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REDUCTION OF CHEMICAL OXYGEN DEMAND FROM PULP MILL WASTEWATER WITH INTEGRATED MEMBRANE FILTRATION

Faculty of Engineering and Natural Sciences
Bachelor's Thesis
January 2019

ABSTRACT

Linda Määttä: Reduction of Chemical Oxygen Demand from Pulp Mill Wastewater with Integrated Membrane Filtration
Bachelor's Thesis
Tampere University
Bachelor's Degree Programme in Environmental and Energy Engineering
January 2019

The pulp industry generates high volumes of wastewater from 10 to 90 m^3 per tonne of produced pulp. The wastewater contains large quantities of various organic compounds which total amount can be measured, for example, with a chemical oxygen demand test. The organic compounds can cause environmental degradation if they are discharged into the near water bodies, and because of that, the treated wastewater has to have high and consistent quality.

This result can be achieved, for example, with membrane filtration process, which can be in use in the tertiary treatment of the wastewater treatment. The membrane processes include micro-, ultra-, nanofiltration and reverse osmosis, which can remove contaminants from water very effectively. The effectiveness of the membrane filtration is, however, highly affected by membrane fouling, which restrains the usage of the membrane processes in the field of the wastewater treatment. During the membrane fouling process, the membrane flux is decreased fast, which causes a decline in the filtration performance of the membrane.

The aim of this thesis is to investigate the suitability of the integrated membrane filtration system for the wastewater treatment of the case study's pulp mill. The integrated membrane filtration system contains a membrane bioreactor, that combines biological wastewater treatment with membrane filtration, and a membrane filtration unit, which can be, for example, ultrafiltration. In this study, the compounds of the pulp mill's wastewater, which can still cause membrane fouling in the membrane filtration unit, are also investigated. For example, lignin, adsorbable organic halides, colored compounds and wood extractives, are the possible foulants, because they are challenging to remove from the wastewater with the conventional wastewater treatment processes.

The suitable options for the membrane fouling reduction are also suggested from the aspect of the case study's pulp mill. The suggested options, which are simple, effective and cost-effective, include optimizing the operating conditions of the membrane filtration unit and the membrane bioreactor and elevating the hydrophilicity of the membrane surface by the membrane material selection or precoating the membrane surface with a surfactant. With a help of the above-mentioned methods, the lowest level of the membrane fouling can be obtained, when the integrated membrane filtration system can be a very suitable option for the wastewater treatment of the pulp mill.

Keywords: pulp mill, wastewater, COD, membrane filtration, membrane fouling

TIIVISTELMÄ

Linda Määttä: Sellutehtaan kemiallisen hapenkulutuksen hallinta integroidulla kalvosuodatus-tekniikalla
Kandidaatintyö
Tampereen yliopisto
Ympäristö- ja energiatekniikan kandidaatin tutkinto-ohjelma
Tammikuu 2019

Selluteollisuus muodostaa huomattavia määriä jätevettä, jonka määrä vaihtelee välillä 10–90 m^3 tuotettua sellutonnia kohden. Jätevesi sisältää runsaasti erilaisia orgaanisia yhdisteitä, joiden kokonaismäärää voidaan kuvata esimerkiksi jäteveden kemiallisen hapenkulutuksen avulla. Orgaanisten yhdisteiden päästessä valumaan läheisiin vesimuodostumiin, ne voivat aiheuttaa ympäristön tilan heikentymistä, jonka johdosta puhdistetun jäteveden laatu tulee olla korkea ja yhtenäinen.

Kyseiseen puhdistustulokseen voidaan päästä esimerkiksi käyttämällä kalvosuodatustekniikkaa jäteveden puhdistuksen tertiäärivaiheessa. Kalvosuodattimiin kuuluvat mikro-, ultra-, nano- ja käänteisosmoosisuodatus, jotka puhdistavat jätevettä tehokkaasti. Kalvosuodatuksen tehokkuuteen vaikuttaa kuitenkin suuresti kalvon tukkeutuminen, joka rajoittaa kalvojen käyttöönottoa jäteveden puhdistuksessa. Kalvon tukkeutuessa kalvon vuo pienenee nopeasti, mikä aiheuttaa kalvosuodatuksen suorituskyvyn laskua.

Työn tarkoituksena on tutkia integroidun kalvosuodatussysteemin soveltuvuutta tapaustutkimuksen sellutehtaan jäteveden puhdistukseen. Integroitu kalvosuodatussysteemi sisältää membraanibioreaktorin, joka yhdistää jäteveden biologisen puhdistuksen kalvosuodatukseen, sekä erillisen kalvosuodattimen esimerkiksi ultrasuodattimen. Työssä selvitetään myös ne sellutehtaan jäteveden yhdisteet, jotka voivat vielä aiheuttaa kalvopinnan tukkeutumista kalvosuodatimessa. Näihin mahdollisesti tukkeutumista aiheuttaviin yhdisteisiin kuuluvat esimerkiksi ligniini, orgaaniset halogeeniyhdisteet, värilliset yhdisteet sekä puun uuteaineet, jotka ovat haastavia poistaa puhdistettavasta jätevedestä tavallisilla puhdistusmenetelmillä.

Työssä esitellään myös tapaustutkimuksen sellutehtaan näkökulmasta suositeltavat vaihtoehdot kalvon tukkeutumisen vähentämiseen. Näihin yksinkertaisiin, tehokkaisiin ja kustannustehokkaisiin vaihtoehtoihin kuuluvat kalvosuodattimen ja membraanibioreaktorin käyttöolosuhteiden optimointi, kalvopinnan hydrofiilisyyden kasvattaminen kalvomateriaalin valinnalla tai kalvopinnan esipäällystyksellä. Näiden edellä mainittujen vaihtoehtojen avulla voidaan saavuttaa alhaisin taso kalvon tukkeutumiselle, jolloin integroitu kalvosuodatussysteemi vaikuttaa olevan hyvin sopiva vaihtoehto sellutehtaan jäteveden puhdistukseen.

Avainsanat: sellutehdas, jätevesi, COD, kalvosuodatus, kalvon tukkeutuminen

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LIST OF SYMBOLS AND ABBREVIATIONS

AOX	Adsorbable Organic Halides
BDCOD	Biodegradable Chemical Oxygen Demand
BOD	Biochemical Oxygen Demand
CAS	Conventional Activated Sludge
COD	Chemical Oxygen Demand
MF	Microfiltration
MBR	Membrane Bioreactor
MLSS	Mixed Liquor Suspended Solid
MLVSS	Mixed Liquor Volatile Suspended Solid
NBDCOD	Non-Biodegradable Chemical Oxygen Demand
NBDPCOD	Non-Biodegradable Particulate Chemical Oxygen Demand
NBDSCOD	Non-Biodegradable Soluble Chemical Oxygen Demand
NF	Nanofiltration
NOM	Natural Organic Matter
POP	Persistent Organic Pollutant
RBCOD	Readily Biodegradable Chemical Oxygen Demand
RO	Reverse Osmosis
SBCOD	Slowly Biodegradable Chemical Oxygen Demand
SRT	Sludge Retention Time
SS	Suspended Solids
TCOD	Total Chemical Oxygen Demand
ThOD	Theoretical Oxygen Demand
UF	Ultrafiltration
VOC	Volatile Organic Compound
VRF	Volume Reduction Factor
WWTP	Wastewater Treatment Plant

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1. INTRODUCTION

Pulp industry is a field of industry which uses high volumes of water in its manufacturing processes (Adnan *et al.* 2009; Gönder *et al.* 2012). Pulp mills have been estimated to generate 10–90 m^3 of wastewater per air dry tonne of pulp (ADt) (European Commission 2015). In addition to a high formation of wastewater, the wastewater from pulp mills also contains various potential pollutants, such as organic matter, which can be measured as chemical oxygen demand (COD) (Ali & Sreekrishnan 2001; Metcalf & Eddy 2014, p. 123). The pollutants of the wastewater can cause environmental degradation if they are discharged into the near water bodies (Ali & Sreekrishnan 2001).

Because of the formation of large volumes of polluted wastewater, the pulp industry is forced to introduce new advanced treatment processes (Gönder *et al.* 2012). The pressure to seek these new processes has developed from costs of fresh water and possible deficiency of fresh water as well as from tightened environmental regulations which regulate the wastewater effluent standards (Adnan *et al.* 2009; Gönder *et al.* 2011). These new advanced treatment processes include membrane filtration processes which have high range of various applications, from medical usage to wastewater treatment (Cheryan 1986, cited in Shi *et al.* 2014). The use of membrane processes is increasing in wastewater treatment of pulp industry because these processes can remove contaminants from water very effectively, for example, ultrafiltration (UF) process has obtained COD removal rate of even 85–90% (Zaidi *et al.* 1992; Gönder *et al.* 2012).

