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Master's thesis

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Evaluation of CTMP mill wastewaters and handling methods

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TIIVISTELMÄ

Lappeenrannan teknillinen yliopisto
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Kemitermomekaanisen sellutehtaan jätevesien ja mahdollisten jätevedenkäsittely menetelmien tarkastelu

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Työssä selvitettiin kemitermomekaanisen sellutehtaan jätevesien koostumusta ja koostumuksen vaikutuksia jäteveden käsittelymenetelmän valintaan. Työn tavoitteena oli selvittää jätevedestä löytyviä komponentteja ja selvittää onko niistä jokin rajoittava tekijä jäteveden käsittelymenetelmän valinnassa. Näiden tietojen perusteella tavoiteltiin perusteluja käsittelymenetelmän valinnalle ja parhaalle menetelmälle kyseisten vesien käsittelyyn.

Kirjallisuusosassa tarkastellaan CTMP prosessia, jäteveden epäpuhtauksien alkuperiä prosessissa ja jäteveden koostumusta. Mahdolliset jäteveden käsittelymenetelmät käydään läpi ja tutkitaan niiden hyötyjä sekä haittoja ja puhdistustehokkuutta. Myös tavoiteltava jäteveden laatu käydään lyhyesti läpi. Kokeellisessa osassa tutkitaan kahden eri CTMP tehtaan jätevesiä. Jätevesistä määritetään erilaisia komponentteja sillä perusteella, mitä kirjallisuusosassa on löydetty käsittelyn rajoittaviksi tekijöiksi. Kokeellinen osa sisältää myös Excel työkalun, jonka avulla voidaan karkeasti arvioida tutkittujen vedenkäsittelymenetelmien (aerobinen ja anaerobinen biologinen käsittely sekä haihdutus) sopivuutta kyseisille jätevesille.

Tulosten perusteella aerobinen jäteveden käsittely olisi CTMP vesien käsittelyyn parhaiten soveltuva ja käyttöhyödykkeiden kannalta kannattavin. Myös aerobisen ja anaerobisen menetelmän yhdistelmä olisi toimiva ratkaisu. Haihdutuksen energiankulutus on niin paljon suurempi kuin biologisten menetelmien, että sitä ei nähty kannattavana muissa tapauksissa, kuin jos päästörajat ovat erittäin tiukat tai vettä halutaan kierrättää prosessissa.

ABSTRACT

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Evaluation of CTMP mill wastewaters and handling methods

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Keywords: chemithermomechanical pulp, CTMP, wastewater, wastewater treatment, water purification

The aim of this work was to evaluate the characteristics of chemithermomechanical pulp (CTMP) mill wastewaters and their impact to the selection of the treatment method. Target for this work was to find out what kind of components the wastewaters contain and are there any limiting factors among them that could affect to the treatment method selection. With this information, justifications for the treatment methods selection were looked.

In the theoretical part CTMP process, origins of the wastewater impurities and the characteristics of the wastewater are examined. Possible treatment methods are described shortly and their benefits and challenges are presented. The requirements for the purified water are also described shortly. In the experimental part, softwood CTMP wastewaters from two different mills are analyzed. Experimental part includes also an Excel tool, which can be used to roughly evaluate treatment methods (aerobic, anaerobic and evaporation) suitability for wastewaters in question.

On the ground of the results, the aerobic method seems to be the best alternative to treat CTMP wastewaters. Also, a combination of aerobic and anaerobic method could be profitable solution. The energy demand in evaporation is so high, that it was not seen to be a reasonable treatment method, otherwise than in cases where discharge limits are strict or water needs to be circulated.

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Sonja Rantanen
Kouvola, 24th July 2018

Contents

1. Introduction

Chemithermomechanical pulping (CTMP) is a pulping method that combines chemical treatment with mechanical refining. CTMP process is nowadays the predominant chemimechanical pulping process. It produces high-yield mechanical pulps, which have better properties than conventional mechanical pulps. Compared to other mechanical pulps, CTMP has better cleanliness, absorbency and strength properties. (Lindholm, 2009)

In a world, that battle with climate change and water pollution by plastics, the future trend is to develop more and more sustainable products with environmentally friendly methods, to replace the oil based products. For example plastics are very commonly used in food packaging and those could be replaced with wood-based materials. Because of the cleanliness of the CTMP, it is much desired material in the food packaging markets. It is also very high strength material, and commonly used in all kinds of packaging material production, for instance in cardboard boxes middle layer, where the strength is needed. The growing trend in internet shopping has increased the demand for cardboard, which makes CTMP even more desired.

CTMP effluents tend to be quite challenging to deal with. The effluents have high load of COD and suspended solids, but also dissolved resin and fatty acids and residues from the impregnation and bleaching chemicals. The dissolved compounds cause problems in the wastewater treatment plants and it is not even possible to use all wastewater treatment alternatives due to these toxic dissolved compounds. The effluents tend to be very toxic, so those need to be well purified before discharging them into the receiving waters. (Suhr, et al., 2015) Effluents from pulp and paper industry in general have reported to cause slime growth, thermal impacts, scum formation, color problems and increased amount of toxic substances which cause death and other health issues for zooplankton and fish. (Pokhrel & Viraraghavan, 2004)

There are few possible alternatives that can be selected for the treatment method for CTMP wastewaters. In this work, three methods were selected to be examined; aerobic treatment, anaerobic treatment and evaporation. The content of the CTMP effluent is examined from the point of the treatment methods needs and limitations. The aim is to find out what kind of wastewater comes from different processes and what are the limiting factors in the water for possible treatment methods. The meaning of this work is to examine the best methods to match the effluents, to ease the design process when considering wastewater treatment plants for CTMP mills.

2. Chemithermomechanical pulping (CTMP) process

Chemithermomechanical pulping is a combination of thermomechanical and chemical pulping processes. The process is like a typical thermomechanical pulping process, where the wood chips are refined with rotating refining plates in certain temperature and pressure, but the wood chips are treated with chemicals before the refining. The wood chips are treated with an alkaline solution and cooked for a short period, like in the chemical pulping process. (Suhr, et al., 2015) The chemical treatment of the chips combined with mechanical refining leads to pulp properties that are intermediate of chemical and mechanical pulp properties. Also, the yield for CTMP pulp is higher than chemical pulps but lower than mechanical pulps, ranging from 80% to 95%. (Blechschmidt, et al., 2006)

In figure 1, a simple CTMP process diagram is presented and the main parts of the process are described in the chapters 2.1.-2.5.

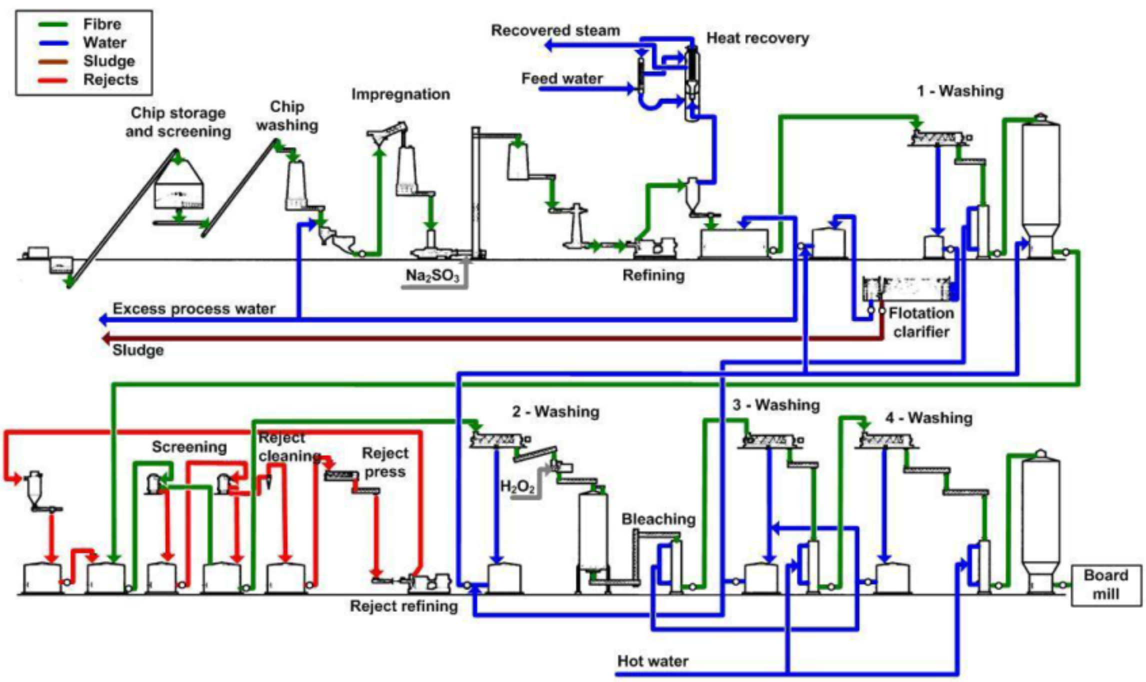


Figure 1 CTMP process diagram with the main unit operations. Different streams are described with different colors; fiber stream with green, water stream with blue, sludge stream with brown and reject stream with red. **(Suhr, et al., 2015)**

2.1. Wood handling

The CTMP process is a chip-refining process, so the wood must be in a chip form before it can be refined. The wood can be delivered to the mill already chipped or as a round wood. If the wood is delivered to the mill in a round wood form, it must be de-barked and chipped before the refining process. Otherwise, the chips can be delivered to the mill from sawmills or as a ground wood, and then it only needs to be screened and stored before refining. (Suhr, et al., 2015)

The wood handling part also includes the washing of the chips before the impregnation stage. The CTMP plant uses counter-current water flow, so the washing water is get from the later stages of the process. (Suhr, et al., 2015) The water flow in the process is described in the figure 1. with the blue line.

2.2. Impregnation

Impregnation means the penetration of chemicals into the wood structure (Blechschmidt, et al., 2006). In the impregnation part, the chips are treated with alkaline chemicals, usually with sodium sulphite (Na_2SO_3) or alkaline peroxide (NaOH, H_2O_2). The used chemical depends on the raw material used for the pulp (softwood, hardwood). A weak sodium sulfite is most commonly used for softwood and the stronger alkaline peroxide for the hardwood. (Suhr, et al., 2015)

The chips are cooked with the chemicals, like in the chemical pulping process, with a short retention time. The CTMP process conditions are pretty much the same in every process. (Lindholm, 2009) Recommended conditions for chemical treatment of softwood and hardwood CTMP is presented in table I.

Table I Recommended process conditions for impregnation stage in CTMP process **(Lindholm, 2009)**.

Condition	Softwood	Hardwood
Na_2SO_3 charge	2 – 4 % on b.d. wood chips	0 – 4 % (+ 1 – 7% NaOH)
pH	9 – 10	12 – 13
Temperature	120 – 135 °C	60 – 120 °C
Retention time	2 – 15 min	0 – 30 min

2.3. Refining

The CTMP process utilizes rotating refining plates. The chemically treated chips are fed between two rotating plates, where they are defibrated into pulp under pressure. The chips are lead into the center of the plates and they move between the plates towards to the disc sides, where they are removed and transferred to the next stage of the process. (Blechschmidt, et al., 2006)

The refining process can be carried out with one- or two-stage process. Process conditions in these stages vary. These conditions are optimized for the raw material used, since there are differences in the cell structures between different wood species. The cell structure affects to the optimal defibrillation of the wood. (Blechschmidt, et al., 2006)

2.4. Screening and cleaning

The pulp from the refining process is not homogeneous, but includes insufficiently pulped fragments. To optimize the product quality, these fragments must be screened off from the pulp. (Blechschmidt, et al., 2006) The screening process is executed in high dilutes, meaning that the dry content is below 1%. After the screening, the undesirable fragments are refined and returned to the main fiber line. (Suhr, et al., 2015)

The pulp washing is an important part of the total process. The aim of the washing is to separate the organic material dissolved in refining from the fibers but also to purify the pulp from the chemicals used in impregnation and bleaching (Bajpai, 2010). The water used in washing is circulated in the process counter-currently, which means that the clean water is fed to the last washing step and is flows against the pulp flow to the first step of the process, where it is removed and moved into the wastewater treatment plant (Suhr, et al., 2015). The washing step is really important factor in the pulp quality, and it can be enhanced by adding more washing steps in series. Also the amount of washing water can be increase, but this increases the use of water and also increases the dissolving of the organics into the wastewater, which affects to the COD load in the effluent. (Bajpai, 2010)

In the washing steps, the impurities, dissolved organics and solids are transferred from the pulp into the effluent. Also, some of the fiber material is lost in the washing stage. (Bajpai, 2010)

2.5. Bleaching

The bleaching of mechanical pulps is based on a lignin-saving method. This means, that otherwise than in the bleaching of chemical pulps, the lignin is not tried to be removed but changed into colorless form. Because of this, the bleaching effect is not permanent and the product will turn into yellow color over time. (Suhr, et al., 2015)

Typical bleaching chemicals in CTMP bleaching are sodium dithionite ($Na_2S_2O_4$) and hydrogen peroxide (H_2O_2) (Blechschmidt, et al., 2006). Chemical for the process is chosen by the brightness level demanded. With hydrogen peroxide better brightness can be reached. Hydrogen peroxide bleaching is performed in alkaline conditions, which are reached by adding sodium hydroxide. Calcium and magnesium hydroxides can also be used, but sodium hydroxide is the most commonly used chemical. When using calcium or magnesium hydroxides, the COD load is a bit smaller. Sodium silicate ($NaSiO_3$) is used as a stabilizer in bleaching and chelating agents EDTA ($C_{10}H_{16}N_2O_8$) and DTPA ($C_{14}H_{23}N_3O_{10}$) as additives. Other stabilizers and additives are also used, but those are not very common in CTMP plants. (Lindholm, 2009)

3. CTMP wastewater

CTMP effluent comes from different sources from the whole plant and the total effluent is a collection of all these different kinds of waters. The final effluent that goes to the wastewater treatment plant varies depending on the used technology and the used chemicals in the plant. Also the used raw material affects to the composition of the effluent.

3.1. Sources of pollutants and wastewater in CTMP plant

The final effluent that needs to be purified in the wastewater treatment plant consists of multiple streams from the whole process. The main sources of pollutants are presented in the figure 2. Basically, the effluent comes out from the process after the washing stages, but the dissolved compounds and chemicals in the effluent originate from different process stages. From figure 2 it can be seen, that the composition of the effluent varies a little between the sources. Basically the main components in the effluent are fibers, dissolved organics, nutrients that originates from the wood and residues of the used chemicals. Also, during the process, the components of the wood react with the chemicals used, so there are reaction products in the effluent. (Manner, et al., 2009)

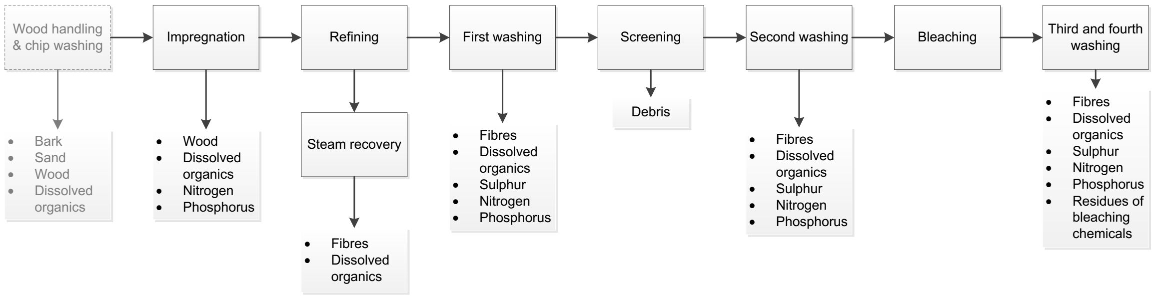


Figure 2 Sources of pollutants in the CTMP plant. Modified from (**Suhr, et al., 2015**).

The de-barking process has a big role in the effluent pollution. The effluent from de-barking consists of bark, sand, wood and dissolved organics. Because of the toxic nature of the bark, these effluents are usually kept outside the other parts of the CTMP process. The de-barking effluent can also be treated separately, to ease the treatment of less toxic effluents. (Manner, et al., 2009) (Suhr, et al., 2015) The wood handling part of the process is left outside consideration in this work.

Alkaline treatment of wood in impregnation stage affects to the dissolution of organics. The alkaline conditions dissolve more organics from the wood. Compared to other mechanical pulps, in CTMP effluent there are more lignin dissolved in the water, due to the sulphonation of the lignin in the impregnation stage. Also, at pH above 8, deacetylation of glucomannans (softwoods) and xylans (hardwood), and methylation of pectins takes place, which affects to the amount of acetic acid, methanol and pectic acids in the effluents. CTMP impregnation is executed usually around pH 9, so these reaction products can also be found from the effluents. (Manner, et al., 2009)

Bleaching is also executed in alkaline conditions. This means, that also in the bleaching, the dissolution of organics is quite high. Also, alkaline peroxide bleaching is noticed to increase the dissolution of wood extractives, so those kinds of compounds also exist in the bleaching effluents. Alkaline peroxide bleaching is also known to dissolve acetic acid from the pulp (Konn, et al., 2002). Silicate in the effluent originates from the bleaching, where sodium silicate is used as an additive. With alkaline solutions and bleaching chemicals, chelating agents are added. These chelating agents also exist in the bleaching effluents. The nitrogen in the effluents originates from the wood but also from the nitrogen based chelating agents, EDTA and DTPA. Dithionite is also used as a bleaching chemical. Dithionite bleaching is carried out in lower pH (5-6) and does not dissolve so much organics from the pulp. For the yield losses in dithionite bleaching are though conflicting opinions, some studies show little yield loss and other negligible. Because of the nature of the chemical in dithionite bleaching, more salts are dissolved into the effluents. (Manner, et al., 2009)

3.2. The effect of the pulp raw material into the wastewater

Different wood species have a different kind of chemical composition. In general, wood consist of carbon, oxygen, hydrogen, nitrogen, potassium, calcium, magnesium, phosphorous and sulphur. First four of them are the main components, and the others exist in lower concentrations. (Snow, 2011) The main polymers and substances (cellulose, hemicelluloses, lignin and extractives) consist from these compounds. The amount of these polymers varies between different wood species. The wood properties also vary depending on the location in the wood. For example, the chemical composition in the stem wood and knot wood is different. (Sjostrom, 1993) In table II, there is presented chemical compositions for some wood species.

Table II Chemical composition of different wood species **(Knowpap, 10.0.)**

Constituent (%)	Spruce	Pine	Birch	Eucalyptus	Acacia
Cellulose	42	42	40	50	50
Hemicellulose	28	26	37	20	24
Lignin	28	27	20	27	23
Extractives	2	5	3	3	3

In general, hardwood pulp effluent contains more dissolved organics than softwood pulp effluents. This is due the amount of hemicelluloses, pectins and acetic acid dissolution. Also, the higher chemical demand for hardwood has an impact to the amount of dissolved compounds. The amount of extractives in the effluent depends from the wood species and how much of these are available in the wood. For example it has been noticed, that pine wood releases more resins than spruce wood, and that correlates straight to the amount of extractives in those species. (Manner, et al., 2009)

Since the wood consists of carbon, oxygen, hydrogen, nitrogen, potassium, calcium, magnesium, phosphorous and sulphur, it can be assumed, that all of these elements exist in some amounts dissolved in the effluents. Generally it can be said, that hardwood contains more inorganics than softwood, though exceptions exist. (Pettersen, 1984) This means, that in general, hardwood effluent contains more inorganics than softwood effluents.

3.3. Wastewater characterization

The wastewater from the CTMP process contains lignin, hemicellulose, carbohydrates, tree extractives (resin and fatty acids), inorganic compounds, chemicals used in bleaching and impregnation and breakdown compounds from all of these materials. (Roy-Arcand & Archibald, 1995) (Suhr, et al., 2015) From the impregnation chemicals, sulfite is dissolved in the process water. Also, in the impregnation stage, nitrogen, phosphorous and salts, which originates from the wood, are dissolved into the water. (Suhr, et al., 2015) In the bleaching stage, the bleaching chemical reacts with the pulp and the dissolved compounds in the effluent. The reaction with the effluent depends on the nature of the bleaching chemical. If chlorine based bleaching chemicals are used, the residual lignin forms adsorbable organic halides (AOX) with the chlorine or chlorine compounds (Badar & Farooqi, 2012). When using chemicals with high alkalinity, like NaOH, which is typically used together with peroxide bleaching, the amount of dissolved organics is higher. Dithionite bleaching does not increase the amount of organics significantly, but the amount of salts in the effluent is higher. This is due the sodium in the bleaching chemical (Manner, et al., 2009)

3.3.1. Chemical oxygen demand (COD)

Chemical oxygen demand (COD) is very commonly used variable in the wastewater characterization. COD refers to the amount of oxygen that is consumed under specific conditions by chemical oxidation of organics and oxidisable inorganic matter in the wastewater. (Bahadori & Smith, 2016)

The CTMP effluent is a very high concentration effluent. It has a high COD compared to other mechanical pulps. This is due the chemical treatment, which dissolves more organics from the wood and thus increases the COD load. COD load in CTMP wastewaters is assumed to consist of polysaccharides (10 – 15 %), lignin (30 – 40 %) and organic acids (35 – 40 %) (Rintala & Puhakka, 1994). In the table III COD loads for wastewaters from different kind of mechanical pulping processes are presented.

