarking waters enhances the reduction of both COD_{CR} and BOD₇ in anaerobic treatment, COD_{CR} reduction is greater than BOD₇ reduction. With lower initial chemical oxygen demand, methane gas production is increased. (Savolainen 1992)

Table XIII Reduction of COD_{CR} and BOD₇ in debarking waters after laccase + flocculation and anaerobic treatment (Savolainen 1992)

COD _{CR} , mg/L	Reduction of COD _{CR} , %	Reduction of BOD ₇ , %
10 500	50	82
5 500	72	85

Zender et al. (1994) studied the effect of aerated lagoon treatment system with aerobic and anaerobic phases to resin acids found on effluents of bleached kraft pulp and paper mill. Aerated lagoon system was able to remove 96 % of resin acids from effluents. They also discovered that 40 % of resin acids in the outlet of the treatment system were transformed resin acids such as hydrogenated or hydroxylated resin acids. In aerobic phase of treatment system, the removal rate was highest for DHAA and lowest for isoprimary acid. The removal rate sequence is similar to solubility sequence of resin acids presented by Peng & Roberts (2000).

3.5.3 Oxidation processes

El-din et al. (2006) oxidized abietic acid and linoleic acid with ozone to see the effect of oxidation to the toxicity of resin and fatty acids. Abietic and linoleic acids were oxidized with different amounts of ozone to determine oxidized percentage of the acids. Increase of pH and temperature increased the oxidation rate of the acids and in so affected the

toxicity. Oxidation of abietic acid increases the toxicity (Figure 13). Before 40 % oxidized abietic acids, the toxicity increases rapidly and after that it slightly begins to lower, however staying at increased toxicity after full oxidization. Inverse reaction can be seen with linoleic acid, where toxicity decreases slowly until around 55 % oxidization and then the decrease rate increases. Overall oxidation decreases the toxicity of linoleic acid. (El-din et al. 2006) These results are for almost pure compounds and their relation to actual debarking waters cannot be accurately compared, but they give indication to what happens to resin and fatty acids during oxidation.

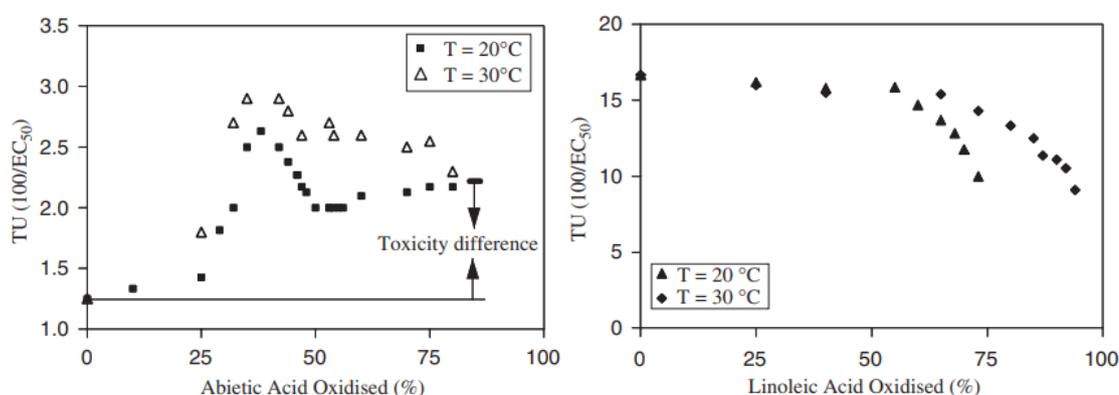


Figure 13 Effect of oxidized amount of abietic and linoleic acids on their toxicity at pH 11 and temperatures 20 °C and 30 °C (El-din et al. 2006).

Tanskanen et al. (1997) studied the effect of ozone and ozone/hydrogen peroxide on the toxicity of debarking waters. Debarking waters used in the experiments were highly concentrated with BOD 6 400 mg/L and COD_{CR} 15 000 mg/L and EC₅₀ < 5 % for *D.magna*. Ozone alone didn't remove any BOD and removed maximum of 15 % of COD_{CR}. Combination of ozone and H₂O₂ was able to reduce maximum of 5 % of BOD and no reduction of COD_{CR}. Both AOP methods didn't affect the toxicity of the debarking water. Low reduction percentages can be described because these processes just reduce the size of organic compounds. (Tanskanen et al. 1997)

Ozone was used in oxidation of debarking waters in another study by Korhonen & Tuhkanen (2000). COD of the debarking water used was 10 000 mg/L and it included 67 mg/L of resin acids. 90 % of resin acids removal required 0.2 mg_{O3}/mg_{COD} ozone dosage,

which equals to 2 000 mg/L of ozone for the debarking water. COD reduction in the ozone treatment was around 30 %. (Korhonen & Tuhkanen 2000)

Roy-Arcand & Archibald (1996) removed resin and fatty acids with ozone from mechanical pulp mill effluent. Used process effluent was the total effluent of the mill with COD of 1 300 mg/L and BOD₅ of 350 mg/L. Ozone removed resin and fatty acids selectively resulting that only 1 – 5 % of required ozone load to oxidize COD completely was necessary for the removal of high amounts of resin and fatty acids. At 100 mg/L ozone charge, the process was able to remove 50 – 90 % of resin acids, with highest removal of levoprimary and palustric acids and lowest dehydroabietic. With fatty acids the highest removal achieved was 80 % for linoleic acid and lowest 20 % for stearic acid. COD removal was at the highest 20 %. (Roy-Arcand & Archibald 1996) Removal efficiencies of different ozone charges are shown in Figure 14.

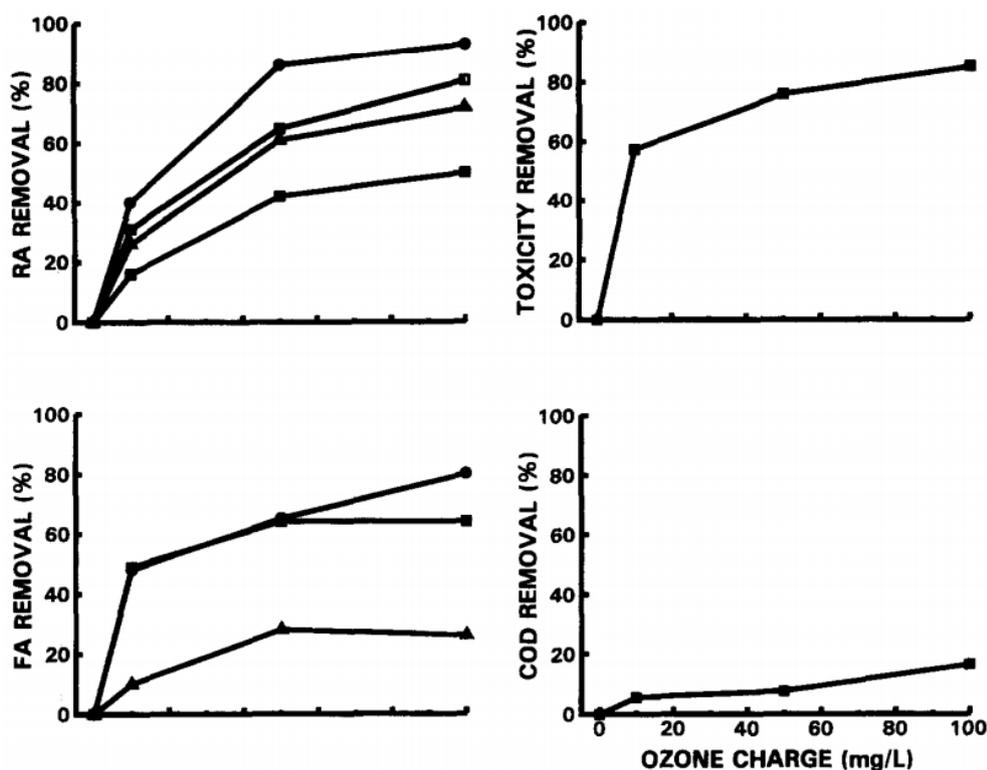


Figure 14 Effect of used ozone concentration to the removal of resin and fatty acids, toxicity and COD of mechanical pulp mill total effluent. Resin acids; □: abietic, ■: dehydroabietic, ▲: pimaric, sandaracopimaric and isopimaric, ●: levoprimary and palustric. Fatty acids; ■: oleic, ▲: stearic, ●: linoleic. (Roy-Arcand & Archibald 1996).

Toxicity of the total effluent was reduced efficiently by the ozone treatment. At 50 °C and pH 7.7 toxicity was reduced by 88 %. The removal of resin and fatty acids and the removal of toxicity showed high correlation of 0.92, but further analyses indicated that the toxicity of the effluent didn't come only from resin and fatty acids. (Roy-Arcand & Archibald 1996) These results are directly conflicting with the results of El-din et al. (2006) where oxidizing abietic acid raised its toxicity. One possible explanation why the total toxicity of the effluent in experiments by Roy-Arcand & Archibald (1996) decreases might be on the composition of resin to fatty acid ratio.

Amat et al. (2005) found that the efficiency of the degradation of COD by ozone is highly dependent on the ratio of fatty acids to phenols. Ozone reacts more easily with phenols than fatty acids, which leads to lower degradation in effluents with high fatty acids/phenols -ratio. It was also found that low oxidation increased the biodegradability of effluent whereas high amount of COD decrease or oxidation, lead to decrease in biodegradability (Amat et al. 2005)

Ledakowicz et al. (2006) used aqueous solutions of different resin acids to study their removal with ozone. Various concentrations of resin acids were added to the solutions to see the effect of concentration to the efficiency of ozone treatment. Maximum COD reduction of 35 % was achieved with solutions where the resin acids concentrations were lowest, in a solution of only resin acids, the COD reduction was only 3.7 %. Required ozone dose for the reduction of 90 % resin acids was determined to be 0.1 – 0.7 mg_{O₃}/mg_{COD} depending on the concentration of resin acids. It was also noted that DHAA was the hardest resin acids to be degraded with ozone. Ledakowicz et al. (2006) studied additionally the combination of ozone and UV. With the addition of UV, irritation the reduction of resin acids increased to 100 %. At the same time usage of UV increases the consumption of required ozone. Required ozone for reducing more than 90 % of resin acids was more than 10-times more with O₃+UV than with only O₃ (1.74 mg_{O₃}/mg_{COD} vs. 0.1 mg_{O₃}/mg_{COD}). Ozone consumption in combined process can be reduced effectively with the increase of temperature. (Ledakowicz et al. 2006)

Ahmed et al. (2009) used UV with combination of H₂O₂ to degrade various pollutants from paper and pulp mill effluents. Studied effluents had TOC of 270 – 2 680 mg/L. UV

+ H₂O₂ was able to remove >90 % of COD from the effluent with lowest TOC and only 25 % from highest TOC effluent after 300 minutes. The increase of initial TOC of tested effluents didn't have significant results on the reduction of color, which was due to lignin derivatives and tannins.

Wet oxidation is usually used to treat black liquor of paper and pulp mills. It has shown to be effective method at reducing high amounts of COD from the wastewaters and it is suitable for toxic effluents. (Mishra et al. 1995) However traditional wet oxidation does not oxidize all the pollutants completely. Catalysts can be used in the process to improve the oxidation efficiency. Dhakhwa et al. (2012) used traditional and catalytic wet oxidation with coagulation to treat pulp mill effluent with 5 120 mg/L COD. Traditional process without coagulation was able to remove 32 % of COD and addition of catalyst increased the removal efficiency to 51 %. Combining catalytic wet oxidation with coagulation improved the COD reduction to 77.5 % and the treatment was able to remove 87 % of color. Anang (2011) used catalytic wet oxidation to treat paper mill debarking waters. Used debarking waters had COD concentrations of 1 000 – 3 000 mg/L. Catalyst used was 1 % Pt on activated carbon. Highest COD reduction of 74 % was achieved with 3 000 mg/L COD debarking water at 180 °C and 10 bar. At these process conditions, TOC removal was 54 %, lignin/tannin content 97 % and color 90 %. It was concluded that removal of lignin/tannin was the main cause of color in the debarking water. (Anang 2011)

3.5.4 Membrane processes

Ultrafiltration of wood extractives has been studied. Puro et al. (2011) used regenerated cellulose (RC) and polyethersulphone (PES) membranes in filtrating paper and pulp mill, using softwood and hardwood, effluents. TC of these effluents was 3 800 – 8 900 mg/L. Wood extractives were greatly reduced in the filtration, despite their molar mass being significantly under the cut off value of the membranes. Used membranes were able to remove >97 % of resin and fatty acids, >90 % of sterols and 40 – 90 % of lignans from the softwood effluents. Resin acids contributed mostly on the fouling of the membranes in the experiments. On another study with the same membranes, TC retention was 73 – 92 % (Puro et al. 2010).

Elefsiniotis et al. (1997) also used ultrafiltration to filtrate simulated paper and pulp mill effluent with 3020 – 4170 mg/L COD. Used membranes had MWCO of 10 kDa and 100 kDa. Overall removal efficiency COD and TOC was greater with smaller MWCO membrane (37 % vs 21 % and 33 % vs 16 %), but the removal of resin and fatty acids was lower (55 % vs 69 %). In both membranes resin acids removal was more than two times lower than fatty acids removal.

Tanskanen et al. (1997) used ultrafiltration to study its effect on acute toxicity of debarking water. Used debarking water had 3 200 mg/L BOD and 10 300 mg/L COD_{CR} with LC₅₀ of <5 % for *D.magna*. Ultrafiltration was able to reduce BOD by 12 % and COD_{CR} by 33 %. Toxicity of the debarking waters reduced to >10 % LC₅₀. Ultrafiltration was also used on debarking water by Hakala (2014). Studied debarking water had COD of 1 585 mg/L and MWCO of membranes studied were 1 000 – 30 000 Da. COD retention with ultrafiltration membranes used was around 50 % and TC reduction around 20 %. In the same study nanofiltration was used to treat the same debarking water. Used nanofiltration membrane had MWCO of 300 – 400 Da. Nanofiltration worked efficiently with more than 80 % removal of COD and TC. (Hakala, 2014)

3.5.5 Other processes

Lipophilic extractives can be adsorbed from the debarking water. Leiviskä et al. (2012) adsorbed lipophilic extractives from debarking plant wastewater with Finnish kaolin and talc. Kaolin was able to remove up to 42 % of lipophilic extractives and talc removed 46 %. Residual lipophilic extractives after the adsorption consisted mostly of triglycerides and resin acids. Adsorption did not remove other wood extractives. They also studied coagulation-flocculation with chitosan and kaolin. Chitosan alone was able remove 85 – 89 % of lipophilic extractives. Kaolin addition improved settling velocity and raised the removal efficiency to 87 – 91 %. Remaining lipophilic extractives after coagulation with chitosan and kaolin were almost completely fatty acids and oxidized resin acids. (Leiviskä et al. 2012)

Coagulation with cationic polyelectrolytes has been studied in removal of wood extractives from chemical pulp bleaching filtrate. Leiviskä & Rämö (2008) were able to remove 92 % of wood extractives. Main wood extractives remaining in the water after

coagulation were resin and fatty acids. Results are similar to the study by Leiviskä et al. (2012), even though different kind of paper and pulping wastewater was used.

Combination of resin and fatty acid, sterols, BOD and COD removal of different water treatment methods applied to various waters in paper and pulp mills is shown in Table XIV.

Table XIV Removal efficiencies of resin and fatty acids, sterols, BOD and COD of different wastewater treatment techniques used in paper and pulp industry.

Treatment	Water used	Removal %					Reference
		Resin acids	Fatty acids	Sterols	BOD	COD	
Activated sludge	Debarking + bleaching	79	53	54	60 – 80	-	Junna et al. 1982
Activated sludge	Debarking	99	95	-	85	99	Saunamäki & Savolainen 1999
Activated sludge	ECF pulp mill	94	-	41	98	82	Kostamo & Kukkonen 2003
Aerobic and anaerobic	Pulp and paper	96	-	-	-	-	Zender et al. 1994
Enzymatic pretreatment + anaerobic	Debarking	-	-	-	85	72	Savolainen 1992
Ozone	Debarking	90	-	-	-	30	Korhonen & Tuhkanen 2000
Ozone + UV	Synthetic	99	-	-	-	46	Ledakowicz et al. 2006
Ultrafiltration, MWCO 100 kDa	Synthetic	41	94	-	-	21	Elefsiniotis et al. 1997
Ultrafiltration, MWCO 30 – 50 kDa	Chemithermomechanical pulp	>97	>97	>90	-	-	Puro et al. 2011

4 Wastewater treatment in Anjala paper mill

Wastewater treatment plant in Anjala paper mill treats wastewater from Anjala paper mill and Ingerois board mill. Wastewater treatment in Anjala paper mill is done with mechanical and biological treatment. Treatment is based on activated sludge system with addition of two moving bed biofilm reactors. Flowsheet of the wastewater treatment system is shown in Figure 15. Combined wastewater flow to the treatment is around 25 000 m³/d. At first, wastewaters flow in to 1 400 m³ neutralization tank. There are also emergency basins to diminish effects of unwanted emission levels. Before combining debarking plant wastewater to other wastewaters, there is an additional clarifier to reduce the amount of solids in the debarking wastewater. Due to the toxicity and concentration of the wastewater, most of the debarking wastewater from the clarifier is recycled back to the debarking process and only small amount flows to the wastewater treatment plant.

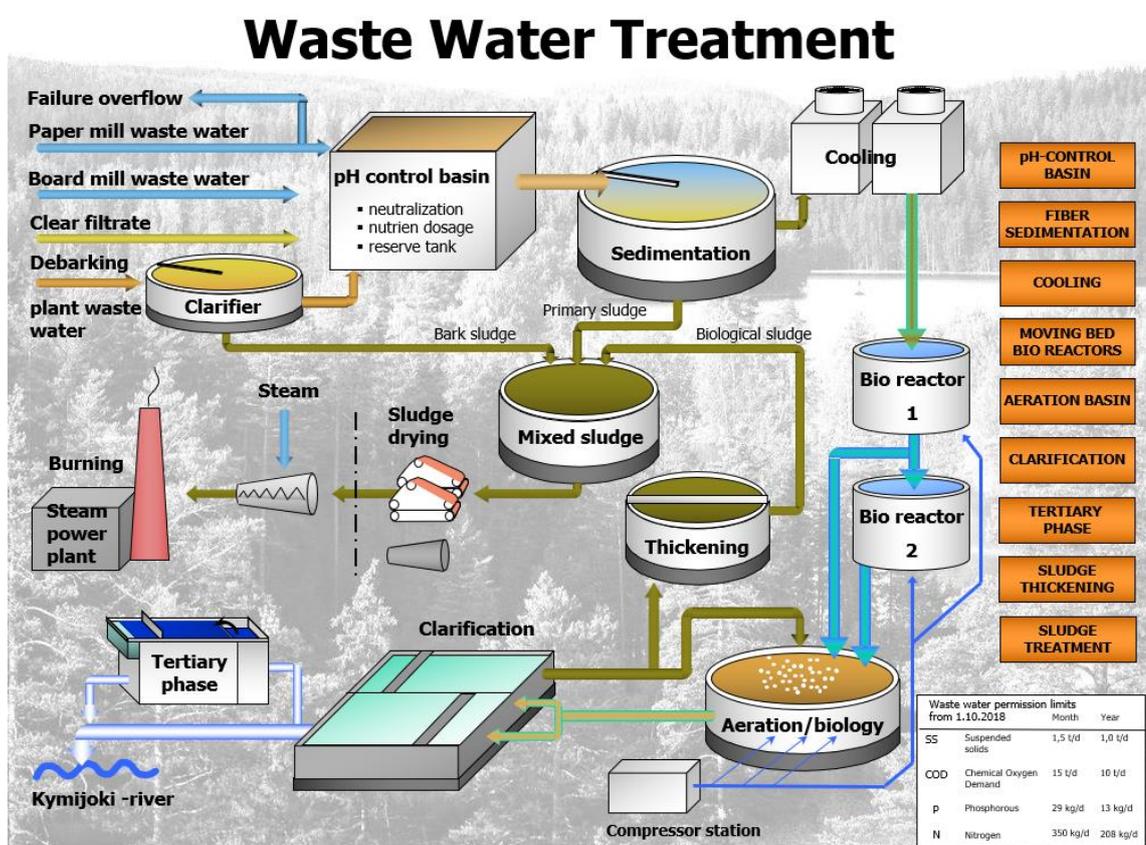


Figure 15 Wastewater treatment system in Anjala paper mill.