The membrane processes are introduced in use in pulp mills' wastewater treatment plants (WWTP) which operate internal process water recycling as well as the treatment of wastewater effluents (Adnan *et al.* 2009; Gönder *et al.* 2012). Currently, the wider applications of membrane processes are, however, limited by membrane fouling (Gönder *et al.* 2011). During the membrane fouling process, the membrane flux is decreased fast, which causes a decline in the filtration performance of the membrane (Gönder *et al.* 2011; Shi *et al.* 2014). Membrane fouling process is caused by foulants, such as biological substances, and it can be divided into four general forms: particulate fouling, scaling, organic fouling and biological fouling (Amy 2008; Metcalf & Eddy 2014, pp. 1198–1199). Membrane fouling is a limiting factor in the membrane processes because it affects the process operation, pretreatment demands of the wastewater and cleaning of the membrane (Metcalf & Eddy 2014, p. 1198). The above-mentioned membrane fouling factors with increased need of energy may cause higher operational costs for pulp mills (Metcalf & Eddy 2014, p. 1198; Shi *et al.* 2014).

The aim of this study is to investigate the suitability of the integrated membrane filtration system for the wastewater treatment of a pulp mill. The result of the wastewater treatment is especially examined by the removal rate of the COD. The integrated membrane filtration system contains a membrane bioreactor (MBR), which fuses biological wastewater treatment with membrane filtration, and a membrane filtration unit. Because both components of the integrated membrane filtration system contain a membrane surface that may foul, the other aim of this study is to investigate which factors lead to membrane fouling, and how to reduce it.

Chapter 2 focuses on the wastewater of the pulp mill. In this chapter, the different pollutants and factors affecting the pulp mill wastewater are characterized. Chapter 3 focuses on the technique of the membrane processes and the fouling of the membranes. In chapter 4, the case study, the quality of its wastewater after the MBR and the emission standards of the wastewater are introduced. This chapter focuses also on the alternatives that can reduce the fouling of the membranes in the WWTP of the case study. In the end the of the thesis the conclusions, considering the integrated membrane filtration system in the pulp mill wastewater treatment, are presented.

2. CHARACTERIZATION OF PULP MILL WASTEWATER

The pulp industry is a water intensive industry similarly, for example, to metal and chemical industry (Roppola *et al.* 2009; Gönder *et al.* 2011; Gönder *et al.* 2012; Subramonian *et al.* 2014). In addition to voluminous water consumption and wastewater generation, pulp industry also generates notable quantities of potential pollutants: gaseous, aqueous, particulate and solid waste. The aqueous effluents are the greatest concern of the potential pollutants, because the manufacturing processes generate large amounts of wastewater which have high pollutant concentration, for example, bleaching pulp mill can generate 4033 kg of colored compounds per tonne of produced pulp (Yen *et al.* 1996, cited in Pokhrel & Viraraghavan 2004; Ali & Sreekrishnan 2001). Therefore, the focus of this thesis is on aqueous effluents.

The wastewater of the pulp mills contains high amounts of COD, which is the focus of the next chapter. The wastewater contains also high quantities of biochemical oxygen demand (BOD), suspended solids (SS), toxic compounds such as adsorbable organic halides (AOX), and colored compounds such as humic acids (Ali & Sreekrishnan 2001; Pokhrel & Viraraghavan 2004). Some of the pollutants occur naturally in wood such as lignin and fibers, and some, for instance, chlorinated lignins and dioxins, are formed during the pulp manufacturing process (Ali & Sreekrishnan 2001).

2.1 The Chemical Oxygen Demand of the Wastewater

COD is a sum parameter that is used to approximate the quantity of organic matter in wastewater (ISO 1989) The organic matter of the wastewater contains various organic compounds with different qualities (Wentzel *et al.* 1999). In the COD test, organic matter is chemically oxidized by dichromate or by permanganate in acid conditions. The quantity of oxidant, which is used in the COD test, is equivalent to the oxygen demand quantity of the organic matter. (ISO 1989) This specified amount of oxygen, is oxygen consumed by organic matter of the wastewater under specific reaction conditions (Metcalf & Eddy 2014, p. 123; Choi *et al.* 2017).

COD of the water can also be estimated by calculating the theoretical oxygen demand (ThOD) value, which is amount of oxygen that is required to oxidize an organic compound to its final oxidation form (Metcalf & Eddy 2014, p.116). ThOD can be calculated if the chemical formula of the organic matter is known (Horan 1990, p. 12). ThOD is determined with the balanced equation of endogenous respiration, for example, the equation for cellulose, which is an essential structural constituent of wood, is

$$(C_6H_{10}O_5)_n + 6\text{n}\, O_2 \rightarrow 6\text{n}\, CO_2 + 5\text{n}\, O_2 \quad (1)$$

where one mole of cellulose ($(C_6H_{10}O_5)_n$) requires 6n moles of oxygen (O_2) to form 6n moles of carbon dioxide (CO_2) and 5n moles of water (H_2O), in the endogenous respiration process (Biermann 1996, p. 406; Metcalf & Eddy 2014, pp. 116, 125–126). The experimentally measured COD value of the water is, however, lower than ThOD value because in the ThOD calculation it is assumed that the whole amount of the organic compound is oxidized into the final oxidation form (Horan 1990, p. 12). In reality, the biodegradability of the organic compound, the conditions and the metabolism of the organisms affect to the COD of the organic compound (Horan 1990, p. 12; Choi e*t al.* 2017).

The total COD (TCOD) of the wastewater is separated, according to their biodegradation character, into two main fractions: biodegradable COD (BDCOD) and non-biodegradable COD (NBDCOD) (Figure 1) (Choi *et al.* 2017). The main fractions both have two subfractions. BDCOD is divided into readily biodegradable COD (RBCOD) and slowly biodegradable COD (SBCOD), and NBDCOD is divided into non-biodegradable soluble COD (NBDSCOD) and non-biodegradable particulate COD (NBDPCOD). (Wentzel *et al.* 1999; Choi *et al.* 2017) The behavior of the COD fractions in wastewater treatment process can be assumed by their qualities (Wentzel *et al.* 1999). In biological wastewater treatment, RBCOD is readily degraded by microbes, over 60% of the COD in 28 days, whereas SBCOD is degraded slower by microbes with several stages of microbial operations, such as hydrolysis (OECD 1992; Choi *et al.* 2017). NBDSCOD is non-biodegradable and soluble, therefore it passes through the biological treatment, while NBDPCOD can be removed from treated water by sedimentation and then participated into sludge production (Choi *et al.* 2017).

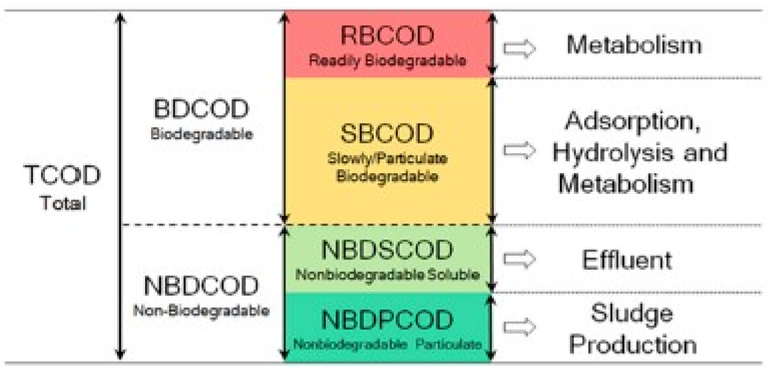

Figure 1. *Partition of TCOD's fractions and their roles in biological treatment, adapted from (Choi et al. 2017).*

The manufacture of pulp contains many unit processes which generate wastewater with different COD concentrations, for example, wastewater from thermo-mechanical pulping can contain 7210 mg/l of COD (Bajpai 2000, cited in Pokhrel & Viraraghavan 2004). Although the different unit processes generate different kinds of wastewater, pulp mill wastewater is generally characterized by high COD concentration, for example, bleaching pulp mill wastewater can contain 2572 mg/l of COD (Yen *et al.* 1996, cited in Pokhrel & Viraraghavan 2004). The COD of the pulp mill wastewater is also characterized by higher concentrations of NBDCOD, and especially NBDSCOD, than domestic wastewater. NBDSCOD covers about 80% of the pulp mill wastewater's TCOD, while NBDPCOD and SBCOD cover together only about 20% of the TCOD, as shown in the Figure 2. (Choi *et al.* 2017)