Table III Typical COD loads in the wastewater before treatment for different types of mechanical pulps **(Suhr, et al., 2015)**.

Pulp type	COD (kg/t of pulp)
Refiner mechanical pulp (RMP)	40-60
Thermomechanical pulp (TMP)	50-80
Chemithermomechanical pulp (CTMP)	60-100
Bleached softwood CTMP	80-130
Bleached hardwood CTMP	120-200

As seen in the table III, the COD load in bleached CTMP effluents is higher than in the unbleached ones. This is due the alkalinity of the bleaching chemicals. The alkalinity affects to the woods chemical composition and dissolves organics compounds from the pulp. (Suhr, et al., 2015) The reason to the differences between bleached softwood and hardwood COD loads is in the higher amount of hemicelluloses in the hardwoods species and their tendency to dissolve into the effluent in alkaline conditions. Also, as the name already tells, the wood material is harder in hardwood species, so it requires higher chemical doses to soften the wood. This affects to the COD load. (Manner, et al., 2009) The amount of COD varies depending on the process. Bajpai have reporter, that for the CTMP process, typical COD load in mg/liter of wastewater is between 6000-9000 (Bajpai, 2017). Other reported values for COD in CTMP wastewaters are 12 000 mg/L (Dufresne, et al., 1996), 2520 – 7930 mg/L (Stephenson, et al., 1994) and 2100 – 13 000 mg/L (Stephenson, et al., 1994).

3.3.2. Biochemical Oxygen Demand (BOD)

Biochemical oxygen demand (BOD) is a variable, which is used to determine the amount of oxygen that is consumed by microorganism in the water to decompose organic matter. The BOD value is can be determined for a five day period, when the used term is BOD_5 or for a seven day BOD used for example in Scandinavia, the term is BOD_7. (Bahadori & Smith, 2016)

For the CTMP process, typical BOD_5 load in mg/liter of wastewater is between 3000-4000 (Bajpai, 2017). BOD_5 loads for different mechanical pulping processes are presented in table IV.

Table IV Guidelines for BOD_5 loads in the wastewater before treatment for different types of mechanical pulps (**Suhr, et al., 2015**).

Pulp type	**BOD_5 (kg/t of pulp)**
Refiner mechanical pulp (RMP)	10-15
Thermomechanical pulp (TMP)	13-22
Chemithermomechanical pulp (CTMP)	17-30
Bleached softwood CTMP	25-50
Bleached hardwood CTMP	50-80

3.3.3. Total Suspended solids (TSS)

Total suspended solids are a measure for all suspended solids in the wastewater. (Bahadori & Smith, 2016) It consists of settleable and nonsettleable compounds. If discharged into receiving waters, TSS can settle to the bottom of the receiving waters and disturb the culture medium of flora and fauna in the water. Suspended solids in the CTMP wastewaters are mainly fibers or fiber debris. (Mathys, 1991)

The CTMP effluent has a very high suspended solids amount compared to other mechanical pulp effluents. For CTMP effluents TSS values have been reported to be 180 – 490 mg/L (Larsson, et al., 2017), 1200 mg/L (Dufresne, et al., 1996), 600 – 1000 mg/L (Welander, et al., 1988), 200 – 2000 mg/L (Cornacchio & Hall, 1988), 180 – 5000 mg/L (Stephenson, et al., 1994) and 4.4 – 72 kg/t (Novatec Consultats Inc.; Hydroqual Consultats Inc.; Sandwell Swan Wooster Inc., 1987).

3.3.4. Total nitrogen

Total nitrogen is a measure for the complete nitrogen content in the wastewater. It includes nitrate (NO_3^-), nitrite (NO_2^-), ammonia (NH_3), ammonium (NH_4^+), nitrogen gas (N_2) and organic nitrogen compounds in the water. (Bahadori & Smith, 2016) Some of these compounds exist in the CTMP effluent, but are typically presented only in total nitrogen amount, not separately.

Nitrogen in the wastewater originates from the wood and the used chelating agents (EDTA, DTPA) that contain nitrogen. The amount of nitrogen in the effluents depends on the used raw material and its chemical composition, but also the pulping method affects to the amount of dissolved nitrogen. (Suhr, et al., 2015) In table V, nitrogen loads in wastewaters from different kind of pulping processes are presented. As it can be seen from the table, if chemical treatment is used, more nitrogen is dissolved into the effluents.

Table V Typical nitrogen loads in the wastewater before treatment for different types of mechanical pulps from spruce **(Suhr, et al., 2015)**.

Pulp type	**Nitrogen (g/ADt of pulp)**
Refiner mechanical pulp (RMP)	90-110
Thermomechanical pulp (TMP)	100-130
Chemithermomechanical pulp (CTMP)	110-140
Bleached softwood CTMP	130-400

Reported values for nitrogen in the CTMP wastewaters are 110 – 400 g/ADt (Suhr, et al., 2015) and 14 – 50 mg/l (Ruutiainen, 1987).

Aerobic bacterial fermentation requires a BOD:N:P ratio of 100:5:1. (Mathys, 1991) According to Cornacchio and Hall (Cornacchio & Hall, 1988), CTMP wastewaters usually offer a COD/N ratio between 100:0.67 and 100:4. The amount of nitrogen in the effluents is so small that it does not fulfill the nitrogen need as a nutrient in the activated sludge process. The nitrogen in the effluent can also be in a form, in which bacteria cannot utilize it. If aerobic method is used for the wastewater treatment, nitrogen needs to be added to the process to optimize the process conditions (Suhr, et al., 2015).

For anaerobic treatment, typical need for nitrogen is 10 mg per 100 mg of biomass and the COD:N:P ratios is around 500:5:1. To maintain the methanogenic activity, 50 mg/L of nitrogen in liquid phase is needed. (Tchogobanoglous, et al., 2003) These needs are not fulfilled in CTMP wastewaters, so this method also needs nitrogen addition to work properly.

3.3.5. Total phosphorous

Total phosphorous in the wastewater is a sum of all forms of phosphorous existing in the effluent. (Bahadori & Smith, 2016)

Phosphorous in the wastewater originates from the wood structure. The phosphorous dissolves into the effluent during chemical and mechanical treatment and the amount of phosphorous depends on the wood species used as a raw material. (Suhr, et al., 2015) Table VI presents the amounts of phosphorous in effluents from different kind of mechanical pulping processes. The amount in the chemically treated pulps is a little higher, but not significantly.

Table VI Typical phosphorous loads in the wastewater before treatment for different types of mechanical pulps from spruce **(Suhr, et al., 2015)**.

Pulp type	Phosphorous (g/t of pulp)
Refiner mechanical pulp (RMP)	20-30
Thermomechanical pulp (TMP)	30-40
Chemithermomechanical pulp (CTMP)	35-45
Bleached softwood CTMP	50-60

For CTMP effluents, phosphorous load is reported to be 35 g/ADt to 60 g/ADt (Suhr, et al., 2015), 0.5 – 32 mg/l (Ruutiainen, 1987). According to Cornacchio and Hall, CTMP wastewaters usually offer a COD/P ratio from 100:0.093 to 100:0.5 (Cornacchio & Hall, 1988). The amount of phosphorous in the effluents is so small that is does not fulfill the phosphorous needs of the activated sludge process. If that method is used for the wastewater treatment, phosphorous needs to be added to the process to optimize the process conditions (Suhr, et al., 2015). As so, the amount of phosphorous is so small that it shouldn’t cause big problems when considering the wastewater discharge.

3.3.6. Adsorbable organic halides (AOX)

Adsorbable organic halides (AOX) is a general definition for all the organics that contain one or more atoms of halogens. These compounds are stable and non-reactive, but toxic to environment if discharged within the wastewaters. (Bahadori & Smith, 2016) In the case of pulp and paper industry, the AOX compounds are mainly chlorinated organic compounds.

AOX are only generated in chlorine based bleaching, not in totally chlorine free bleaching. These compounds can be removed with aerobic wastewater treatment methods in some amounts. The removal efficiency depends on the process conditions. Usually, anaerobic methods are not used to purify chlorine bleached wastewater, because of the sensitiveness of the anaerobic process. (Bajpai, 2010) Since chlorine is not typically used in mechanical pulp bleaching, these compounds can be left without consideration in this work.

3.3.7. Resin and Fatty acids

Resin acids are weak hydrophobic acids, which can be found in the wood. These are toxic compounds and can cause even 60-90% of the toxicity in mechanical pulping effluents. Even though resin acids are hydrophobic, they are found in the CTMP wastewaters at concentrations of several hundreds milligrams per liter. (Liver & Hall, 1996) Addition of sodium sulphite and oxidizing agent is known to increase the dissolution of resin and fatty acids, so the amount of chemicals used in the process has a connection to the amount of extractives in the effluent (Gaarder, 1991). According to Puro et al.'s research the amount of resin acids in softwood CTMP wastewaters vary between 330-770 mg/l and in a mixture of hardwood and softwood CTMP wastewaters between 270-570 mg/L. (Puro, et al., 2011) Bathija have presented resin acids amount of 42 mg/L for some softwood BCTMP process (Bathija, 1989) and Ismailov 90 mg/L for softwood CTMP process waters (Ismailov, 2013).

According to Puro et al.'s research, the amount of fatty acids in softwood CTMP wastewaters vary between 110-420 mg/l and in a mixture of hardwood and softwood CTMP wastewaters between 60-210 mg/L (Puro, et al., 2011). Bathija's research shows amount of fatty acids to be around 70 mg/L for some softwood BCTMP process (Bathija, 1989). Ismailov have presented in his study fatty acids amount in some softwood process to be 385 mg/L (Ismailov, 2013). Total amount of wood extractives in CTMP effluents can vary from 12 to 1200 mg/L (Stephenson, et al., 1994).

As it can clearly be seen, the reported values for resin and fatty acids vary a lot. The differences in these values can be explained either by different kind of pulping processes or the analyzing methods. Extractives can be in some parts connected into the solids in wastewaters, so if the analyzing method does not take solids into account, the amount can be smaller than in reality. There is also couple of different kind of methods for the extractives analysis, so they can give different kind of results.

Resin and fatty acids are known to be inhibitors in anaerobic (Bajpai, 2017) and aerobic treatment and affects to the activity of the sludge (Hynninen, 2008). These are also considered to act as a foulants in filtration (Puro, et al., 2011). Resin and fatty acids are found in the evaporation deposit also, so they work as foulants in that technology too (McKeough & Fagernäs, 1999).

3.3.8. Sulphur compounds

Sulphur in the wastewaters originates from the chemicals used in the impregnation and dithionite bleaching. Sulphur exists in the effluents as sulphonated organics, sulphide S^{2-}, sulphite SO_3 and sulphate SO_4. According to Ruutiainen, SO_4 amount in the wastewater varies in a wide range between 181-2700 mg/l and SO_3 amount in the wastewater varies from 5 mg/l to 790 mg/l (Ruutiainen, 1987). The total sulphur content in the wastewaters can be between 65-1198 mg/l (Ruutiainen, 1987). Pichon et al. (1988) have also reported that sulphur in the wastewaters is mainly present as sulphate. Pichon et al. have reported a sulphate amount of 0.75 kg/m^3 of wastewater. Sulphur has also been found from CTMP wastewaters as lignosulphonates, at a concentration of 0.1 kg/m^3 of wastewater. (Pichon, et al., 1988). Stephenson et al. (1994) have reported SO_4, SO_3, S_2O_3 and S^{2-} concentrations to be 525 – 1565 mg/L, 10 – 30 mg/L, 0 – 10 mg/L and 0.7 – 3.3 mg/L respectively. They have also reported some literature values without reference. These values for SO_4 and SO_3 are 200 – 1590 mg/L and 0 – 225 mg/L respectively.

Sulphur is an inhibiting compound in anaerobic treatment. The presence of sulphur reduces the COD removal efficiency, when COD/S ratio is below 20. It can be degraded by sulphur-degrading bacteria, which form hydrogen sulphide H_2S, from sulphite and sulphate. The use of sulphur-degrading bacteria decreases the formation of methane, since the bacteria use the same energy source as the methane-producing bacteria. (Pichon, et al., 1988) Another way to reduce sulphur and H_2S is to chemically treat the water and precipitate the sulphur compounds. This increases the chemical amount consumed in the process. This method is usually used in aerobic treatment. In the aerobic conditions, the sulphur compounds are oxidized into odorless sulphate. This increases a little the oxygen consumption. The sulphate is precipitated and removed from the process with the sludge. This may affect to the applicability of the sludge. (Lebrecht & Hannay, 2015)

Biogas that is formed in the anaerobic treatment process may need purification because of the hydrogen sulphide's toxic and polluting nature. (Pichon, et al., 1988) The need of purification depends on the purpose of use of the gas. Specific purification is needed only if the gas has high purity demands.

3.3.9. EDTA & DTPA

Ethylenediamine tetraacetic acid (EDTA) and diethylenetriamine pentaacetic acid (DTPA) are used with bleaching chemicals to maximize the bleaching efficiency by removing the negatively affecting metals. They form complexes with the metal ions to remove those from the pulp. Unreacted chemicals exist in some amounts in the wastewaters. (Bajpai, 2017) In the pulp mills, 25-40 % of the chemical used in the process is detected in the effluents. If 2 kg/ADt of EDTA or DTPA is used, it correlates to 150 - 220 g/L of additional nitrogen per ton of pulp in the wastewater. (Suhr, et al., 2015) Stephenson and Duff have reported DTPA concentrations to be between 20 to 500 mg/L in the BCTMP effluents (Stephenson & Duff, 1996a).

There are several toxicity researches, that claim EDTA and DTPA and metal ions cause no significant environmental threat. Conflicting opinions also exist. The effect of these chelating agents after they are released into receiving waters is not so well known, so the purification of these compound needs to be considered and actions need to be made to purify the water from these compounds before discharge. (Bajpai, 2010)

3.3.10. Salts

CTMP wastewater includes inorganic salts, that originates from the wood and chemicals used in the process. For example sodium salts and silicates originate from the pulping chemicals and calcium and magnesium from the wood. (Li & Watkinson, 2009) Salts in the effluents tend to be a problem in the wastewater treatments, if evaporation is used as a treatment method (Li & Watkinson, 2009).

Manganese ions exist in some amounts in the water and cause a catalytic decomposition of peroxide in the bleaching stage. Since counter current method is used in the CTMP mills, the effluent from the bleaching stage is fed to the unbleached stage and the manganese sticks to the pulp. That way the ions stay in the process. (Vinje & Kuntz, 2000). For this reason, the harmful salt ions need to be removed, so that they don't stay in the water circulation and cause problems in the process or in the evaporation based wastewater treatment system. For biological wastewater treatment methods, salts should not be a problem, since addition of different kind of salts is used as a pretreatment method for example in anaerobic treatment, to remove compounds that are toxic for methanogenic bacteria (Welander, 1988).

3.3.11. Heavy metals

Heavy metals are specified to be metals, which have high atomic mass and can be precipitated by hydrogen sulfide in acidic conditions. These metals are lead, silver, gold, mercury, bismuth, copper, cadmium and zinc. (Bahadori & Smith, 2016)

Metals are known to be toxic when discharged into receiving waters. Some amounts of different metals have been found from the CTMP wastewaters. Metals can originate from the wood (copper, zinc, mercury, cadmium) or related dirt, like impurities in the chemicals used, from piping or other process equipment. The amount of metals is quite low compared to other toxic components, and does not significantly increase the total toxicity in the effluents. Also, metals require acidic environment to be solubilized and since CTMP process is operated in slightly alkaline conditions, the dissolving into effluents is not favorable for metals. (Gaarder, 1991)

3.3.12. H_2O_2

Hydrogen peroxide is used as a bleaching chemical in some plants. If the bleaching stage is not operating correctly, it is possible that the hydrogen peroxide is not totally consumed in the process and then it can get into the washing water. This should happen only in fault situations, not in normal operations. Small amounts of hydrogen peroxide residues are still quite typically found in the waters, even when the process operates normally. (Ruutiainen, 1987)

Hydrogen peroxide is known to be harmful for aerobic biosludge in high concentrations (Hynninen, 2008). For anaerobic processes, hydrogen peroxide is also known to be an inhibitor at certain concentrations. According to Ruutiainen, even 100 mg/l of H_2O_2 in the wastewater does not affect to the production of methane in the anaerobic process (Ruutiainen, 1987). Conflicting information about the inhibiting concentration is available. Though it may not affect to the methane yield, it can make the process slower by inhibiting hydrolysis, acidogenesis or acetogenesis stages.

If high amounts of hydrogen peroxide exist in the effluent, it can be treated with anaerobic catalase enzyme, which catalyzes the decomposition of hydrogen peroxide to water and oxygen, as presented below.

$$2\,H_2O_2 \xrightarrow{catalase} 2\,H_2O + O_2 \tag{1}$$

Stephenson and Duff have reported H_2O_2 concentrations between 50-1000 mg/L in BCTMP effluents (Stephenson & Duff, 1996a).

3.4. Conclusion of the pollutants in the wastewater

In table VII is collected together all the parameters and pollutants, and their concentration ranges in the wastewater.

Table VII Summary from the typical parameters and pollutants, and their concentrations, in the CTMP wastewater (1) **(Stephenson, et al., 1994)**, (2) **(Suhr, et al., 2015)**, (3) **(Bajpai, 2017)**, (4) **(Ruutiainen, 1987)**, (5) **(Novatec Consultats Inc.; Hydroqual Consultats Inc.; Sandwell Swan Wooster Inc., 1987)** , (6) **(Puro, et al., 2011)** , (7) **(Stephenson & Duff, 1996a)**.

Pollutants	**Amount in the wastewater**	
	mg/L	**kg/ADt of pulp**
Chemical oxygen demand (COD)	2100 – 13000(1)	80 – 130 (softwood) 120 – 200 (hardwood)(2)
Biological oxygen demand (BOD)	3000 – 4000(3)	25 – 50 (softwood) 50 – 80 (hardwood)(2)
Total suspended solids (TSS)	180 – 5000(1)	4.4 – 72(5)
Total nitrogen	14 – 50(4)	0.11 – 0.4(2)
Total phosphorous	0.5 – 32(4)	0.035 – 0.06(2)
Resin acids	42 – 770 (softwood)(6)	-
Fatty acids	60 – 420 (softwood) 60 – 210 (hardwood+softwood)(6)	-

Total extractives	Up to 1200[1]	-
Sulphide, S^{2-}	0.7 – 3.3[1]	-
Sulphite, SO_3	5 – 790[1]	-
Sulphate, SO_4	181 – 2700[1]	-
DTPA & EDTA	20 – 500[7]	-
H_2O_2	50 – 1000[7]	-

From the table VII it can easily be seen, that the amounts of pollutants vary a lot. This only confirms the fact that CTMP effluents are quite difficult to classify. There are multiple parameters that affect to the nature of the effluent. From different kind of processes, different types of effluents are discharged. Because of this, there is no straightforward answer to the question what is the one and only, and the best, way to treat CTMP effluents.

3.5. Water purity objectives

When treating water, there is always some kind of purity level that needs to be reached. This level can be for discharged water or for process equipment, if water is recycled at the mill. For discharged water, the levels are defined in environmental permit and for process equipment. Manufacturers can set levels for the process equipment, to secure the functioning of the equipment.

3.5.1 Objectives for discharge water

European Union has set guidelines to minimum limits for measureable parameters in wastewater discharged from CTMP pulp mills. The levels for COD, TSS, nitrogen and phosphorous are listed in table VIII.

Table VIII BAT-associated levels for the direct waste water discharge to receiving waters **(EU, 2014)**.

Parameter	Yearly average, kg/ADt
Chemical oxygen demand, COD	12 – 20
Total suspended solids, TSS	0.5 – 0.9
Total nitrogen	0.15 – 0.18 [1]
Total phosphorous	0.001 – 0.01

(1) When biodegradable or eliminable chelating agents cannot be used due to pulp quality requirements (e.g. high brightness), the emissions of total nitrogen might be higher than this BAT-AEL and should be assessed on a case-by-case basis.