After addition of required compounds and neutralization, the wastewater goes through primary clarification where about 90 % of suspended solids are removed and form primary sludge. Sedimentation happens gravitationally in 8 500 m³ circular tank with a drag scraper. If necessary, the clarified wastewater is cooled in order to reach the appropriate operation temperature of 37 – 38 °C in the biological phase. Cooling towers are followed by equalization basin equipped with the nutrient feed facility.

Moving bed biofilm reactors (MBBRs) are used to reduce the load coming to the activated sludge system. In MBBR there are freely moving carrier elements into which biological culture forms, called biofilm. Carrier elements are small, which provides a high surface area of the biofilm. As a result of the high surface area, the treatment efficiency is high in MBBRs. In Anjala paper mill there are two 4 000 m³ aerobic MBBR units in sequence where aeration comes from the bottom. Two bottom aerated bio reactors remove the easily biodegradable organic matter (BOD) and the aeration basin, also bottom aerated, removes the more slowly biodegradable organic matter (COD).

Aeration occurs in 34 000 m³ aeration basin with bottom aeration. In the basin there is biomass in which are different microbes that use substrates in the wastewater. Effluent from the aeration basin flows to two 5 600 m³ secondary clarification basins. In the clarification, part of formed sludge is returned to the aeration basin and surplus sludge is pumped to sludge thickening. Sludge thickening happens in a sedimentation tank. In case of exceptional situations with a risk for increase in emissions there is an option for tertiary treatment by flotation with or without chemicals.

For sludge treatment, bark sludge from the bark wastewater clarifier, primary sludge from primary clarifier and biological sludge from sludge thickener are combined in mixed sludge tank. From the tank mixed sludge is dried with one belt press and a screw press. Dried sludge is used as a fuel in the mill.

5 Membrane filtration

5.1 Principles of membrane filtration

Membranes are defined as semipermeable films which have specific pore size. Membrane filtration can be classified based on the pore size or molecular cut-off value (MWCO). Basic pressure driven membrane filtration processes are micro-, ultra- and nanofiltration and reverse osmosis. Microfiltration (MF) membranes have largest pores in a size of 0.05 – 10 μm and therefore requires minimal pressure (< 2 bar). Ultrafiltration (UF) membranes have smaller pores at around 1 – 100 nm width and requires 1 – 10 bar pressure. Nanofiltration (NF) membranes have pore size of $< 2\text{nm}$ and pressure required 5 – 15 bar. Reverse osmosis (RO) membranes are almost nonporous and they require up to 150 bar pressure. (Mulder 1996, Wagner 2001, Madaeni 2016) Rejections of some typical compounds are presented in Figure 16.

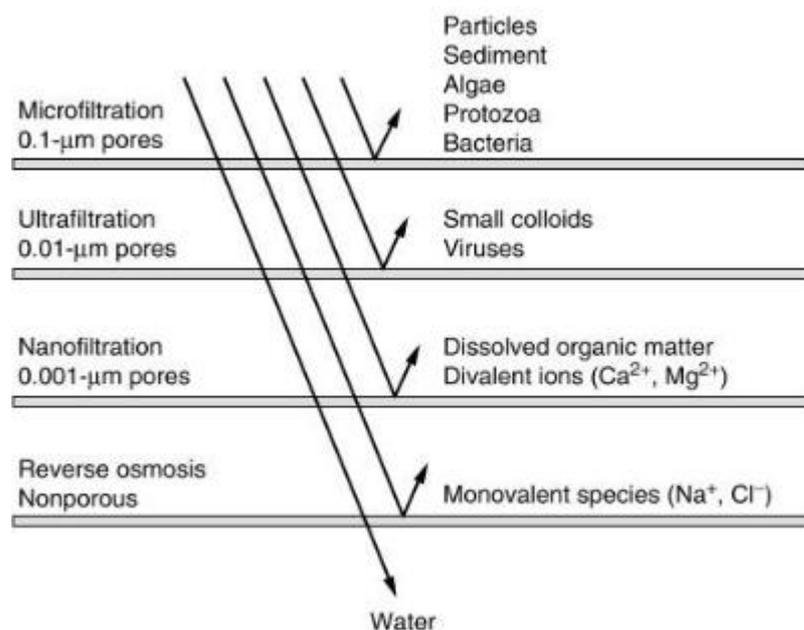


Figure 16 Minimum pore sizes of different membranes and typical compounds that specific membrane rejects (Howe et al. 2012).

There are two types of membrane filtrations based on the angle of feed flow compared to the membrane, dead-end and cross-flow. Pressure is the driving force in both of these filtration types. Depiction of dead-end and cross-flow membrane filtrations is shown in Figure 17. In dead-end filtration, feed flows perpendicular to the membrane surface.

Water and particles that have passed the membrane form permeate. Dead-end filtration is a batch process as a cake of the filtrated material forms on the surface of the membrane or fouling occurs, blocking the flow through. Two different filtration methods can be used with dead-end filtration, constant flux or constant pressure. Constant flux through the membrane can be achieved with gradually increasing pressure as more pressure is required to keep steady flux as membrane becomes more blocked. Constant flux operation is done often industrially whereas constant pressure is kept usually in laboratory scale processes. (Mulder 1996, Li & Li 2016b)

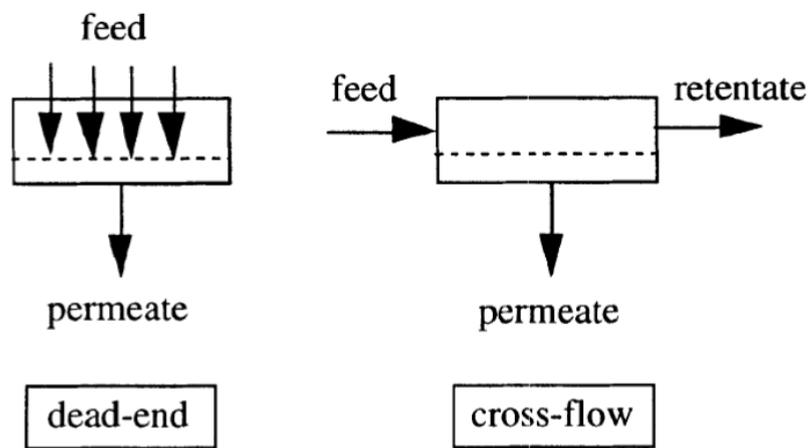


Figure 17 Principles of dead-end and cross-flow membrane filtrations (Mulder 1996)

In cross-flow filtration feed comes from the side of the membrane and flows tangential to the membrane surface. Pressure is added perpendicular to the membrane. After crossing the membrane, feed stream becomes retentate or concentrate stream. Retentate is concentrated partition of the feed stream. Like in dead-end filtration, layer of particles builds up at the surface of membrane during filtration decreasing the flux through (Figure 18). Due to the cross-flow stream, this cake layer reaches maximum depth after some time and steady flux is achieved. This enables continuous filtration if no fouling occurs during filtration. Cross-flow filtration is used more in industrial applications than dead-end filtration. (Mulder 1996, Li & Li 2016a)

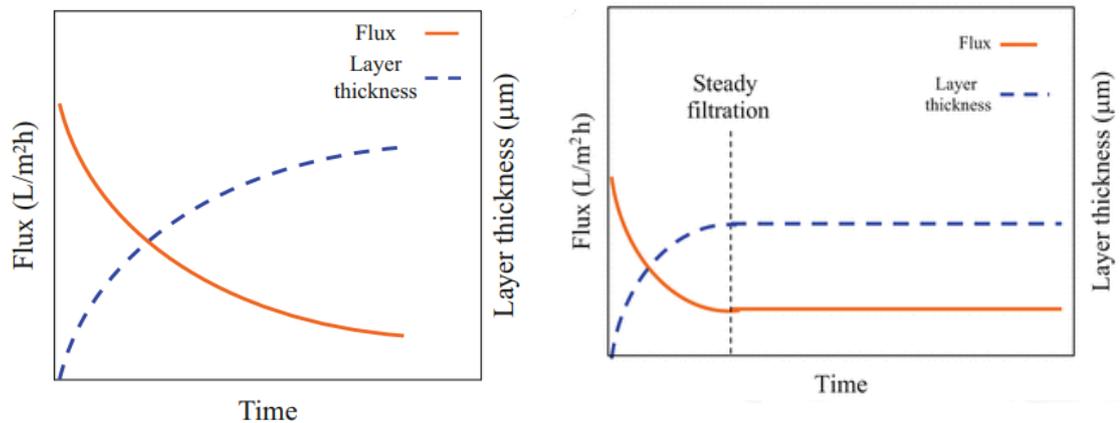


Figure 18 Formation of cake layer on to membrane surface and its effect on flux in dead-end (left) and cross-flow (right) filtrations (Li & Li 2016b, Li & Li 2016a)

Membrane pore size is not the only parameter to affect how well membrane performs. Hydrophobicity of membrane influences how water passes the membrane. In general, hydrophobic membranes have higher fouling tendency than hydrophilic membranes. Charge of membrane surface and pores affects the rejection of charged species in water. Same charge for membrane and particles improves rejection of the membrane and can reduce fouling. (Mulder 1996, Howe et al. 2012)

There are various kinds of membranes and modules made from membranes. Flat sheet membranes are single sheets which are placed on flat surface. These kinds of membranes are simplest and have been developed longest due to their simplicity. Filtration can be done in dead-end and cross-flow. Modules made from flat sheet membranes can contain one or multiple membranes. Modules containing multiple flat sheet membranes are called plate-and-frame module. In plate-and-frame module, membranes are separated from each other with spacer in between and feed flows between membranes. (Mulder 1996) Advantages of plate-and-frame are simplistic design and ability to exchange single membranes from the module, but the module has low packing density and high pressure drop (Balster 2016b).

More advanced module configuration using flat sheet membranes is high shear rate module. These modules can be cross-rotational (CR) or vibratory shear enhanced processing (VSEP). CR modules have multiple stacked flat sheet membranes and in between them is a spinning rotor. Spinning rotor can reach peripheral velocity of 13 m/s

and this motion creates turbulent conditions inside the module. Spinning motion also helps to keep membrane surface from clogging and reduces fouling. (Mänttari et al. 2010) Figure 19 shows basic structure of CR filtration module. One single module can have up to 140 m² membrane area (Valmet 2017). In VSEP, membranes are stacked flat sheet membranes like in CR module. The whole membrane stack undergoes torsional vibration which means that in the module movement of fluid is minimal . Vibration of membranes causes less fouling as particles do not stick to the membrane surface so easily. (Mänttari et al. 2010)

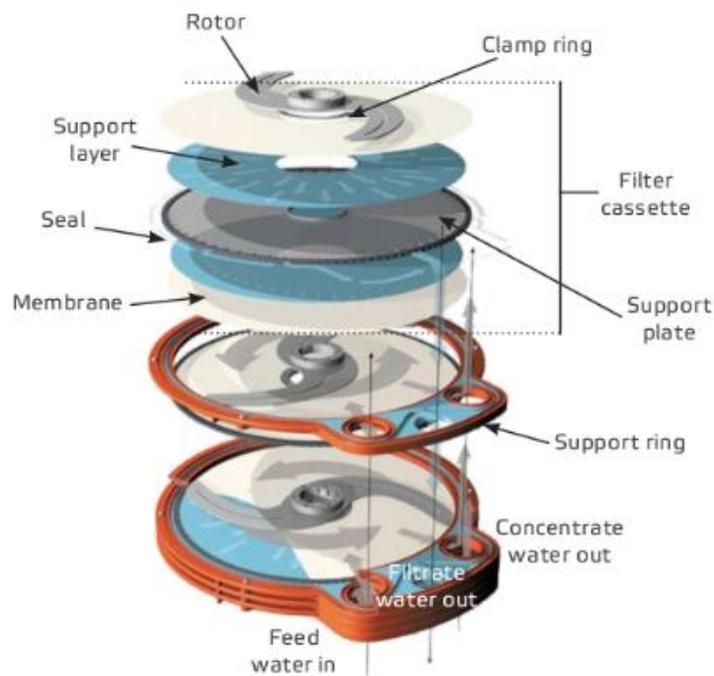


Figure 19 Structure of industrial cross-rotational membrane module (Valmet 2017).

Modification of using flat sheet membranes in module is spiral wound module. In spiral wound module multiple flat sheet membranes are stacked around central pipe with holes. Schematic of spiral wound membrane module is in Figure 20. Feed flows axially through the module and permeate flows to the center pipe. Spiral wound modules have high membrane area compared to space required for the module. Multiple modules can be combined in single pressure vessel to improve filtration, number of modules (up to 8 modules) increases as the required pressure increases. Spiral wound modules achieve higher packing density than normal plate-and-frame modules. Due to the structure of the

module it is weak against high pressure drops and susceptible to fouling often needing pretreatment. (Ismail et al. 2015, Mulder 1996, Wagner 2001)

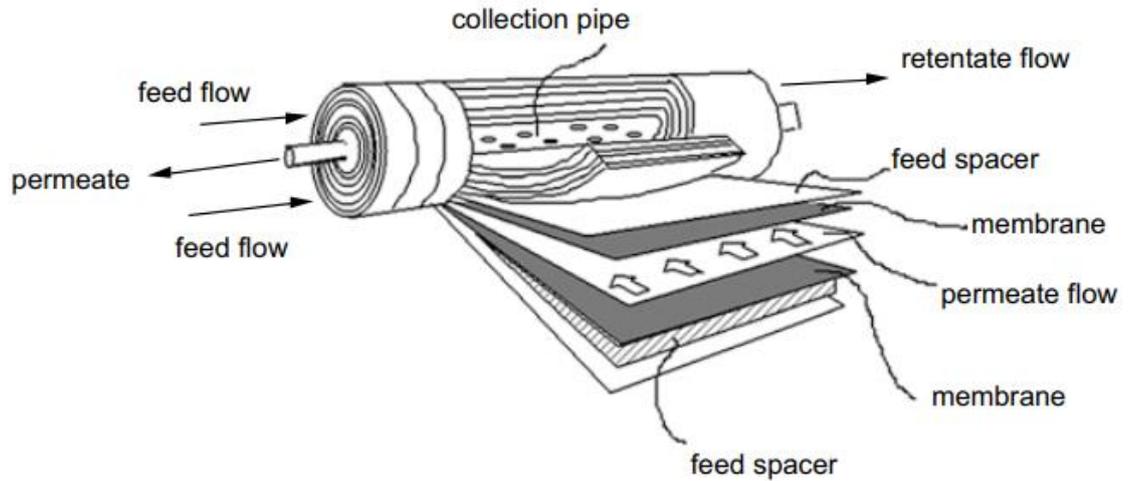


Figure 20 Schematic of spiral wound membrane module (Ismail et al. 2015).

Tubular membranes are tube which consist of supporting material and membrane layer. Diameter of tubular membranes is usually 5 – 25 mm. Feed flows through the center of tubes and becomes retentate at the end of the tubes. Permeate exits through the tube walls. Tubular membrane module can typically have 4 – 18 tubes. Multiple tubes are packaged inside a larger vessel where there is exit point for permeate (Figure 21). Tubular membrane modules have good flow conditions and are resistant to fouling. These modules however have high costs and require a lot of space which leads to low packing density. (Mulder 1996, Wagner 2001)

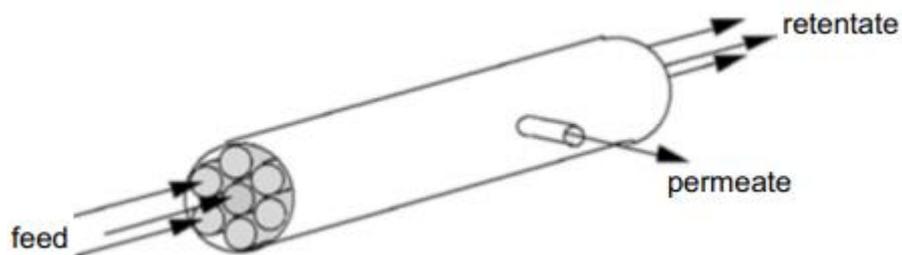


Figure 21 Schematic of tubular membrane module (Ismail et al. 2015).

As the name suggests, hollow fiber membranes are long thin tube membranes which are hollow in the middle. These membranes have inner structural layer and outer active layer. Surface of a hollow fiber membrane can be smooth, or it can have e.g. pentagonal shape. When using hollow fiber membranes, the feed can be fed to center of the membrane or to outer layer of the membrane (Figure 22). (Mohamed 2016) Hollow fiber modules are packages of numerous hollow fiber membranes where ends of the fibers are joined together. Hollow fiber modules are cheap and have high membrane area to volume ratio, but they can have low pressure resistance based on application. (Balster 2016a)

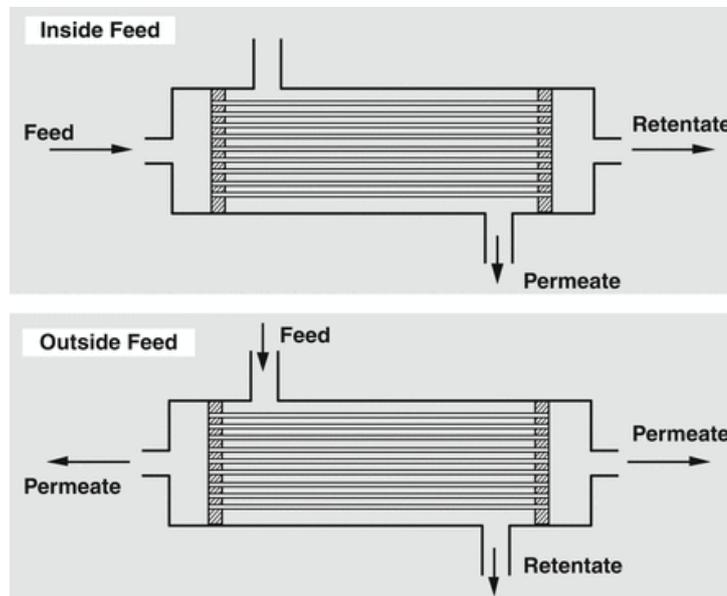


Figure 22 Schematic of inside and outside feed hollow fiber membrane modules (Scholz et al. 2011).