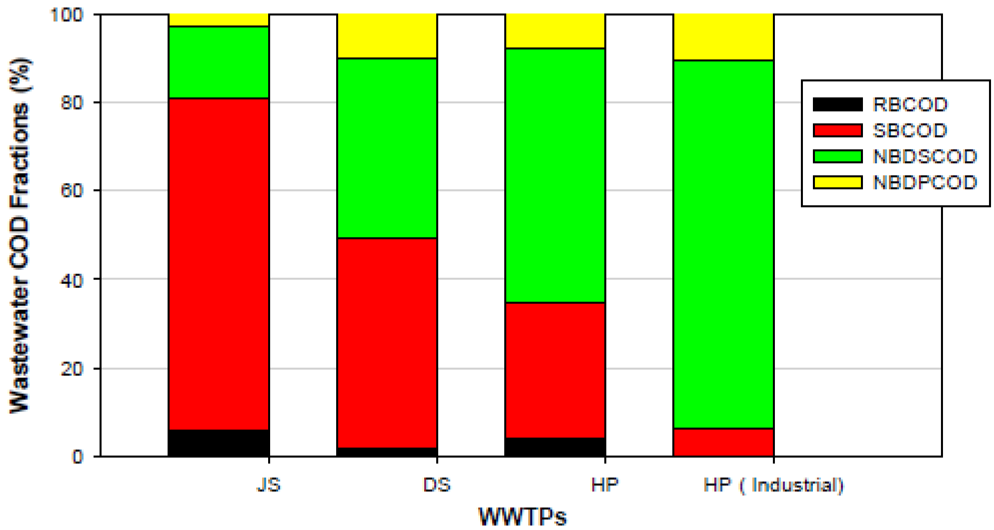

Figure 2. *Assessed WWTPs' influent COD fractions from Jisan (JS), Dalseocheon (DS), Hyunpoong (HP) and HP's industrial discharge, which is generated in the pulp mills (Choi et al. 2017).*

The NBDCOD of the wastewater is formed, for example, from lignin, lignin derivates, carbohydrates and extractives, which have low biodegradability (Pokhrel & Viraraghavan 2004; Choi et al. 2017). The compounds which form NBDCOD are transferred into the pulp mill wastewater from mechanical pulping, pulp washing, bleaching and pulp drying (Pokhrel & Viraraghavan 2004; AVI 2015, p. 21). In addition of NBDCOD formation in the manufacturing processes, NBDCOD is also formed in the biodegradation process of BDCOD. In the biodegradation of organic matter, all biodegradable organic matter of the wastewater is not mineralized entirely but is biotransformed into NBDCOD. (Roppola *et al.* 2009) Some of these products of biotransformation, such as the oxidation products of resin acid, can be even more toxic and persistent than the initial reactants (Lindholm-Lehto *et al.* 2015).

2.2 Factors Affecting the Quality of Wastewater

Wastewater treatment of pulp mills can be difficult to optimize because its quality of the wastewater varies (Ali & Sreekrishnan 2001; Pokhrel & Viraraghavan 2004). In the manufacturing process of pulp, there are various unit processes which generate different kinds of aqueous effluents, which are mixed together in the WWTPs of the pulp mills (Ali & Sreekrishnan 2001). For example, the pulp production of a bleached sulfate pulp mill contains debarking and chipping, chemical pulping, pulp washing, bleaching, pulp drying and baling of the finished pulp (Figure 3) (Biermann 1996, p. 55; Pokhrel & Viraraghavan 2004). First the wood is debarked and chipped, then the wood chips move to chemical pulping where the chips are cooked with a solution of white liquor, which can, for example, consist of sodium hydroxide (NaOH) and sodium sulfate (NaS_2) (Pokhrel & Viraraghavan 2004). After the chemical pulping and pulp washing where the cooking chemicals and dissolved wood is separated from the fibers, the produced pulp is whitened in a bleaching process, for example, with chlorine dioxide, (ClO_2), oxygen (O_2), sodium hydroxide (NaOH) and hydrogen peroxide (H_2O_2). In the final step of the pulp production, the pulp is dried in a drying machine and baled. (Biermann 1996, pp. 92, 93)

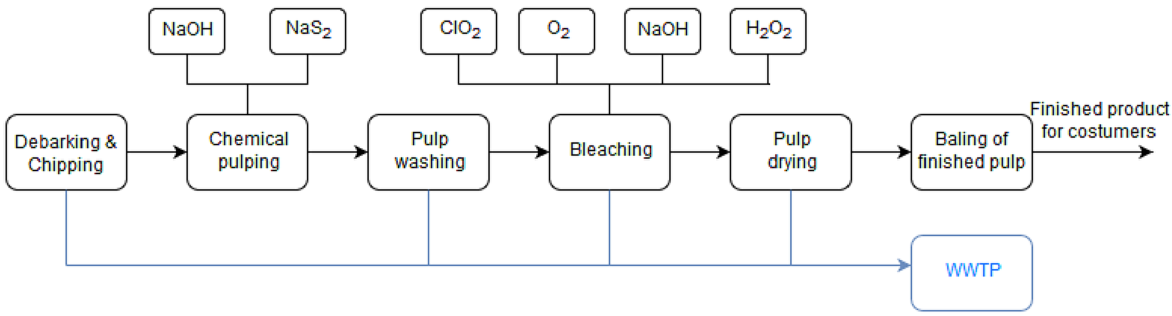

Figure 3. *Flowchart of the bleached sulfate pulp mill's manufacturing process, adapted from (Biermann 1996, pp. 55, 92, 93; Pokhrel & Viraraghavan 2004).*

Effluents from debarking and chipping are characterized by high concentration of BOD, COD, SS, dust and fibers (Ali & Sreekrishnan 2001; Pokhrel & Viraraghavan 2004). In chemical pulping, in turn, the wastewater, which is formed in the cooking process, is called black liquor (Biermann 1996, p. 88). The black liquor can be characterized by high concentrations of COD, color, fatty acids, lignin derivates, resin acids and volatile organic compounds (VOC), which are formed from cooking chemicals and dissolved wood (Pokhrel & Viraraghavan 2004; Lehto & Alén 2015). The wastewater from pulp washing is alkaline and contains effluents from former unit processes, while the bleaching process generates wastewater with COD, SS, nutrients, lignin, cellulose and other carbohydrates, color, inorganic chlorine and chlorinated organic compounds, such as chlorite (ClO_2^-) and chlorinated hydrocarbons (Pokhrel & Viraraghavan 2004; Lindholm-Lehto e*t al.* 2015).

In addition to unit processes, the composition of the wastewater is also affected by wood type and structure (Ali & Sreekrishnan 2001; Pokhrel & Viraraghavan 2004; Lindholm-Lehto e*t al.* 2015). Wood contains cellulose, hemicellulose and other carbohydrates, lignin and extractives (Biermann 1996, p. 13). Wood can be classified as hardwood or softwood, and they differ in structure and composition (Lindholm-Lehto e*t al.* 2015). Hardwood is wood from dicots and softwood is wood from conifers (Biermann 1996, p. 16).

The bark of hardwood contains two to ten times more ash, and the fibers are about three times shorter. Hardwood is also commonly more difficult to chip, and the morphology of the wood is also more complicated than that of softwood. (Biermann 1996, pp. 14, 16, 25) Lignin, which is a group of various polyphenolic compounds, can also be divided into softwood or hardwood lignin (McKague 1981, cited in Hubbe *et al.* 2016; Lindholm-Lehto e*t al.* 2015). The natural lignin can form AOX during bleaching, depending on the ratio of hardwood and softwood, and the quantity of lignin and chemicals which are used in the bleaching processes (Kringstad & Lindström 1984, cited in Lindholm-Lehto e*t al.* 2015; Gregov *et al.* 1988, cited in Ali & Sreekrishnan 2001).

2.3 Environmental Effects of the Wastewater

Suitable wastewater treatment in the pulp mills is crucial. If the effluents flow from the mills into close by water bodies, the pollutants can have an influence on aquatic environment for a long time. (Ali & Sreekrishnan 2001) In the water bodies, the pollutants first affect directly in the water phase but then eventually end up in a sediment by sorption from water (Meriläinen & Oikari 2008; Lindholm-Lehto e*t al.* 2015). The sediment can first act as a pollutant sink, but after a while the pollutants begin to desorb back to water from the sediment, and again the pollutants become available to the aquatic organisms (Meriläinen & Oikari 2008).