The BAT conclusions set levels only for parameters that are supervised without exception. There are several possible discharge parameters, like toxic compounds or pH, to be controlled and supervised, but these parameters are set locally and on case-by-case basis.

Though EU has set general guidelines for wastewater discharge, there might be different kinds of regulations in different EU countries. For example in all the Nordic countries, Finland, Norway and Sweden, the environmental permit requirements are set on case-by-case basis. Some of the countries in EU have developed a permit system based on a technology, so for example for CTMP plants or pulping plants in general some guidelines exist. Usually these are only the maximum levels and tighter limits are set for individual plants. (OECD, 1999)

The discharge levels and regulations vary a lot between different countries around the world. There are some guidelines set in every country, for example in USA by Environmental Protection Agency, but these are not as straightforward as EU's BATC. The discharge limits and standards can be set based on the technology used or in general for all types of technologies used in the certain industry area. Typically, if the limits are based on the technology, the limits for CTMP are set based on mechanical pulping technology. There might be difficulties to match the CTMP technology to the limits since chemicals are used. The technology does not match the chemical pulping either, so the limits set for that technology can't either be used. This is one reason, why the CTMP wastewaters tend to cause problems when designing the mill. It is very common to set the limits on a case-by-case basis in the environmental permission. When set on case-by-case basis, the designing comes a bit easier.

The controlled and supervised parameters, and the ways to present these values, vary between countries and continents. For example when BAT-conclusions present the limits in kg/ADt of pulp for the whole discharges, in U.S. the limits are categorized further for continuous discharges and non-continuous discharges.

Table IX Effluent limitations for mechanical pulp facilities where pulp and paper groundwood chemi-mechanical mill are produced **(U.S. Environmental Protection Agency, 2018)**.

Pollutant	kg/t of product		
	Continuous discharges		Non-continuous dischargers (annual average)
	Maximum for any 1 day	Average of daily values for 30 consecutive days	
BOD5	13.5	7.05	3.96
TSS	19.75	10.65	5.85

The wastewater discharge limits around the world are quite hard to interpret in general basis. For example in Asia, the limits are a lot tighter than in USA (Song, et al., 2015). After all, all over the world the last decision on the limits comes from the environmental authorities.

3.5.2 Objectives for recycling water

Water used and purified in the pulp and paper mills is not only discharged into receiving water bodies, but also recycled and reused in the mill. This can be achieved for example by using evaporation or other technologies. Due to recirculation, the fresh water consumption in the mill can be decreased. The quality limits for process waters depends a lot on the product produced, the use of the water and the equipment used in the process. Equipment suppliers can set some limits for the water used within the equipment. In the table X is some values for different processes in pulp and paper mills, that the used water needs to fulfill. Typical values that are controlled are hardness and alkalinity of the water, because these might cause scaling in the machines and water circuits. Silica is also a source for scaling, so that can also be monitored. Some metals (Fe, Al, Mn), chlorine and sulphate are corrosive and also can cause scaling, so these also needs to be controlled. If thinking the values in the table X, the pH range suitable for different processes is quite big, so that should not be a problem with these kinds of waters. The TSS is high in CTMP waters (up to 5000 mg/L), and the limits presented in table X are quite strict. This can cause problems in circulation, if enough TSS can not be removed.

Table X Water quality requirements in different pulp and paper making processes **(Blanco, et al., 2016)**.

Parameter	Cooling	Boiler	Sealing	Mechanical pulping	Pulp and paper bleached	Chemical unbleached pulp
pH	6.9 – 9.0	8.5 – 9.5	> 7.0	6 – 10	6 – 10	6 – 10
TSS (mg/L)	100	-	-	40	10	10
Turbidity (NTU)	50	-	-	70	40	40
Color (PCU)	-	-	-	30	10	10
Hardness (mg$CaCO_3$/L)	650	0 – 0.3	200	100 – 200	100	100
Alkalinity (mg$CaCO_3$/L)	350	-	-	75 – 150	75	75
Si (mgSiO_2/L)	50	-	-	50	50	50
Cu (mg/L)	-	0.01 – 0.05	-	-	-	-
Fe (mg/L)	-	0.10 – 0.01	-	0.3	0.1	1
Mn (mg/L)	-	-	-	0.1	0.05	0.5

When using biological wastewater treatment, some of the microorganisms may occur in the water after the purification process, and these are harmful for the pulping process and may produce biofilms and odor problems. (Blanco, et al., 2016) Because of these problems, usually biologically treated water is not recycled and reused in the mill. If recycled, some tertiary treatments, like membrane filtration or chemical purification, are needed.

4. Wastewater treatment methods

CTMP wastewaters are quite challenging to purify, because of the high COD, suspended solids and the toxicity of the water. There are few alternatives for the treatment methods that can be used. Usually, the total treatment is a combination of several treatment methods. Recommended treatment methods in BAT are; aerobic treatment with activated sludge, internal chemical treatment of the white water of the first washing stage and activated sludge process for the rest, combination of aerobic and anaerobic treatments, evaporation of the most contaminated water and activated sludge for the rest, evaporation of all the effluents and incineration of the concentrates in a recovery boiler. (Suhr, et al., 2015)

4.1. Evaporation

Evaporation is a technique for wastewater handling, where heat is used to vaporize the liquid phase and the solids are concentrated. Temperature used in the evaporation is optimized to vaporize the water, but of course compounds which evaporate in lower temperatures can also be found in the evaporated phase. (Bahadori & Smith, 2016)

It is possible to use evaporation as the main treatment method, or treat only part of the effluents with evaporation. When using evaporation as the only treatment method, it leads to zero liquid discharge situation, where liquid is evaporated and circulated in the process and none of it is discharged into receiving water bodies. In this type of evaporation, a by-product of concentrated waste is produced. This can be incinerated in a recovery boiler to recover chemicals and produce steam that can be utilized elsewhere in the process. (Suhr, et al., 2015) (Forsberg & Jansen, 1993)

Evaporation is typically executed in multiple stages for better steam economy. The vapor from the first stage is utilized as at heat source in the second stage etc. This method is called multiple-effect evaporation (Krotscheck & Sixta, 2006). The secondary condensate from the first stages is the most impure, and contains for example methanol which is formed during the pulping process. The most impure fractions from the evaporation are typically stored in foul condensate tanks and the cleaner in clean condensate tanks. Secondary condensate from the foul tank can be further purified for example by stripping and then mixed with the clean condensate. (Forsberg & Jansen, 1993)

Acetic acid can also be found as an impurity in the condensates, but it exists in notable amounts only in later evaporation stages and in lower concentrations in the pre-evaporator condensates (Forsberg & Jansen, 1993). Larsson, et al. have reported acetic acids values for CTMP wastewaters produced from spruce, aspen and birch. These values vary between 1330 to 6950 mg/L, the highest values being from hardwood wastewaters. (Larsson, et al., 2017) Forsberg and Jansen have presents in their patent (Forsberg & Jansen, 1993), that with recycling of the green liquor, pH can be controlled and significant decrease in the acetic acid concentration in the condensates can be reached. With concentration level of 35%, when feed pH is lifted from 9.12 to 10.45, the concentration of acetic acid in condensate decreases from 50.3 mg/L to 6.7 mg/L.

For wastewater treatment, the most commonly applied evaporation technology is the falling film type evaporators. For high-viscosity liquors or liquor that tends to foul, forced circulation evaporators are also used. In falling film type evaporators, plates or tubes are used as heating elements. The effluent is fed into the top of the evaporator with circulation pump, where it falls downwards on the hot surface of the plates or tubes by gravity. The water is evaporated and collected from the top and the concentrate from the bottom of the evaporator. (Krotscheck & Sixta, 2006)

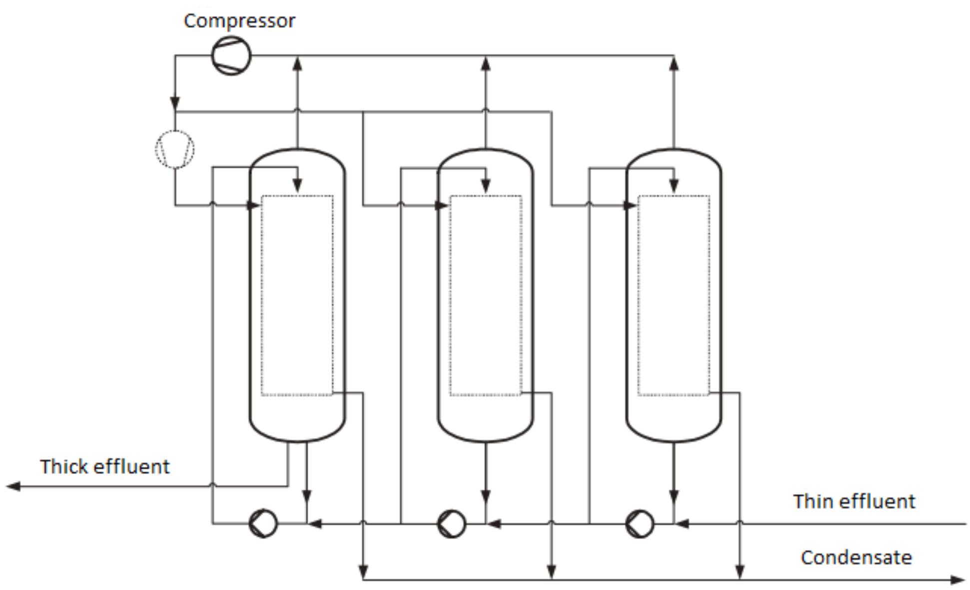


Figure 3 Principle of the mechanical vapor recompression (MVR) system (**Krotscheck & Sixta, 2006**).

Mechanical vapor recompression (MVR) technology is the most commonly used method in wastewater treatment evaporation plants. The method is based on a process where evaporation is driven by electrical power. The vapor that is formed from the wastewater in the liquid side of the evaporator is compressed and recycled to the steam side for condensation. The liquid is pumped from body to body. The difference between multiple-effect plants and mechanical vapor recompression plants is in the flow rates between the bodies. In multiple-effect plants the flowrates of condensate from all bodies are similar, but in MVR the highest condensate flow rate is from the thin effluent stage and the lowest flow rate from the thickened effluent stage. The MVR process principle is presented in figure 3.

The zero-liquid discharge method seems quite a good alternative, because the demand for fresh process water is a lot smaller than with typical biological treatment options. The water recycling system for zero liquid effluent discharge is presented in figure 4. As seen in the figure, the only fresh water addition to the process is the amount of water lost as a water vapor in the pulping process (Bajpai, 2010) (Suhr, et al., 2015).

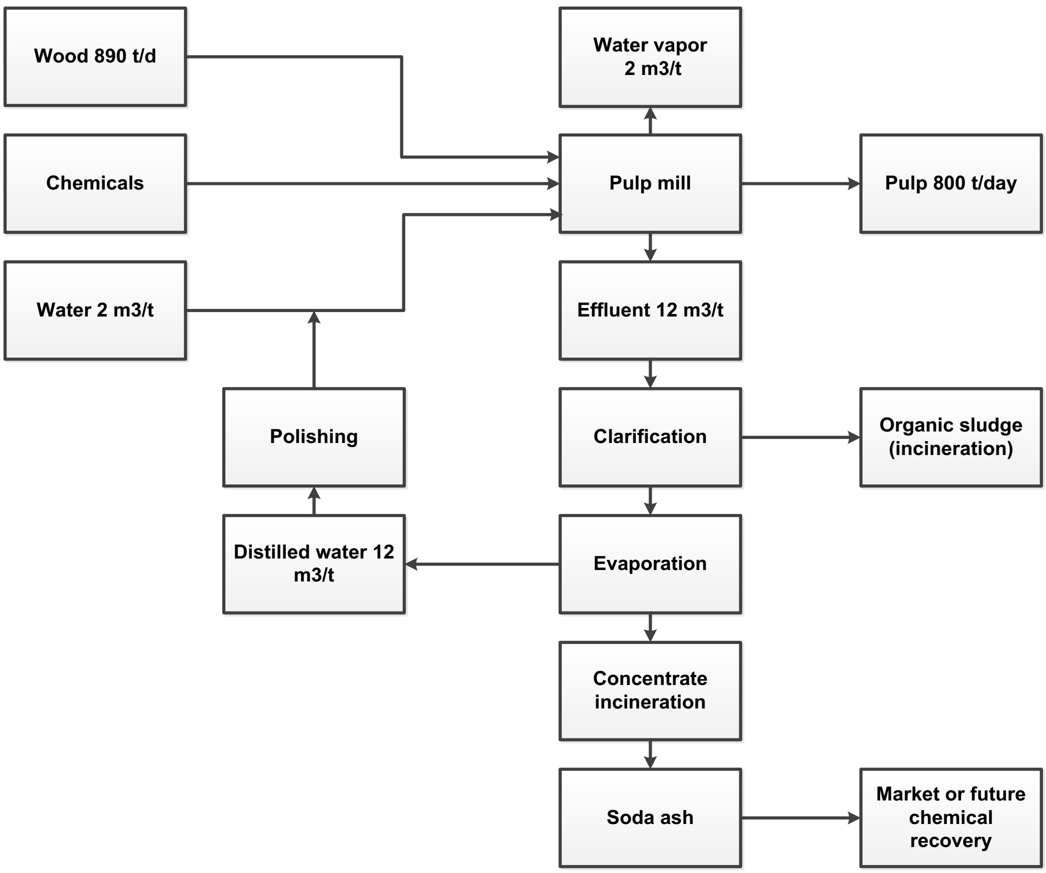


Figure 4 Process chart of a zero discharge water recycling system in Meadow Lake BCTMP mill **(Suhr, et al., 2015)**.

The benefits of this method are even 80% recycling of the water and the possibility to recover chemicals and nutrients in a recovery boiler. (Suhr, et al., 2015) This method seems quite tempting when there is no receiving waters near the mill for the discharge or when limited amount of water is available. Also, when very tight regulations for the discharge water are set, and other purification methods seem not to reach the targets, this method could be utilized.

The closed loop zero effluent discharge system is possible to execute both in old and new plants. The biggest limitation though, is the high investment costs. The evaporation and recovery boiler technology is pretty expensive, and often other cheaper solutions are chosen for the water treatment. (Bajpai, 2010) Also, in already existing plants, there might not be a lot of free space for the evaporation plant. Thought the evaporation process itself does not require that much space, when compared for example to aerobic treatment which needs big lagoons, it needs to be located close to the CTMP plant. (Bajpai, 2010)

Problems in the evaporation method are fouling and deposit formation. The organic and inorganic solids in the effluent tend to cause fouling in the evaporator surfaces. Due to this, the efficiency of the equipment decreases. (Li & Watkinson, 2009) Possible foulants in the CTMP wastewaters found in the research of McKenough & Fagernäs are calcium carbonate, silica, fibers, fatty and resin acids and alcohols (McKeough & Fagernäs, 1999). For the performance of the evaporators, it is very important to remove the fibers in the effluent before entering the evaporators. Fibers cause deposit formation in the evaporator and can block the heating elements. Fibers can be removed by clarifiers (SUEZ, 2017) or by filters.

Table XI Benefits and challenges in the evaporation technology.

Method	Benefits	Challenges
Evaporation	– zero liquid discharge – chemical recovery – suitable for most waters without big problems – no impact for aquatic environment	– fouling and deposit formation – high investment costs – high energy demand – equipment needs quite a lot of space near the CTMP plant – recycling water may affect to the product quality – may increase the air pollution load

4.2. Biological treatment

Biological treatment is based on a process, where microbes are grown in a fixed and controlled environment. In this environment, harmful degradable compounds are transformed into non-harmful form. (Kokko, 2017a)

For CTMP wastewaters, biological aerobic treatment method is the most commonly used one (Suhr, et al., 2015). CTMP wastewaters have also a very high potential for methane production with anaerobic plants, but because of the difficult nature of the water, it can be quite challenging to treat in anaerobic conditions. (Bajpai, 2017)

4.2.1. Aerobic treatment

Biological aerobic treatment, as the name already suggests, is a wastewater treatment method which utilizes microorganisms in the presence of air, or preferable oxygen. These microorganisms are called aerobes, and they use free and molecular oxygen from the wastewater to degrade the organics into carbon dioxide, water and biomass. (Mittal, 2011) Figure 5 presents the simplified principle of the aerobic process.

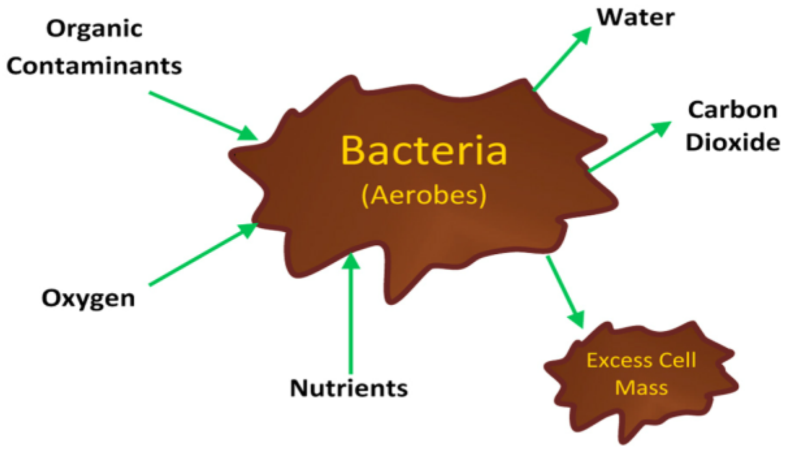


Figure 5 Principle of the biological aerobic treatment **(Mittal, 2011)**.

The reactions which describe the functioning of the wastewater treatment by the aerobic treatment process are presented in equations 2 and 3. Equation (2) describes the oxidation and synthesis of the organics into products and biomass, and equation (3) describes the biomass decomposition which occurs during the process. (Kokko, 2017a)

$$COHNS + O_2 + nutrients \rightarrow CO_2 + NH_3 + C_5H_7NO_2 + others \qquad (2)$$

$$C_5H_7NO_2 + O_2 \rightarrow 5\ CO_2 + 2\ H_2O + NH_3 + energy \qquad (3)$$

As seen from the figure 5 and from the equations above, the aerobic process requires nutrients to work. The optimal nutrient ratio (BOD:N:P) for aerobic processes is 100:5:1. To maintain this ratio, nutrients can be added or the organic loading increased. Other process parameters that affect to the functionality of the process are pH, temperature, inhibiting factors and oxygen availability. (Kokko, 2017b)

Aerobic treatment process consists of three main units; the aerobic treatments tanks, the clarifier part where the sludge is separated from the water and the circulation system where part of the sludge is circulated back to the process and the excess sludge is removed. Before the aerobic treatment effluent needs to be purified with some primary treatments, to protect the biological treatment plant from toxic pollutants but also to make the flow more balanced when considering the organic loads, temperature and pH. (Suhr, et al., 2015)

A basic line diagram of the typical aerobic treatment units without the preliminary and tertiary treatments is presented in figure 6.

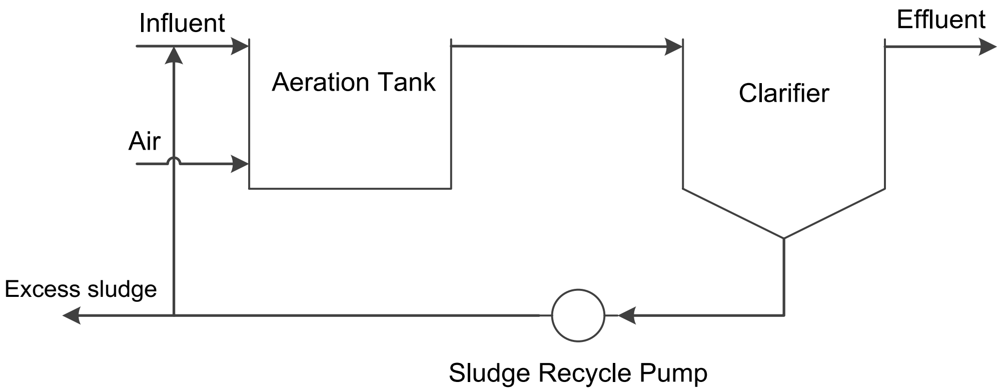


Figure 6 Simple process chart of the aerobic treatment process (**Mittal, 2011**).

In the case of CTMP water, for example the toxic resin acids, EDTA and DTPA can be harmful for the activity of the bacteria used in the aerobic treatment, so to optimize the operations of the biological plant; these pollutants should probably to be removed by some primary treatment method before entering the biological part of the process. (Bajpai, 2010)

Activated sludge process method is one, and the most commonly used way to biologically treat CTMP effluents. Activated sludge process is a simple aerobic process, which can be presented as presented in figure 6. The activated sludge method is found to be very effective in the removal of COD and BOD. Even 98% of BOD and 85% of COD can be removed with this treatment from the CTMP effluents. (Suhr, et al., 2015) Achieved results for CTMP wastewater purification by activated sludge process is presented in table XII.