5.2 Usage of membranes in paper and pulp wastewater treatment

Membranes have many applications in water and wastewater treatment. Membrane filtration enables removal of harmful substances and efficient water purification. Process effluents and different kinds of municipal wastewater often contain solids and various size compounds so normally membrane treatment is used as tertiary treatment. In water treatment membranes are used in e.g. desalinating seawater, water softening and recovery. (Mulder 1996, Howe et al. 2012)

In paper and pulp industries membranes have wide variety of usages. For maximum purification of process or raw waters RO or NF can be used. These membrane processes use usually spiral wound modules and need extensive pretreatment for proper operation in paper and pulp mills. Most common pretreatment methods are biological treatment and physical treatment such as flocculation and sedimentation. NF and RO spiral wound modules have usually flux of 5 – 40 L/(m²*h). Micro- and ultrafiltration membranes can be used as hollow fiber, tubular or high shear rate modules. Hollow fiber modules are mostly used in membrane bioreactors to treat total mill effluents. Tubular UF modules are used in treatment of various paper and pulp mill effluents such as bleaching effluents or total mill effluent. High shear rate membrane modules are used to treat circulating water, also known as white water, and coating effluents. These membrane processes can withstand suspended solids and fibers and have relatively high fluxes. (Mänttari et al. 2010) High cost coating effluents like TiO₂ can be effectively recovered with cross-rotation ultrafiltration at high fluxes such as 200 L/(m²*h) (Jönsson et al. 1996). Membrane filtration with UF and NF membranes for the removal of wood extractives in paper and pulp industry was discussed in Chapter 3.4.4.

6 Advanced oxidation processes

6.1 Principles of advanced oxidation processes

Advanced oxidation processes (AOP) are based on formation of free radicals in aqueous solutions. These radicals are often hydroxyl radicals (HO^\bullet) which are nonselective, highly reactive and can degrade recalcitrant pollutants. Hydroxyl radicals are capable to totally mineralize many organic compounds. HO^\bullet reacts with organic molecules by radical addition (1), hydrogen abstraction (2), electron transfer (3) and radical combination (4). (Srivastava 2019)



where R reacting organic compound.

Hydroxyl radicals are generated by oxidizing agents such as ozone and hydrogen peroxide, catalysts such as Fe^{2+} or by irradiation such as UV or ultrasound. Oxidation potential of hydroxyl radical is 2.80 V. (Deng & Zhao 2015)

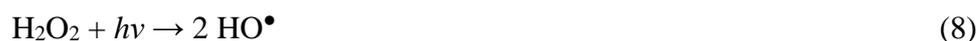
Ozonation can be classified as conventional or advanced oxidation process. In ozonation ozone (O_3) is used as primary hydroxyl generator. Ozone has oxidation potential of 2.07 V. Energy is required to generate ozone from oxygen in air. Ozone reacts selectively with dissociated and ionized organic compounds. (Deng & Zhao 2015) Overall reaction for hydroxyl radical generation by ozone is given at Equation (5) (Gottschalk et al. 2009).



Ozone reacts in wide pH range and has fast reaction rates. It is also effective against various organic, inorganic and microbial pollutants. Limiting factor to ozone usage is that ozone generating systems have high capital and operational costs. (Oram 2014) Ozonation efficiency can be improved with increasing pH above 8 and combining it with other AOPs such as H₂O₂ and UV. Combining ozone and hydrogen peroxide is called peroxonation. Addition of H₂O₂ reduces the required dosage of O₃. Peroxonation increases the hydroxyl radical formation as hydroperoxide (HO₂⁻) is formed from H₂O₂ based on Equations (6) and (7). (Deng & Zhao 2015)



In UV radiation based advanced oxidation processes hydroxyl radicals are generated by catalysts like TiO₂ or oxidants. With oxidants such as ozone or H₂O₂, UV can cleave molecules and produce more hydroxyl radicals (8). UV can also solely generate hydroxyl radicals by H₂O photolysis (9). (Deng & Zhao 2015)



where $h\nu$ light.

Metals can produce hydroxyl radicals in water by activating H₂O₂. Most common metal ion used is Fe²⁺ in a process called Fenton process. In Fenton process Fe²⁺ generates strong reactive species, mostly hydroxyl radicals but also other substances like Fe³⁺ ions. Hydroxyl radicals are generated through electron transfer in Fenton process. Traditional Fenton process requires acidic conditions for effective generation of hydroxyl radicals. Fenton process can be combined with UV irradiation to reduce produced Fe³⁺ ions back to Fe²⁺ ions. This process is called photo-Fenton. (Pignatello et al. 2006)

Every AOP works differently in every water treatment case. Often combining different AOPs such as O_3 , UV and H_2O_2 enhances the effectiveness of the treatment, but this depends largely on the treated water and pollutant. This can be seen in Figure 23 where various AOPs are compared for degradation of phenol. Combination of $O_3/UV/H_2O_2$ has higher removal than O_3/H_2O_2 or O_3/UV , but O_3 alone has also higher removal efficiency than O_3/H_2O_2 or O_3/UV processes. (Esplugas et al. 2002)

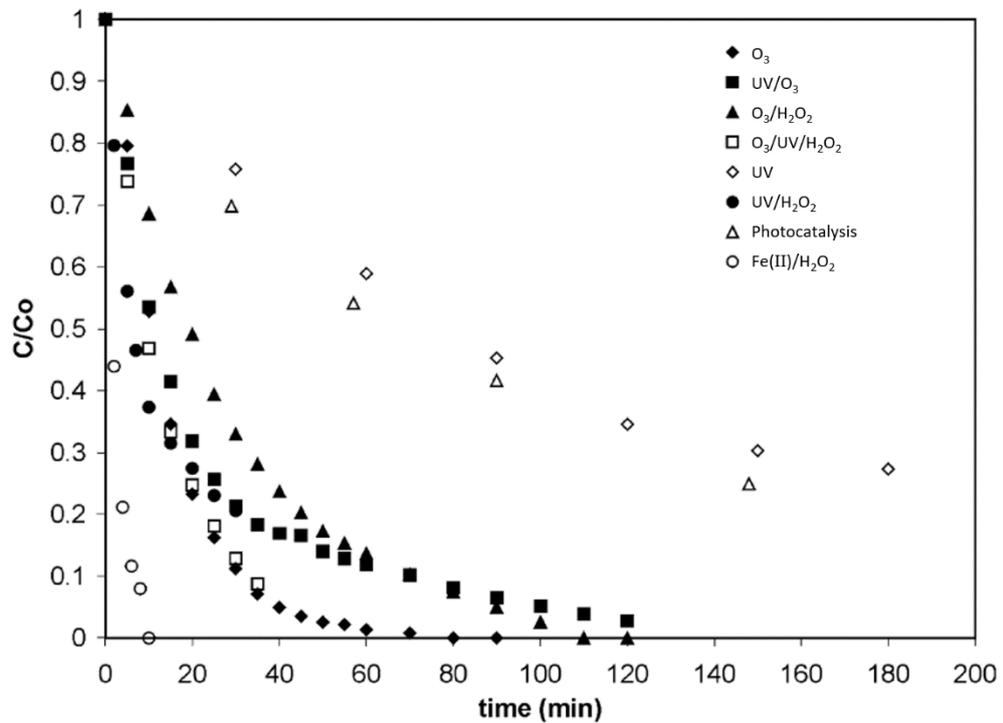
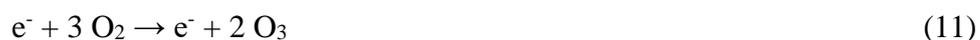


Figure 23 Phenol concentration removal of different AOPs (Esplugas et al. 2002, modified).

6.2 Pulsed corona discharge

6.2.1 Principle of pulsed corona discharge

Pulsed corona discharge (PCD) is advanced oxidation process based on non-thermal plasma (NTP). In non-thermal plasma process, short duration electric discharge is pulsed to a gaseous gap at atmospheric pressure which leads to strong electric field to form in the gas. Temperature of surrounding gas phase does not increase during the process. Plasma in NTP generates hydrogen ions, hydroxyl radicals, oxygen radicals and ozone during the process. These all act as oxidizing agents which leads to effective removal of pollutants. Formation of radicals in NTP is presented in Equations (10) – (12). (Preis et al. 2013)



In addition to free radicals, plasma in NTP generates UV radiation and high-pressure shockwaves. UV radiation comes from relaxation of excited species to lower energetic states. Effects of UV radiation to organic compounds was discussed in Chapter 6.1. Shockwaves are generated when plasma channels expand against surrounding water. Shockwaves can cause chemical and pyrolytic reactions due to electrohydraulic cavitation which causes dissociation of water and generates more radicals such as OH^{\bullet} . Degradation of compounds can happen directly due to high temperatures in the electrical discharge which contribute to more radical formation from water dissociation as well as directly degrade pollutants. (Gupta 2007, Jiang et al. 2014)

Pulsed discharges are nanosecond or microsecond long in NTP systems. Electrical discharge is produced between two electrodes where usually one is high-voltage point and other is grounded plate. Discharge travels from point electrode to grounded plate electrode. Configuration of these two electrodes are important. When both electrodes are in liquid phase the radicals can directly interact with pollutants, but transport rates are

low in liquid phase. Point electrode and in so electrical discharge in gas phase and plate electrode in liquid phase promotes the generation of ozone from oxygen in the gas phase, but gas-liquid interface has steep boundary layer. Most efficient configuration has been reported to be when point electrode is in liquid phase and plate electrode is in gas phase. In this configuration radicals and H_2O_2 are formed in the liquid phase and when electrical discharge reaches gas phase it forms active species and ozone from oxygen in the air. (Kušić et al. 2005, Jiang et al. 2014)

There are many parameters affecting pollutant removal efficiency of PCD treatment in both gas phase and liquid phase. Liquid phase parameters are composition of solution, pH, temperature and flow rate. pH of the solution affects the formation of hydroxyl radicals and H_2O_2 . More radicals are formed in neutral or alkaline pH whereas hydrogen peroxide production favors lower pH. (Thagard et al. 2009) Lower temperature of the solution has been reported to increase degradation of phenol and methyl blue (Chen 2004, Jiang 2012). On the other hand, higher solution temperature increases formation of radicals. Conductivity of the solution decreases the formation of hydrogen and H_2O_2 , so lower conductivity is beneficial for PCD. (Jiang et al. 2014)

Configuration of PCD system also affects its efficiency. In PCD unit, water can be fed through a perforated plate or aerosol nozzle which break down water stream to droplets. This increases surface-to-volume ratio of water with air which increases mass transfer and energy efficiency. Industrially electrodes preferred are wires rather than pinpoint electrodes like needles because wire electrodes distribute plasma more uniformly. Number of electrodes also increases efficiency. Gap distance of electrodes is important because shorter gap increases electric field generation but decreases plasma generation zone. (Jiang et al. 2014)

6.2.2 Pulsed corona discharge as a water treatment method

PCD can be used to remove pollutants from gas phases as well as liquids. Advantage of PCD compared to other AOPs is that all the radicals and ozone are generated in situ which eliminates the need for e.g. additional ozone dosage. PCD has been reported to be more energy efficient method than traditional ozonation for phenol degradation. (Preis et al.

2013) Due to still being a novel process, no wide scale industrial applications of PCD exist (Ajo et al. 2018).

PCD is effective especially in micropollutant removal. Arola et al. (2017) studied the degradation of micropollutants with PCD in membrane bioreactor (MBR) permeate treating municipal wastewater. Degradation of almost all micropollutants studied in the study reached more than 90 % with 0.2 kWh/m³ energy usage. Ajo et al. (2018) studied the removal of pharmaceutical residues from hospital wastewaters. Used wastewaters contained untreated and biologically treated wastewaters. 27 pharmaceuticals were analysed from untreated wastewater and total removal was 59 % at 30 W and 1.0 kWh/m³ PCD treatment. It was observed that caffeine is highly resistant of oxidation, without it the total removal was 87 %. Total removal from biologically treated wastewater was 91 % from 17 pharmaceuticals analysed at 0.1 kWh/m³ energy usage. (Ajo et al. 2018)

EXPERIMENTAL PART

7 Materials and methods

7.1 Bark water

Bark water used in experiments was collected from Anjala Paper mill in 24.1.20, 30.3.20 and 7.5.20. Analysed parameters from these batches are presented in Table XV. Bark water batch from 24.1.20 was more concentrated than the batches from 30.3.20 and 7.5.20 due to warmer water used in debarking.

Table XV Properties of used bark water from Anjala Paper mill.

	24.1.20 batch	30.3.20 batch	7.5.20 batch
pH, -	5.3	5.3	5.6
Conductivity, $\mu\text{S}/\text{cm}$	2 800 – 2 900	2 350 – 2 480	1 900
Color, PtCo	7 900 – 8 700	5 800 – 5 900	7 300
Turbidity, FAU	3 300 – 3 800	2 500	2 600
COD, mg/L COD	20 600 – 23 000	17 650 – 18 850	11 500
TOC, mg/L	21 000	-	17 000
BOD ₇ , mg/L	9 000	-	5 000
EC ₅₀ , %	0.6	-	0.6

7.2 Membranes

RC70PP and NF270 membranes were selected based on their known good performance with debarking plant wastewater (Hakala 2014). Properties of used membranes are shown in Table XVI.

Table XVI Used membranes in the experiments and their properties. [1] Alfa Laval 2020, [2] DuPont 2020.

Membrane	Maker	Material	MWCO, Da	T, °C	P, bar	pH, -
RC70PP ^[1]	Alfa Laval	Regenerated cellulose acetate	10 000	5 – 60	1 – 10	1 – 10
NF720 ^[2]	Dow	Polyamide	200 – 400	< 45	< 41	2 – 11

7.3 Filtrations

Used equipment for filtrations was CR-250 cross-rotational membrane module unit. The principle of the unit is same as CR module presented in Chapter 5.1 with one rotor and two membranes. Filtration area is 0.09 m^2 divided to the two membranes. Operation pressure is $0.5 - 10 \text{ bar}$ and rotor tip speed is up to 17.5 m/s . Schematic of the filtration unit is presented in Figure 24. Feed tank is heated by oil jacket, temperature and mixing speed of the tank can be adjusted. Pump used is peristaltic pump which is equipped with nitrogen pulse dampener to reduce pressure pulses. Permeate is collected from both membranes with two tubes. Concentrate can be circulated back to the feed tank or removed from the unit. Filtration pressure is adjusted with two valves and rotor speed with changing motor frequency.

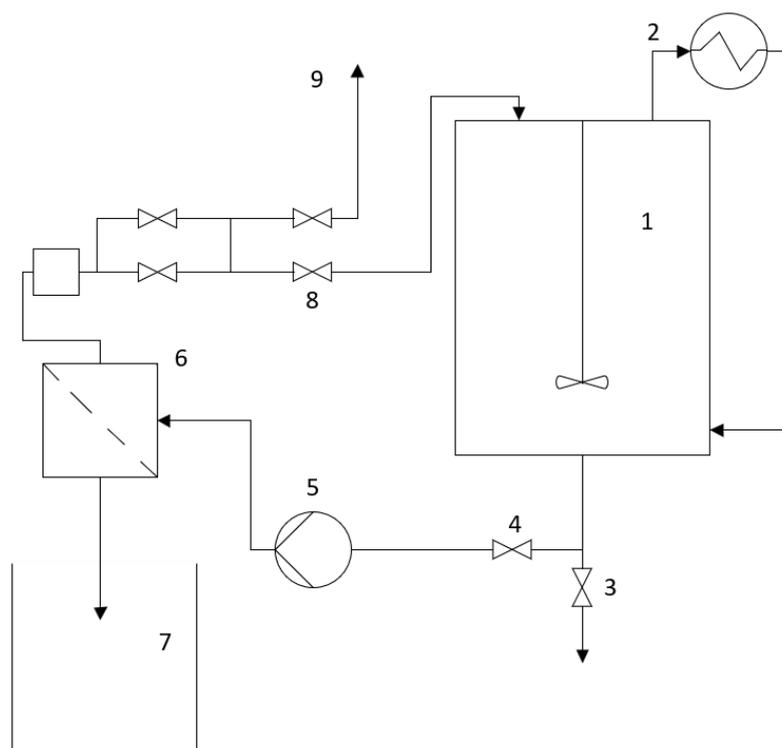


Figure 24 Schematic of used CR-250 filtration unit. 1: feed tank, 2: heating, 3: feed discharge, 4: feed to CR, 5: pump, 6: filtration unit, 7: permeate tank, 8: concentrate circulation, 9: concentrate outlet.

Small scale filtrations were done with dead-end filtration cell with 400 mL volume. Schematic of the cell is shown in Figure 25. Material of the cell is stainless steel. Pressure is adjusted with nitrogen flow. Temperature and mixing are adjusted with heated magnetic plate under the cell. Cell is operated as batch process.

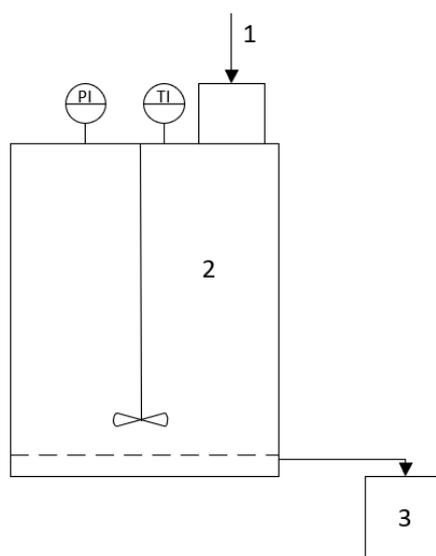


Figure 25 Schematic of used dead-end filtration cell. 1: feed, 2: cell, 3: permeate tank.

Small scale experiment for the effect of activated carbon (AC) as a pretreatment for nanofiltration was done in the dead-end filtration cell. Filtrations were done with 100 mL bark water filtrated through 1.6 μm glass microfiber filter and 100 mL bark water with 10 g/l added AC and 1.6 μm filtration. Bark water with AC was mixed for 30 min at 20 °C. Used AC was Norit SAE 2 activated carbon.

Regular and modified saw dust were tested to adsorb components from bark water and in so increase flux and reduce fouling during membrane filtration. Experiments were done in dead-end filtration cell. Saw dust was added to around 100 mL bark water, concentration used was 10 m-% of saw dust. Solution was stirred for 30 min at room temperature and pressure and then twice filtrated through a 1.6 μm glass microfiber filter. Two batches of saw dust bark water solution was made.

Saw dust used in filtration experiments was spruce saw dust from a sawmill. It was screened through 5.6 mm mesh and then extracted for 2 h at 160 °C and 4:1 liquid/solids -ratio. Both extract and saw dust were cooled together and then saw dust was pressed with 4 MPa pressure to ~45 % moisture content. Saw dust was further dried at open container at room temperature to 10 – 30 % moisture content. Used saw dust had moisture content of 6 – 8 % during experiments.

7.4 Pulsed corona discharge

PCD unit used in experiments is described in Figure 26. Pulse generator frequency can be changed between 50 – 833 Hz and power 6 – 100 W. Used pulse configuration during experiments was 300 Hz and 36 W. Feed tank was in ambient temperature and pressure. Flow of liquid to PCD reactor or back to feed tank can be adjusted with hand valves. Flow to reactor is monitored with a rotameter. The PCD reactor has two grounded plates and in between them 31 stainless steel wires which act as electrodes. Flow to reactor is monitored with a rotameter. The PCD reactor has two grounded plates and in between them 31 stainless steel wires which act as electrodes.