Some of the pollutants of the pulp mills can be acute or chronic toxins, which can have negative effects on ecosystems and health of organisms (Ali & Sreekrishnan 2001; Metcalf & Eddy 2014, p.161). The pollutants of the pulp mills can potentially have some toxic effects, such as respiratory stress and mutagenicity, on different fish species (Lindström-Seppä e*t al.* 1998). The pollutants can also have an impact on plankton and benthic invertebrate communities (Yen *et al.* 1996, cited in Pokhrel & Viraraghavan 2004; Meriläinen & Oikari 2008). A few pollutants of the pulp mill wastewater can be toxic to humans, for example, International Agency for Research on Cancer has classified dioxins, which are chlorinated organic compounds, as carcinogenic to humans (Ali & Sreekrishnan 2001; IARC 2012). Some of the pollutants can be persistent organic pollutants (POP) which are resistant to microbial degradation and tend to persist in the environment and in the bodies of the organisms for a long time (Ali & Sreekrishnan 2001). The pulp mill effluents can also cause oxygen deficiency, thermal varieties and color changes in water bodies, into which the effluents have been flowing to (Pokhrel & Viraraghavan 2004).

3. MEMBRANE FILTRATION IN PULP MILL WASTEWATER TREATMENT

The pulp mill wastewater treatment can be divided into pretreatment, primary treatment, secondary treatment and tertiary treatment (Figure 4) (Biermann 1996, pp. 287, 289). In addition to different stages of the treatment, the sludge of the primary clarification and the concentrate of the membranes, are also collected (Metcalf & Eddy 2014, pp. 1454–1457). In the pretreatment, the pulp mill wastewater is treated with screening. In the screening process the coarser particles are separated with screens. (Davis 2011, p. 13-9) In the primary treatment the wastewater is treated with primary clarification, which separates SS and organic matter from the water phase, and the wastewater is neutralized (Biermann 1996, p. 288; De Wever *et al.* 2007; Metcalf & Eddy 2014, p. 529). In the secondary treatment the wastewater is treated with a biological treatment, in which microbes degrade biodegradable pollutants, and with a secondary clarification (Biermann 1996, p. 288; Davis 2010, p. 18-2; Choi *et al.* 2017). In the secondary treatment, more effective MBR, for example, internal MBR, can be used to replace a conventional activated sludge process (CAS) (De Wever *et al.* 2007).

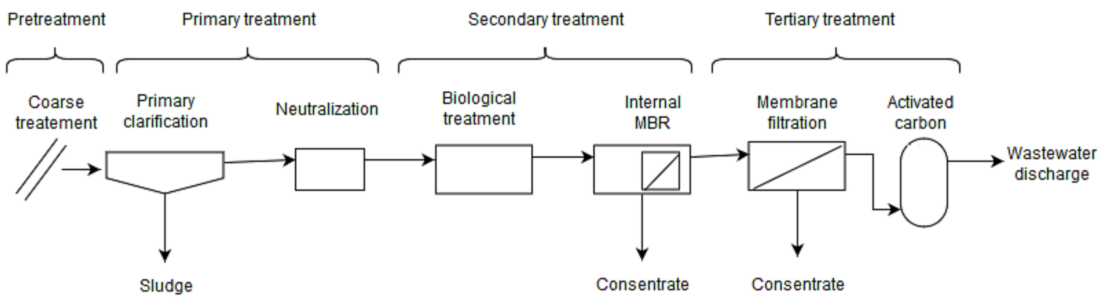

Figure 4. *Flowchart of pulp mill's wastewater treatment, which contains integrated membrane filtration system, adapted from (Biermann 1996, pp. 287, 289; De Wever et al. 2007).*

However, for achieving the quality of wastewater, which can obtain strict environmental regulation values, the tertiary treatment with advanced treatment methods is usually required (Biermann 1996 p. 289; Gönder et al. 2011; Gönder et al. 2012). In the tertiary treatment the wastewater can be treated, for example, with membrane filtration and activated carbon filter, which reduce the concentrations of more challenging pollutants, such as AOX and colored compounds (Pokhrel & Viraraghavan 2004; Gönder et al. 2012; Metcalf & Eddy 2014, pp. 1224–1225).

3.1 Membrane Bioreactor in Wastewater Treatment

The MBR consists of two phases (Metcalf & Eddy 2014, p.704). In the first phase, microbes degrade biodegradable pollutants in a suspension form in a bioreactor. The conditions of the bioreactor can be aerobic or anaerobic. (Alturki *et al.* 2010; Metcalf & Eddy 2014, p.704) The second phase consist of a membrane, which filtrates organic matter and particles from the wastewater (Judd 2008). The membrane is usually UF or MF, and it can be internal, when the membrane is submerged into the bioreactor, or external, when the membrane is separated from the bioreactor (Adnan *et al.* 2009). The MBR generates high quality and clear permeate. It is also able to function at higher concentrations of mixed suspended solids (MLSS) than CAS. (Judd 2008) The MBR can treat wastewater efficiently because MLSS of the bioreactor can absorb pollutants, when their sludge retention time (SRT) in the MBR is prolonged, for example, the SRT in the MBR is usually 30–70 d (De Wever *et al.* 2007; Davis 2010, p. 16-95).

The MBR is a suitable option for replacing the CAS, especially in the WWTPs of the pulp mills, because the MBR can elevate the removal rates of microorganisms, chlorinated aromatics and the enzymes of cellulose from the wastewater of the pulp mills, in comparison to CAS (Galil & Levinsky 2007). For example, the removal rate of *Escherichia coli* has been detected to be over two times higher in the MBR than in the CAS (De Luca *et al.* 2013). The prolonged SRT in the MBR, can also increase the degradation rate of the pollutants, which have intermediate biodegradability (De Wever *et al.* 2007). In the wastewater treatment process of the MBR, the removal rates of SS, ammonia and total phosphorus have been detected to be about 99%, 90% and 17%, and the removal rates of COD, BOD and TOC have been detected to be about 86%, 98% and 93% (Yao-po *et al.* 1998, cited in Galil & Levinsky 2007; Berube & Hall 2000, cited in Pokhrel & Viraraghavan 2004; Zhang *et al.* 2009). The MBR can operate as only biological unit process in the pulp mill WWTP or it can be placed after the biological treatment, when the effluent can obtain even a higher quality. For example, the removal rate of COD, in the anaerobic process combined with the MBR, can be about 95%, which is about 12% higher than MBR's itself. (Stahl *et al.* 2004; Zhang *et al.* 2009)

Lignin is the most challenging wood component for biodegradation in the wastewater of the pulp mills (Kumar *et al.* 2010, cited in Hubbe e*t al.* 2016). The lignin content varies between the wood types. Hardwood is generally better wood type for pulping because it has, for example, a lower lignin content. The lignin content of hardwood is 18–25%, whereas the lignin content of softwood is 25–35%. (Biermann 1996, pp. 18, 32) Lignin degrades during the manufacturing process of pulp and generates various high, medium and low molar mass compounds (McKague 1981, cited in Hubbe *et al.* 2016; Wallberg *et al.* 2003). In the biological treatment, low molar mass organic compounds are presumed to have high removal rates, while the removal rates of high molar mass compounds, which primarily cause the color and toxicity of the wastewater, have stayed relatively low (Mänttäri *et al. 2*008; Costa *et al.* 2017). Singhal & Takur (2009) have, for example, studied lignin biodegradation in biological treatment with four different fungi, and the removal rate of the lignin has been detected to be about 37%. UF, which can be the membrane unit of the MBR, has been detected to have 45–80% removal rate of lignin, depending on the material and the porosity of the membrane (Wallberg *et al.* 2003). Because the MBR fuses biological treatment with membrane filtration, according to the above-mentioned studies, it seems to be possible that effluents of the MBR can still contain lignin. Lignin of the MBR effluents can form gel on the surface of the membrane and cause fouling of the membrane in the tertiary treatment (Shi *et al.* 2014).

3.2 Membrane Filtration Methods

The membrane processes, particularly MF, UF, nanofiltration (NF) and reverse osmosis (RO), are getting new applications in purification of pulp mill wastewater (Gönder *et al.* 2012). The membrane is semipermeable, therefore it is more permeable to some pollutants in the wastewater and less permeable to others (Davis 2010, p. 6-2). The feed wastewater is pushed with a pressure against the surface of the membrane (Metcalf & Eddy 2014, pp. 1181, 1183). The permeable components, which are called a permeate, filtrate through the membrane and impermeable components stay on the other side of the membrane and form a concentrate (Figure 5) (Davis 2010, p. 6-2).