Table XII Emission achievements for CTMP wastewater purification with activated sludge process (**Bajpai, 2010**).

Parameter	Value
Flow (m^3/t)	8 – 40
BOD5 (kg/t)	0.5 – 9
COD (kg/t)	12 – 30
Total phosphorous (g/t)	5 – 50
Total nitrogen (g/t)	200 – 500
TSS (kg/t)	0.1 – 12

For the nitrogen and phosphorous, emissions after activated sludge treatment are reported to be 117-182 g/ADt for nitrogen and 2-8 g/ADt for phosphorous (Suhr, et al., 2015). According to Bajpai (Bajpai, 2010), the emission are though a little bit higher (Table XII.). Overall, the removal efficiency for nutrients tends to be quite low. Usually some chemical treatment is combined with aerobic treatment to fulfill the purity requirements for the discharged water. (Bajpai, 2010) EDTA and DTPA are resistant to aerobic biodegradation. Those does not absorb into the sludge, so they pass the aerobic treatment without degradation. The biodegradation can be increased by raising the alkalinity in the aerobic treatment tanks (Bajpai, 2010), or some primary or tertiary treatments can be applied to remove these compounds. For example, effluent treatment with aluminum sulfate has noticed to reduce the amount of EDTA by 65% (Saunamäki, 1995).

Activated sludge process is the most used one, but there are other aerobic process options that can be used. These are aerated lagoons, sequencing batch reactors (SBR) and rotating biological contactors (RBC) and membrane bioreactors (MBR). These are not most commonly used, but promising results in effluent purification has been shown (Dubeski, et al., 2006) (Mathys, 1991). Membrane bioreactors are emerging and can be a future option for wastewater treatment. Membrane bioreactors system combines bioreactor and microfiltration into one unit process. With membrane bioreactors, there is no need for secondary clarifiers or effluent filtration in separate units, but this all happens in the MBR unit itself. These reactors have two basic configurations: 1) the integrated bioreactor, where membrane unit is immersed inside the bioreactor and 2) the recirculated MBR, where mixed liquor is pumped through a membrane unit outside the reactor. (Tchogobanoglous, et al., 2003) Schematic diagrams of these two configurations are presented in figure 7.

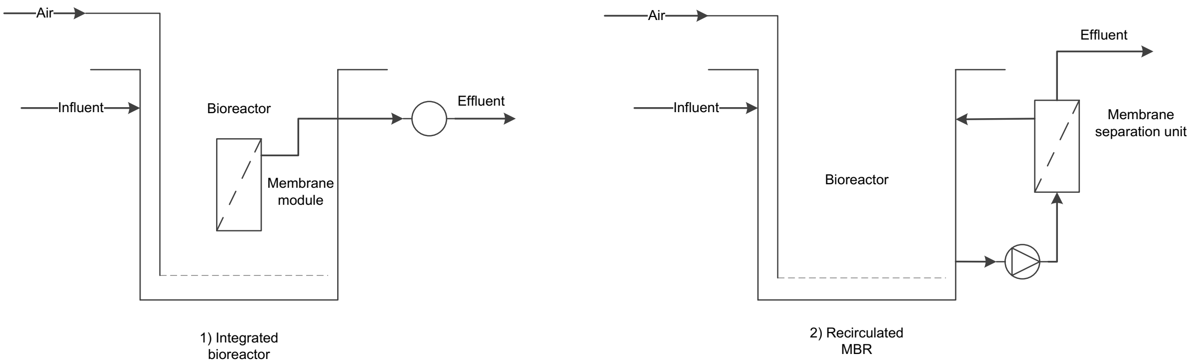


Figure 7 Schematic diagrams of integrated bioreactor and recirculated MBR configurations **(Tchogobanoglous, et al., 2003)**.

Drawbacks in using aerobic method are the high amount of sludge formed during the process and the fact that all components in the effluents are not biodegradable in aerobic conditions. The sludge formed in the aerobic treatment plants needs to be disposed also, so that forms another waste disposal problem.

Table XIII Benefits and challenges in the aerobic biological treatment methods.

Method	**Benefits**	**Challenges**
Aerobic treatment	– efficient reduction of COD and TSS – can reach the current discharge regulations – does not affect to the product quality (no recycling to the process)	– lot of sludge formed – may have long-term impacts in environment – does not treat EDTA&DTPA – extractives are inhibitors

4.2.2. Anaerobic treatment

Anaerobic treatment is a wastewater treatment method, which utilizes micro-organism in the absence of molecular and free oxygen. Microorganisms that are used in anaerobic conditions are called anaerobes. (Mittal, 2011) Anaerobic treatment can be operated in two temperature areas: 29 °C – 38 °C (mesophilic) and 49 °C – 57 °C (thermophilic). A simplified figure of the anaerobic treatment principle is presented below in figure 8.

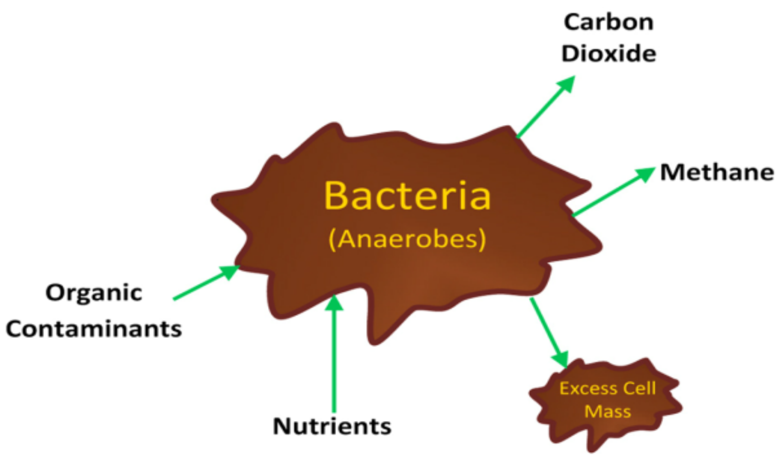


Figure 8 Principle of the biological anaerobic treatment **(Mittal, 2011)**.

The organic substances in the wastewater are broken down in steps, which are called hydrolysis, acidogenesis, acetogenesis and methanogenesis. In these reaction steps, large organic polymers are step by step broken down into smaller pieces, leading to the production of methane, carbon dioxide, hydrogen, nitrogen, hydrogen sulfide and biomass. (Hynninen, 2008) (Bajpai, 2017) In figure 9 is presented the anaerobic pathway by which the anaerobic bacteria degrades the organics in the wastewater.

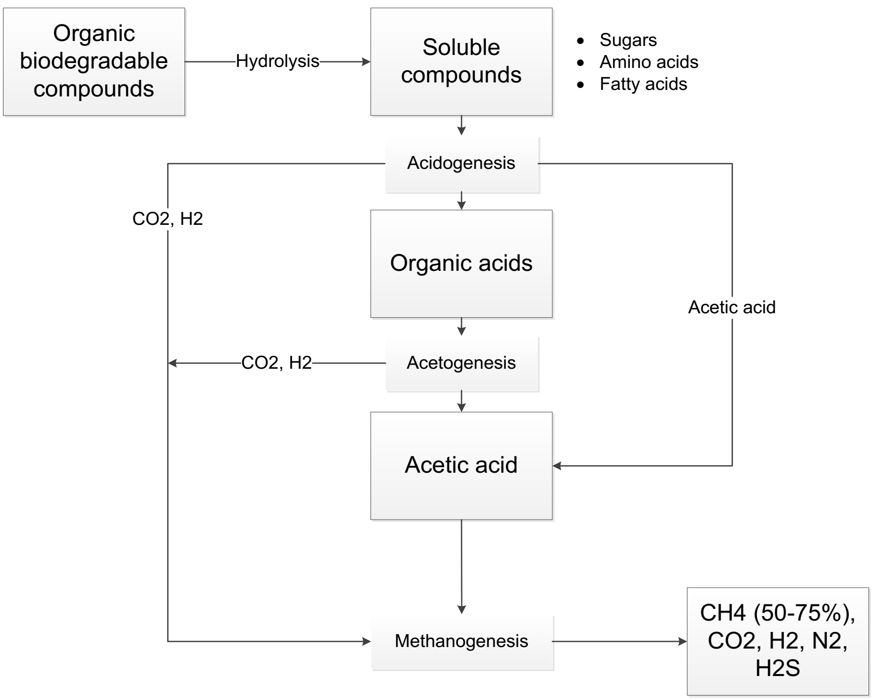


Figure 9 Anaerobic pathways **(Kamali, et al., 2016)**.

In hydrolysis, organic biodegradable compounds, in the case of CTMP wastewaters basically cellulose, hemicellulose and lignin, are depolymerized by acidogenic bacteria or hydrolytic enzymes into smaller compounds. Hydrolysis simply means reaction with water. In equation (4), reaction that occurs in the hydrolysis is presented. (Bajpai, 2017)

$$C_6H_{10}O_4 + 2H_2O \rightarrow C_6H_{12}O_6 + H_2 \quad (4)$$

The hydrogen that is formed in the hydrolysis can straight be used by the methanogenic bacteria to produce methane. The hydrolysis step is comparatively slow, and the base for all the other reactions, so it can slow down the methane formation. (Bajpai, 2017)

Straight after hydrolysis, acidogenesis step follows. In the acidogenesis step, smaller water soluble compound are converted by acid-forming bacteria to organic acids. Reactions occurring in the acidogenesis are presented in equations (5), (6) and (7). (Bajpai, 2017)

$$C_6H_{12}O_6 \leftrightarrow 2\ CH_3CH_2OH + 2\ CO_2 \quad (5)$$

$$C_6H_{12}O_6 + H_2 \leftrightarrow 2\ CH_3CH_2COOH + 2\ H_2O \quad (6)$$

$$C_6H_{12}O_6 \rightarrow 3\ CH_3COOH \quad (7)$$

Acetic acid, hydrogen and carbon dioxide that are formed during these reactions can straight be utilized in the methanogenesis step. (Bajpai, 2017)

The higher organic acids, which are formed in the acidogenesis, need to be converted into acetic acid. This happens in the acetogenesis by acetogenetic bacteria. Reactions for this step are presented in equations (8), (9) and (10). (Bajpai, 2017)

$$CH_3CH_2COO^- + 3\ H_2O \leftrightarrow CH_3COO^- + H+ + HCO_3^- + 3\ H_2 \quad (8)$$

$$C_6H_{12}O_6 + 2\ H_2O \leftrightarrow 2\ CH_3COOH + 2\ CO_2 + 4\ H_2 \quad (9)$$

$$CH_3CH_2OH + 2\ H_2O \leftrightarrow CH_3COO- + 3\ H_2 + H^+ \quad (10)$$

In the last step, methanogenesis, methane is produced by methanogenic bacteria. Methanogenic bacteria can convert formic acid, acetic acid, methanol, carbon monoxide and carbon dioxide and hydrogen into methane. The reactions are presented below in equations (11), (12) and (13). (Bajpai, 2017)

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad (11)$$

$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O \quad (12)$$

$$2\ CH_3CH_3OH + CO_2 \rightarrow CH_4 + 2\ CH_3COOH \quad (13)$$

Methanogenic bacteria are the most sensitive ones in the whole process for changes in the environment. Methanogenesis is the critical step in the anaerobic digestion process, and is often the slowest one of all the four steps. (Bajpai, 2017)

Process parameters affecting the anaerobic digestion are anaerobic condition, optimal temperature and pH, presence of inhibiting compounds, availability of nutrients and sufficient mixing. (Kokko, 2017b) Compounds that inhibit the anaerobic digestion are ammonium, light metal ions, inorganic sulphur compounds (sulphate, sulphite, and sulphide), oxidants (oxygen, hydrogen peroxide), low molecular weight organics (volatile fatty acids, sugars, and alcohols), heavy metals, molecular hydrogen, wood constituents (lignin, resin acids) and DTPA. (Bajpai, 2017) Some inhibiting compounds are presented in table XIV to present the concentrations in which they are harmful for the process. These compounds can in some amounts be found in the CTMP effluents.

Table XIV Inhibiting compounds and their concentrations [(1)] **(Kokko, 2017b)**, [(2)] **(Sierra-Alvarez, et al., 1994)**, [(3)] **(Tchogobanoglous, et al., 2003)**.

Compounds	Inhibitory concentration for 50% methanogenic activity decrease (mg/L)
[1]**Sulfite**	125
[1]**Sulfide**	50
[2]**Resin acids**	21 – 400
[2] **Fatty acids**	250 – 1235
[3]**Na^+**	3500 – 5500 (moderately) 8 000 (strongly)
[3]**K^+**	2500 – 4500 (moderately) 12 000 (strongly)
[3]**$Ca2^+$**	2500 – 4500 (moderately) 8 000 (strongly)
[3]**Mg^{2+}**	1500 – 1500 (moderately) 3 000 (strongly)

EDTA and DTPA are inhibitors in the anaerobic treatment process, so preliminary treatment to remove these compounds could be needed. The harmfulness of these compounds depends on the amount of the chemicals in the wastewater. (Bajpai, 2017) According to Ruutiainen, 200 mg/l dose of DTPA does not affect into the activity of the sludge in the anaerobic treatment (Ruutiainen, 1987). This means that in those amounts of these compounds, these chelating agents does not affect to the operation of the anaerobic treatment.

Sulphur management needs to be considered, since the sulphur compounds are highly toxic to the anaerobic process. Stephenson et al. have proposed the removal of sulphide from the produced gas to be the most effective option for sulphur management in the anaerobic process. The removal is executed by recycling part of the produced hydrogen sulfide-free gas back into the reactor. By scrubbing and recycling the gas, the amount of total dissolved sulphide concentration can be decreased and higher TOC removals can be achieved. (Stephenson, et al., 1994) The idea of this sulphur management method is presented in figure 10. Other methods that were tested by Stephenson et al. were pH controlling in the acidogenic reactor and inhibiting the sulphur reducing bacteria, didn't show as good results in total sulphur management as the gas scrubbing. (Stephenson, et al., 1994)

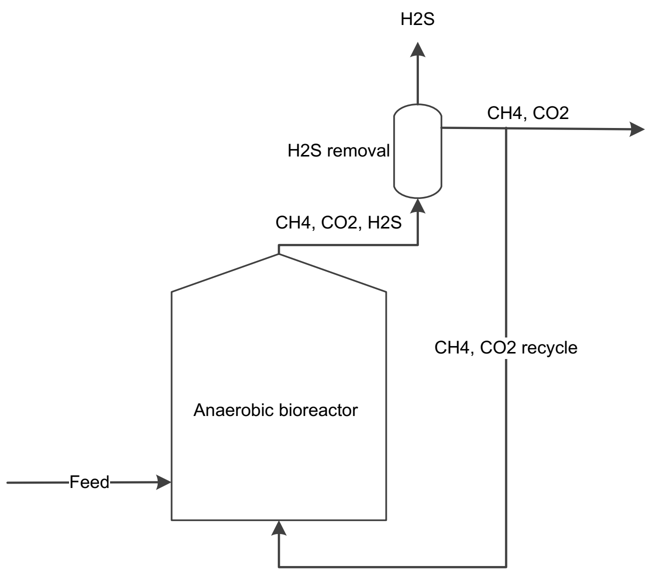
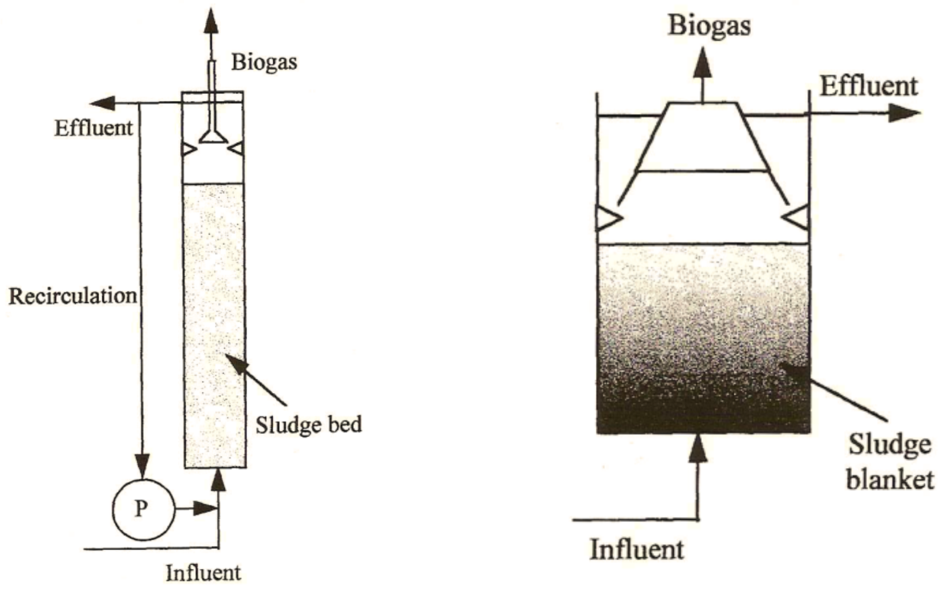


Figure 10 Sulphur management in anaerobic process by hydrogen sulphide scrubbing and gas recycle **(Stephenson, et al., 1994)**.

In the case of CTMP water, there are several substances in the effluent that are inconvenient for anaerobic process, for example resin and fatty acids and residues from impregnation and bleaching chemicals. Anaerobic treatment is not typically used on its own for this type of wastewaters, but can be combined with aerobic treatment or some chemical treatments prior anaerobic parts of the process (Suhr, et al., 2015).

There are few process designs available for anaerobic treatments: fixed bed reactor, sludge contact process, anaerobic upflow sludge blanket (UASB), expanded granular sludge blanket (EGSB) and internal circulation (IC) reactors. The main difference in these designs is the technology to ensure the high concentration of biomass within the reactors. In contact reactors, this is ensured by recycling washed out biomass after settling in an external separator and in fixed bed reactors by attaching the biomass to a supporting media with the reactor. UASB and EGSB reactor utilizes granular biomass that produces auto-immobilization. (Suhr, et al., 2015) UASB technology is quite old, but still widely in use. EGSB reactors are becoming more general. The basic principle in UASB process is that the wastewater is fed to the bottom of the reactor, where it travels through a sludge blanket as an upflow. The gas and the effluent are removed from the top of the reactor. (Tchogobanoglous, et al., 2003) The EGSB reactor is an upgraded version of the UASB reactor. The main difference between these two reactors is the upflow velocity, which is higher in EGSB reactor. (Lim, 2018) Schematic diagrams of these two most common reactor types are presented in figure 11.



EGSB UASB

Figure 11 Schematic diagrams of EGSB and UASB reactors **(Lim, 2018)**.

The main thing to evaluate when considering the best wastewater treatment method is the removal efficiency or the purification results that can be achieved. For a CTMP wastewater that contains COD of 2500 – 13 000 mg/L, anaerobic degradability has been reported to be 40-60 % (Pokhrel & Viraraghavan, 2004). Purification efficiencies can vary, depending on the process design used. Some reactor types, wastewater characteristics and removal efficiencies are presented in table XV.

Table XV Anaerobic processes removal efficiencies for CTMP effluents **(Larsson, et al., 2017)**.

Wastewater type	**Reactor type**	**HRT (h)**	**OLR (kg COD/m^3 day)**	**COD reduction (%)**	**Methane production (NmL/gCOD)**
Bleached spruce, Na_2SO_3 & H_2O_2	Lab scale, upflow hybrid reactor	16-24	10-15	49	300
Bleached aspen, Na_2SO_3 & H_2O_2	Pilot scale, anaerobic fixed bed film reactor	12-16	20	60	300
Bleached spruce, Na_2SO_3 & H_2O_2	Pilot scale, anaerobic fixed bed film reactor	48-72	3	60	200
Bleached spruce	Pilot scale, upflow blanket filter reactor	48	4.7	45	100

The overall working for organics removal seems to be quite good. As seen in the table XV, the COD removal efficiency can vary a lot depending on the process parameters and chosen technology and also the raw material used, so the use of anaerobic reactor can be either good or a bad choice. COD removal of 45% is not even near the desired results, but 60% at least pretty near. Depending on the design used, the high amount of suspended solids can cause problems in the anaerobic systems. If the amount of suspended solids is higher than 200-500 mg/L, problems can occur and the process is not working properly and effectively. (Bajpai, 2015) From this it can be concluded, that the working of the anaerobic reactor should be well studied in case-by-case basis.