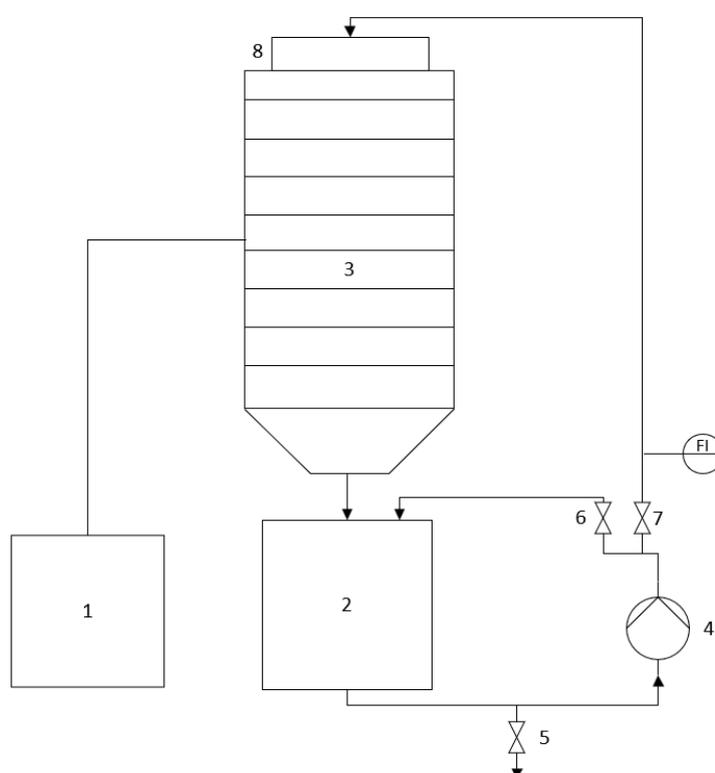


Figure 26 Schematic of used PCD unit. 1: pulse generator, 2: feed tank, 3: electrode wires and grounded plate, 4: pump, 5: outlet and sampling point, 6: feed circulation, 7: feed into PCD unit, 8: perforated plate.

7.5 Analysis methods

pH and conductivity were analysed from feed, concentrate and permeate from filtrations and samples from PCD treatments. Analyses were done in room temperature and ambient pressure. Conductivity analysis was done with Knick Konduktometer 703 conductivity meter and pH analysis with Metrohm 744 pH-meter.

Color and turbidity were analysed from feed, concentrate and permeate from filtrations and samples from PCD treatments. Analyses were done in room temperature and ambient pressure. Both analyses were done with Hach DR/2010 portable datalogging spectrophotometer which has programmed colorimetric measurements for multiple different analyses. Color was analysed with APHA platinum-cobalt standard method at 455 nm wavelength and samples were diluted to be in color range of measurement. Turbidity was analysed as FAU units at 860 nm wavelength.

COD measurements were done with Spectroquant[®] COD-tubes made by Merck. In this method potassium dichromate in the tube reacts with oxidizable substances in sample and produces oxygen. Formed Cr^{3+} ions are determined photometrically corresponding DIN ISO 15705 method. Used COD tubes were for COD concentrations of 0 – 1 500 mg/L COD and samples were diluted to suitable COD concentrations. COD was analysed from feed, concentrate and permeate from filtrations and samples from PCD treatments. Feed and concentrate samples from filtrations were filtered through 0.45 μ m RC filter to remove solids. Analyses were done in room temperature and ambient pressure. Sample size was 2.0 mL. COD concentrations were measured with Hach DR/2010 portable datalogging spectrophotometer at 620 nm wavelength.

TOC analysis was done with Shimadzu TOC-L analyser with Shimadzu ASI-L autosampler. Analyser oxidizes organic carbon in liquid sample catalytically to carbon dioxide from which carbon content is measured. TOC was analysed from feed, concentrate and permeate from filtrations and samples from PCD treatments. Feed and concentrate samples from filtrations were filtered through 0.45 μ m RC filter to remove solids. Samples were diluted prior analysis and diluted to 20 times concentration during analysis to obtain TOC concentration below 400 mg/L.

UV-Vis analysis was used to determine compound changes in samples from experiments. Analysis was done with Jasco V-670 Spectrophotometer. UV-Vis analysis was done to

feed, concentrate and permeate from filtrations and samples from PCD treatments. Feed and concentrate samples from filtrations were filtered through 0.45 µm RC filter to remove solids. Samples were diluted prior analysis to obtain absorbance in range of 0.25 – 3.75. Polyphenol concentrations were determined from UV-vis spectra at 280 nm. Concentrations were calculated with Equation (13) where nonphenolic absorbance is corrected with 4 (Wrolstad 2001).

$$C_{phenol} = [Abs_{280nm} * DF * (\frac{1cm}{b})] - 4 \quad (13)$$

where C_{phenol} Polyphenol concentration, -
 Abs_{280nm} Absorbance at 280 nm, -
 DF Dilution factor, -
 b Path length in cuvette, cm.

BOD and toxicity analysis were done by Kymen Ympäristölaboratorio Oy. BOD was analysed as BOD₇-ATU according to SFS-EN 1899-1:1998 standard. For analysis samples are diluted with water containing large amounts of dissolved oxygen, microorganism seeds and nitrification suppressor. Sample is then incubated in complete darkness for 7 days at 20 °C and dissolved oxygen concentration is measure before and after incubation. Toxicity was analysed for *Vibrio fischeri* EC₅₀ for 30 min according to SFS-EN ISO11348-3:2009 standard. Different concentrations sample are introduced to luminescent bacteria suspension in a test tube. Luminescence is then measured after 30 min and inhibitory effect is presented as EC₅₀ value.

Permeate flux of the membranes was calculated for filtrations. Flux presents the amount of permeate obtained in an hour with 1 m² membrane area. Permeate flux is calculated with Equation (14).

$$J = \frac{m_p}{A_f * t} \quad (14)$$

where J Permeate flux, kg/m²h,
 m_p mass of the permeate, kg,
 A_f membrane area, m²,
 t filtration time, h.

Volume reduction factor (VRF) describes the amount of concentration occurred in filtration or how lower volume original feed is reduced. VRF is calculated with Equation (15).

$$VRF = \frac{m_f}{m_f - m_p} \quad (15)$$

where VRF Volume reduction factor, -,
 m_f mass of the feed, kg.

Retentions were calculated from the analyses. Retention describes how effectively components have separated during filtration, i.e. relation of component concentrations in feed and permeate. Retentions are calculated with Equation (16).

$$R = 1 - \frac{C_i^p}{C_i^f} \quad (16)$$

where R Retention of component, -,
 C_i^p concentration of component i in permeate, -,
 C_i^f concentration of component i in feed, -.

8 Results

8.1 CR module filtrations

Filtrations were done using CR250 filter with RC70PP and NF270 membranes. Evolution of membrane flux using bark water as feed with no pretreatment at 20 °C and 40 °C and using RC70PP permeate as feed for NF270 are shown in Figure 27. With RC70PP pressure used was 2, VRF of 17.6 was reached with good flux. In nanofiltrations with NF270, based on the low flux and therefore long filtration time required filtrations were stopped early. Using RC70PP permeate as NF270 feed increased the NF270 permeate flux by 20 – 35 %. As bark water in Anjala Paper mill during winter can reach to temperatures of around 40 °C, filtrations with RC70PP and NF270 were done at that temperature. Increase of temperature increased the flux with RC70PP by 35 – 50 %. In filtration with NF270 at 40 °C flux increase was around 100 %, however filtration was done with 11.7 m/s tip speed rather than 6.5 m/s used in 20 °C filtration and at 8.5 bar.

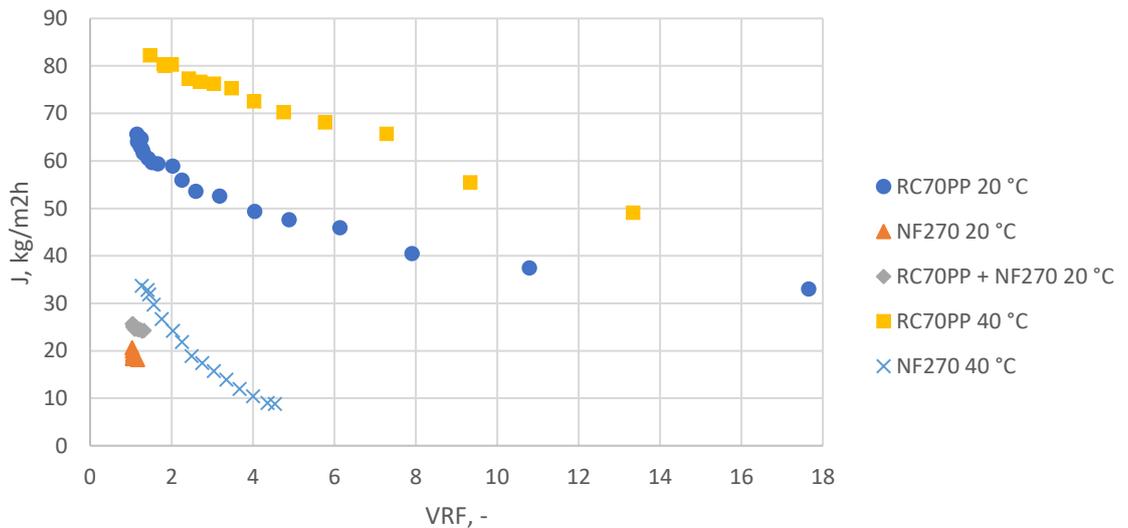


Figure 27 Permeate flux as function of VRF for RC70PP at 2 bar and 20 °C and 40 °C, NF270 20 °C at 8 bar, NF270 40 °C at 8.5 bar and NF270 using RC70PP permeate as feed at 8 bar. CR tip speed was 6.5 m/s on all the other filtrations than NF270 40 °C where it was 11.7 m/s.

8.2 Effect of different parameters on the fouling and capacity of membranes

Fouling of membranes was determined by measuring water flux (WF) before and after filtrations and calculating membrane permeability. WFs for RC70PP were measured at 1, 2 and 3 bar pressures and NF270 were measured at 8, 6 and 4 bar pressures. WFs for were measured at same temperature that filtrations were done.

Water permeabilities of RC70PP and NF270 membranes before and after filtrations and after washing are presented in Figure 28. NF270 filtration at 20 °C and RC70PP permeate NF270 filtration at 20 °C were done with the same membrane sheet, with basic NF270 filtration done first.

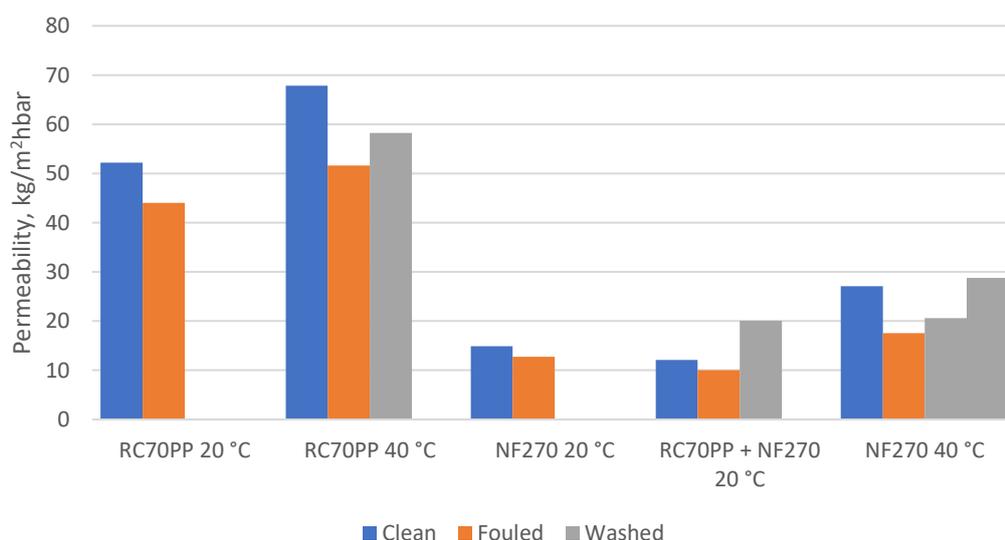


Figure 28 Water permeabilities before and after filtration and after washing.

Fouling of membranes during filtration and real fouling after washing for filtrations with RC70PP and NF270 is presented in Figure 29. Fouling is modest in both ultra- and nanofiltrations.

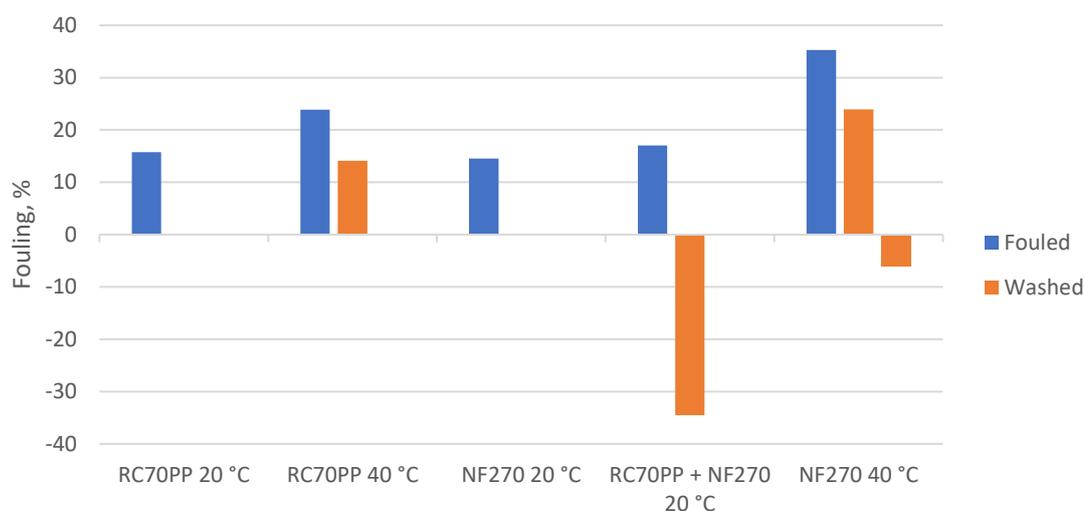


Figure 29 Membrane fouling during filtrations and after washing for different CR module filtrations.

Washing conditions of CR module filtrations is shown in Table XVII. 0.2 % Ultrasil 110 wash was enough to reverse any fouling occurred at 20 °C NF270 filtrations. However, washing NF270 membrane after 40 °C filtration with 0.2 % Ultrasil 110 was not enough to completely remove fouling. Fouling resistance increase in this filtration might be attributed to increased temperature and higher VRF. 0.5 % solution removed fouling effectively after 0.2 % washing. Washing of RC70PP after 40 °C filtration with 0.5 % Ultrasil 110 did not fully restore membrane permeability.

Table XVII CR module filtrations, their washing parameters and permeability after washing compared to permeability of clean membrane.

Filtration	Ultrasil 110 wash at 1 bar	Permeability change, %
NF270 20 °C + RC70PP perm 20 °C	0.2 %, 30 °C, 20 min	34
NF270 40 °C	0.2 %, 40 °C, 25 min + 0.5 %, 40 °C, 30 min	6
RC70PP 40 °C	0.5 %, 40 °C, 20 min	-14

8.2.1 Feed volume

Filtrations were done with 60 L and 12 L bark water feed to see the effect of feed volume to fouling of NF270 membrane. Temperature during filtration was 40 °C and pressure 9 bar. Same membrane was used for both filtrations and it was washed between the filtrations. Filtrations were continued to 4 VRF which equals around 25 h for 60 L filtration and 4 h for 12 L filtration. Evolution of fluxes during filtrations is shown in Figure 30. Fluxes decreased similarly during filtration, in 60 L filtration flux decreased by 77 % and in 12 L filtration the decrease was 73 %.

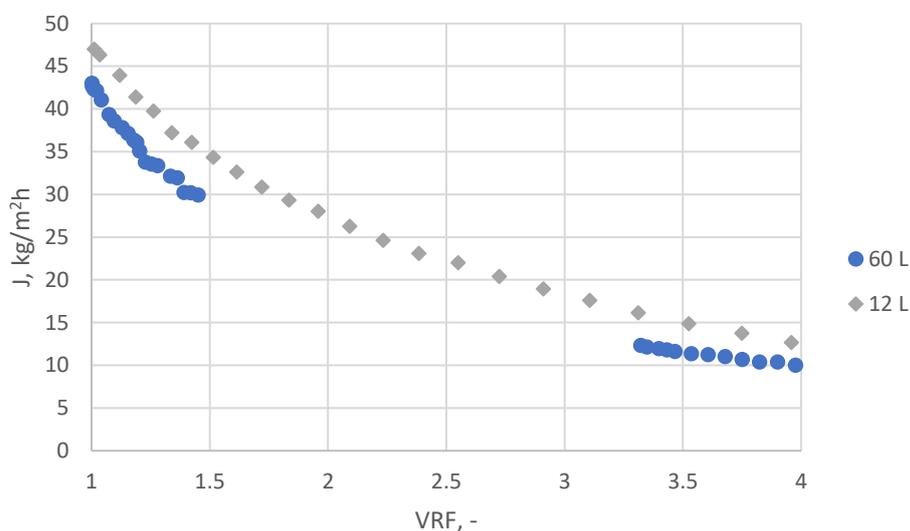


Figure 30 Filtrations with 60 L and 12 L bark water using NF270 membrane at 40 °C, 9 bar and 11.7 m/s tip speed.

Water permeabilities were measured before and after filtrations, after 15 h in water and 3 d in water (Figure 31). Fouling was 39 % after 60 L filtration and 17 % after 12 L filtration. Higher feed volume and longer filtration time seems to have an effect on the fouling of NF270 membrane. Washing the membrane with 0.5 % Ultrasil 110 at 40 °C for 20 min after 60 L filtration can influence the fouling during 12 L filtration.

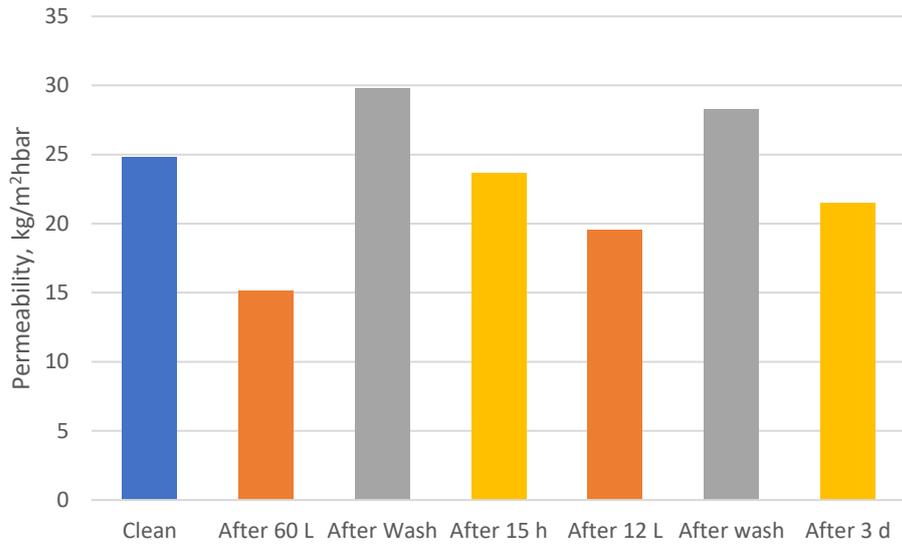


Figure 31 Permeabilities of NF270 membrane during different parts of 60 and 12 L filtrations at 9 bar, 40 °C and 11.7 m/s tip speed.