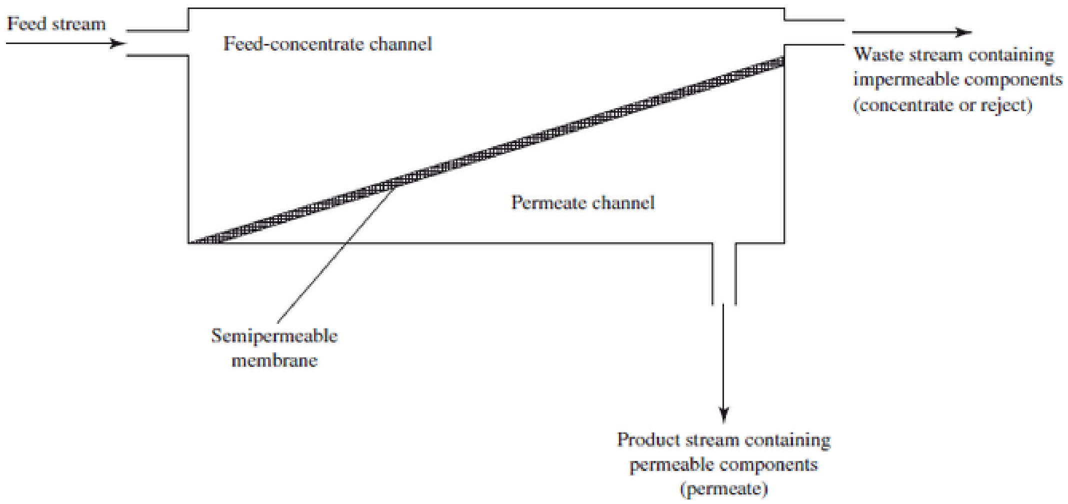

Figure 5. *Schema of the membrane filtration process (Davis 2010, p. 6-2).*

In the membrane filtration process, the membrane can be organic, such as polyamide, composite or inorganic material, such as aluminium oxide (Davis 2010, pp. 9-7 – 9-9; Metcalf & Eddy 2014, p. 1182). There are four different membrane types: tubular, hollow fiber, spiral wound and plate and frame. In the tubular membrane module, the membrane is placed inside of the support tube. (Metcalf & Eddy 2014, p. 1184) In the hollow fiber membrane module, the membrane is in configuration of a hollow fibers which form bundles, that consist hundreds to thousands of hollow fibers. In the spiral wound configuration, two membranes are in the spiral form and they are separated with permeate spacer

(Davis 2010, p. 6-6). In the plate and frame form, the membranes are in the flat sheet configuration and they are supported by plates (Metcalf & Eddy 2014, p. 1184). The main purposes of the membrane types are to create the largest possible membrane surface area, stable flow and minimize the energy consumption (Davis 2010, pp. 6-6 – 6-7; Metcalf & Eddy, pp. 1182–1185).

MF and UF are the coarse membranes, which remove pollutants, such as bacteria, viruses and small colloids, from the wastewater mainly by sieving (Scott 1998, p. 24; Davis 2010, pp. 6-2 – 6-3). The typical pore size of MF is about 0.1 µm, whereas the pore size of UF is about 0.01 µm (Figure 6) (Davis 2010, p. 6-3). The operating ranges of the MF and UF are 0.07–2.0 µm and 0.008-0.2 µm (Metcalf & Eddy 2014, p.1183). NF and RO are finer membranes which remove pollutants, such as dissolved organic matter and ions, with reverse osmosis technique (Davis 2010, pp. 6-2 – 6-3; Metcalf & Eddy 2014, p. 1883). In the reverse osmosis technique, the higher operational pressure of the feed, such as 60 bar, is required (Adnan *et al.* 2009). The typical pore size of the NF is about 0.001 µm, whereas, the membrane surface of the RO is such dense that it is classified as nonporous (Figure 6) (Davis 2010, p. 6-3). The typical operating range is 0.0009–0.01 µm for NF and 0.0003–0.002 µm for RO (Metcalf & Eddy 2014, p.1183).

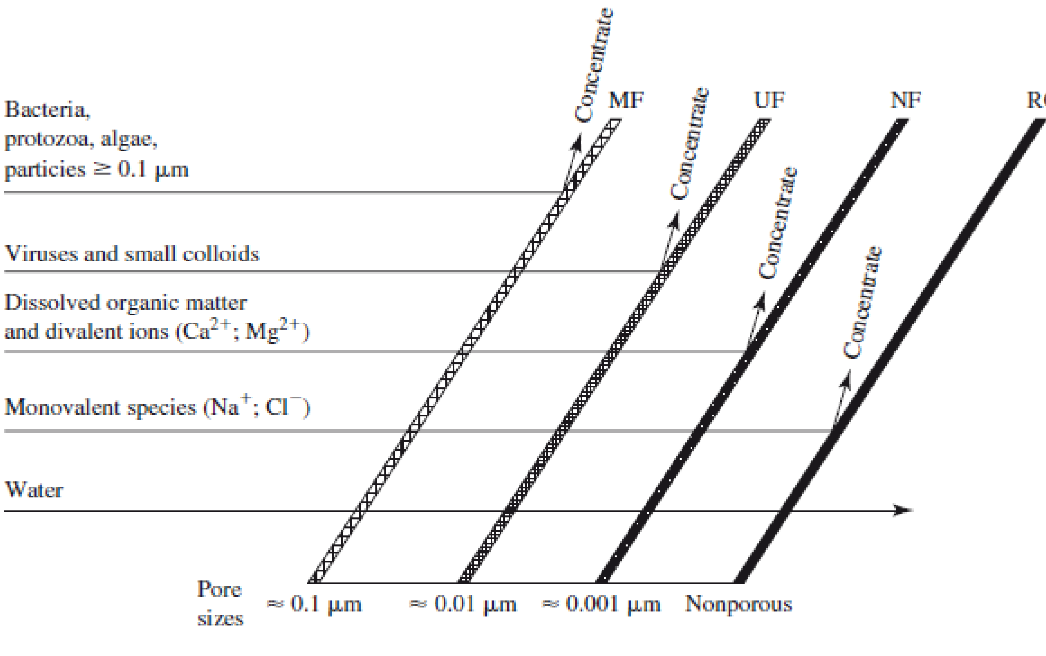

Figure 6. *The pore sizes and the common pollutants removed by the membrane filtration processes (Davis 2010, p. 6-3).*

All the membrane filtration processes can be in use in WWTPs of the pulp mills, depending on the other unit processes and the location of the membrane filtration in the wastewater treatment process (Adnan *et al.* 2009; Alturki *et al.* 2010; Gönder *et al.* 2011; Gönder *et al.* 2012). For example, the membrane surface of MF is too coarse to be the only membrane process in the wastewater treatment of the pulp mill, but it can be used as pretreatment for UF, NF or RO (Zhang *et al.* 2009; Davis 2010, pp. 9-2 – 9-3). UF can be used in secondary treatment, for example in the MBR, or in tertiary treatment (Adnan *et al.* 2009; Gönder *et al.* 2012). Finer NF and RO can be used only in tertiary treatment, because their pores are easily clogged by the larger particles of the wastewater (Zhang *et al.* 2009; Gönder *et al.* 2011).

3.3 Membrane Processes in Tertiary Treatment

In the tertiary treatment the remaining pollutants, especially colored and non-biodegradable organic compounds, are removed from the wastewater (Biermann 1996, p. 289; Hubbe *et al.* 2016). The membrane processes are beneficial in the tertiary treatment because they are efficient in purifying the pulp mill wastewater even from small suspended pollutants, which have passed through the previous treatments (Hubbe *et al.* 2016). UF can remove 77% of SS and 85–90% of COD, NF 88% of SS and 87% of COD and RO about 100% of SS and 83,6–97% of COD (Table 1) (Lopes *et al.* 2005; Zhang *et al.* 2009; Huang *et al.* 2011; Gönder *et al.* 2012; Kiril Mert & Kestioglu 2014). As seen in Table 2, the removal rate of the COD is slightly increased between the membrane processes, whereas the removal rate of the SS increases about 10 % from UF to NF and from NF to RO.

Table 1. *The removal rates of UF, NF and RO, adapted from (Lopes et al. 2005; Zhang et al. 2009; Huang et al. 2011; Gönder et al. 2012; Kiril Mert & Kestioglu 2014).*

The membrane process	COD removal (%)	SS removal (%)
UF	85–90	77
NF	87	88
RO	83,6–97	about 100

The membranes can also remove efficiently more challenging pollutants, for example, 90% of colored compounds and AOX (Pokhrel & Viraraghavan 2004; Gönder *et al.* 2012). AOX, which have been formed during the chemical pulping and the bleaching, can be challenging to remove from the wastewater because they are likely to be non-biodegradable, and they can inhibit microbes during the biological treatment (Ali & Sreekrishnan 2001). The colored compounds are also challenging to remove from the wastewater, because their carbon-to-carbon biphenyl linkages are hard to biodegrade (Ali & Sreekrishnan 2001; Hubbe *et al.* 2016). Because of these above-mentioned examples, membrane process of the tertiary treatment can be crucial for reaching the emission standards of the treated wastewater.