Benefits of anaerobic treatment are reduction of COD with less energy than in aerobic treatment, and formation of methane. Methane formation from the COD reduces the amount of excess sludge compared to aerobic treatment (Suhr, et al., 2015). The CTMP wastewater is high on COD and indicates for a good methane production possibilities. When COD load is higher than 1300 mg/L, anaerobic treatment can be considered. Usually it is though favored to have more than 2000 mg/L COD in the effluent, to provide enough methane production to ensure the heating of the reactor with the produced methane. Otherwise, external fuel source is needed (Tchogobanoglous, et al., 2003).

Ekstrand et al. presents a 40-50 % methane yield of the theoretical potential. The theoretical methane potential was calculated to be 940 Nml/g TOC. (Ekstrand, et al., 2013) Hardwood pulp effluents have proven to have higher yields in methane production than softwoods (Larsson, et al., 2017). Methane production in Larsson et al.'s research is presented in table XVI. From the table it can be seen, that the amount of produced methane is higher for hardwood, but the difference between softwood is not that significant.

Table XVI Production of methane for different type of CTMP wastewaters **(Larsson, et al., 2017)**.

Wood species	Methane production (Nml/g TOC)
Undiluted bleached aspen	400 ± 12
Diluted bleached aspen	440 ± 42
Diluted bleached birch	500 ± 42
Bleached spruce	360 ± 33

The aspect of the anaerobic treatment to reduce the amount of excess sludge is very tempting. The management and disposal of the sludge tends to be a problem for the pulp mills, and the costs can be even 60% of the mills total waste treatment costs (Kamali, et al., 2016).

Table XVII Benefits and challenges in anaerobic treatment methods.

Method	Benefits	Challenges
Anaerobic treatment	– less energy needed – lower addition of nutrients(vs. aerobic) – less sludge formation (vs. aerobic) – methane production – does not affect to the product quality (no recycling to the process)	– inefficiency because of the inhibiting compounds in the effluent – sensitive for changes in the process conditions – long start-up time – odour formation – need for further treatment(aerobic) – may have long-term impacts in environment

4.3. Physicochemical treatment

Physicochemical treatment is a combination of physical and chemical treatment (Bahadori & Smith, 2016). Its meanings are to remove suspended solids, colloidal particles, floating matters, colors and toxic compounds by multiple treatment methods, which utilize physicochemical way of action. These treatment methods can be sedimentation, flotation, screening, adsorption, coagulation, oxidation, ozonation, and electrolysis or membrane filtration. (Pokhrel & Viraraghavan, 2004) These methods are used as primary or tertiary treatment methods, and should be considered only if the main purification technology does not reach to the purification targets or notable improvement in the secondary treatment stage can be achieved by pre-treating the effluent. What to be noticed also, is that physicochemical treatment should not affect to the efficiency of the main treatment method. For example biodegradable material is not wanted to be removed before it enters the biological reactor, since then it decreases the purification efficiency of the biological reactor.

Table XVIII Physicochemical processes and their removal function in CTMP effluent purification.

Process	Removal function	Source
Sedimentation/flotation	Dissolved and suspended solids	(Samer, 2015)
Coagulation & precipitation	Dissolved and suspended solids, phosphorous removal, toxicity, turbidity and color removal	(Samer, 2015) (Suhr, et al., 2015) (Stephenson & Duff, 1996b) (Stephenson & Duff, 1996a) (Lei, et al., 2010)
Adsorption	Toxic compounds, color	(Samer, 2015)
Oxidation	Toxic compounds (resin and fatty acids)	(Samer, 2015) (Roy-Arcand & Archibald, 1995)
Membrane filtration	Dissolved inorganics, COD, AOX, color	(Samer, 2015) (Pokhrel & Viraraghavan, 2004)

4.3.1. Sedimentation/flotation

Sedimentation and flotation are methods for removing solids and suspended particles from the water. Sedimentation means settling the solid material in the wastewater. The settling is accomplished by gravity, when flow velocity of the water is decreased and the solid have time to settle in the bottom of the sedimentation tank by gravity. Otherwise than in sedimentation, in flotation suspended particles are raised to the surface of the water. This is usually accomplished by using air as a carrier. (Bahadori & Smith, 2016)

These methods are typically used as a pretreatment method, to reduce the amount of suspended solids in the water. Sedimentation can reach up to 80% removal of the total suspended solids, and flotation with dissolved air has been reported to remove even 95% of the total suspended solids. (Pokhrel & Viraraghavan, 2004) These methods seem to be very usable in the suspended solids removal.

To maximize the separation, some coagulants or flocculants can be used with the sedimentation or flotation step. (Bahadori & Smith, 2016) (Suhr, et al., 2015) Coagulants have been used for removal of resin and fatty acids. Even 90% removal for resin acids and 94% removal of fatty acids have been reached by using cationic polymers. Other coagulants have also been used, like anionic albumin, gelatin, alginate and alginic acid, and these coagulants also show good results. (Roberts, 1994). This method could be used to remove these compounds prior the secondary treatment methods, where these compounds work as inhibitors or foulants.

4.3.2. Coagulation & precipitation

In coagulation, the main idea is to use chemicals to neutralize the charges of the fine particles in the wastewater. When the charges are neutralized, the particles can get closer to each other, causing them to form larger flocs. Precipitation means the phenomenon, where substances dissolved in the water is turned into a solid form. Electricity can also be used with chemicals to enhance the coagulation and precipitation treatments. (Bahadori & Smith, 2016) When using coagulation or precipitation, the formed solids and flocs can be removed by sedimentation or flotation. (Samer, 2015)

Multiple coagulants have been tested for BCTMP wastewaters. Stephenson and Duff presented the usability of iron and aluminum salts as coagulants. They proved 88% removal of total carbon and 90-98% removal of color and turbidity. The also noticed, that when using these coagulants, the influence of operating pH is significant. The pH should be for ferric chloride between 4 – 6.5, for ferrous sulphate above 7.4, aluminum chloride between 5 – 6 and for aluminum sulphate (alum) between 5.8 to 6.8. (Stephenson & Duff, 1996a) Ganjidoust et al. compared the removal efficiency of alum and synthetic and natural chitosan, and preferred the chitosan with 90% removal of color and 70% removal of TOC (Ganjidoust, et al., 1997). Also Rohella et al. discarded the use of alum and stated that polyelectrolytes should preferably be used, because of the lower sludge formation and the better dewatering possibility of the sludge (Rohella, et al., 2001).

4.3.3. Adsorption

Adsorption is a process, where molecules dissolved in the water are removed by attaching them into a surface of solid substrate. The molecules attached are called adsorbates and the surfaces they are attached are called adsorbents. Adsorbents have different kind of properties, physical and chemical, but the mutual property for all adsorbents is the high specific surface area. The high surface area is needed to provide maximal removal efficiency for the desired compounds. (Samer, 2015)

Adsorption processes can be used to remove color and COD. Adsorption is quite an expensive method to maintain, because of the expensive adsorption materials and the need to recover them once in a while. Adsorption is not usually used in pulp and paper industry wastewater treatment, but laboratory experiments show good results in color and COD removal. For example activated charcoal, fuller's earth, coal ash and activated coke are tested, and show even 90 % removal for color and COD. (Pokhrel & Viraraghavan, 2004)

4.3.4. Conventional and advanced oxidation

Conventional chemical oxidation is a wastewater purification method, where chemicals are added into the water to cause an oxidation-reduction reaction (Bahadori & Smith, 2016). Common chemicals used as oxidants are chlorine, potassium permanganate and ozone (Deng & Zhao, 2015). Advanced oxidation then, is based on creating a hydroxyl radical (OH·) which is a very strong oxidizer. (Bahadori & Smith, 2016) Hydroxyl radical has oxidizing potential between 2.8 V (pH 0) and 1.95 V (pH 14). It is very nonselective, so it can oxidize multiple different substances. (Deng & Zhao, 2015)

Ozone is a very typical oxidant used in wastewater treatment. It has the capability to oxidize a wide range of organics and inorganics in the wastewater. (Samer, 2015) Compared to advanced oxidation processes and their oxidizing capacity, ozone is though much more selective than hydroxyl radical. It prefers the ionized and dissociated form of organic compounds, not so much the neutral form. Oxidation potential of ozone itself is 2.07 V. There are also advanced oxidation methods that utilize ozone to create hydroxyl radical. Then the oxidation is enhanced and is much more efficient. (Deng & Zhao, 2015) Main problem in the use of ozone is the unstable nature of the molecule. It should be generated at the time of usage, so ozone plant should be constructed near the wastewater treatment plant and it can't be delivered to the plant as other possible oxidants. It is quite expensive oxidant to produce and difficult to handle. (Samer, 2015)

Laboratory scale results from using ozonation in wastewater purification have been reported. Ozonation can be used to remove COD, TOC, toxicity (Yeber, et al., 1999), resin acids (Korhonen & Tuhkanen, 2000) and EDTA (Korhonen, et al., 2000) from the wastewaters. There are several researches done by using ozone alone as an oxidant, or by using ozone as a medium to create hydroxyl radicals, when direct ozone oxidation also occurs. (Deng & Zhao, 2015) Yeber et al. have reported good removal efficiency for COD, TOC and toxicity.

Also, the biodegradability has increased significantly, while ozone is used. (Yeber, et al., 1999) Korhonen et al. have examined the effect of ozone oxidation in EDTA. The results show, that even 90% removal of EDTA is possible by ozonation. At the same time, COD was reduced for 65%. (Korhonen, et al., 2000) The removal of EDTA is very important, since it's not biodegradable with aerobic methods and acts as an inhibiting compound in anaerobic treatment. Ozonation seems to be quite a good alternative when considering the removal of EDTA from the wastewater. Other harmful compound in the wastewater, resin acids, which are toxic when released into receiving waters and inhibiting compound in anaerobic treatment, can also be removed with ozonation. Korhonen and Tuhkanen have reported 90% removal of resin acids with 0.2 mgO_3/mgCOD dosage in ozonation (Korhonen & Tuhkanen, 2000).

Ozone and hydroxyl radical can also be used at the same time. Pulsed corona discharge technology is one of these technologies that utilize both ozone and hydroxyl radical. High voltage pulses are used to create electrical discharge and generate ozone and hydroxyl radicals from water and oxygen. (Panorel, 2013) The reactions are presented in formulas below.

$$e^- + H_2O \rightarrow e^- + \cdot H + \cdot OH \quad (14)$$

$$e^- + 3O_2 \rightarrow e^- + 2O_3 \quad (15)$$

$$O + H_2O \rightarrow 2OH \quad (16)$$

The pulsed corona discharge method is quite new technology for water treatment. It is considered as a better option based on energy efficiency. It has proven to be very good method for removal of organics from the wastewaters. (Panorel, 2013)

4.3.5. Membrane filtration

Membrane is a semipermeable film, which divides the feed stream into two phases, concentrate/retentate and permeate. Permeate is the stream that passes the membrane. Driving force that forces permeate to pass the membrane can be pressure, concentration, temperature or electrical difference between the two sides of the membrane. (Mulder, 1996) Typically in pulp and paper wastewater treatment, pressure driven membrane processes are utilized. A schematic of membrane process is presented in figure 12.

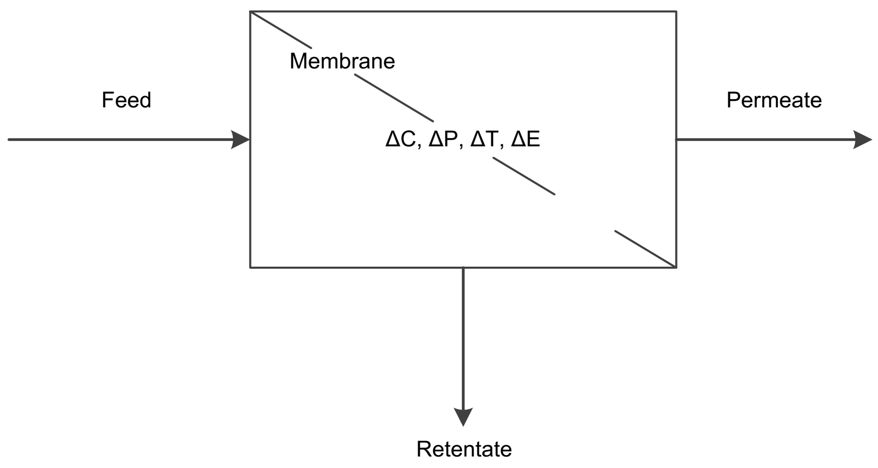


Figure 12 Schematic membrane process presentation **(Mulder, 1996)**.

Pressure driven membrane processes can be divided into four groups; microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Difference in these processes is the pore size. In the same order from microfiltration to reverse osmosis, the pore size diminishes, and the separated particles are though smaller. Pore sizes are for microfiltration 0.05 – 10 μm, ultrafiltration 1 – 100 nm and for nanofiltration and reverse osmosis < 2 nm. In micro- and ultrafiltration, the separation is based on the particle size, but in nanofiltration and reverse osmosis on the difference in solubility and diffusion. (Mulder, 1996)

Membrane filtration can be utilized in the CTMP effluent purification as a tertiary treatment method or included in the secondary treatment. Chemical oxygen demand, suspended solids, inorganics and color are possible to reduce by using membrane filtration. From pulp and paper wastewaters in general, with ultrafiltration TOC, color and SS have been removed by 54%, 88% and 100% respectively. Reported values for COD and BOD are 88% and 89% respectively. Also heavy metals have been removed successfully from pulp and paper mill wastewaters by nanofiltration or reverse osmosis. (Pokhrel & Viraraghavan, 2004) With different kind of membrane technologies, different purity levels can be reached.

One drawback in membrane filtration is, that the harmful substances in the wastewater is not transformed into less harmful form or adsorbed into some other material, but those are only separated into different streams. The stream where the removed pollutants exist need still be treated or disposed somehow. (Mulder, 1996) Second drawback in membrane filtration is the fouling of the membrane. In CTMP wastewaters, there are high amounts of resin and fatty acids, that tend to act as foulants in membrane processes. (Puro, et al., 2011)

4.4 Selection of the wastewater treatment method

The selection of the “best” treatment method is a complex process in which many parameters needs to be taken into account. The design of the wastewater treatment process needs to be in co-operation with the pulping process engineers and the pulping process itself affects to the selection of the wastewater treatment process. Environmental impacts and regulations work as a basis for the design, with the characteristics of the wastewater. In figure 13, a chart of the wastewater treatment process selection is presented in red blocks and in black blocks the process engineering parts. There are interactions between all the blocks, so the selection procedure in reality is not quite so straight-forward.

The selection and design of the wastewater treatment starts when process is ready and all the process parameters are known. The selection and design can be started from many points. One possibility is to start from the wastewater characterization. Important part of this step is to find the source for the contaminants, and check if these can be reduced by making small changes in the process. One possibility is to recycle some water to minimize the amount of pollutants discharged.

Second possible manner of an approach is to evaluate the environmental impacts and find out the regulations or if recycled, the impact on the product quality. Further investigation of the receiving water may be needed to evaluate the possible environmental impacts. For example toxicity is pH dependent, so toxicity tested in other pH than in the receiving water’s pH is not telling the real toxicity in the receiving water. The sensitivity of the receiving waters ecosystem to pollutants may affect to the selection of the method.

Third step is, based on the information from the previous steps, to select all possible method alternatives. It is important to make some kind of forecast on the environmental regulations also in this stage. If for example the liquid effluent regulations are assumed to tighten and the purification efficiency of conventional biological method is not enough, evaporation may be the best solution. When all the alternatives, and their benefits and difficulties, are evaluated, the fourth step is to make an economical comparison between these alternatives. This may be the most important step, since usually economics play a big role in the final decisions made.

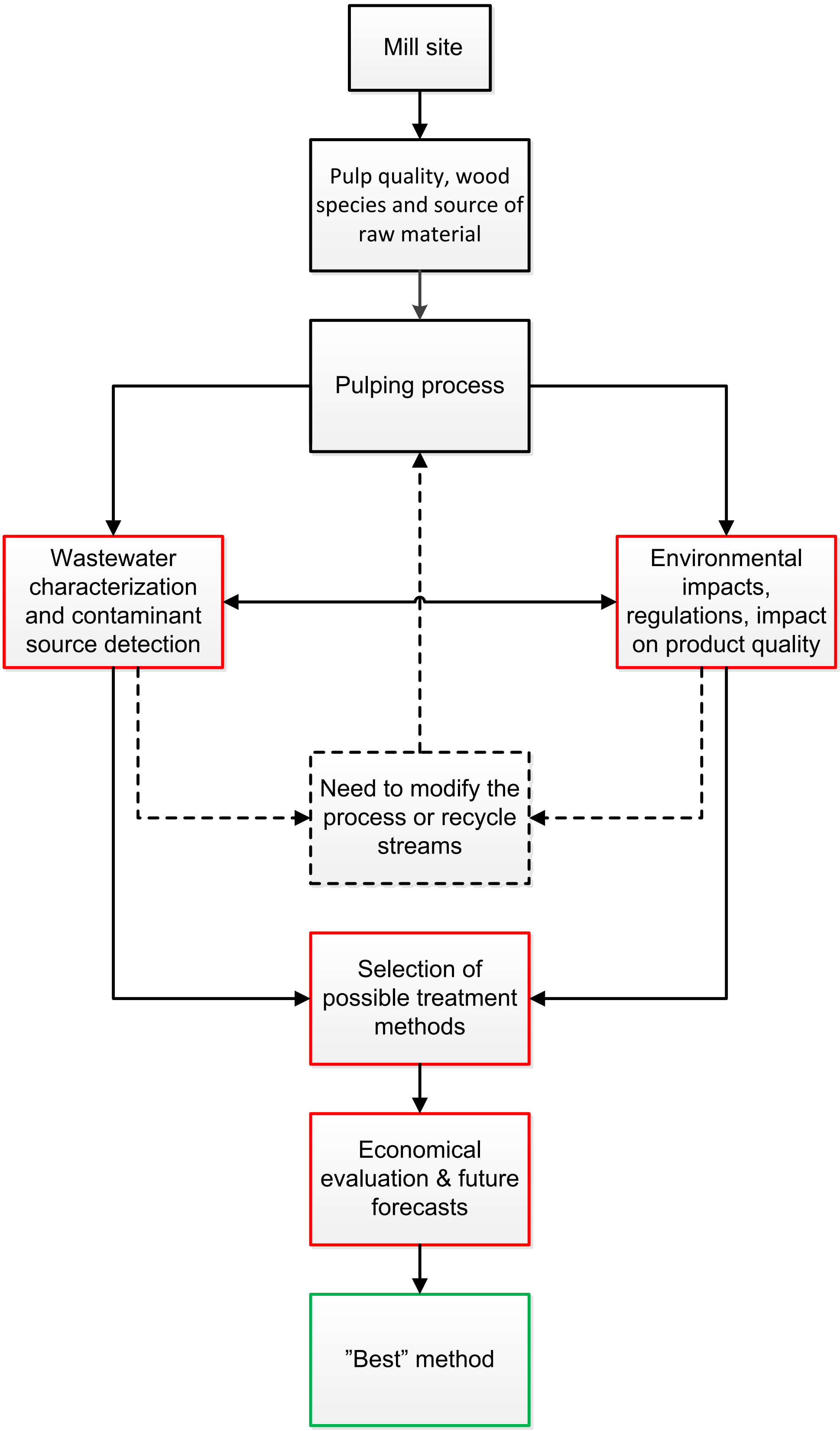


Figure 13 Wastewater treatment method’s selection procedure.

EXPERIMENTAL PART

The experimental part in this thesis consists of laboratory analyses of CTMP wastewaters and creating excel tool to predict possible solutions for the wastewater handling method. In this experimental part, information from the mills, sampling and analysis methods are described and the results are presented. Excel tool is described and the information of its operations is explained.

5. Materials and methods

Wastewaters from different mills from Finland were analyzed in laboratory at Lappeenranta University of Technology. Samples were collected from two different CTMP mills in Finland. These mills are named in this work as mill 1 and 2.

Analyzed characteristics where pH, conductivity, dissolved organic carbon, suspended solids, total amount of organics and inorganics, composition of inorganics and resin and fatty acids. The amount of these compounds in the wastewaters was determined. These compounds where chosen for further analysis based on the literature research; the compounds are either typical wastewater characteristics, like suspended solids or total organic carbon, or found to be inhibitors or foulants in the literature. With these characteristics, basic information from the water is get for better identification of the water. Resin and fatty acids were determined because they are harmful compounds in the biological wastewater treatment methods. The inorganics are analyzed because they create problems in the evaporation causing scaling.