The effect of feed volume on the adsorptive fouling was tested on small dead-end filtration cell. NF270 membranes were kept in 100 mL, 500 mL and 1000 mL of bark water at 20 °C and ambient pressure for 24 h. Additional experiments were done where mixing was added to 500 mL and 1000 mL solutions to enhance mass transfer. Pure water permeabilities were measured before and after bark water adsorption. Fouling caused by different volume of bark water is shown in Figure 32. In CR filtrations, feed volume did not affect the permeate flux during filtration, but increased fouling, possibly due to addition of longer filtration time. When membrane sheets were submerged in different volumes of bark water, no increase in adsorptive fouling was measured in dead-end filtrations at higher volumes.

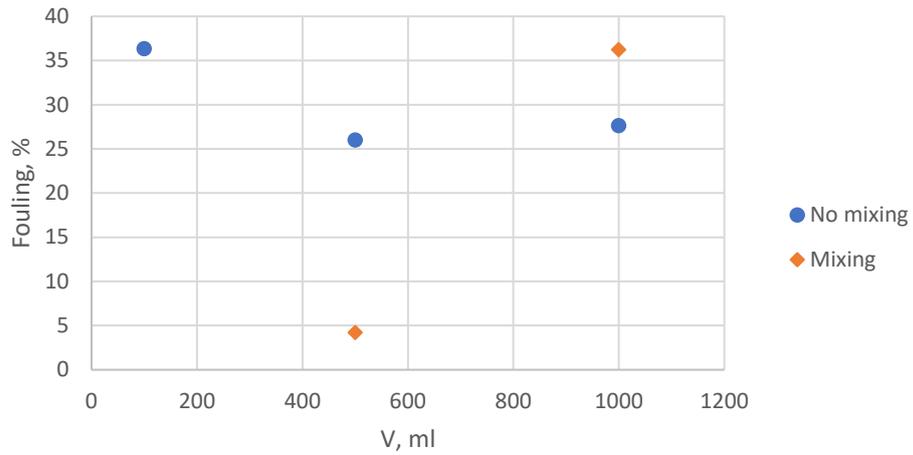


Figure 32 Fouling of NF270 membranes submerged in different volumes of bark water at 20 °C and ambient pressure for 24 h.

8.2.2 Temperature

Temperature was observed to increase fouling in filtrations so small-scale experiment with NF270 was done to see how much of the temperature induced fouling was based on adsorption. Membranes were suspended in 400 mL of bark water and pure water at 20 °C and 50 °C for 22 h. Effect of bark water temperature on pure water permeabilities of NF270 is shown in Figure 33. At 20 °C bark water did not reduce permeability whereas at 50 °C fouling was 65 %. Pure water at 20 °C and 50 °C had negligible effect on permeabilities.

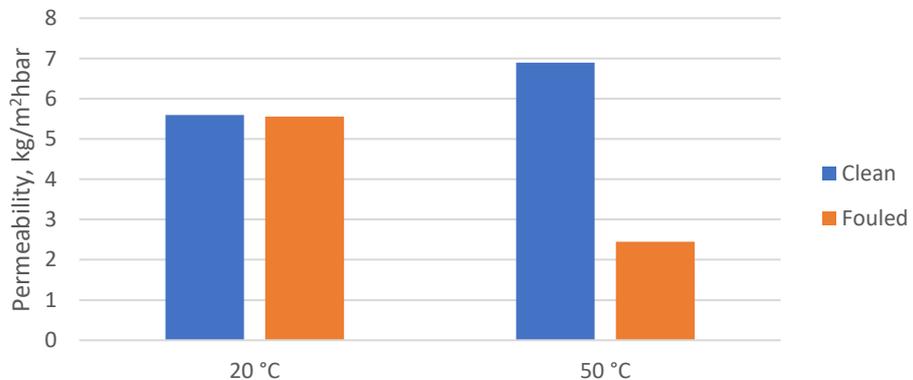


Figure 33 Pure water permeabilities of NF270 membrane before and after 22 h in 400 mL bark water at 20 °C and 50 °C.

One experiment was done to see how temperature affects the turbidity of bark water. 400 mL samples of bark water were heated to 3 °C, 20 °C and 50 °C and turbidity was then measured. Turbidity increases with increasing temperature (Figure 34).

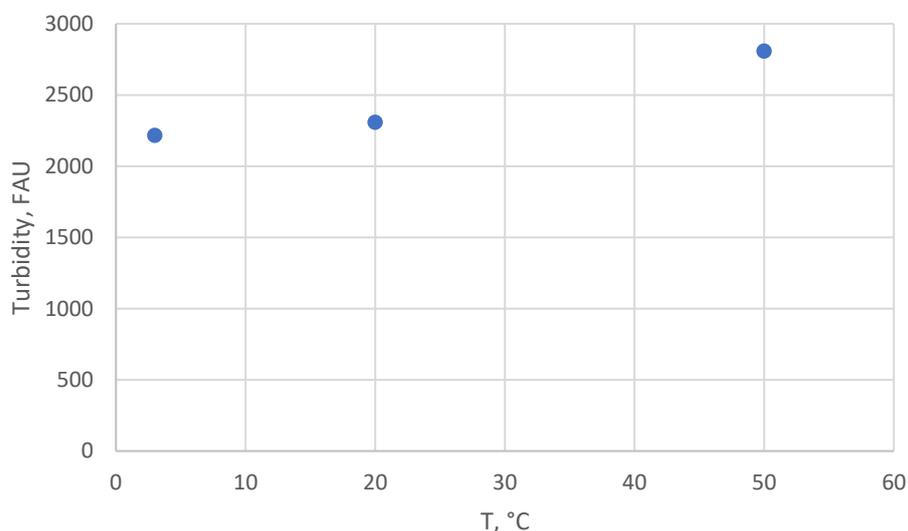


Figure 34 Effect of temperature on the turbidity of bark water.

Increase of fouling due to higher feed temperature was seen clearly with NF270 membrane. Most of the fouling can be attributed to adsorptive fouling, as membranes were only submerged in bark water, no external force was applied to the system. As turbidity of bark water increases with higher temperature more colloidal material dissolves to bark water and more adsorption occurs on to the membrane surface. In CR filtrations, increase in temperature increased permeate flux as well as fouling in ultra- and nanofiltration significantly. Fouling increase was lower in CR filtration than in dead-end filtration cell possibly due to high shear rate reducing adsorption on to membrane surface.

8.2.3 CR tip speed

10 L batches of untreated bark water was filtrated with CR-250 and NF270 membrane at 40 °C and 9 bar. Filtrations were done with tip speeds of 6.5, 11.5 and 15.6 m/s. Effect of tip speed on flux during filtration is shown in Figure 35. Increase of tip speed from 6.5 m/s to 11.5 m/s increases flux by around 30 % during the whole filtration. Increase from 11.5 m/s to 15.6 m/s increases flux 20 – 30 %. It should be noted that during 15.6 m/s

filtration, after VRF 2.5 temperature of bark water increased gradually from 40 °C to 43.4 °C at VRF 3.7. This can slightly increase the flux.

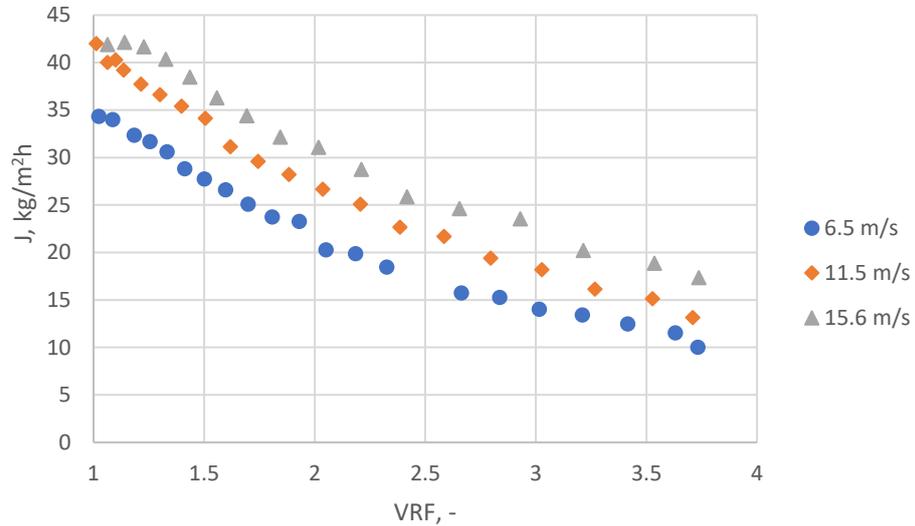


Figure 35 Evolution of flux during filtrations at tip speeds of 6.5, 11.5 and 15.6 m/s. Used membrane was NF270 at 40 °C and 9 bar.

Permeabilities of used membranes before filtration, after filtration, after washing and after 15 h in water are shown in Figure 36. When looking at difference of permeabilities before and after filtration, fouling seems to reduce as CR tip speed during filtration increases. On the other hand, the only difference in permeabilities is between clean membranes, all permeabilities after filtration are almost the same. Permeabilities after washing and 15 h in water follow the same pattern as with clean membranes. No definitive result on the effect of CR tip speed on the fouling of membrane can be concluded from these results.

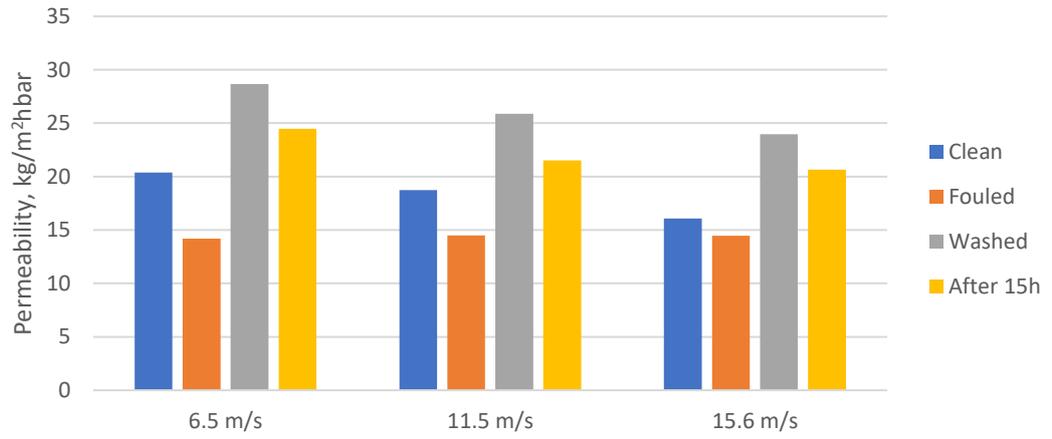


Figure 36 Permeabilities of NF270 membranes used in filtrations with different CR tip speeds at 9 bar and 40 °C.

8.3 Effect of pretreatment on the fouling and capacity of membranes

Adsorption to activated carbon, regular saw dust and modified saw dust were used as pretreatment methods in small scale filtrations. Fluxes during filtration with NF270 membrane at 40 °C and 8 bar is shown in Figure 37. Filtrations with modified saw dust pretreated bark water achieved 2 – 3 times higher flux than filtration with regular bark water. Regular saw dust produced similar flux to modified saw dust at the beginning of filtration, but the flux decrease was greater as VRF increased. Activated carbon pretreatment resulted in flux evolution between modified and regular saw dust during filtration where at start flux increase was more than 100 % higher and flux decrease during concentration was higher than with modified saw dust but lower than regular saw dust.

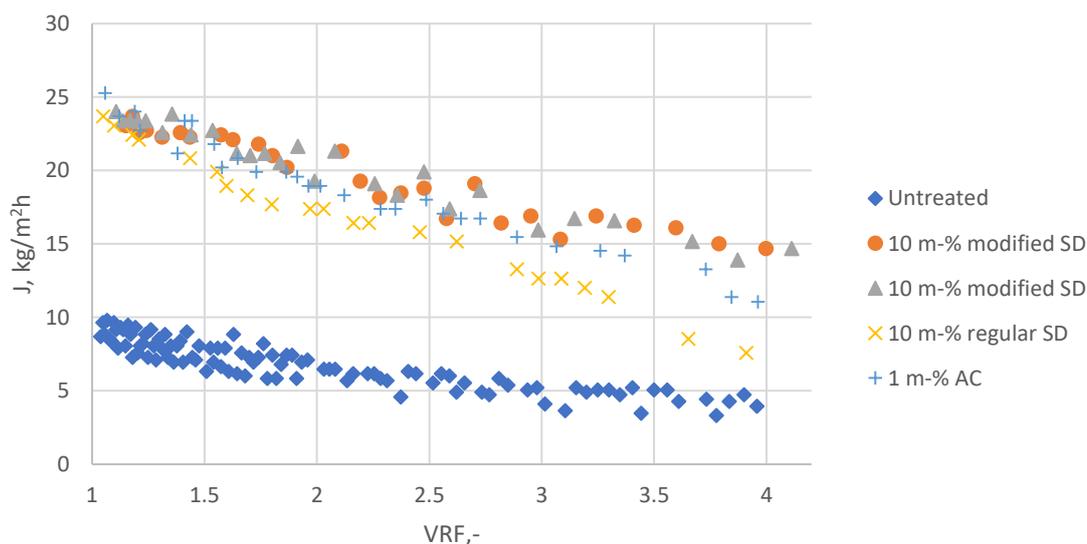


Figure 37 Permeate flux as function of VRF in NF270 filtration at 40 °C and 8 bar for untreated bark water, and bark water pretreated with 10 m-% regular and modified saw dust and 1 m-% activated carbon as adsorbents.

Pure water permeabilities and fouling of NF270 membranes for AC, regular and modified saw dust pretreatment filtrations are shown in Figure 38. All pretreatment methods reduce fouling drastically. Two experiments with 10 m-% modified saw dust pretreatment provided similar results, fouling in both cases was 34 %. Least amount of fouling, 10 %, was in filtration with regular saw dust, AC pretreatment also resulted in low fouling, 12 %. Low amount of fouling can partly come from lower permeate flux during filtration. More

experiments are needed to verify the results for regular saw dust and activated carbon pretreatments.

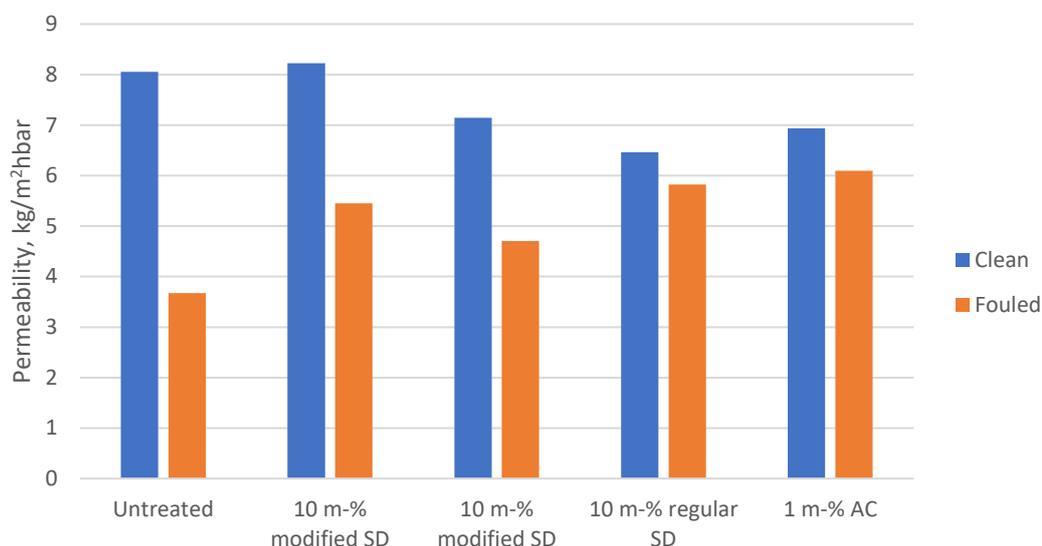


Figure 38 Permeabilities of NF270 membranes before and after bark water filtrations in dead-end filtration cell at 8 bar and 40 °C.

Pretreatment with modified saw dust was tested on larger scale with CR-250 module. 128 kg of bark water from 7.5.20 batch was mixed with 10 kg of modified saw dust for 30 minutes at 40 °C and then saw dust was let to settle on the bottom of the mixing tank. Treated bark water was separated from saw dust through a fine mesh.

60 L of treated bark water was used for RC70PP filtration at 3 bar, 40 °C and 15.6 m/s tip speed. Permeate flux during filtration is shown in Figure 39. Combined effect of increased pressure, CR tip speed and saw dust treated bark water increased the flux by 70 – 100 % during whole filtration when compared to filtration shown in Figure 27.

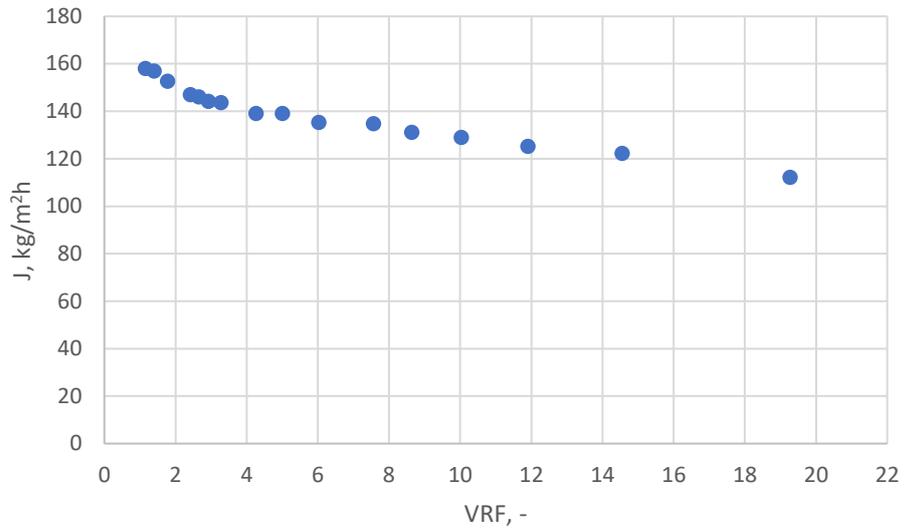


Figure 39 Permeate flux as a function of VRF for RC70PP membrane when filtrating modified saw dust treated bark water at 3 bar, 40 °C and 15.6 m/s tip speed.

Permeabilities before and after filtration and after washing are shown in Figure 40. Fouling during filtration was 21 %, which is slightly lower than in 40 °C RC70PP filtration shown in Figure 27. Washing with 0.5 % Ultrasil 110 at 1 bar and 40 °C for 20 minutes only reduced fouling to 14 %.

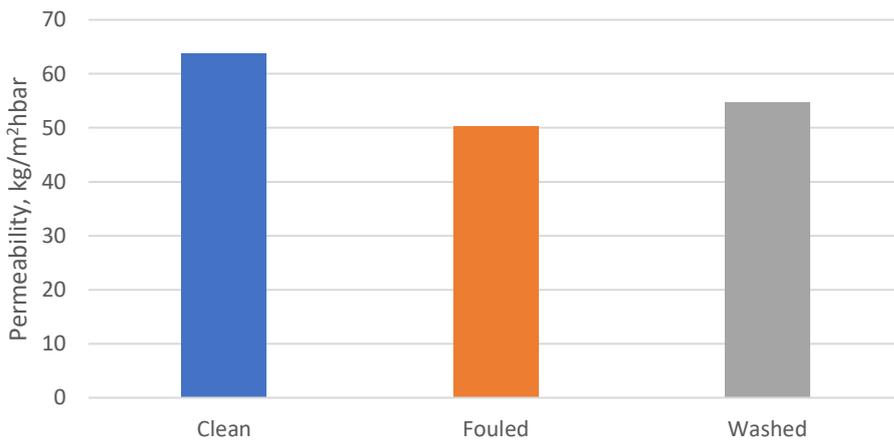


Figure 40 Water permeabilities of RC70PP membrane before and after filtration with modified saw dust treated bark water, and after washing.