The permeate recovery of the individual element is fairly low, for example, the permeate recoveries of the spiral wound configuration and the hollow fiber configuration are 5–15% and about 30 %. Therefore, the membrane elements in the tertiary treatment can be arranged in series, for example, the membrane elements, which are in spiral wound configuration, are typically arranged in series of four to seven elements. (Davis 2010, p. 6-6; Metcalf & Eddy 2014, p. 1191) The membrane elements can also be placed in parallel, when the individual parallel elements form a stage, if higher yield is needed (Metcalf & Eddy 2014, p.1195). The membrane elements can be arranged in stages and in series, as in Figure 7, if achieving a high permeate recovery ratio and permeate yield is essential. The typical recovery ratio is, for example, for one stage membrane process under 50%, whereas, typical recovery ratios for two and three stage membrane processes are 50–75% and over 90%. (Davis 2010, p. 6-15; Metcalf & Eddy 2014, p. 1195)

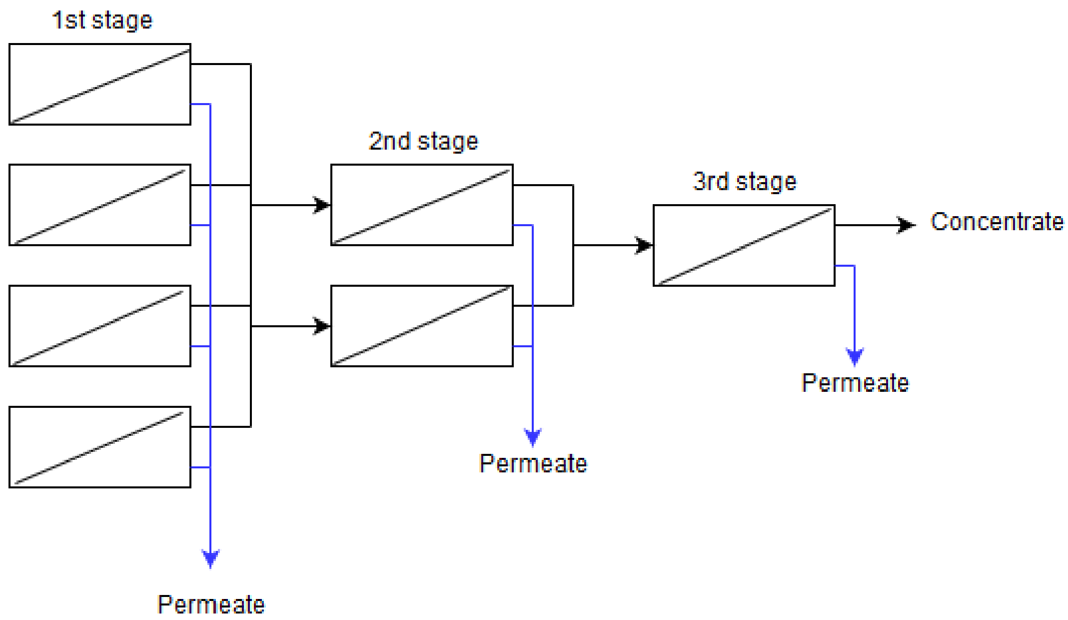

Figure 7. *Three stage membrane process, adapted from (Davis 2010, p. 6-10).*

The membrane modules are placed in containment vessels (Metcalf & Eddy 2014, p. 1185). There are two types of containment vessels: pressurized and submerged (Davis 2010, p. 9-9). The pressurized vessel supports the membrane element or elements inside it, isolates the feed water and permeate from each other, prevents leaks and pressure losses and minimizes fouling of the membranes. In the submerged vessel type the membrane elements are submerged in a feed water tank, which is open to the atmosphere and the permeate is drawn through the membrane by a vacuum. (Davis 2010, p. 9-9; Metcalf & Eddy 2014, pp. 1186–1188) The operating pressure of the submerged type vessel is limited by the atmospheric pressure, therefore the maximum transmembrane pressure for the submerged type is about 50 kPa (Metcalf & Eddy 2014, pp. 1187–1188).

3.4 Membrane Fouling

Membrane fouling is a process in which suspended or dissolved solids deposit on a membrane surface (Metcalf & Eddy 2014, p. 1198). The deposition of the solids cause decrease in performance of the membrane (Gönder *et al.* 2012). During the fouling, the flux of the membrane is rapidly declined (Shi *et al.* 2014). The flux of the membrane is related to a net transmembrane pressure and a membrane resistance coefficient as follows

$$J = \frac{\Delta P}{\mu * R_m}. \tag{2}$$

In the equation 2, J is the flux of the membrane ($m^3/h*m^2$), ΔP is the net transmembrane pressure (kPa), μ is the dynamic viscosity of the water (Pa*s) and R_m is the membrane resistance coefficient (m^{-1}). As seen in equation 2, the flux begins to decrease when the membrane resistance coefficient increases due to the fouling of the membrane. (Davis 2010, p. 9-5) During the fouling, the flux of the membrane is maintained as constant as possible by increasing the net transmembrane pressure. However, the increase of the net pressure will be eventually lower than the increase of the membrane resistance coefficient, and from that point the flux of the membrane begins to decrease. (Davis 2010, p. 9-5; Shi *et al.* 2014)

There are four different types of fouling: particulate fouling, scaling, organic fouling and biological fouling, which can occur simultaneously (Metcalf & Eddy 2014, p. 1199). During the particulate fouling, the particles, such as organic colloids and oxidized metals, block the pores of the membranes partially or completely (Metcalf & Eddy 2014, p. 1199; Shi *et al.* 2014). The particulate fouling can happen by three different mechanisms: pore narrowing, pore plugging and gel/cake formation (Metcalf & Eddy 2014, p. 1200). In the pore narrowing and plugging, the particulates, which are smaller than the pores, get stuck in the pores or attach in the inner surface of the pores (Davis 2010, p. 9-8; Metcalf & Eddy 2014, p. 1200). In the gel/cake formation the particles of the feed water are larger than the pores, therefore the particles begin to form highly concentrated layers on the surface of the membrane (Metcalf & Eddy 2014, p. 1200; Shi *et al.* 2014). The particulate fouling can occur rapidly in the initial stages of the filtration process, when the surface of the membrane is clear from foulants and the particulates can interact directly with pores of the membrane (Shi *et al.* 2014). During the scaling, concentration of the salts, such as calcium carbonate ($CaCO_3$) and silica (SiO_2), is locally increased due to removal of the salts at the surface of the membrane. In the scaling process, the concentration of the salts exceeds the solubility limits locally, when various salts begin to precipitate. (Metcalf & Eddy 2012, p. 1200) During the organic fouling, dissolved or colloidal organic matter, such as natural organic matter (NOM) and organic polymers, accumulate on the surface of the membrane (Scott 1998; Kent e*t al.* 2011). In the organic fouling, the stable organic layer on the surface of the membrane can escalate the fouling and decrease the water permeability of the membrane (Metcalf & Eddy 2014, p. 1200; Shi *et al.* 2014). In the biological fouling the microorganisms grow on the surface of the membrane and form a biofilm. The biofilm consists of living and dead microorganisms and extracellular polymeric substances, which are extracted by the microorganisms. (Kent *et al.* 2011) The growth of the biofilm is able to occur because the concentrations of the organic matter and nutrients are increased on the surface of the membrane (Metcalf & Eddy 2014, p. 1201). The biofilm growth on the surface of the membrane reduces the water permeability of the membrane and the extracellular polymeric substances of the biofilm can interact with other foulants (Kent *et al.* 2011; Metcalf & Eddy 2014, p. 1201).

The foulants are divided into four types: particles, macromolecules, salts and biological substances. There are two types of particles, which cause fouling: large suspended particles and small colloidal particles. (Shi *et al.* 2014) The sizes of the particles vary from 1nm to 1 µm, and they have solid form (Metcalf & Eddy 2014, pp. 1999–1200; Shi *et al.* 2014). The particles cause fouling by cake formation, pore narrowing and plugging (Metcalf & Eddy 2014, p. 1200). The macromolecules, such as proteins, are large molecules which molecular mass is over couple of thousand grams per mole (g/mol) (Shi *et al.* 2014). Because macromolecules are bigger than the pores, they form cake or gel on the surface of the membrane (Metcalf & Eddy 2014, p. 1200). Salts cause fouling by scaling, and some of them, for example, calcium cations can ease the fouling process of the macro-molecules (Scott 1998; Shi *et al.* 2014). The biological substances cause biological fouling by growth of the biofilm. The biological substances are hard to manage because only a few cells can form a biofilm on the surface of the membrane (Flemming *et al.* 1997).