5.1. Sampling from the mills

The samples from each mill were taken into two plastic 1 liter sample containers. The containers were taken as full as possible, to avoid excess air in the samples, and closed carefully. Samples from the mill 1 were frozen, before samples from the mill 2 was get and the analyses could be done at the same time. The samples from the mill 2 were stored at cool temperature in refrigerator before analyses. Though there is a possibility that contaminants in the water may precipitate into the suspended solids (Puro, 2018), that is not taken into account in this work. As a justification for this is the fact, that all of the contaminants that may precipitate are anyway removed in some amounts in the wastewater purification systems before the secondary treatment method. It can also be assumed, that the amount of settled contaminants is not significant for the purpose of this thesis.

From the mill 1, the samples were taken from two different sampling points. First sample is CTMP clear filtrate. Second sample is from a channel, which collects up chip washing water, CTMP plug screw filtrates and recycling water from the heat recovery system. These samples should give a proper view of the CTMP process effluents, since this is the total wastewater flow, which is purified at the wastewater treatment plant. A simplified process chart including the sampling points is presented in figure 14. Blue line presents the water flows which are collected up to samples. At mill 1, before the water enters to the CTMP process, it has gone through the board mill, which exists at the mill integrate. This needs to be taken into account, since the chemicals used in the board mill can affect to the water and its chemical composition. The chemicals can possibly be seen in the inorganics analysis, so these results needs to be noticed if there is any unaccountable in the results.

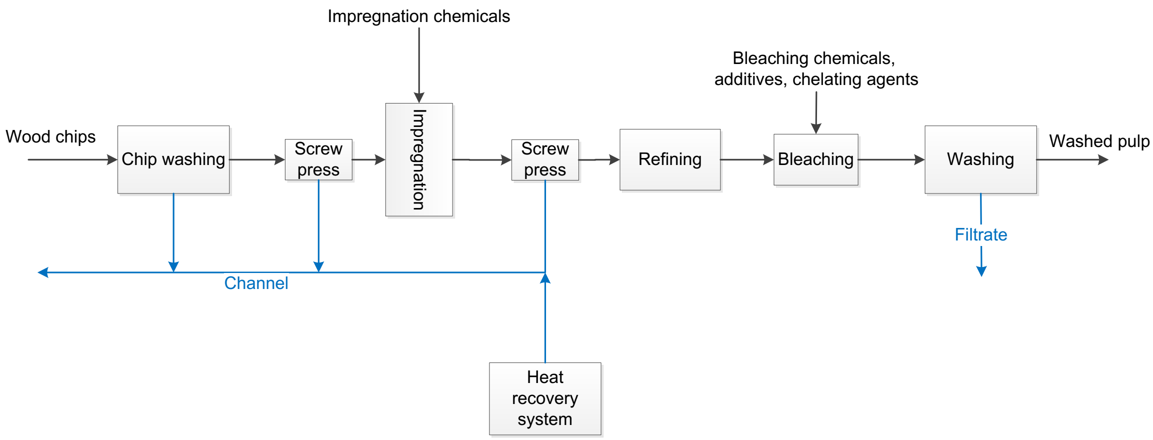


Figure 14 Simplified figure about the sampling points, where samples were taken from the mills.

Process description and some process parameters at the time of sampling for mill 1, are presented in table XIX.

Table XIX Process information from the mill 1.

Mill 1.	
Raw material	Spruce chips, sapwood
Used chemicals	Na_2SO_3 8 kg/t EDTA 3.8 kg/t Dithionite 3.5 kg/t
CTMP production	19 ADt/h
Total water usage	60 L/s
Refining EOP	750 kWh/t
Wastewater flow	
Clear filtrate	40 L/s
Channel sample	39 L/s
Wastewater treatment process now used	Flotation – MBBR – aeration – clarifier - flotation
Problems detected at the moment	High COD load High TSS If dry-barking does not work correctly, bark gets into the process with chips and causes red color to the water

From the mill 2, the samples were taken from two different sampling points, as at the mill 1. First sample is filtrate from third screw press from the washing stage after bleaching. Second sample is from a channel, and is equal to mill 1 channel sample. The water used in the process is raw water and water from the power plant. Mill 2 has a microflotation system for recirculating CTMP filtrates, where chemicals are added to the water and the formed sludge is removed from the top of the flotation pool. The sludge goes to the activated sludge treatment and the clarified water is recycled at some parts of the CTMP process. Process description and selected process parameters at the time of sampling are presented in table XX.

Table XX Process information from the Mill 2.

Mill 2.	
Raw material	Spruce, mostly chips from sawmills
Used chemicals	Na_2SO_3 35 kg/t H_2O_2 24 kg/t DTPA 3 kg/t Caustic soda 27.5 kg/t Natrium silicate 5 kg/t
CTMP production	610 ADt/d = 25,4 ADt/h
Total water usage	Raw water 113 L/s + power plant water 36 L/s
Refining EOP	Refiner 1, 878 kWh/t Refiner 2, 757 kWh/t Reject refiner, 772 kWh/t
Wastewater flow	
Filtrate Channel sample	47.5 L/s 81 L/s
Wastewater treatment process now used	microflotation + activated sludge treatment
Problems detected at the moment	COD load is high, but it's easily treated at the activated sludge plant compared to other streams going there, so no significant problems.

Both mills make wastewater quality analyses for certain parameters on their own. These analyses are also used in this thesis. These results are from a short time period and are presented in table XXI for both mills, as an average from all the results. The samples for these analyses are collected from a pipeline, in which both channel and filtrate samples exist.

At mill 2, the sample is taken after the microflotation from the stream going to the wastewater treatment plant. That can explain the differences between the phosphorous and nitrogen values from different mills. In reality, the nutrients amount at mill 2 is smaller. Since the nutrient values were not measured from the whole flow, it can skew the results in the excel tool part in this work.

Table XXI Wastewater quality analyses average results for mill 1 (from time period 5.2.2018 – 16.4.2018) and for mill 2 (from time period 1.4.2018 – 3.5.2018).

	Mill 1	**Mill 2**
Production, ADt/d	-	395
Wastewater, m3/d	-	5805
pH	-	7.7
SS, mg/l **SS, t/d** **SS, kg/t**	-	2180 12 46
COD, mg/l **COD, t/d** **COD, kg/t**	4345 - -	7881 45 164
H2O2 residue, g/l	-	0
P, mg/l	3.0	10
N, mg/l	15.6	180

Mill 2 has reported the residue H_2O_2 to be around zero. This is of course an ideal situation, but in reality can be quite rare. This thought depends on the residence time. If the residence time is long enough, all the hydrogen peroxide have time to react. Since the residue hydrogen peroxide value is also analyzed after the microflotation, it is possible that the residue hydrogen peroxide is circulated back to the process in the microflotation clarifier stream. To verify this, more analysis should be done and more knowledge of the process itself should be collected. The possibility of hydrogen peroxide residues in the wastewater should still be considered, since they might cause trouble in some treatment methods.

5.2. Analysis methods

Different kinds of methods were used in the laboratory analyses. These methods and used equipment are briefly described in this chapter. To avoid faults in the measurements and to detect mistakes, two corresponding measurements were made for each sample. Average and standard deviation were calculated from these two measurements and then with these the coefficient of variation was calculated with equation 14.

$$v = s/x * 100\% \tag{14}$$

where v is the coefficient of variation

s is the standard deviation

x is the average.

Accepted value for coefficient of variation was 5% and if this was exceeded, more measurements were made.

5.2.1 pH and conductivity

pH and conductivity are measured based on SFS-standards. Conductivity measurements are based on SFS-EN 27888 standard and pH on SFS-EN ISO 10523 standard. Both measurements were done at temperature 21 °C with a digital pH and conductivity meters.

5.2.2 Total suspended solids

Total suspended solids were measured according to SFS-EN 872 standard. Samples were measured at room temperature. Glass fiber filters used in this experiment were washed with water and dried in oven. After that the filters were weighted. Sample volume used in the filtration was 20 ml. Using a vacuum filtration apparatus, samples were filtered through glass fiber filters and then dried at 105 °C, cooled in desiccator and then weighted.

The amount of suspended solids can be calculated from equation

$$SS = \frac{1000 \cdot (b - a)}{V}$$

where SS is the suspended solids, mg/L

b is the mass of the filter after filtration, mg

a is the mass of the filter before filtration, mg

V is the volume of the sample, ml

1000 is the reduction factor.

5.2.3. *Dissolved organic carbon, DOC*

Dissolved organic carbon was determined according to standard SFS-EN 1484. The samples were first centrifuged and then filtered through 0.45 μm membrane filter. Samples were diluted into 1:100 dilutions and then analyzed with Shimadzu Total Organic Carbon Analyzer, TOC-L. Standard solutions were analyzed before and after the samples and based on the standard solution results, correlation factor was determined. Correlation factor was used to correct the fault in the analyzed results. Correlation factor was calculated to be 0.89 and the results were divided with the correlation factor to correct the fault in the measurements.

5.2.4. *Total solids, organics, inorganics and the chemical composition of the inorganics*

Organics and inorganics were measured according to what is presented in SFS-EN 872 standard. First, samples were weighted into porcelain crucibles and dried at 105 °C for two hours. The residue was cooled in desiccator and weighted with 0.1 mg accuracy. Then, the residue was annealed for two hours in 550 °C, cooled in desiccator and weighted with 0.1 mg accuracy.

Total solids can be calculated with equation

$$X_1 = \frac{1000\ (m_2 - m_1)}{V}$$

where X_1 is total solids, mg/L

m_1 is weight of the sample container, mg

m_2 is weight of the sample container and the dry matter, mg

V is the volume of the water sample, ml

1000 is the reduction factor.

The amount of organics and inorganics can be calculated from the annealing residue equation. The annealing residue contains only inorganics and can be calculated from equation

$$Y_1 = \frac{1000\,(m_3 - m_1)}{V}$$

where Y_1 is amount of inorganics, mg/L

m_1 is weight of the sample container, mg

m_3 is total weight of the sample container and the annealing residue, mg

V is the volume of the water sample, ml

1000 is the reduction factor.

The amount of organics in the sample can be calculated from the total solids result and the amount of inorganics with equation

$$Z_1 = X_1 - Y_1$$

where Z_1 is amount of organics, mg/L

X_1 is amount of total solids (organics and inorganics), mg/L

Y_1 is amount of inorganics, mg/L

Chemical composition of the inorganics was analyzed from the annealing residue. Analyzes were made by LUT employee, with scanning electron microscope (SEM). The sample was grinded into fine powder and piled up. The pile was scanned with the microscope from the surface and analyzed with energy dispersive x-ray spectroscopy (EDS) technique. The results are presented as weight percent, and converted into milligrams per liter. This is a very harsh number, since it's not analyzed straight from the liquid, but gives some estimate of the existing inorganic compounds in the water and guides to the direction of how much these compounds could exist in the effluents.

5.2.5. Extractives

The analyses for the extractives in the wastewaters were made by isolating the extractives from the solutions by liquid-liquid extraction and further analyzed with gas chromatography (GC). Method includes the removal of fibers and fines by centrifugation, extraction with methyl tert.-butyl ether (MTBE), silylation and gas chromatography determination. (Orsa, 1994)

First, pH of the water samples was adjusted with on drop of 1M sulphuric acid to 3-3.5. Then, 4 mL of MTBE and 300 μL of standard solution were added. Standard solution contained heneicosanoic acid, betulinol, cholesteryl heptadecanoate and 1,3-dipalmitoyl-2oleoyl glycerol, each 100 mg/L in MTBE. The samples were shaken for 7 min in a shaker machine. The clear MTBE layer was pipetted off, evaporated in a nitrogen stream and freezed until analysis could be continued. The samples had to be silylated before the GC analysis with solution of BSTFA [bis-(trimetholsilyl)-trifluoroacetamide] and TMCS (trimethylchlorosilane) in 2:1 ratio. 150 μL of the solution was added. The samples were kept in an oven at 70 °C for 45 min and then analyzed with GC.

The GC analysis was performed with 6 m/0.53 mm i.d. wide-bore capillary column with a nonpolar phase (MTX-1HT), film thickness 0.15 μm. The samples were injected with an autoinjector directly in the column at injection temperature 85 °C. The column temperature was 85°C, 1 min-12°C/min-345°C, 5.5 min, 100°C/min-365°C/5 min. The flame ionization detector (FID) temperature was 370 °C. Hydrogen was used as a carrier gas.

The amount of extractives in mg/L was calculated from the equation

$$\frac{Extractives,\ mg}{Volume,\ L} = \frac{(Sample\ peak\ area)(Standard\ amount, mg)}{(Standard\ peak\ area)(Volume,\ L)}$$

5.3 Excel tool

The purpose of this part of the work is to show the causal connections of the wastewater characteristics to different treatment methods operating costs, and with that information to give some guidelines for the selection of the wastewater treatment method. The investment costs are left without consideration and the guidelines are set only by factors like the need for commodities, for example power and chemicals and formation of beneficial or unwanted by-products, like biogas or sludge. This kind of comparison of the methods is very harsh, but can help when justifying possible methods for clients, and to help think about future solutions or possibilities when updating the mill site or process.

This excel tool is purposed to be used with the table of the limiting factors in anaerobic part. The limiting factors show, if the method is overall even possible and the excel tool gives some values related to operating costs and purification efficiency. Other methods, evaporation and aerobic treatment, don’t have significant limiting factors.

For every treatment method, different factors were chosen. For example for evaporation, the only factor that describes the operations of the method is the power demand. The power demand was calculated for aerobic and anaerobic methods also, but in evaporation it is a lot bigger factor than in the biological methods. Though there is different kind of weighting values and methods that could be used to improve the comparison of different treatment methods, the factors were not weighted. This is due the fact, that it's up to the observer from which point of view the methods are examined and what weights are given to the factors. This excel tool carried in this master's thesis only gives values that can be compared and considered when justification for the treatment method selection is needed. This tool is only harsh evaluation to give some guidelines for the pre-design or survey to the client when treatment methods are considered.

The main idea of this tool is, that you feed process and wastewater parameters to the excel tool and it calculates values for different kind of factors, which can be compared and the usability of the method can be estimated for that process and water. In the tool, red values are the ones that need to be fed to the tool. Blue block are marked in specific worksheet, and these values are basically the variables that can be changed, like electricity price, power demand or sludge formation. Green values are the ones that the excel tool calculates when red and blue variables are changed.

5.3.1 Factors and calculations

Factors that were chosen to be examined in the excel tool are described below. The calculation basis for these factors is also presented and explained. Some calculations are based on references and some on common knowledge at Pöyry designers.

Power demand was calculated for all the three treatment methods. This factor was considered to be quite important, since power demand defines a big part of the operating expenses. The calculations were made based on the common knowledge at Pöyry designers. For evaporation, MVR evaporator values were used. The value is defined for situation where 0.5% solid matter solution is concentrated into 15 % solution. For aerobic treatment, the value is for activated sludge process, since it's the most common process. The value consists mainly on the demand for aeration, which means air feed blower power demand, and other pumps needed in the process. Anaerobic treatment power demand is also based on the power demand of the pumps needed to pump the water and sludge etc. Different calculation basis are presented below. As it can be seen from the formulas, the power demand in aerobic method depends on the COD removal rate. This needs to be taken into account in the calculations and when considering the suitability of the process for the treatment method.

Evaporation: 17 kWh/t H_2O (0.5% → 15%)

Aerobic: 0.046 kWh/kg COD removed

Anaerobic: 0.35 kWh/t H_2O

Cost estimation for power use was calculated based on the electricity price for medium size industry case, based on the value got from Statistic Finland webpage (Statistics, 2018).

Electricity price = 7.3 snt/kWh

For aerobic treatment, the *sludge formation* is one big disadvantage of the method. This factor was chosen, since it affects to the costs of the process, since the sludge needs to be handled somehow or disposed. This increases the operating expenses. Disposal costs are evaluated based on information found from Pöyry Environment Oy's report (Pöyry Environment Oy, 2007). The value is edited from treatment costs with different techniques presented in the survey. The disposal costs are calculated to be an average of all these different techniques. Disposal costs are evaluated to be 81 €/ton of sludge.

Based on the common knowledge at Pöyry, the *sludge formation* for aerobic treatment was valued to be 0.29 kg sludge formed per kg COD removed. Similar values can also be seen in the literature (Tchogobanoglous, et al., 2003). The amount of sludge is also dependent on the COD removal efficiency and that needs to be taken into account. For anaerobic treatment, the sludge formation is assumed to be zero and complete reaction of the COD into methane, carbon dioxide and sulphur dioxide (equations 4 – 13) is assumed.

Other factors calculated in the tool for biological methods are *nutrient demand or nutrient removal need*. Typically the pulp and paper wastewater does not fulfill the demand of nutrients in the biological methods and, therefore, nutrients need to be added to the process to ensure the optimal operation. If there is nutrients available in the effluent that much, that it needs purification other than addition, the cost estimation will then give a zero value. The excel tool does not notice the additional purification in the calculations, so it needs to be evaluated separately. The amount of nitrogen or phosphorous does not tell the real amount of the substances that can be utilized by bacteria. That is why this is a very harsh estimation of the demand.

Nutrient demand for aerobic treatment is calculated based on the BOD:N:P ratio found in the literature (Tchogobanoglous, et al., 2003). The ratio between these compounds is assumed to be 100:5:1. With this ratio on the calculated BOD value, minimum amount of nitrogen and phosphorous needed in the process can be estimated. These values were estimated also for anaerobic treatment method, but the ratio is a bit different than in aerobic treatment. The used ratio is COD:N:P and is estimated to be 500:5:1. This ratio is also based on literature (Tchogobanoglous, et al., 2003).

Urea (CH_4N_2O) is used for nitrogen and phosphoric acid (H_3PO_4) for phosphorous calculations. Urea contains 46% of nitrogen and phosphoric acid contains 32% phosphorous. These values can be calculated from the molar mases. Prices for urea and phosphoric acids are from Pöyry’s database.

Urea = 380 € / ton

Phosphoric acids = 500 € / ton

Quality demand for effluent defines the usability of the purification process. In this work, these calculations are based on COD removal efficiency. The efficiency can vary and can be changed in the excel tool based on laboratory or pilot plant experiments if needed.

For evaporation, it is assumed that 10 % of the COD goes into the condensate stream, which means 90% COD removal. One source presents even 99% removal (H2O, 2018), when using vacuum in the evaporation. The total COD removal is evaluated to be a bit smaller than this literature value, since no vacuum is used. The removal rate depends on the condensate handling and purification, and can vary a lot depending on the case. This value was estimated to be an average of all possible cases.

The value used in this work for aerobic treatment is based on literature (Suhr, et al., 2015) and is assumed to be

COD removal = 85 %.

To reach the BAT-limits for COD (12-20 kg COD/ADt) by using only aerobic treatment with 85% removal efficiency, the wastewater can contain maximum 80 to 133 kg COD/ADt.

These calculations are also done for anaerobic method and like in the aerobic treatment these values also vary a lot depending on the wastewater characteristic and process parameters etc.

Based on literature, the COD removal efficiency can vary a lot, but is typically between 45-60 % (Larsson, et al., 2017) . In this work the calculations in excel tool are made using COD removal of 60%.

COD removal = 60 %.

The value was chosen to be 60%, based on the Larsson, et al. research where pilot scale tests gave this value for both hardwood and softwood. The real COD removal values can be smaller, depending on the process and raw material.

To reach the BAT-limits for COD (12-20 kg COD/ADt) by using only anaerobic treatment with 60% removal efficiency, the wastewater can contain maximum 30 to 50 kg COD/ADt.

The biggest advantage in anaerobic treatment is the *methane formation* and that is calculated in the excel tool. This factor has a positive effect on the operating expenses, since the biogas can be used in the CTMP plant to replace at least a part of the natural gas bought, or it can be sold further. CTMP wastewaters theoretical methane potential is calculated by Ekstrand et al..

Theoretical methane potential = 0.94 m^3/kg TOC removed

Ekstrand et al. proposes that the methane production is about 40-50% of the total methane potential. A medium of this was used in the calculations, so about 45% of TOC was evaluated to be removed by anaerobic method.

Natural gas is typically used as energy source in pulp mills. Profit from the methane production is calculated based on a natural gas price found from Statistics Finland webpage (Statistics, 2018).