Filtrations with modified saw dust treated bark water was also done with NF270 in CR unit at 9 bar, 40 °C and 15.6 m/s tip speed. Permeate of RC70PP filtration was additionally filtrated with NF270 to see the effect of ultrafiltration prior nanofiltration. One filtration was done with untreated bark water, as the used bark water for modified saw dust pretreatment was different batch than previously used. Fluxes of these filtrations are shown in Figure 41.

Modified saw dust pretreatment increased the flux by 90 – 100 %. Using modified saw dust pretreated RC70PP permeate as feed for NF270 does not affect the flux compared to straight nanofiltration, slightly lower flux could be the result of different membrane sheet used. Flux when filtrating bark water from 7.5.20 batch is around 20 % higher than when filtrating bark water from 30.3.20 batch (Figure 35). This is possibly due to the bark water from 30.3.20 batch having higher temperature during debarking resulting in more concentrated water and in so higher osmotic pressure during filtration.

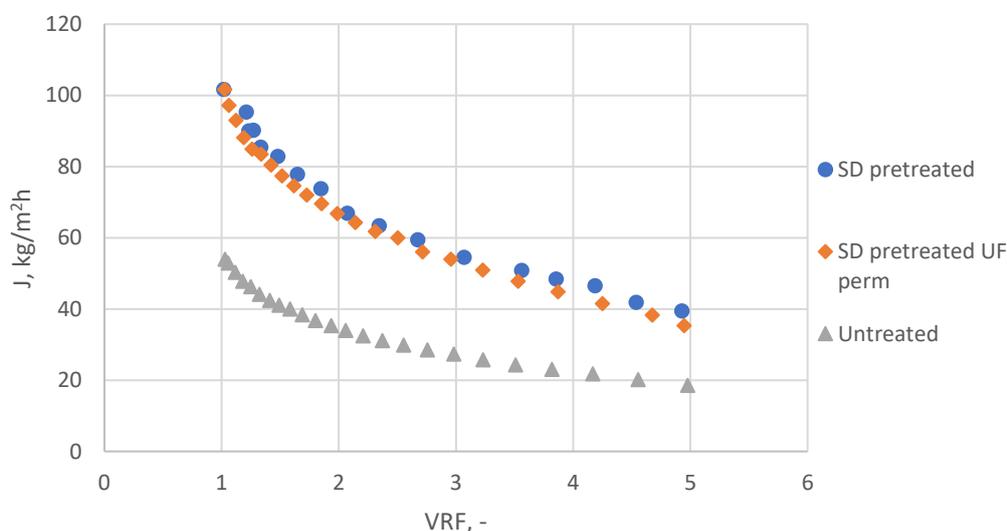


Figure 41 Permeate flux as a function of VRF for NF270 filtration in CR unit at 9 bar, 40 °C and 15.6 m/s tip speed.

Water permeabilities of filtrations are shown in Figure 42. Percentual fouling is 10 % for untreated, 31 %, for saw dust pretreated and 37 % for saw dust pretreated UF permeate. However, the difference comes only from measured water permeability of clean membranes. Permeabilities of fouled membranes are almost the same. Fouled membrane

permeabilities are same as shown in Figure 36. No clear reduction of fouling due to modified saw dust pretreatment can be seen in CR filtrations. Higher disruptive forces during filtration in CR than in dead-end filtration cell can mean that adsorptive pretreatment does not affect fouling prevention during filtration.

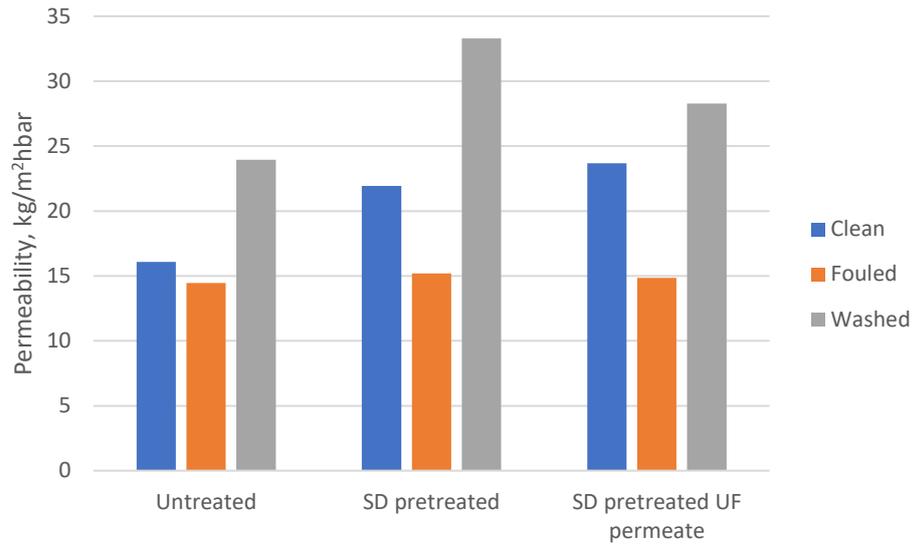


Figure 42 Water permeabilities of NF270 membranes before and after filtration and after washing.

8.4 Effect of pulsed corona discharge on debarking water and filtration

PCD was used for bark water filtrated through a 41 μm filtrating cloth (Figure 43). Significant changes were observed for color and turbidity, which increased during treatment, and toxicity which reduced during treatment. No real change of COD or TOC was observed, PCD does not remove any of those compounds, but it can possibly change molecular structure of the compounds or cleave molecules.

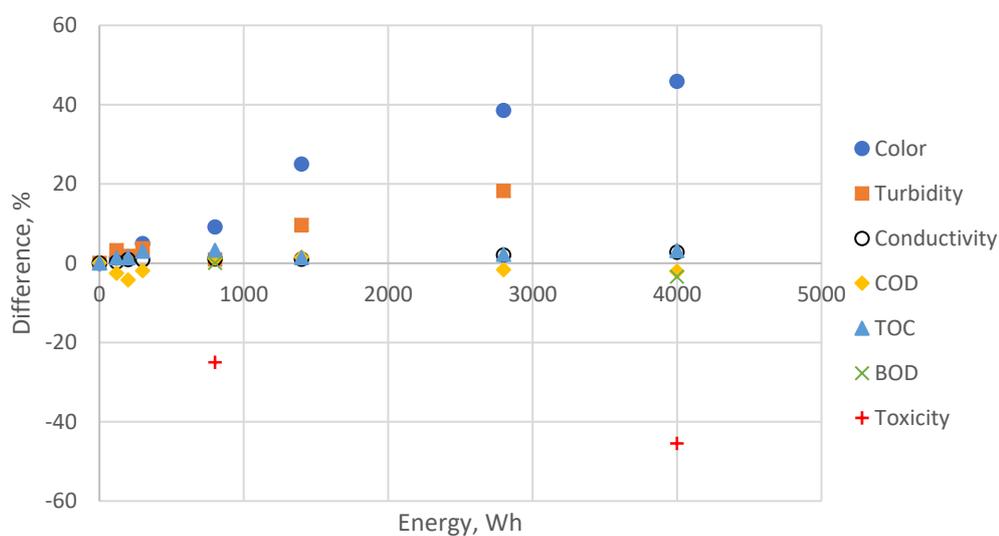


Figure 43 Effect of PCD treatment energy on color, turbidity, conductivity, COD, TOC, BOD and toxicity of 41 μm filtrated bark water at ambient pressure and 20 $^{\circ}\text{C}$.

Filtration with PCD pretreated bark water was done at 40 $^{\circ}\text{C}$, CR tip speed was 11.7 m/s and pressure at start 9 bar and then dropped to 8.5 bar. Permeate flux for this filtration is presented in Figure 44. Flux with PCD pretreated bark water was around 50 % greater than flux with bark water without pretreatment (Figure 27).

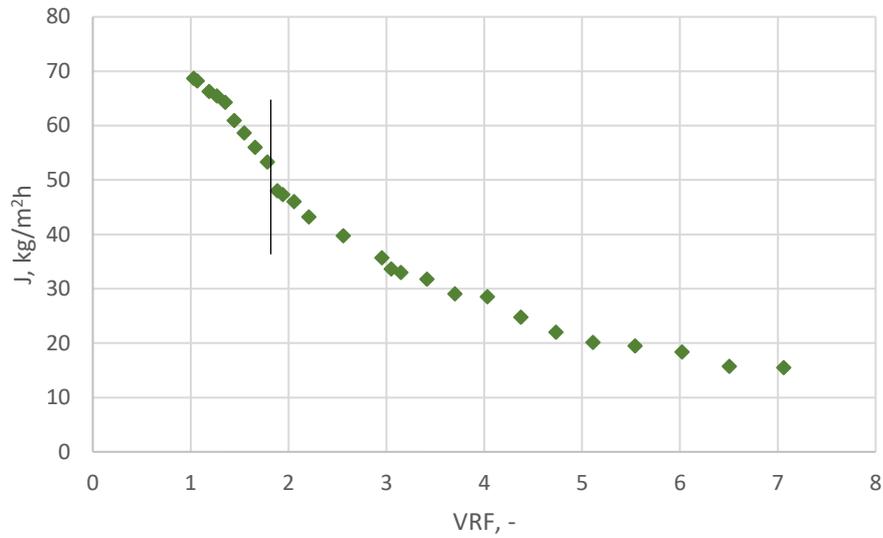


Figure 44 Permeate flux as function of VRF for NF270 membrane with PCD pretreatment. CR tip speed was 11.7 m/s and temperature 40 °C. Pressure at start was 9 bar and point of drop to 8.5 bar is presented with vertical line.

Water permeabilities before and after filtration and after washing are shown in Figure 45. Fouling during filtration was 30 % when without PCD pretreatment it was 35 % (Figure 29). VRF in PCD pretreated filtration was 7, and 5 without PCD, which means that PCD reduced fouling significantly as higher VRF should lead to increased fouling.

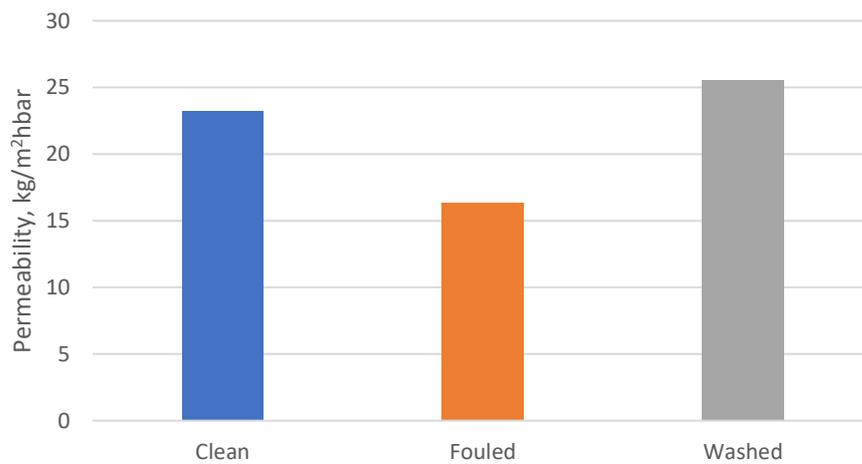


Figure 45 Water permeabilities for NF270 membrane before and after PCD pretreated bark water filtration and after washing.

Dark color of bark water could possibly hinder the effect of PCD, especially reducing the effectiveness of UV. Another PCD treatment was made on the permeate of NF270 filtration done at 40 °C (Figure 27). Only noticeable change was again in color and toxicity. Color increased rapidly at the beginning of the treatment and then started slowly declining after 2 000 Wh energy was used. Lower energy is required to reduce toxicity when treating nanofiltration permeate. At 4 000 Wh toxicity reduction is only 45 % when treating untreated bark water, when 94 % reduction is achieved at 2 000 Wh with nanofiltration permeate. Toxicity reduction slightly decreases when more energy is used in oxidation, at 10 000 Wh the reduction is 89 %. This is possibly due to formation of new toxic compounds. Slight correlation with color change is seen with toxicity change during oxidation in both untreated bark water and nanofiltration permeate.

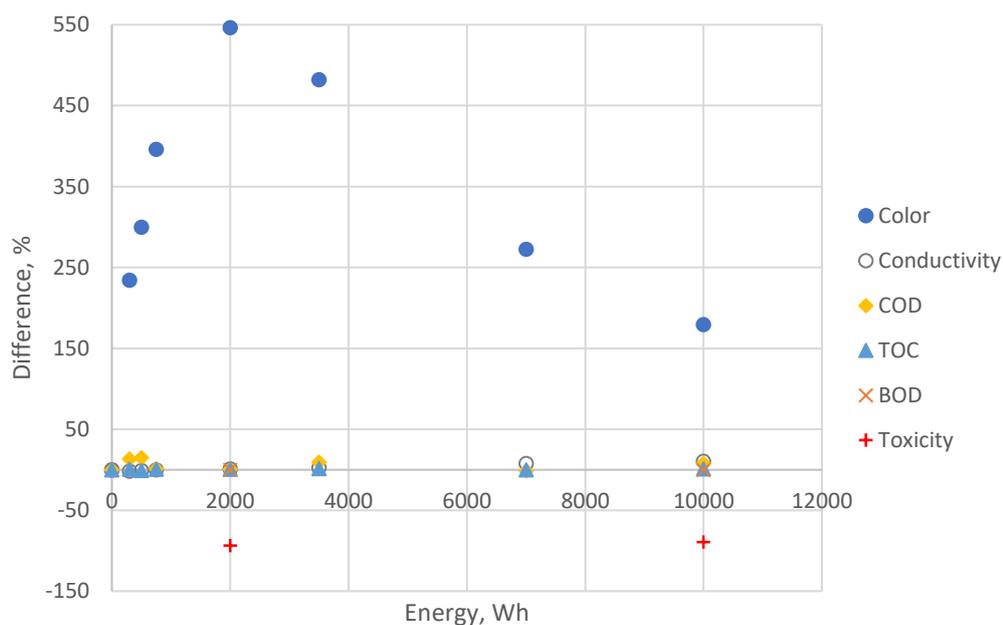


Figure 46 Percentage difference of color, conductivity, COD, TOC, BOD and toxicity as a function of energy used in PCD treatment for treating NF270 bark water permeate. Temperature and pressure during treatment were ambient.

More accurate analysis on the effect of PCD for bark water was done with UV-Vis spectroscopy. UV-vis spectra on bark water treated with PCD is presented in Figure 47.

Higher energy amounts result clearly to lower absorption in 300 – 340 nm range. In other wavelengths only slight differences can be seen.

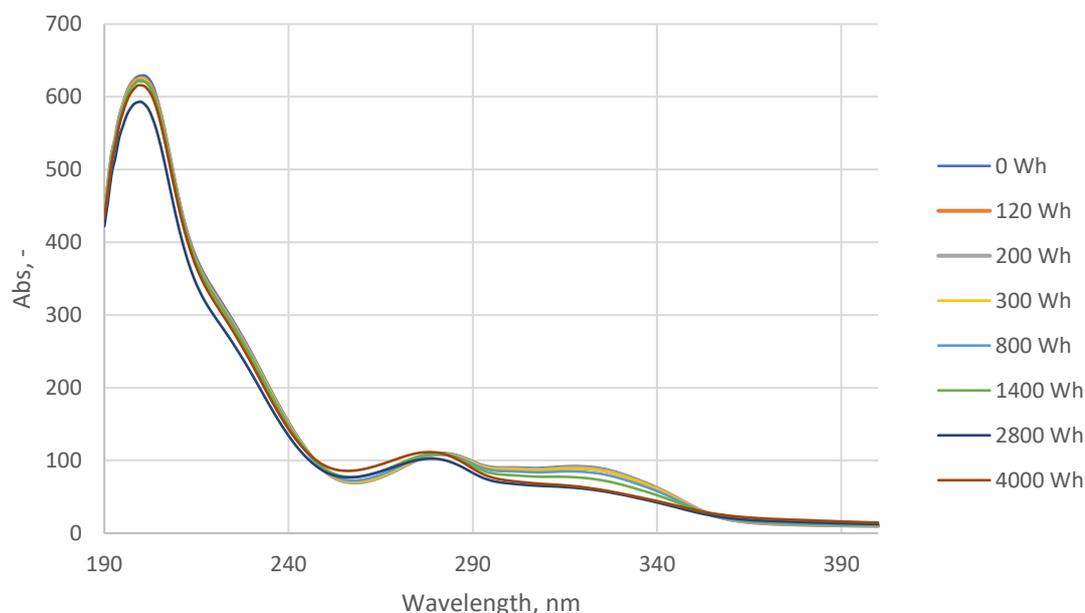


Figure 47 UV-Vis spectra of bark water treated with PCD at different energy amounts.

UV-Vis spectra for PCD treated NF270 permeate is shown in Figure 48. More clear changes in spectra can be seen than when treating bark water (Figure 47). UV absorbance in 260 – 350 nm range decreased with the used PCD energy. No clear peaks can be seen anymore at around 220 and 280 nm in 7 000 and 10 000 Wh spectra. Higher energy also lowers the absorbance in biggest peak at 200 nm. Further analysis is required to see compound level changes in the permeate.

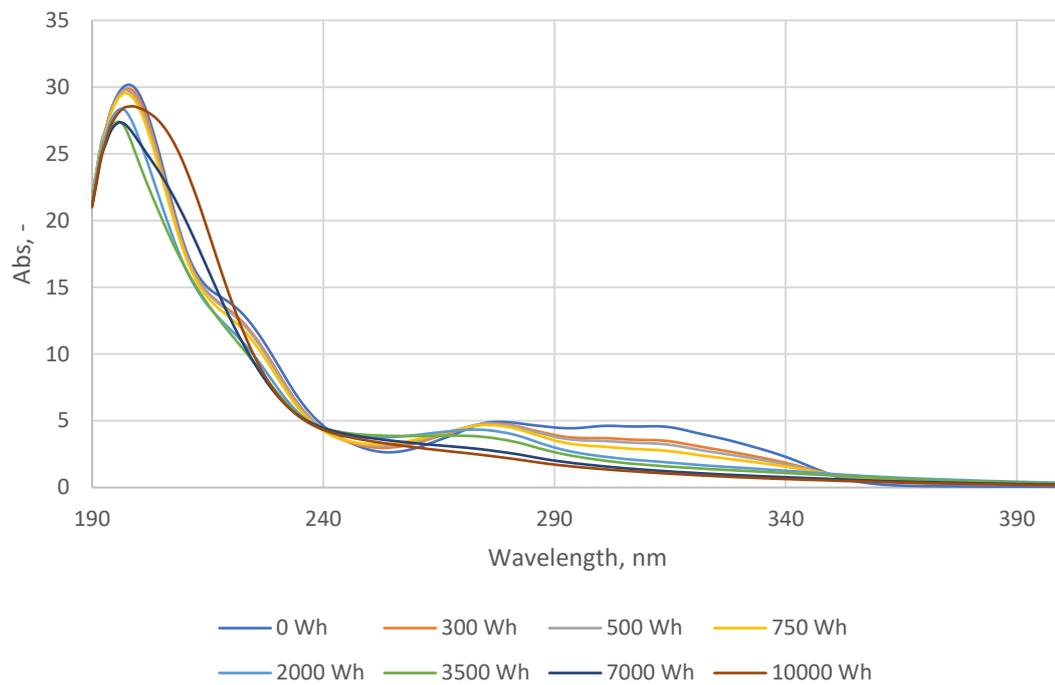


Figure 48 UV-Vis spectra of permeate of bark water filtrated through NF270 membrane treated with PCD at different energy amounts.