The fouling can be reversible or irreversible (Davis 2010, p. 9-6). In the reversible fouling, the flux of the membrane is able to recover, whereas, in the irreversible fouling the flux of the membrane cannot be recovered by backwashing or chemical cleaning (Shi *et al.* 2014). The irreversible fouling of the membranes increases over time during the filtration, and eventually the membranes have to be replaced by the new ones, for example, service life of the MF and UF can be 5–10 years, depending on the use of them (Davis 2010, p. 9-12). It is not possible to completely avoid membrane fouling, when membrane processes are in use, but it is possible to reduce it (Metcalf & Eddy 2014, p.1198; Gönder *et al.* 2012). The main ways to control the membrane fouling are pretreatment of feed water, membrane backflushing and chemical cleaning (Metcalf & Eddy 2014, p.1201). In the pretreatment the SS, colloidal material and microorganisms of the feed water are reduced, for example, with coagulation, flocculation and clarification (Davis 2010, p. 9-13). The pretreatment chemicals, such as anti-scalants and biocides, are also often inserted into the feed water. In the membrane backflushing, water and/or air is pumped backwards through the membrane. (Metcalf & Eddy 2014, p. 1201) The backflushing can work in the flux recovery only if the typical working flux is over two times higher than the typical filtration flux. If the working flux is lower, the chemical cleaning is required. (Shi *et al.* 2014) In the chemical cleaning, the hydraulically irreversible foulants are removed either by replacing the feed water with cleaning solution or by chemical treatment (Metcalf & Eddy 2014, p. 1201).

4. THE CASE STUDY

The case study is a bleached sulfate pulp mill, which is currently build, in North-Western Russia. The pulp mill will produce 1,33 air dry tonne of pulp per year (ADt/a). 80% of the pulp will be produced from hardwood, which is birch or aspen, and 20% of softwood, which is pine or spruce. The pulp will be made from birch 145 d/a, from aspen 80 d/a and from softwood 125 d/a. The softwood, which will be used in the manufacturing processes during the year, is 25% of pine and 75% of spruce. The manufacturing processes of the pulp mill will contain the same unit processes, as presented in Figure 3. The effluents from different unit processes will be mixed together and directed to the WWTP, expect the alkaline and bark press filtrates which will be directed to the recovery cycle. In the recovery cycle, the chemical products are converted into the fresh chemicals, which can be used again in the manufacturing processes of the pulp mill. In the WWTP of the pulp mill, the unit processes of the wastewater treatment will be also same, as in Figure 4.

The aim of the case study is to investigate the fouling of the membrane in the membrane filtration unit, which belongs to the integrated membrane filtration system with the MBR, using the emission values of the influent wastewater and the assessed pollutant values after the MBR. In the case study, the possible foulants after the MBR, are estimated, and the possible methods to reduce the fouling are suggested. The membrane process option for the membrane filtration unit, which is suitable for the pulp mill, is also suggested.

4.1 Emission Values of the Influent Wastewater

The normal average of the total inflow to the WWTP of the pulp mill will be 60 000 m^3/d for softwood and 70 000 m^3/d for hardwood, whereas, the maximum average inflow will be 80 000 m^3/d and maximum hourly inflow will be 100 000 m^3 per day and 4170 m^3 per hour (Table 1). The temperature of the influent wastewater will be 60 °C and pH will be 3,5 because alkaline filtrates from pulp washing will be directed to the recovery cycle. The pollutants of the wastewater are expressed as in loads per day. The COD load of the softwood will be 125 t/d, whereas the COD loads for birch and aspen will be 155 t/d and 135 t/d. The differences between the COD loads are explained by the differences between the structure of the wood types (Biermann 1996, p. 43-44). The loads of SS and AOX will be 12 t/d and 1,8 t/d**,** and the loads are estimated to be about the same for different wood types.

The pollutant values can also be expressed as in concentrations. The average COD concentration for softwood is calculated with softwood's normal average inflow, whereas the average COD concentrations for birch and aspen are calculated with hardwood's normal average inflow. The average SS and AOX concentrations are also calculated with hardwood's normal average inflow, because 80% of the pulp is produced from hardwood. As in Table 2, the COD concentration will be 2080 mg/l for softwood, 2210 mg/l for birch and 1930 mg/l for aspen and the SS and AOX concentrations of the wastewater will be 171 mg/l and 25,7 mg/l.

Table 2. *The parameters of the influent wastewater.*

Parameter	**Value**	**Unit**	**Value**	**Unit**
Normal average inflow for softwood	60 000	m^3/d		
Normal average inflow for hardwood	70 000	m^3/d		
Maximum average inflow	80 000	m^3/d		
Maximum hourly inflow	100 000 4170	m^3/d m^3/h		
Temperature	60,0	°C		
pH	3,50			
COD for softwood	125	t/d	2080	mg/l
COD for birch	155	t/d	2210	mg/l
COD for aspen	135	t/d	1930	mg/l
SS	12,0	t/d	171	mg/l
AOX	1,80	t/d	25,7	mg/l

The characters of the influent wastewater depend on the wood type being used, the unit manufacturing processes, the process technology, internal water recycle, and the amount of water required in the manufacturing process (Pokhrel & Viraraghavan 2004). Therefore, pollutant concentrations of the different pulp mills cannot be compared directly with each other. However, the pulp mills, which have same kind of wood type composition as a source of the pulp and same kinds of manufacturing processes, can have fairly similar pollutant concentrations. If the pollutant concentrations of case study's bleached sulfate pulp mill are compared to other bleached pulp mills, it seems that the bleached sulfate pulp mill's pollutant concentrations of the influent wastewater will be fairly typical for bleached pulp mills (Pokhrel & Viraraghavan 2004; Farooq & Ahmad 2017, p. 127). The COD, SS and AOX concentrations can, for example, be 1450 mg/l, 342 mg/l and 31,6 mg/l for a bleached pulp mill (Farooq & Ahmad 2017, p. 127).

4.2 Effluent Wastewater Emission Standards

The emission standard for COD concentration of the pulp mill wastewater will be 76 mg/l. Because the pulp mill of the case study is in construction stage, there are not any current COD concentration values of the effluent wastewater which could be compared to the regulated emission standard. For calculating the required removal rate of the COD concentration during the wastewater treatment, the COD concentration values of the softwood and hardwood are used to form a weighted arithmetic mean for the COD concentration of the influent wastewater. Because the percentage values of the birch and aspen are unknown, the mean COD concentration value of the hardwood is first calculated from the COD concentration values of birch and aspen. The COD concentrations and the weights of hardwood and softwood are presented in the Table 3. When the weighted values are summed together the weighted arithmetic mean will be 2072 mg/l, and therefore the required removal percentage of the COD concentration will be 96,3%.

Table 3. *The COD concentrations and the weights of different wood types.*

The wood type	The COD concentration (mg/l)	The weight (%)
Softwood	2080	20
Hardwood	2070	80

In the study of Stahl *et al.* (2004) the MBR combined with the anaerobic treatment have achieved 95% COD removal. The result of this study is used to estimate the COD removal before the membrane filtration unit because the processes of this study are closest to the processes of the case study's WWTP, compared to the other found studies. When the COD removal is 95%, the COD concentration after the MBR can be assessed to be about

104 mg/l, when the COD concentration's weighted mean of the influent wastewater is used (Stahl *et al.* 2004). If the emission standard of the effluent COD is wanted to be achieved, the maximum removal rate of the final filtration unit, after the MBR, has to be 31%. For achieving this required removal rate, the suitable membrane filtration unit can be UF, because its removal rate is higher than the required removal rate, as seen in the Table 1, and the energy consumption is lower than for NF and RO, which need higher operational pressures (Zhang *et al.* 2009; Gönder *et al.* 2012; Metcalf & Eddy 2014, p.1183).

The emission standard for the pH of the effluent wastewater will be between 6,5–8,5. The emission standard is set, so that the wastewater would not have an effect on pH of the water in the close by water bodies (Ali & Sreekrishnan 2001). The pH value of 6,5–8,5 is also required to achieve a necessary biological wastewater treatment process. Because the wastewater will be acidic in the beginning of the treatment process, the wastewater will be treated with the neutralization process, which elevates the pH value of the acidic wastewater. (Cox *et al.* 2007, pp. 45–46) The other parameters of the effluent wastewater from Table 2 can be adjusted by the final process concept.