Natural gas price = 25.5 eur/MWh

To compare these three treatment methods, costs per kg COD removed was calculated. These numbers consists of different factors in different methods. For evaporation, the equation used for calculations is

$$Costs\ \left(\frac{eur}{kgCODremoved}\right) = \frac{Power\ (\frac{eur}{d})}{COD\ removed\ (\frac{kg}{d})}$$

For aerobic treatment, the equation is

$$Costs\ \left(\frac{eur}{kgCODremoved}\right)$$

$$= \frac{Power\ \left(\frac{eur}{d}\right) + Sludge\ disposal\ \left(\frac{eur}{d}\right) + Nutrients\ demand\ (\frac{eur}{d})}{COD\ removed\ (\frac{kg}{d})}$$

And for anaerobic treatment formula is

$$Costs\ \left(\frac{eur}{kgCODremoved}\right)$$

$$= \frac{Power\ \left(\frac{eur}{d}\right) + Nutrients\ demand\ \left(\frac{eur}{d}\right) - Profit\ from\ biogas\ (\frac{eur}{d})}{COD\ removed\ (\frac{kg}{d})}$$

6. Results and discussion

This chapter includes results from the laboratory analysis done in this thesis and the results from the excel tool, which was created during this thesis work.

The excel tool can be used for any kind of CTMP wastewaters and processes, when the wastewater parameters are known. In this thesis, the examined wastewaters were got from two different mills, so these two mills are used as an example. The excel tool is used for the summary of the two streams where the samples were collected from mills. Since these two mills are softwood CTMP mills, the third case is based on literature values for hardwood CTMP, just to estimate the differences in softwood and hardwood wastewaters. The results and discussion does not take into account existing wastewater treatment at the mills or the effects of different departments at integrate to the water. Only the CTMP part of integrate is discussed. Location and the size of the equipment is not either taken into account.

6.1. Laboratory results

Results from all the analysis performed in this thesis work are presented in table XXII.

Table XXII Results from the laboratory analyses described in chapter 5.2.

	Mill 1. Channel	**Mill 1. Filtrate**	**Mill 2. Channel**	**Mill 2. Filtrate**
pH	7,5	6,7	7,7	8,6
Conductivity, mS/cm	2,928	1,861	4,846	4,057
DOC, mg/L	~ 1400	~ 1200	~ 2400	~ 2000
Total solids, mg/L	3940 (3860 – 4020)	5795 (5760 – 5830)	8690 (8590 – 8790)	9110 (9080 – 9140)
Ash (inorganics), mg/L	1540 (1510 – 1570)	2920 (2890 – 2950)	3520 (3460 – 3580)	4195 (4160 – 4230)
Ash composition	O 35 % 540 mg/L, Na 19.7 % 303 mg/L, Si 2.2 % 33 mg/L, S 13.7 % 210 mg/L, Cl 2.8 % 43 mg/L, K 2.3 % 35 mg/L, Ca 2.8 % 43 mg/L	O 38.4 % 1121 mg/L, Na 19.1 % 558 mg/L, Si 10.5 % 305 mg/L S 8.5 % 248 mg/L, Cl 5.7 % 165 mg/L, K 3.6 % 104 mg/L, Ca 4.5 % 131 mg/L	O 40.8 % 1436 mg/L, Na 31.2 % 1099 mg/L, Si 3.5 % 123 mg/L, S 11.5 % 404 mg/L, Cl 0.4 % 14 mg/L, K 1.4 % 50 mg/L, Ca 1.8 % 62 mg/L	O 40.9 % 1716 mg/L, Na 35.7 % 1498 mg/L, Si 5.1 % 215 mg/L, S 2.2 % 94 mg/L, Cl 0.2 % 8 mg/L, K 0.7% 27 mg/L, Ca 0.8 % 35 mg/L
Organics, mg/L	2400	2875	5170	4915
Organics / Inorganics ratio	1.6	1.0	1.5	1.2
Suspended solids, mg/L	708 (685 – 730)	215 (210 – 220)	1305 (1265 – 1345)	2687 (2630 – 2720)

Resin acids, mg/L	35	13.8	33.2	23
Fatty acids, mg/L	25.6	7.9	23.1	17.5
Lignans, mg/L	21	28.9	33.8	11.2
Lignin residuals*, mg/L	5.4	3.2	10.2	4.0
Sterols, mg/L	3.9	4.3	5.1	2.3
Steryl esters, mg/L	18.6	10.7	64.2	21.5
Triglycerides, mg/L	58.8	57.9	159.8	52.2
Lipophilics, mg/L	142.0	94.6	285.4	116.4

* Does not include polymeric lignin

When comparing the two mills, there are some differences in the analysis results that can be explained by the differences in the processes. For example, mill 2 filtrate sample has higher pH than the filtrate sample from mill 1. This can be explained by the different kind of bleaching chemical used. Filtrates contains washing water after bleaching, and because mill 2 uses hydrogen peroxide and mill 1 dithionite, the bleaching washing water can be assumed to have higher pH because of the more alkaline conditions in hydrogen peroxide bleaching. Also, mill 2 has higher chemical dosing and thus higher total alkalinity in the process than mill 1, so the result in the pH analysis seems reasonable. Chemical dosing difference can be seen in the ash composition results also, since the sodium amount have really big difference between the mills. What was unexpected in pH results, is that in mill 1 the channel sample pH is higher than the filtrate sample, though in the filtrate sample there should be seen the chemical treatments effect on the water. This can be explained either by process water circulation or then there might be some kind of connection to the low Na_2SO_3/EDTA ratio. EDTA is an acid, so it might decrease the pH. When sodium sulfate dosing is quite low and it does not balance the pH decrease caused by EDTA, it could be seen as a lower pH like in this case. When comparing the mill 1 Na_2SO_3/EDTA (8/3.8) and mill 2 Na_2SO_3/DTPA (35/3), it can be seen that the difference is significant.

The effect of the chemical dosing and the nature of bleaching chemical are also seen in the DOC results – higher chemical dosing and alkalinity cause higher dissolution of organics. In the filtrate samples, one noticeable thing is the ratio between organics and inorganics. The ratio in both mills is quite near to 1, so the filtrate contains about same amount of organics and inorganics. This is due the inorganic process chemicals in the washing waters.

Suspended solids are noticeably higher in mill 2 samples compared to mill 1 samples. This can also be explained by the chemical differences. There is a difference between the two mills between the samples from different stages. At mill 1 in the channel sample the SS value is higher than in the filtrate sample, but at mill 2 the filtrate sample's SS value is higher. This difference comes from the higher bleaching level at mill 2.

The ash composition results show clearly the addition of impregnation and bleaching chemicals, but also the additives in the process. At both mills, the addition of silicate in the bleaching stage can clearly be seen from the increasing value of Si between channel and filtrate sample. Other thing to notice from the ash composition results is the difference in sulphur results. Mill 1 uses sulphur containing bleaching chemical, so both the samples contains quite the same amount of sulphur. At the mill 2 then, sulphur is added only in the impregnation and washed away before bleaching, so the filtrate sample contains at much lower amount of sulphur. Other compounds, like potassium, calcium and chlorine can be assumed to origin from the wood, since there is no chemical in which they noticeably exist. The amount of inorganics based on these results is not that high, that it should have effect on the treatment method selection.

The amount of process chemicals in the waters can also be seen by the connection of organics/inorganics ratio, the amount of organics and inorganics and the conductivity. With smaller amounts of inorganics, the conductivity is also smaller. The connection of the process chemicals into the wastewater conductivity is clearly seen from the results – mill 2 having higher chemical dosing has also almost two times higher conductivity in the filtrate samples than mill 1. The connection between conductivity to the amount of organics is not straight-forward, but when comparing the two mills the connections can be seen. This connection is more straight-forward with the conductivity and DOC values. And it is obvious; with higher amount of chemicals, higher dissolution of organics is achieved. The connection between DOC and conductivity is presented in figure 15.

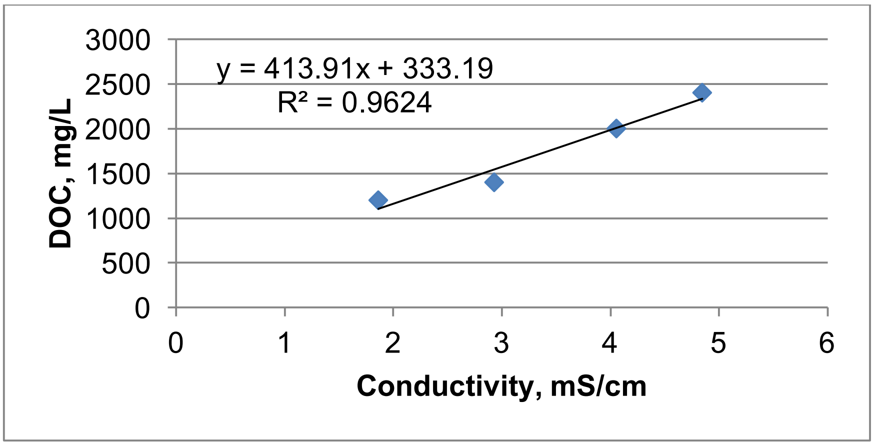


Figure 15 Connection between conductivity and DOC noticed from the laboratory results.

In all the samples, pH is quite near to neutral, except in the mill 2 filtrate sample, little bit higher. In general this pH seems quite good when considering possible treatment methods. Though pH is always adjusted to the right level, when pH is near to the suitable pH value, less pH control chemical is needed.

The results from extractives analysis was a lot smaller than what was expected based on literature. Though, in the literature it is also reported, that the values can vary a lot depending on the process and the analysis method. In the method used in this work, the solids were not taken into account. It is possible, that when the sample was centrifuged, some of the extractives attached to the solids and thus were not along in the analysis. Also, the references don't tell the analysis method used in the research, so we don't know if the results can be compared. Though the results was smaller than expected, the overall amount of resin acids in the total flows from the mills exceed the inhibiting limit in the anaerobic treatment. That needs to be taken into account when selecting the method.

The analysis results converted into different kind of units is presented in table XXIII. From this it is very good to notice, that though the amount seems small in mg/L, is might still produce a high load on a daily basis.

Table XXIII Analysis results converted into different units.

		Mill 1 Channel	Mill 1 Filtrate	Mill 1 total	Mill 2 Channel	Mill 2 Filtrate	Mill 2 total
CTMP Production	Adt/d	456	456	456	610	610	610
Flow	L/s	39	40	79	81	47.5	128.5
	m3/d	3370	3456	6826	6998	4104	11102
	m3/Adt	7	8	15	11	7	18
DOC	mg/L	1400	1200	1299	2400	2000	2252
	kg/d	4717	4147	8865	16796	8208	25004
	kg/Adt	10	9	19	28	13	41
COD*	mg/L	4200	3600	3896	7200	6000	6756
	kg/d	14152	12442	26594	50388	24624	75012
	kg/Adt	31	27	58	83	40	123
BOD**	mg/L	1909	1636	1771	3273	2727	3071
	kg/d	6433	5655	12091	22904	11193	34094
	kg/Adt	14	12	27	38	18	56
SS	mg/L	708	215	458	1305	2687	1816
	kg/d	2386	743	3129	9133	11027	20160
	kg/Adt	5	2	7	15	18	33
Ash	mg/L	1540	2920	2239	3520	4195	3770
	kg/d	5189	10092	15281	24634	17216	41851
	kg/Adt	11	22	34	40	28	69
Ash, Oxygen	mg/L	540	1121	834	1436	1716	1540
	kg/d	1820	3874	5694	10050	7042	17092
	kg/Adt	4	8	12	16	12	28
Ash, Sodium	mg/L	303	558	432	1099	1498	1246
	kg/d	1021	1928	2949	7691	6148	13839
	kg/Adt	2	4	6	13	10	23
Ash, Silicon	mg/L	33	305	171	123	215	157
	kg/d	111	1054	1165	861	882	1743
	kg/Adt	0	2	3	1	1	3
Ash, Sulphur	mg/L	210	248	229	404	94	289
	kg/d	708	857	1565	2827	386	3213
	kg/Adt	2	2	3	5	1	5
Ash, Chlorine	mg/L	43	165	105	14	8	12
	kg/d	145	570	715	98	33	131
	kg/Adt	0	1	2	0	0	0
Ash, Potassium	mg/L	35	104	70	50	27	41
	kg/d	118	359	477	350	111	461
	kg/Adt	0	1	1	1	0	1
Ash, Calcium	mg/L	43	131	88	62	35	52
	kg/d	145	453	598	434	144	578
	kg/Adt	0	1	1	1	0	1
Organics	mg/L	2400	2875	2641	5170	4915	5076
	kg/d	8087	9936	18023	36182	20171	56353

	kg/Adt	18	22	40	59	33	92
Total solids	mg/L	3940	5795	4879	8690	9110	8845
	kg/d	13276	20028	33304	60816	37387	98204
	kg/Adt	29	44	73	100	61	161
N* **	mg/L	-	-	15.6	-	-	180
	kg/d	-	-	106.5	-	-	1998.4
	kg/Adt	-	-	0.2	-	-	3.3
P* **	mg/L	-	-	3	-	-	10
	kg/d	-	-	20.48	-	-	111.0
	kg/Adt	-	-	0.04	-	-	0.2
Resin acids, mg/L	mg/L	35	13.8	24.3	33.2	23	35.4
	kg/d	117.9	47.7	165.6	232.3	161.0	393.3
	kg/Adt	0.3	0.1	0.4	0.4	0.3	0.6
Fatty acids, mg/L	mg/L	25.6	7.9	16.5	23.1	17.5	25.6
	kg/d	86.3	26.6	112.9	161.7	122.5	284.1
	kg/Adt	0.2	0.1	0.2	0.3	0.2	0.5
Lignans, mg/L	mg/L	21	28.9	24.6	33.8	11.2	28.4
	kg/d	70.8	97.4	168.1	236.5	78.4	314.9
	kg/Adt	0.2	0.2	0.37	0.4	0.1	0.52
Lignin residuals, mg/L ****	mg/L	5.4	3.2	4.2	10.2	4	9.0
	kg/d	18.2	10.8	29.0	71.4	28.0	99.4
	kg/Adt	0.04	0.02	0.06	0.1	0.05	0.16
Sterols, mg/L	mg/L	3.9	4.3	4.0	5.1	2.3	4.7
	kg/d	13.1	14.5	27.6	35.7	16.1	51.8
	kg/Adt	0.03	0.03	0.06	0.1	0.03	0.08
Steryl esters, mg/L	mg/L	18.6	10.7	14.5	64.2	21.5	54.0
	kg/d	62.7	36.1	98.7	449.3	150.5	599.8
	kg/Adt	0.1	0.1	0.22	0.7	0.2	0.98
Triglycerides, mg/L	mg/L	58.8	57.9	57.6	159.8	52.2	133.6
	kg/d	198.1	195.1	393.2	1118.3	365.3	1483.7
	kg/Adt	0.4	0.4	0.9	1.8	0.6	2.4
Lipophilics, mg/L	mg/L	142.0	94.6	116.8	285.4	116.4	253.3
	kg/d	478.5	318.8	797.2	1997.3	814.6	2812.0
	kg/Adt	1.0	0.7	1.7	3.3	1.3	4.6

* Calculated from DOC values by multiplying with coefficient 3
** Calculated from COD values by dividing with coefficient 2.2
*** Values from mills reports
**** Does not include polymeric lignin

6.2. Case 1: Mill 1

Case 1 results from the excel tool can be seen in table XXIV. Case 1 CTMP process has quite light chemical treatment and thus lower amount of water is needed in the washing stage, when compared to case 2. The amount of water used in the process affects to the evaporation power demand. The results show, that evaporation needs a lot of energy, and the operation costs are very high. Annual costs for power demand would be over 2 million euros.

In this value, only evaporation part is taken into consideration, so the concentrated waste handling will increase the expenses. The total cost for evaporation and concentrate disposal would be even higher. It is not profitable to use evaporation and it should be selected only in cases where biological treatments are not possible to execute. These kinds of cases could be very tight discharge limits that can't be reached with biological methods, or if water needs to be reused as efficiently as possible.

There are some possible solutions that could be studied, if biological treatment can't be used and evaporation by itself is too expensive. It would be tempting to use for example membrane filtration to pretreat the wastewater and then treat the retentate with evaporation. The amount of water, that needs to be evaporated, decreases when membrane is used, so the evaporation power demand would decrease. The quality of permeate from the membrane treatment needs to be examine, if it could be recycled at least into some parts of the CTMP process. More calculations and research should be done to ensure the usability and profitability of this kind of combination.

Biological methods are a lot more economical solutions than evaporation, when considering the power demand. Based on excel tool results, the aerobic treatment seems to be the best alternative for this case. Power demand is reasonable, 1040 kWh/d would cost 76 € daily, which is a lot less than evaporation would consume (83159 kWh/d and 6071 €/d). The sludge formation is quite small and the costs from the disposal are not significant. The COD discharge reaches the BAT-limit, actually COD going even under the recommended values. Costs per kg COD removed is reasonable for aerobic method, though it does not make profit like anaerobic treatment. In future, if sludge based products take place at the markets, sludge could be sold further for some manufacturers or products could be even refined by the company near the wastewater treatment plant. This would affect to the profitability of the aerobic method, if incomes could be created from waste streams. This though needs time, but it is the future trend to refine products from waste streams. Nutrient demand for the aerobic process is also quite high. The total amount of additional nitrogen and phosphorous is almost 600 kg daily. The need for additional nutrients does not affect outstandingly to the total operating costs, since the chemicals are quite cheap and easily available.

Table XXIV Excel tool results for Mill 1 total flow (spruce CTMP wastewater).

Process parameters	
Production, Adt/d	456
Water flow, L/s	79
Water flow, m3/Adt	15

Wastewater parameters	
sTOC, mg/L	1299
COD/TOC	3
COD, mg/L	3897
COD/BOD	2.2
BOD, mg/L	1771
N, mg/L	15,8
P, mg/L	3
sTOC, kg/d	8866
COD, kg/d	26599
BOD, kg/d	12091
N, kg/d	108
P, kg/d	20
sTOC, kg/Adt	19
COD, kg/Adt	58
BOD, kg/Adt	27
N, kg/Adt	0.2
P, kg/Adt	0.04

Evaporation	
Power demand	
Power, kWh/d	83159
Cost, eur/d	6071
Cost, eur/a	2155054
Purification efficiency / Condensate quality	
COD removal %	90
Condensate	
COD, kg/d	2660
COD, kg/Adt	6
Costs(+) & profit(-), eur/kg COD removed	
Daily	0.25
Annual	90

Aerobic treatment	
Power demand	
Power, kWh/d	1040
Cost, e/d	76
Sludge formation	
Sludge t/d	6,6
Disposal eur/d	530
Nutrient demand (+) or purification need (-)	
N, kg/d	497
P, kg/d	100
Urea and phosphoric acid costs	
Urea, eur/d	4.1
Phosphoric acid, eur/d	1.6
Purification efficiency / Effluent quality	
COD removal %	85
Effluent	
COD, kg/d	3990
COD, kg/Adt	9
Costs(+) & profit(-), eur/kg COD removed	
Daily	0.03
Annual	9.6

Anaerobic treatment	
Power demand	
Power, kWh/d	2389
Cost, e/d	174
Biogas / Methane production	
Methane, m3/d	3751
Biogas, m3/d	5770
Biogas, kWh/d	59303
Biogas, MWh/d	59
Profit, e/d	1512
Nutrient demand (+) or purification need (-)	
N, kg/d	158
P, kg/d	33
Urea and phosphoric acid costs	
Urea, eur/d	1.3
Phosphoric acid, eur/d	0.5
Purification efficiency / Effluent quality	
COD removal %	60
TOC removal %	45
Effluent	
COD, kg/d	10640
COD, kg/Adt	23
Costs(+) & profit(-), eur/kg COD removed	
Daily	-0.08
Annual	-30

Anaerobic treatment is also promising solution in case 1. The COD discharge is very close to the BAT-limit, being 23 kg/ADt. The COD removal rate is estimated to be quite high, but in case it is lower, the BAT limit can be possibly be reached by some kind of tertiary treatment. The methane potential is the tempting factor in CTMP wastewaters, and the methane formation in case 1 would be around 3750 m^3/d. This would produce a profit or saving of 1500 €/d, when sold forward or deducted from methane bought to the mill. Since the BAT-limit for COD is exceeded, it could be possible to treat the water first with anaerobic and then with aerobic treatment, to reach the same COD removal rate as in aerobic treatment only. This option is presented in figure 16. When combining these two biological methods, it must be noticed, that the overall COD removal can't be more than the optimal COD removal in aerobic treatment. So the total removal rate is 85%, as it would be in the aerobic treatment alone. If anaerobic treatment first removes 60% of the COD, the removal rate of the aerobic stage needs to be calculated with the total removal rate. Then, the aerobic treatment's removal rate is only 63%.