8.5 Purification efficiency of CR filtrations

Results of analysis from the samples of the filtrations shown in previous chapters are shown in Table XVIII - Table XXI. TOC concentrations in some samples are unusually high compared to COD concentrations. It is possible that some errors occurred during the TOC analysis of these samples.

EC₅₀ values for untreated debarking water were 0.6 %. EC₅₀ of whole Anjala mill effluent to wastewater treatment is around 15 %. Debarking water flow to wastewater treatment is around 21.6 m³/h and the total effluent flow is around 1 042 m³/h. Although debarking water flow is minimal compared to the whole mill effluent, it accounts approximately 52 % of the total effluent toxicity. More than 50 % toxicity contribution of debarking to the total toxicity of paper and pulp mills has been previously reported by Savolainen (1992). For nanofiltration permeates at VRF 5, EC₅₀ values were around 3 – 4 %. This reduces the toxic load of debarking by around 86 % and total mill effluent toxic load by 45 %. Toxicity contribution of debarking to the whole mill effluent is then reduced to only 13 %. Ultrafiltration did not reduce toxicity at 20 °C and minimal 10 % reduction was measured for filtration with modified saw dust at 40 °C.

Average of COD of Anjala mill debarking water is around 12 700 mg/L when whole year is taken into consideration. COD concentration of the whole mill effluent to the wastewater treatment at Anjala mill is around 1 800 mg/L. COD concentration contribution of debarking to the whole effluent is around 15 %. Nanofiltration reduces COD concentration in debarking to under 5 000 mg/L. This would reduce COD concentration of the whole mill effluent by around 10 % and reduce the COD contribution of debarking to 5 %.

Table XVIII Results of analysis from the samples of the filtrations when CR tip speed was 6.5 m/s and temperature 20 °C. Used bark water batch was 24.1.20. VRFs were 17.6 for RC70PP, 1.7 for NF270 and 2.3 for RC70PP + NF270. f: feed, c: concentrate and p: permeate.

	Color, PtCo	Turbidity, FAU	Conductivity, $\mu\text{S}/\text{cm}$	COD, mg/L COD	TOC, mg/L	Polyphenols, -	BOD ₇ , mg/L	EC ₅₀ , %
RC70PP f	7 900	3 371	2 869	20 680	21 515	90	9 000	0.6
RC70PP c	-	> 4 500	2 119	125 400	76 350	274	-	-
RC70PP p	2 210	22	2 563	15 800	11 123	60	7 600	0.6
NF270 f	8 700	3 809	2 869	20 600	21 926	92	-	-
NF270 c	-	> 4 500	2 879	32 800	19 503	99	-	-
NF270 p	420	47	825	2 750	3 867	1	1 500	4.9
RC70PP + NF270 f	2 700	32	2 653	16 360	10 910	61	-	-
RC70PP + NF270 c	3 160	92	2 597	23 100	17 602	66	-	-
RC70PP + NF270 p	22	6	743	2 120	898	1	1 400	5.7

Table XIX Results of analysis from the samples of the filtrations when temperature was 40 °C and used bark water batch was 24.1.20. VRFs were 13.3 for RC70PP, 4.9 for NF270 and 7.0 for PCD + NF270. f: feed, c: concentrate and p: permeate.

	Color, PtCo	Turbidity, FAU	Conductivity, $\mu\text{S}/\text{cm}$	COD, mg/L COD	TOC, mg/L	BOD ₇ , mg/L	EC ₅₀ , %
RC70PP c	75 600	> 4 500	3 080	122 500	153 042	-	-
RC70PP p	10 200	29	2 946	19 720	11 486	-	-
NF270 c	45 400	> 4 500	7 073	77 000	57 875	-	-
NF270 p	59	5	1 375	4 290	2 879	2 700	3.0
PCD + NF270 f	28 000	> 4 500	2 875	23 350	20 735	-	-
PCD + NF270 c	84 800	> 4 500	6 900	97 400	85 063	-	-
PCD + NF270 p	38	-	1 840	10 250	4 260	-	-

Table XX Results of analysis from the samples of the NF270 60 L and 12 L filtrations when CR tip speed was 11.7 m/s and temperature 40 °C. Used bark water was from 30.3.20 batch. VRF in both filtrations was 4. f: feed, c: concentrate and p: permeate.

	Color, PtCo	Turbidity, FAU	Conductivity, μ S/cm	COD, mg/L COD
60 L f	5 800	2 534	2 485	17 650
60 L c	26 400	> 4 500	5 725	54 600
60 L p at 1.04 VRF	14	1	7 46	2 340
60 L p at 1.47 VRF	13	2	902	3 130
60 L p final	9	1	1 135	3 450
12 L f	5 900	2 507	2 353	18 850
12 L c	24 000	> 4 500	5 644	60 000
12 L p	9	1	1 080	3 450

Table XXI Results of analysis from the samples of the modified saw dust treatment filtrations with RC70PP and NF270 when CR tip speed was 11.7 m/s and temperature 40 °C. Used bark water was from 7.5.20 batch. VRFs were 19.3 for RC70PP and 5 for RC70PP + NF270 and NF270 filtrations. f: feed, c: concentrate and p: permeate.

	Color, PtCo	Turbidity, FAU	Conductivity, μ S/cm	COD, mg/L COD	TOC, mg/L	Poly phenols, -	BOD ₇ , mg/L	EC ₅₀ , %
Before SD	7 350	2 623	1 945	11 450	17 091	44	5 000	0.6
After SD	5 800	2 902	1 905	13 350	17 682	33	7 000	0.9
SD RC70PP c	102 500	-	2 190	128 500	164 956	255	-	-
SD RC70PP p	3 520	53	1 860	7 300	8 792	26	5 400	1
SD RC70PP + NF270 c	10 240	2 129	4 690	46 000	69 469	118	22 000	0.6
SD RC70PP + NF270 p	79	5	1 020	2 640	3507	1	1 800	8.8
SD NF270 f	3 950	2 861	1 880	17 600	17 964	27	-	-
SD NF270 c	8 000	> 4 500	4 349	100 200	70 277	118	29 000	0.7
SD NF270 p	104	6	1 116	5 170	3 743	3	2 000	3.8
NF270 c	24 200	> 4 500	5 290	43 600	68 024	174	-	-
NF270 p	198	6	812	2 480	3 399	1	-	-

Retentions were calculated for all analysed parameters to see how effectively substances are removed during filtrations. Color, turbidity, conductivity, COD, TOC, BOD, toxicity and polyphenols retentions for filtrations made with 24.1.20 and 30.3.20 bark water batches are presented in Figure 49. With ultrafiltration, retentions clearly decrease as temperature is increased from 20 °C to 40 °C. High color reduction was achieved at 20 C, but no color was retained when temperature was increased to 40 C. TOC reduction is more than 20 percent unit greater than COD in ultrafiltration. Similar reductions for COD and BOD were reported by Tanskanen et al. (1997) where ultrafiltration reduced 33 % of COD and 12 % of BOD from less concentrated debarking water. The highest retention, 99 % in ultrafiltration was measured for turbidity.

All nanofiltrations achieve high retentions. Almost complete removal of color, turbidity and polyphenols are seen. TOC, COD, BOD and toxicity reach around 80 % retention, TOC slightly higher than COD. Hakala (2014) used same nanofiltration membrane on debarking water with 1585 mg/L COD. In her thesis COD and TC retentions were also over 80 %. RC70PP before NF270 filtration slightly increases all retentions. Retentions in PCD pretreated NF270 filtrations are lower due to higher VRF and possibly due to cleaving effect of oxidation on organic molecules. Although toxicity retentions are high in nanofiltrations, the amount of toxicity in permeates is still toxic as EC₅₀ value should be over 40 % to be considered nontoxic.

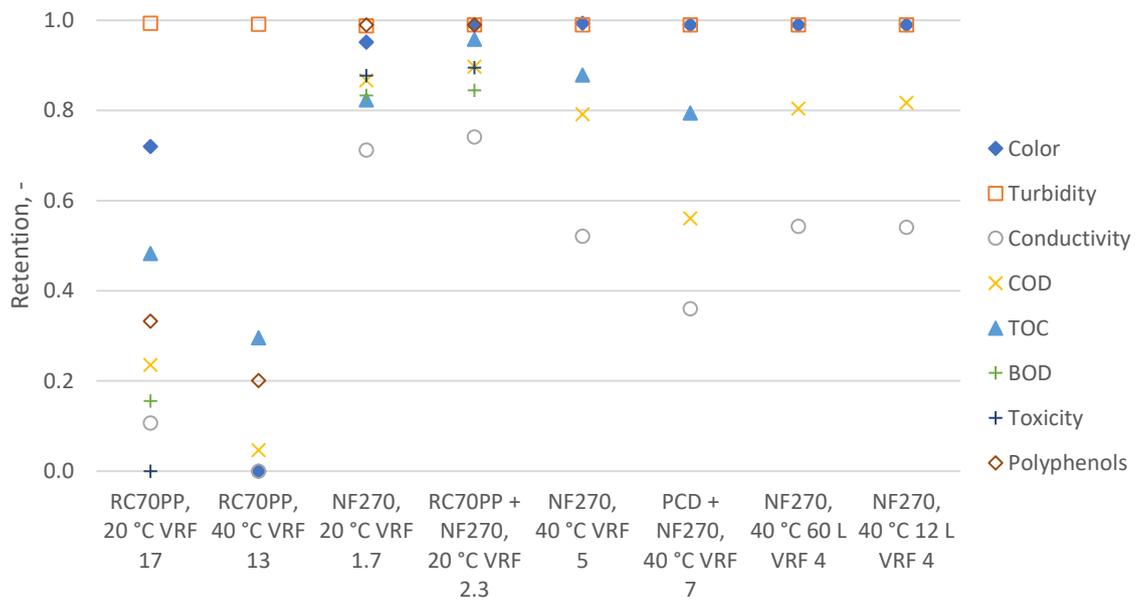


Figure 49 Retentions of color, turbidity, conductivity, COD, TOC, BOD, toxicity and polyphenols for different CR module filtrations made with 24.1.20 and 30.03.20 bark water batches.

It is known that retentions decrease when feed concentration increases due to diffusion in nanofiltration. This was tested during 60 L bark water filtration at 40 °C and 9 bar. Effect of increasing VRF on the retentions of NF270 membrane is shown in Figure 50. Clear decrease on retentions of COD and conductivity can be seen when VRF increases.

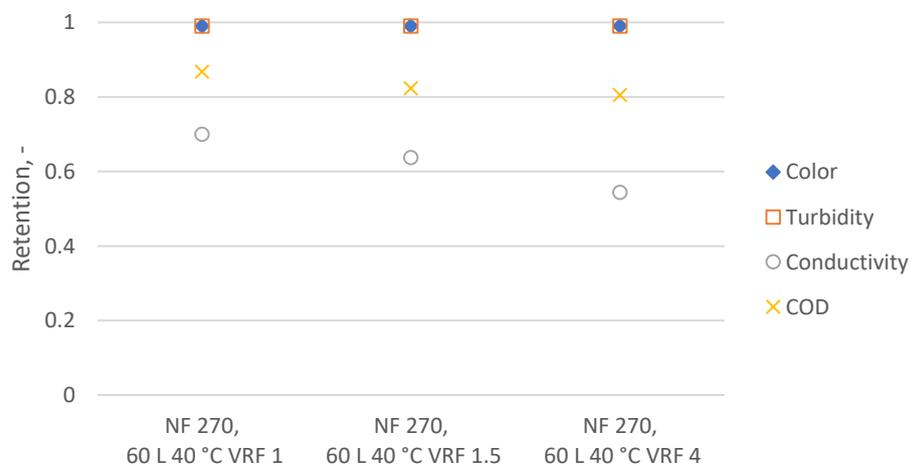


Figure 50 Effect of bark water VRF on the retention of color, turbidity, conductivity and COD for NF270 membrane. Filtration was done at 40 °C and 9 bar.

Retentions of filtrations made with 7.5.20 bark water batch are shown in Figure 51. Ultrafiltration of modified saw dust pretreated bark water retentates COD and TOC more effectively than in filtrations without pretreatment. RC70PP before NF270 again increases all retentions slightly. Normal nanofiltration with NF270 without any pretreatment achieves similar retentions to RC70PP + NF270 filtration. Saw dust pretreatment shows lower retentions compared to filtration without pretreatment in NF270 nanofiltrations.

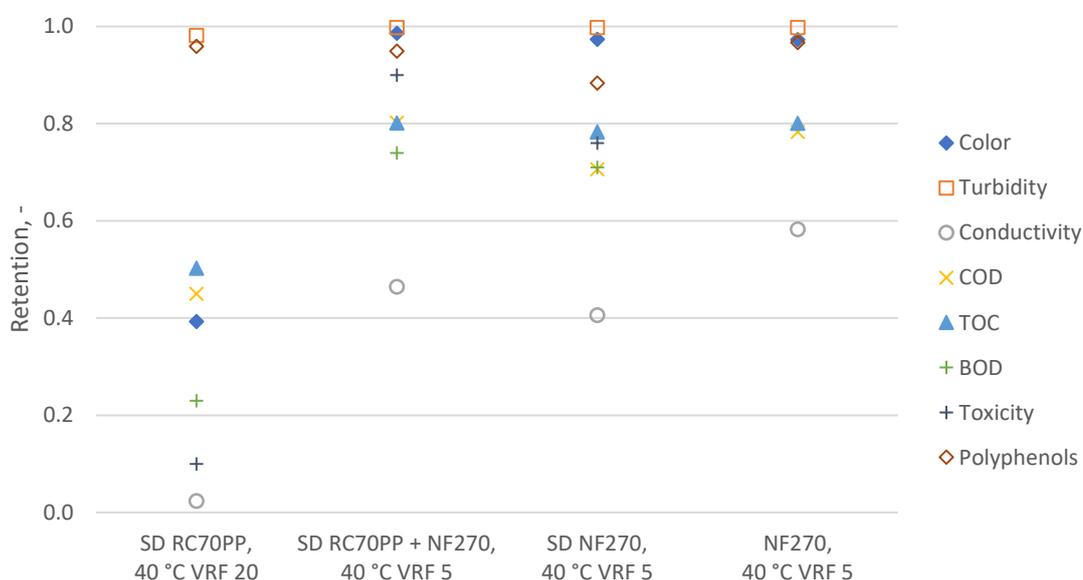


Figure 51 Retentions of color, turbidity, conductivity, COD, TOC, BOD, toxicity and polyphenols for different filtrations made with 7.5.20 bark water batch. SD means modified saw dust pretreatment.

Total retentions were calculated based on color, turbidity, conductivity, COD and TOC retentions. Total retentions for NF270 filtrations are shown in Figure 52. Total retentions for most filtrations are above 80 %. Lower total retention with modified saw dust pretreated NF270 filtration compared to untreated bark water filtration is observed. Retentions decreased only slightly due to higher VRF.

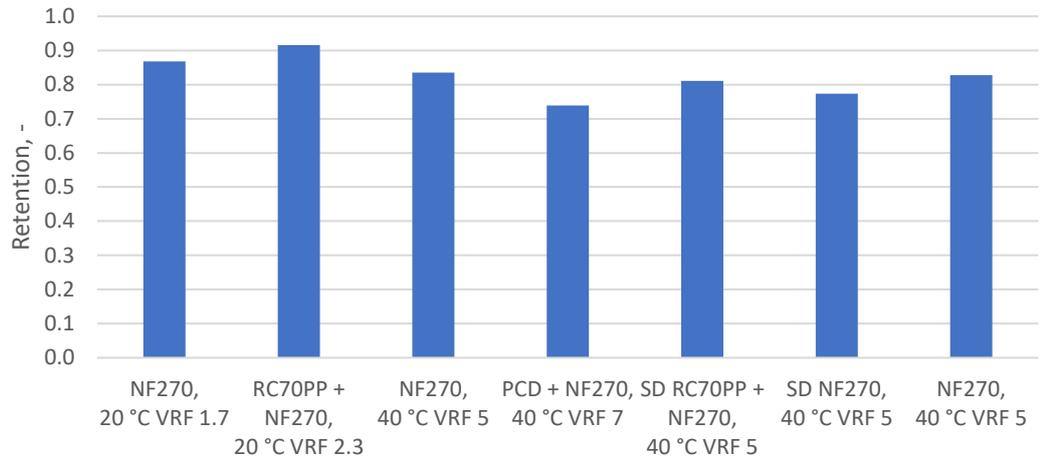


Figure 52 Total retentions for NF270 filtrations.

8.6 Suggested process configurations and cost estimation

Usage of ultrafiltration before nanofiltration slightly increases retentions of nanofiltration and increases nanofiltration permeate flux by 20 – 35 %. Proposed process configurations are shown in Figure 53. Values in process configurations are calculated based on VRF of 20 for RC70PP and VRF 5 for NF270 filtrations at 40 °C obtained during experiments. Single nanofiltration with NF270 membrane produces 17 % less concentrate and 5 % more permeate than NF270 combined with RC70PP. In other words, water recovery with single NF270 filtration is 80 % where in combined process it is 75 %.

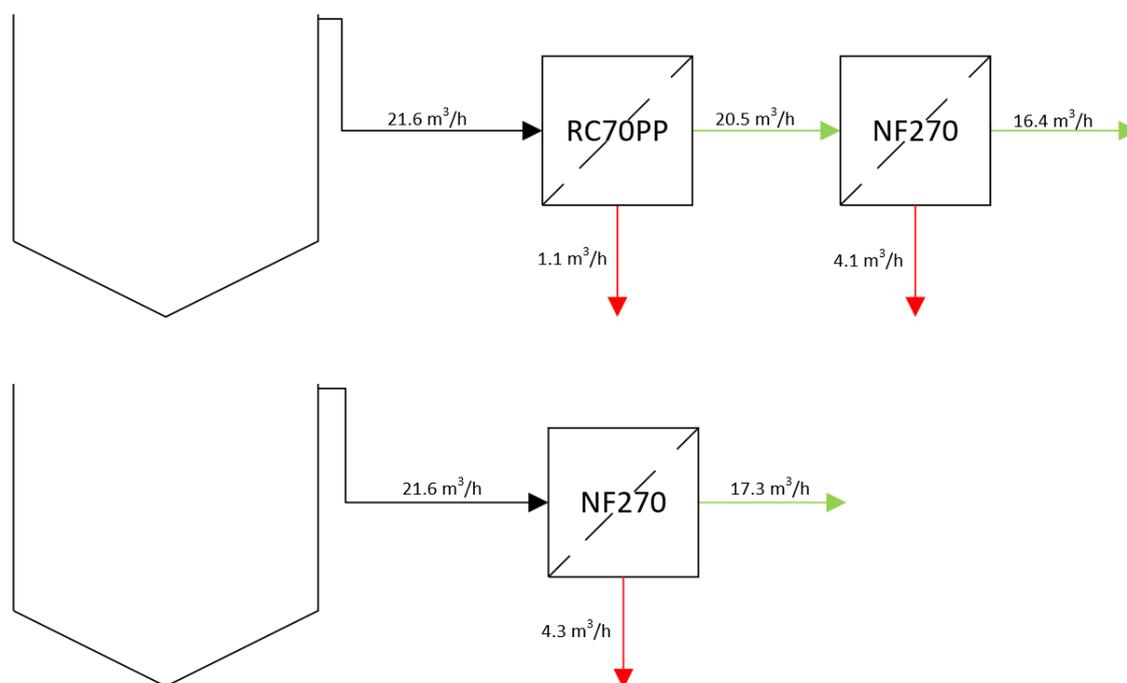


Figure 53 Flow chart of proposed ultrafiltration before nanofiltration and only nanofiltration process configurations. Green arrows represent permeates and red arrows represent concentrates.