4.3 Options for Treatment

Because the COD removal is assessed to be 95% before the membrane filtration unit, most of the biodegradable organic compounds can be assumed to be removed from the wastewater in the primary clarification, in the biological treatment and in the MBR. The pollutants which can still be in the wastewater after the MBR are the compounds which are slowly biodegradable and non-biodegradable soluble organic compounds, because these pollutants are difficult degrade by the microbes in the biological treatment (Choi *et al.* 2017). Because the membrane of the MBR is usually MF or UF, the membrane surface can pass through small colloids, dissolved organic matter and ions, as seen in Figure 6 (Davis 2010, p. 6-3). Due to the above-mentioned information, the pollutants which can still be in the wastewater after the MBR are, for example, lignin, AOX, colored compounds and wood extractives, such as resin acids and sterols. There can also be derivates and metabolites of the above-mentioned compounds in the wastewater after the MBR. (Leiviskä *et al.* 2009) As seen from the list of the possible foulants, the possible foulants are mainly organic compounds, which do not biodegrade properly.

The mitigation of the fouling is critical in the pulp mill, because the membrane fouling can elevate the operational costs of the membrane processes, reduce the effectivity and shorter the operational life of the membranes (Gönder *et al.* 2012; Shi *et al.* 2014). The fouling can be managed, in addition to the conventional washing of the membrane surface, with optimization of the operating conditions, membrane material selection and precoating the membrane surface with a surfactant (Maartens *et al.* 2002; Gönder *et al.* 2012). Determining the optimum operating conditions can be complex, because in the determination process, the interactions between the factors have to be considered. Therefore, the optimization of the operating parameters cannot be done separately one at a time. (Gönder *et al.* 2011) In the study of Gönder *et al.* (2012), where the membrane fouling of UF was studied with the pulp and paper mill wastewater, the optimum conditions for the membrane fouling were 10 for pH, 25 °C for temperature, 6 bar for the transmembrane pressure and 3 for the volume reduction factor (VRF), which is a ratio of the feed water volume and the concentrate.

The membrane material selection can also be complex because the membrane material has to be selected by the characteristics of the wastewater. The material of the membrane can tolerate some factors, such as pH variation, well, but at the same time some other factors, such as high temperatures, poorly. (Shi *et al.* 2014) It is also important that the membrane material has a low fouling tendency (Gönder *et al.* 2012). The tendency to foul can potentially be decreased by increasing the hydrophilic characteristics of the membrane (Shi *et al.* 2014). For example, regenerated cellulose UF membrane has been noticed to have a low fouling tendency, while treating the pulp mill wastewater with it (Kallioinen *et al.* 2010). In the membrane material selection is, however, most important that all the membrane characteristics, such as thermal stability, are at the most optimum level for the wastewater which is treated with the membrane filtration (Gönder *et al.* 2012). In addition of the membrane material selection, the fouling can be mitigated also by precoating the membrane surface with a surfactant, which reduces the surface tension. For example, a surfactant called Pluronic ® F108 can reduce the fouling tendency of the membrane surface and ease the cleaning of the membrane. Pluronic ® F108 has been detected to have no decline in flux in 90 h, whereas the flux decline of the untreated membrane was at the same time 29%. (Maartens *et al.* 2002)

The membrane fouling can also be reduced by improving the pretreatments of the membrane filtration unit. The fouling can be decreased by prolonging the SRT of the MBR. When longer SRT is in use a more various microbial community, which have wider physiological capabilities, is obtained. In the various microbial community, there are generalist and specialist microbes, which lead to effective degradation of many kinds of compounds. (De Wever *et al.* 2007) Because the pollutants of the pulp mill are often hydrophobic and have low biodegradability, the fouling of the membrane can also be reduced by optimizing the concentration of mixed liquor volatile suspended solids (MLVSS) and amounts of excess biosolids (Maartens *et al.* 2002; Galil & Levinsky 2007). The concentration of the MLVSS have to be reduced and the amounts of the excess solids have to be increased to achieve the optimum operating conditions for the MBR in the WWTP of the pulp mill (Galil & Levinsky 2007).

The membrane fouling can also be decreased by using lignin degrading fungi (Leonowicz *et al.* 1999; Costa *et al.* 2017). In nature, there are various ligninolytic fungi, bacteria, which can be potentially used in the field of the wastewater treatment. From these ligninolytic organisms, white rot fungi, such as *Bjerkandera abusta* and *Phanerochaete* *chrysosporium* have been detected of having efficient lignin-degrading enzymes, which can elevate the lignin degradability even up to 97% and 74%. (Costa e*t al.* 2007) The white rot fungi use cellulose of the wood as a carbon source and they secrete enzymes, such as quinone oxidoreductase, which degrade cellulose, hemicellulose and lignin. These enzymes can operate separately or together with each other, effectively degrading lignin and carbohydrates of the wood (Leonowicz *et al.* 1999). Although the ligninolytic white rot fungi have been detected to have a high lignin biodegradability in various studies, there still is a scarce experience from the industrial use of the fungi (Costa *et al.* 2017).

5. CONCLUSIONS

The wastewater of the pulp mills is difficult to treat with conventional wastewater treatment processes if the treated wastewater has to have high and consistent quality because of the tight environmental emission standards. The wastewater of the pulp mills is characterized by complicated matrixes and high pollutant concentrations, which differ among the unit processes of the mill and wood type. Among the pollutants, the organic matter of the pulp mill wastewater is a significant concern because most of it is non-biodegradable or slowly biodegradable compounds, which are difficult to remove from the wastewater only with the conventional wastewater treatment processes.

For achieving high and consistent quality of the treated wastewater, the membrane filtration unit can be combined with the MBR as in the pulp mill of the case study, when a very high quality of the treated wastewater is obtained. The effectiveness of the membrane filtration unit can be, however, affected by membrane fouling, which can, for example, elevate the operational costs. There are various alternatives for reducing the membrane fouling. The suggested options for the WWTP of the case study's pulp mill include optimizing the operating conditions of the membrane filtration unit and the MBR and elevating the hydrophilicity of the membrane surface by the membrane material selection or precoating the membrane surface with a surfactant.

The optimization of the operating conditions is a simple and a cost-effective option for reducing the membrane fouling, because there are no need for additional investments. In the pulp mill of the case study the emission standard for the pH of the wastewater is 6,5–8,5, because the optimum pH for the membrane filtration is 10, the most optimum conditions cannot be completely obtained. However, in the study of the Gönder *et al.* (2012), they have been detected that the membrane fouling is in the lowest point, when the pH is its highest point (10), temperature (25 °C) and VRF (3) are in their lowest points and the transmembrane pressure is its medium level (6 bar). Therefore it can be possible to reduce the membrane fouling by adapting the operating conditions as close to their optimum level as possible. The operating conditions of the MBR can also be optimized, for example, by reducing the MLVSS, when the removal of the low biodegradable compounds from the treated wastewater can be in its the highest level.

The hydrophilic characteristics of the membrane can be improved by a membrane material selection or precoating the membrane surface with a surfactant. Because organic foulants are the biggest concern of the pulp mills' wastewater, the increase of the hydrophilic characteristics of the membrane, which reduces the adsorption of the organic compounds on the membrane surface, is a simple option for reducing the organic fouling of the membrane in the pulp mill of the case study. The surface hydrophilicity of the membrane can be enhanced by selecting a hydrophilic membrane material, such as a regenerated cellulose UF. The other good option for reducing the organic fouling is to precoat the membrane surface with a surfactant. For example, the surfactant Pluronic ® F108 has been detected to reduce the membrane fouling. In addition of the reduction of the membrane fouling, the surfacant can also ease the cleaning of the membrane. In the cleaning process is, however, important to use detergent, which does not remove the surfacant from the surface of the membrane or otherwise the membrane surface has to be recoated with the surfacant.

In addition of the above-mentioned options, white rot fungi can also be used for decreasing the membrane fouling by degrading lignin. However, there is little information about the industrial use of the white rot fungi, therefore the lignin degradation capability of the white rot fungi can still be uncertain on the industrial level.

The above-mentioned methods can be simple, effective and cost-effective options for reducing the membrane fouling compared to the possible added wastewater treatment processes, such as ozonation. With the help of these options the lowest level of the membrane fouling can be obtained. When the membrane fouling is at its lowest level, the integrated membrane filtration system will be a very suitable option for the wastewater treatment of the pulp mill. The integrated membrane filtration system is a competitive option for the WWTP of the pulp mill, because it is a space saving system, which removes very effectively particularly the pollutants which are hard to remove with other more conventional wastewater treatment techniques.

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