Table XXII presents operating parameters for proposed process configurations and required membrane area with number of needed commercial CR units. Pretreatment with saw dust is added as process option to this table. Low capacities with NF270 filtrations equal to high membrane area required for filtrating whole 21.6 m³/h feed flow. Using saw dust as pretreatment greatly reduces the membrane area required.

Table XXII Possible process configurations and their pressures, permeate fluxes and capacities. Required membrane areas for 21.6 m³/h feed and required number of commercial CR units are also shown.

Method	p, bar	J, L/m ² h	A, m ²	140 m ² units, pcs
RC70PP	3	70	309	3
NF270	10	30	720	6
RC70PP → NF270	10	39	554	4
Saw dust → RC70PP	3	140	154	2
Saw dust → NF270	10	60	360	3
Saw dust → RC70PP → NF270	10	60	360	3

Table XXIII shows estimation of operating costs for nanofiltration, ultra- and nanofiltration and nanofiltration with saw dust pretreatment processes based on data from Sutela (2008). Nanofiltration energy consumption is estimated at 50 % higher than in ultrafiltration due to higher operating pressure required. Operating days used in cost estimation are 350 annually. One membrane wash per week and membrane lifetime of 20 months was used in calculations.

In operating cost estimation, energy usage attributes to most of the total cost. RC70PP before NF270 decreases the number of filtration units needed for nanofiltration but required units for ultrafiltration diminish the gains so operating costs for RC70PP before NF270 are slightly higher than in only NF270 filtration. Saw dust as pretreatment for NF270 doubles the permeate flux and in so halves the number of filtration units needed. Total cost reduction with saw dust pretreatment is also 50 %. Real operating cost will be higher because costs of saw dust pretreatment are not included estimation calculations. Estimating operating costs is difficult as no exact energy consumption for CR modules or industrial prices for membranes and washing solution can be found.

Table XXIII Operating cost estimation for different process configurations based on data from Sutela (2008). [1] Eurostat 2020

	NF270	RC70PP -> NF270	Saw dust -> NF270
140 m ² units	6	3 + 4 = 7	3
Electricity consumption, kWh/h	147	98 + 147	147
Electricity price ^[1] , €/kWh	0.0721	0.0721	0.0721
Washing solution, €/kg	2.5	2.5	2.5
Washing consumption, kg/m ² /wash	0.053	0.053	0.053
Energy cost, €/m ³	3.68	1.03 + 2.58 = 3.62	1.84
Washing cost, €/m ³	0.40	0.28 + 0.17 = 0.45	0.20
Membrane cost, €/m ³	0.73	0.52 + 0.31 = 0.83	0.37
Total, €/m ³	4.81	1.51 + 3.38 = 4.89	2.41

Rough estimate on the investment cost of single 140 m² CR unit is 500 000 € (Nurminen 2020). This includes installation, piping, instrumentation etc. Total investment cost is 3 000 000 € for 6 CR units required for NF270 filtration or 3 500 000 € for RC70PP + NF270 filtration. Using saw dust reduces the needed number of CR units to 3 and therefore the investment cost to 1 500 000 €.

PCD pretreatment for nanofiltration was not considered in process configurations as optimisation of required energy for PCD is necessary before it can be utilised for this application. When 4 kWh/m³ energy is used, the operational cost of PCD oxidation would be 0.36 €/m³. Around 50 % increase in nanofiltration permeate flux was observed after PCD pretreatment which reduces required CR units to 4 and operational costs of purification to 3.21 €/m³ + 0.36 €/m³ = 3.57 €/m³. As far as operational costs are concerned, PCD shows promising results for pretreatment of nanofiltration of debarking water.

9 Conclusions

In this thesis high shear rate membrane filtration was used to purify debarking plant wastewater from Stora Enso Anjala paper mill. Used membranes were ultrafiltration membrane RC70PP with 10 000 Da MWCO and nanofiltration membrane NF270 with 200 – 400 Da MWCO. Membrane filtrations were done as concentration filtrations using CR-250 filtration unit. Smaller scale experiments were done with dead-end filtration cell. Activated carbon, saw dust, modified saw dust and PCD were tested as pretreatment to improve the efficiency of filtrations.

Ultrafiltration removes around 20 – 40 % of organic load from bark water at 14 – 20 VRF. Higher removal efficiency is required for the usage of only ultrafiltration. COD and TOC retentions on all nanofiltrations are above 70 % which should drastically reduce the outgoing pollution load to wastewater treatment system. COD concentrations in Anjala paper mill debarking plant outlet during summer are 6 000 – 12 000 mg/L. COD concentrations in NF270 permeates are 2 000 – 5 000 mg/L which are clearly below current COD concentration levels. Toxicity reduction in nanofiltration is also significant but permeate is still toxic.

Washing of RC70PP membranes with 0.5 % Ultrasil 110 did not restore membrane permeability fully. Some decrease of permeability could come from compaction of membrane during filtration. With NF270 membranes washing cleaned fouling and increased water permeabilities. Around 20 % drop of water permeability 1 – 3 days after washing was observed in NF270 membranes when membranes were kept in water. This indicates that swelling of membrane pores occurred during washing.

Usage of modified saw dust as pretreatment greatly increased the permeate flux during both ultra- and nanofiltrations. Slight decrease of fouling was also observed. Unmodified saw dust was also tested in single small-scale experiment. It did not retain high permeate flux as well as modified saw dust, but still increased the flux significantly. Possibility to use unmodified saw dust would benefit industrial scale usage of saw dust as pretreatment because saw dust modification would require additional process infrastructure. Vast amounts of saw dust required for industrial scale can be complicated. Saw dust would require drying after use before it could be applicable for use as energy source.

Used energy during PCD pretreatment was 4 kWh/m³. Pretreatment had high effect on color and turbidity of bark water. Small decrease of toxicity was also seen during treatment. Permeate flux of NF270 increased by around 50 % when filtrating PCD pretreated bark water and fouling was slightly reduced. UV-Vis spectra of treated bark water revealed small changes in the composition of bark water. PCD had stronger effect on the purification of the permeate of nanofiltration than on the original bark water. Color changed the most again in permeate treatment. No reduction of COD or TOC was measured in both PCD oxidations. UV-Vis spectra showed that changes in molecular structure of occurred, meaning that organic compounds were only cleaved during oxidation rather than degraded. More complex changes were seen in UV-Vis spectra of PCD treated NF270 permeate. Dark color, high turbidity and concentrations reduced the effect of PCD when treating bark water.

Due to low feed volumes and permeate fluxes in nanofiltration, operating costs of different membrane process configurations are high. Most of the operating costs comes from the energy consumption of the CR module. Using RC70PP as pretreatment for NF270 increased the permeate flux and in so reduced required NF270 membrane area but did not lower the operating costs as required RC70PP membrane area offsets the reduction for NF270 area. In the cost estimation, modified saw dust pretreatment reduced operating costs by 50 %, but the estimation does not include any costs for the usage of saw dust. PCD pretreatment reduced operational costs of nanofiltration process, but more optimisation of PCD process is required to consider its use in industrial scale.

Treatment for the concentrate generated from ultra- and nanofiltration should be considered when designing membrane filtrations. Additional treatment e.g. oxidation is required before the concentrate can be sent to wastewater treatment plant. Concentrate can be dried or evaporated to remove excess water and then concentrate could be burnt for energy.

One potential option could be the total closure of debarking plant circulating water. If used nanofiltration membrane can retain performance in longer time scale, permeate from filtration could be recycled back to circulating water in debarking plant. This would greatly reduce outgoing waste as only wastewater generated from debarking process would be the concentrate from filtration. Possible concentration of impurities in the circulating water of debarking could still be problematic.

10 Further research

Parameters affecting the membrane filtrations should be more extensively studied to improve permeate flux during filtration. Effects of temperature, CR tip speed and feed volume on permeate flux and fouling during filtrations were evaluated in this study. Feed volumes and filtration times used in this thesis were miniscule compared to industrial scale applications. Even though no harmful effect for increasing filtration time and feed volume was seen, experiments should be conducted on continuous filtrations with cubic meters of feed and filtration times of up to one month. pH is one major parameter affecting nanofiltration, which was not studied in this thesis. Small scale experiments with bark water with pH variation of e.g. 3 – 11 should be conducted to see the effect of pH on permeate flux and retentions.

More detailed analysis on the composition of filtration fractions is suggested to know how well different wood extractives are removed during filtrations. Previous research has shown that ultrafiltration retentates e.g. resin acids effectively, but no research has been done for debarking plant wastewater filtrations. Utilisation of filtration concentrates is not discussed in this thesis. Spruce bark contains many potential compounds, but their extraction can be problematic. UV-Vis analysis of filtration concentrates shows clear concentration of wood extractives e.g. polyphenols. Concentrate could provide high concentrations of useful compounds. Proper analysis of individual compounds is necessary to determine the possibility of economical compound extraction from concentrates.

Optimisation of membrane washing can lead to significant reduction of process operating costs. Volume and concentration of washing solution, temperature and washing time are all parameters that need to be optimised. Possibility to use other washing solution than Ultrasil 110 used in experiments is also possible. There is research about using NaOH as washing solution for membrane fouling. NaOH should be researched in this context as it is used in Anjala paper mill already and could further reduce washing costs.

Usage of saw dust as adsorbent prior to filtrations provided promising results. Optimal concentration of saw dust should be determined as only 10 m-% of saw dust was used in experiments. It is unclear if more saw dust could yield better results or did used concentration reach an equilibrium. To gain better understanding on the adsorption

process, used saw dust should be analysed before and after usage to identify what compounds are adsorbed to the saw dust. Regeneration of used saw dust should be researched to reduce waste formed in the process.

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Appendixes

Appendix I UV-Vis spectra

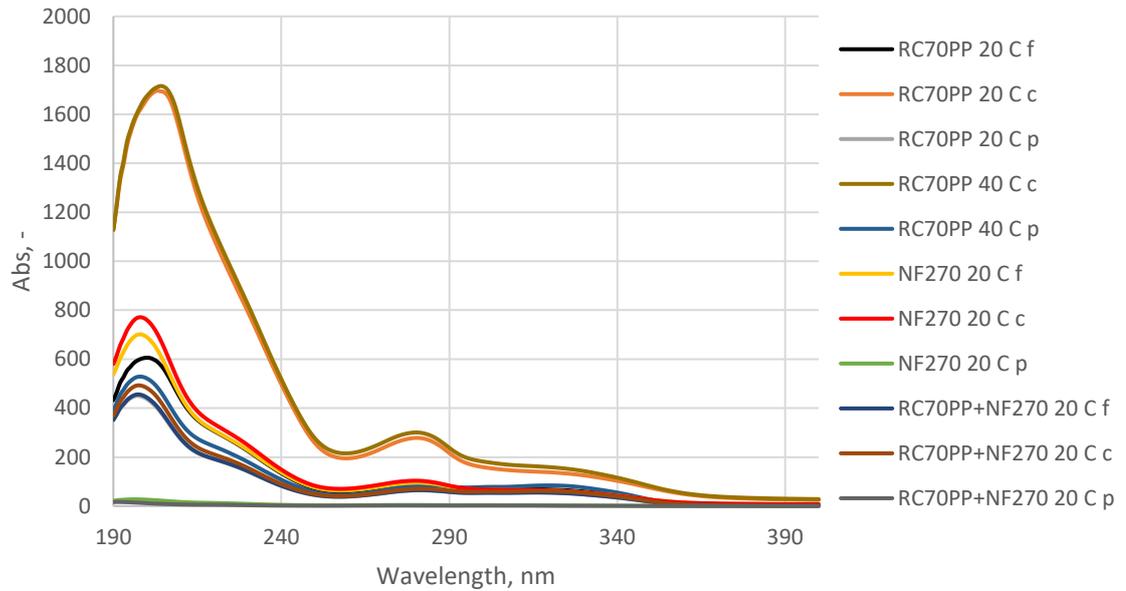


Figure 54 UV-Vis spectra of filtrations shown in Figure 27.

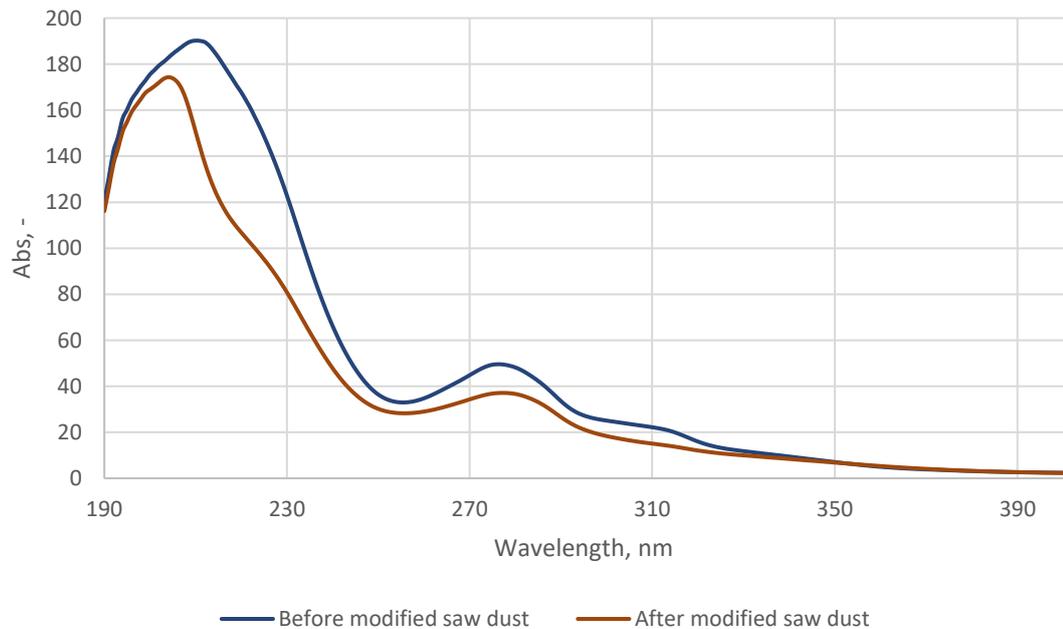


Figure 55 UV-Vis spectra of bark water from 7.5.20 batch before and after modified saw dust treatment.

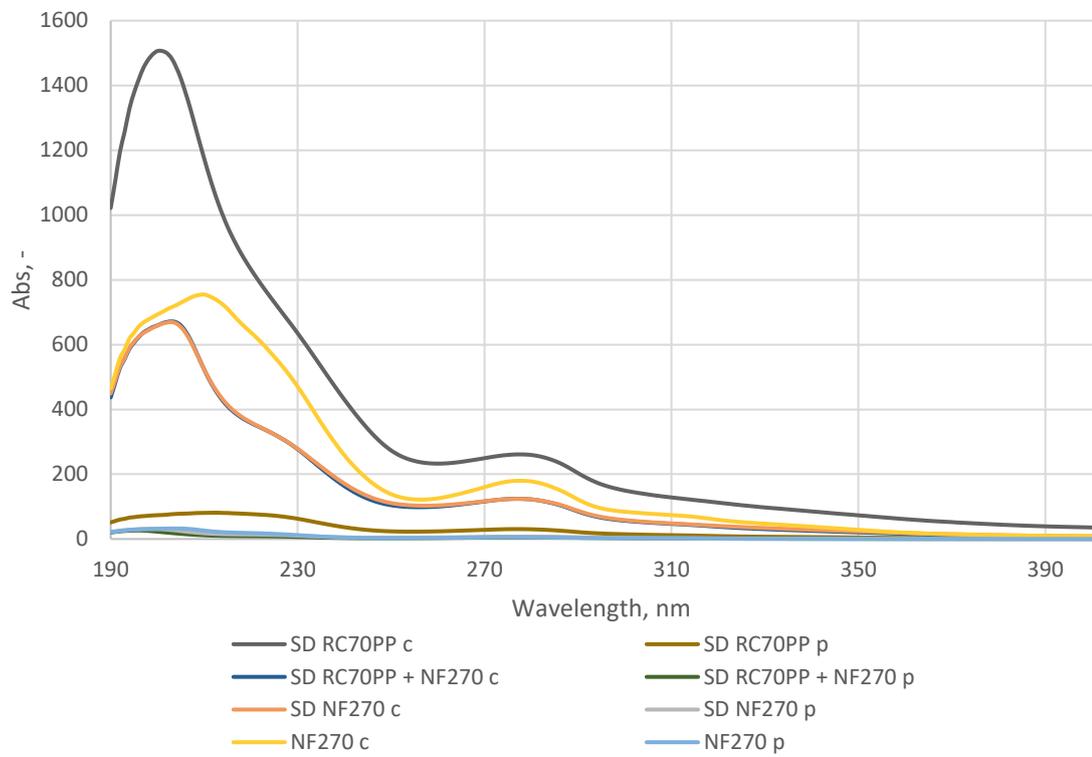


Figure 56 UV-Vis spectra of bark water from 7.5.20 batch filtrations.

Appendix II PCD treatment analyses

Table XXIV Results of analysis from the samples of the bark water PCD pretreatment at different energy amounts.

Energy, Wh/m ³	Color, PtCo	Turbidity, FAU	Conductivity, μ S/cm	COD, mg/L COD	TOC, mg/L	Polyphenols, -	BOD ₇ , mg/L	EC ₅₀ , %
0	19 200	3 807	2 798	23 850	20 099	110	-	-
120	19 450	3 932	2 805	23 250	20 373	108	-	-
200	19 500	3 877	2 824	22 850	20 379	108	-	-
300	20 150	3 950	2 822	23 400	20 700	108	-	-
800	20 950	3 843	2 828	24 150	20 752	109	9 000	0.8
1400	24 000	4 173	2 826	24 200	20 379	109	-	-
2800	26 600	4 500	2 855	23 450	20 537	102	-	-
4000	28 000	4 500	2 875	23 350	20 735	111	8 700	1.1

Table XXV Results of analysis from the samples of the NF270 permeate treated with PCD at different energy amounts.

Energy, Wh/m ³	Color, PtCo	Turbidity, FAU	Conductivity, μ S/cm	COD, mg/L COD	TOC, mg/L	Polyphenols, -	BOD ₇ , mg/L	EC ₅₀ , %
0	73	13	1 365	4 180	3 599	5	2 700	3
300	244	22	1 342	4 740	3 619	5	-	-
500	292	22	1 352	4 810	3 564	5	-	-
750	362	24	1 366	4 230	3 632	5	-	-
2000	472	22	1 379	4 210	3 622	4	2 700	9.4
3500	425	24	1 402	4 570	3 648	4	-	-
7000	272	24	1 474	4 130	3 601	3	-	-
10000	204	29	1 512	4 510	3 638	2	2 600	5.5