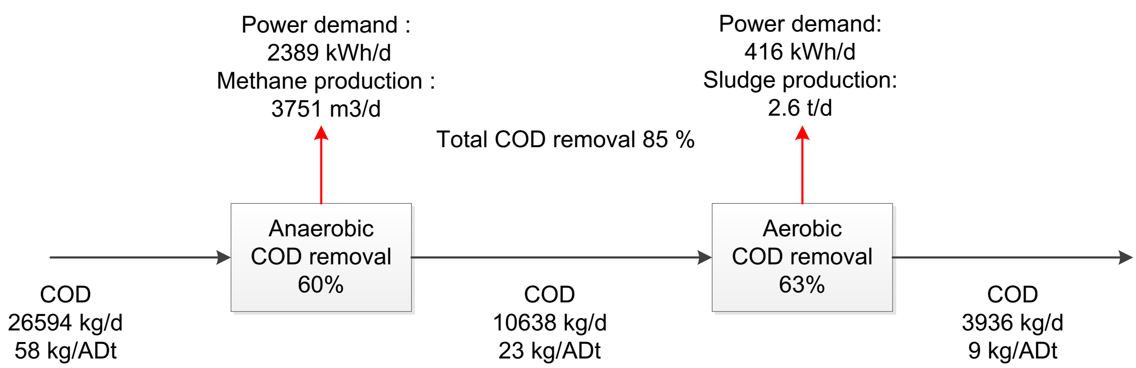


Figure 16 Process option for case 1.

With this kind of process solution presented in figure 16, the total power demand can be decreased, when compared to aerobic treatment alone. This solution offers the profits from the methane produced and degrades the disadvantages from the sludge formation. The amount of sludge is decreased even 4 tons daily. This would make a great saving in the operating costs.

Only questionable thing in the anaerobic treatment is the effect of extractives and other inhibiting compounds to the activity of the bacteria. The total flow at the mill contains extractives that much, that the inhibiting level is exceeded. The amount in the filtrate stream though does not exceed the limit, so it should be safer to treat with anaerobic method, compared to the channel stream or total flow. If the company wants to capitalize on the methane potential of the water, it could consider treating the filtrate stream with anaerobic and channel stream with aerobic method. This option is further presented in figure 17.

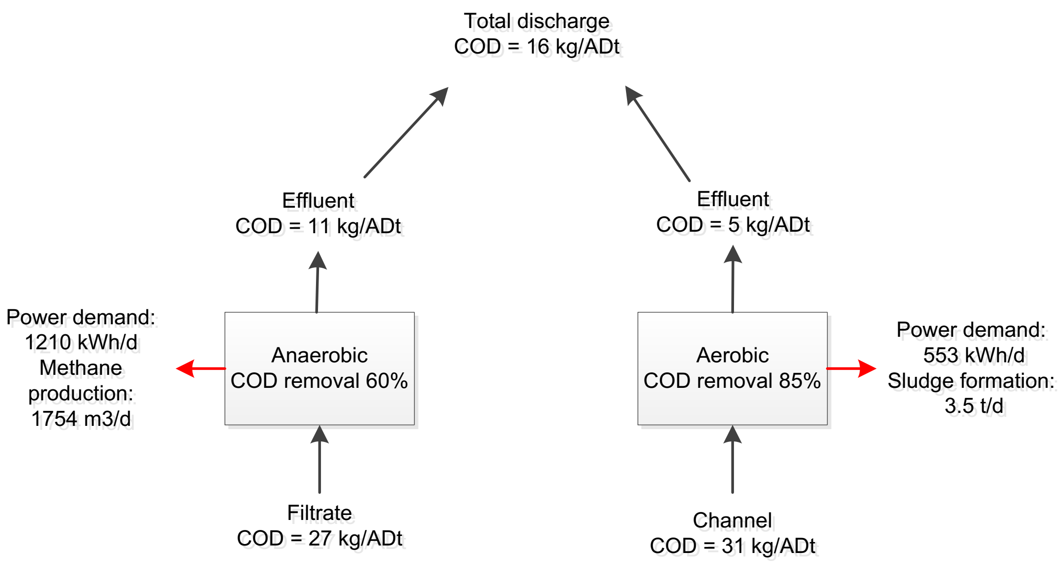


Figure 17 An optional process solution for case 1, where streams are treated separately.

When comparing solution presented in figure 17 with the excel tool results for case 1, the suggested process solution seems quite a good option. The total power demand for the combination of aerobic and anaerobic methods is smaller than for aerobic treatment alone, methane potential could be partly utilized and at the same time, the amount of excess sludge would be halved. The BAT-limit for COD discharge is well undercut for the total discharge, when filtrate and channel streams are treated separately. This could be a good alternative, but needs a bit more investments from the company and it should be well considered if it is profitable to maintain two different operations. More research and calculations should be done, to ensure correct functioning of the anaerobic treatment for the filtrate stream and calculate the profitability and other economical key factors

6.3. Case 2: Mill 2.

Mill 2 uses more chemicals and water compared to mill 1. Due to the high amount of water in the process, the evaporation's expenses rises up to 3.5 million€/year. That is very high price for water treatment, and is profitable basically only in cases where water price is very high or environmental regulations are strict. It will be most likely more profitable to improve biological methods with tertiary treatment, than use evaporation to reach discharge limits or reuse the water in the process.

As in the case 1, the option of pretreating the water prior evaporation is possible and then the operating expenses would be much lower. The water could be pretreated for example with membrane filtration, when only part of the water needs evaporation. This option needs further research and calculations, and should only be considered when for some reason biological methods can not be used.

To be noticed from the biological methods results, the nutrients amount is quite high. That would mean that nitrogen needs to be purified, not added like in case 1. The nitrogen value from mill 2 is from concentrated stream, so this may cause the fault value. Therefore, in this case, the nutrient demand is left out of discussion.

The higher chemical dosing at mill 2 creates higher COD load, so it attracts to choose anaerobic treatment to utilize the methane potential in the wastewater. Total flow has a methane potential of over 10 000 m^3/d. From that, mill could make a good profit. Efficient chemical treatment poses also higher dissolution of extractives which inhibit the anaerobic process and methane production, so it compensates the benefits of high COD. Extractives in the total stream exceed the inhibiting concentration, so they reduce the methane production capacity. Inhibitors also limit the biomass growth and may destroy active biomass, when new biomass may have to be added constantly to the reactors. This may cause high costs to the mill. Even though the utilization of methane potential is tempting, the COD amount is so high, that the anaerobic purification alone can't reach the discharge limits.

Table XXV Excel tool results for Mill 2 total flow (spruce CTMP wastewater).

Process parameters		**Wastewater parameters**		**Evaporation**		**Aerobic treatment**		**Anaerobic treatment**	
Production, Adt/d	610	sTOC, mg/L	2252	***Power demand***		***Power demand***		***Power demand***	
		COD/TOC	3	Power, kWh/d	135264	Power, kWh/d	2933	Power, kWh/d	3886
Water flow, L/s	128,5	COD, mg/L	6756	Cost, eur/d	9874	Cost, e/d	214	Cost, e/d	284
Water flow, m3/Adt	18	COD/BOD	2.2	Cost, eur/a	3505373	***Sludge formation***		***Biogas / Methane production***	
		BOD, mg/L	3071	***Purification efficiency / Condensate quality***					
		N, mg/L	180			Sludge t/d	18.5	Methane, m3/d	10576
		P, mg/L	10			Disposal eur/d	1495	Biogas, m3/d	16271
				COD removal %	90	***Nutrient demand (+) or purification need (-)***		Biogas, kWh/d	167229
				Condensate				Biogas, MWh/d	167
		sTOC, kg/d	25003	COD, kg/d	7501			Profit, e/d	4264
		COD, kg/d	75008	COD, kg/Adt	12	N, kg/d	-294	***Nutrient demand (+) or purification need (-)***	
		BOD, kg/d	34094	***Costs(+) & profit(-), eur/kg COD removed***		P, kg/d	230		
		N, kg/d	1998			***Urea and phosphoric acid costs***		N, kg/d	-1248
		P, kg/d	111	Daily	0.15			P, kg/d	39
				Annual	52				
		sTOC, kg/Adt	41			Urea, eur/d	0	***Urea and phosphoric acid costs***	
		COD, kg/Adt	123			Phosphoric acid, eur/d	3.6		
		BOD, kg/Adt	56					Urea, eur/d	0
		N, kg/Adt	3.3			***Purification efficiency / Effluent quality***		Phosphoric acid, eur/d	0.6
		P, kg/Adt	0.18						
						COD removal %	85	***Purification efficiency / Effluent quality***	
						Effluent			
						COD, kg/d	11251	COD removal %	60
						COD, kg/Adt	18	TOC removal %	45
						Costs(+) & profit(-), eur/kg COD removed		***Effluent***	
								COD, kg/d	30003
						Daily	0.03	COD, kg/Adt	49
						Annual	9.5	***Costs(+) & profit(-), eur/kg COD removed***	
								Daily	-0.09
								Annual	-33

Like in the case 1, the streams could be treated separately. The filtrate sample slightly exceeds the inhibiting concentration in resin acid, but not significantly. This treatment option is presented in figure 17.

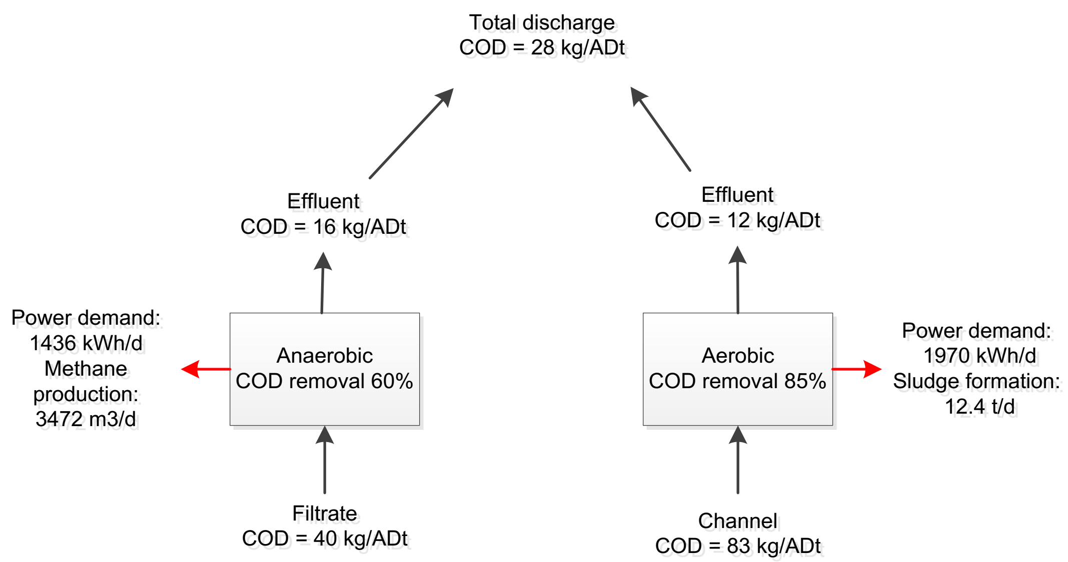


Figure 18 Treatment option for case 2.

From figure 18 it can be seen, that though the COD load is a lot smaller in filtrate sample compared to the channel sample, the anaerobic treatment does not remove COD that much, that the total discharge could be set to BAT-level. This option would need tertiary treatment, which would increase the total costs of the investment and operating costs. It is still good to notice that this kind of solution is possible.

Since the anaerobic treatment alone can not reach the BAT-limits, that can be left without consideration. It is possible though to treat the waters first with anaerobic and then with aerobic method. As mentioned above, there are inhibiting compounds in the waters, so it should be well examined if it is profitable to use anaerobic treatment at all. If it is, the methane potential could be utilized and the amount of sludge formed in aerobic treatment could be decreased. This option is presented in figure 19.

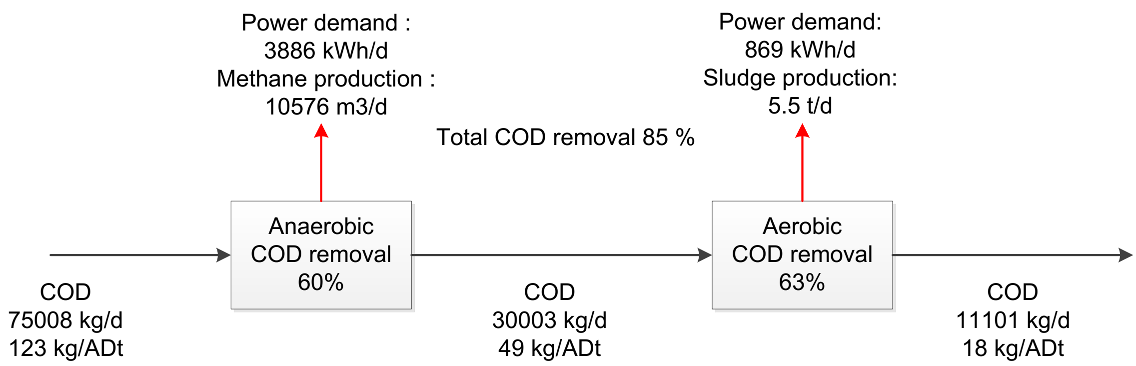


Figure 19 Process option for case 2.

Treatment process presented in figure 19 seems like a good choice. Methane production seems worthwhile and sludge production can be decreased from 18.6 ton to 5.5 ton per day. This is a good saving for the mill, since the sludge disposal is quite expensive.

As in the case 1, the future solutions for sludge use can affect to the selection and total operating costs.

6.4. Case 3: Hardwood

Hardwood case is based on literature, since hardwood CTMP wastewaters were not available. Two species were chosen into observation: aspen and birch. Since there was only literature sources available where process parameters is not told, the process parameters were set as in the case 2. These parameters were chosen, instead of case 1, since the chemical dosing is assumed to be more like in the case 2 based on the literature and the production is bit higher. Process parameters and input values for the excel tool can be seen from tables XXVI and XXVII.

Since the process parameters were set to match the mill 2, the evaporation power demand is the same as in the mill 2. This is due the power demand is calculated from the total water flow, so the wastewater characteristics does not affect to this value. As at mill 2, the evaporation power demand is very high and evaporation is not considered to be profitable method for these kinds of wastewaters. For hardwoods in general, the amount of methanol and organic acids is reported to be higher than for softwoods (Larsson, et al., 2017), so the evaporation would produce impure condensate. Condensate would need better purification before it could be reused in the process. With hardwood CTMP wastewaters, biggest problem is a very high COD load. Since biological methods can’t reach the BAT-limits, the evaporation might be, in some cases, the only possible solution. It should though be well studied, if biological methods can be combined with some tertiary treatment like chemical precipitation, membranes or oxidation, to reach the discharge regulations. Evaporation is very expensive operation and it is possible that an expanded biological method will be more economical choice.

As in the cases 1 and 2, the option of pretreating the water prior evaporation for example with membrane filtration is possible and the operating costs would be much lower. This option needs further research and calculations, but could be a good option since the high COD load.

High COD load affects to the formation of sludge in the aerobic process. The expenses from the sludge disposal would be quite a big cost, up to 3000 €/day. Other disadvantage in aerobic method, caused by high COD load, is the fact that even with removal rate of 85%, the effluent purity does not reach the BAT-limits in COD. COD amount in after purification in the aspen case is 31 kg/ADt and in the birch case 38 kg/ADt. These values are quite near to the BAT-limits (12-20 kg/ADt) and could possibly be reached with some tertiary treatments. There are many researches done in the tertiary treatment options, and good results have been reported for example with coagulation (88% removal of total carbon), adsorption (90 % COD removal) and oxidation. When considering the selection of tertiary treatment, all the harmful compounds that exist in the effluent should try to be removed as efficiently as possible. Since EDTA & DTPA used in the process are not biodegradable, the selection of tertiary treatment method should possibly be done so that these compounds could also be removed. Ozonation for example provides both COD and EDTA removal. Korhonen et al. have proved that with ozone dosing of 1 mgO_3/mgCOD, 65% of COD and 90% of EDTA can be removed. (Korhonen, et al., 2000)

Ozonation, as many other physicochemical treatments, could also be executed prior the biological treatment. This decreases the load in the aerobic treatment plant, so the size of the biological part can be decreased. The pretreatment can also remove harmful compounds, like resin and fatty acids. Korhonen et al. have presented results of 0.2 mgO_3/mgCOD dose to remove 90% of resin acids, but only 30% of COD. Though the COD removal is quite low, that can significantly affect to the final results in the total purification, and BAT-limits could be reached.

Nutrient demand for the aerobic process is quite high in the hardwood cases. Especially the demand for nitrogen is quite big, approx. 2600 kg nitrogen needs to be added daily to the process. The need for additional nutrients does not affect outstandingly to the total operating costs, since the chemicals are quite cheap and easily available.

Since the aerobic treatment can not reach the BAT-limits in COD, it's obvious that these are not reached even near with the anaerobic treatment. The COD values after purification with anaerobic method are for aspen case 83 kg/ADt and for birch case 100 kg/ADt. This method alone can not be used to treat these waters.

The anaerobic method though is very tempting alternative, since the methane production results are very good. Over 20 000 m^3 of methane daily is quite a good amount of gas to be used at the mill or sold forward. The amount of inhibiting compound, like extractives, is smaller in hardwood CTMP wastewaters than in softwood waters. Higher methane formation and lower amount of inhibiting compounds together make such a combination, that anaerobic treatment seems quite reasonable.

Table XXVI Excel tool results for literature values for aspen CTMP wastewater **(Larsson, et al., 2017)** with process parameters from mill 2.

Process parameters		**Wastewater parameters**		**Evaporation**		**Aerobic treatment**		**Anaerobic treatment**	
Production, Adt/d	610	sTOC, mg/L	3790	***Power demand***		***Power demand***		***Power demand***	
		COD/TOC	3	Power, kWh/d	135264	Power, kWh/d	4936	Power, kWh/d	3886
Water flow, L/s	128,5	COD, mg/L	11370	Cost, eur/d	9874	Cost, e/d	360	Cost, e/d	284
Water flow, m3/Adt	18	COD/BOD	2.2	Cost, eur/a	3505373	***Sludge formation***		***Biogas / Methane production***	
		BOD, mg/L	5168	***Purification efficiency / Condensate quality***					
		N, mg/L	24			Sludge t/d	31.1	Methane, m3/d	17799
		P, mg/L	1			Disposal eur/d	2515	Biogas, m3/d	27383
				COD removal %	90	***Nutrient demand (+) or purification need (-)***		Biogas, kWh/d	281438
				Condensate				Biogas, MWh/d	281
		sTOC, kg/d	42078	COD, kg/d	12623			Profit, e/d	7177
		COD, kg/d	126234	COD, kg/Adt	21	N, kg/d	2603	***Nutrient demand (+) or purification need (-)***	
		BOD, kg/d	57379	***Costs(+) & profit(-), eur/kg COD removed***		P, kg/d	563		
		N, kg/d	266					N, kg/d	996
		P, kg/d	11	Daily	0.09	***Urea and phosphoric acid costs***		P, kg/d	241
				Annual	31				
		sTOC, kg/Adt	69			Urea, eur/d	21.5	***Urea and phosphoric acid costs***	
		COD, kg/Adt	207			Phosphoric acid, eur/d	8.8		
		BOD, kg/Adt	94					Urea, eur/d	8.2
		N, kg/Adt	0.4			***Purification efficiency / Effluent quality***		Phosphoric acid, eur/d	3.8
		P, kg/Adt	0.02						
						COD removal %	85	***Purification efficiency / Effluent quality***	
						Effluent			
						COD, kg/d	18935	COD removal %	60
						COD, kg/Adt	31	TOC removal %	45
						Costs(+) & profit(-), eur/kg COD removed		***Effluent***	
								COD, kg/d	50494
						Daily	0.03	COD, kg/Adt	83
						Annual	9.6	***Costs(+) & profit(-), eur/kg COD removed***	
								Daily	-0.09
								Annual	-32

Table XXVII Excel tool results for literature values for birch CTMP wastewater **(Larsson, et al., 2017)** with process parameters from mill 2.

Process parameters	
Production, Adt/d	610
Water flow, L/s	128,5
Water flow, m3/Adt	18

Wastewater parameters	
sTOC, mg/L	4580
COD/TOC	3
COD, mg/L	13740
COD/BOD	2.2
BOD, mg/L	6245
N, mg/L	41
P, mg/L	8
sTOC, kg/d	50849
COD, kg/d	152547
BOD, kg/d	69340
N, kg/d	455
P, kg/d	89
sTOC, kg/Adt	83
COD, kg/Adt	250
BOD, kg/Adt	114
N, kg/Adt	0.7
P, kg/Adt	0.15

Evaporation	
Power demand	
Power, kWh/d	135264
Cost, eur/d	9874
Cost, eur/a	3505373
Purification efficiency / Condensate quality	
COD removal %	90
Condensate	
COD, kg/d	15255
COD, kg/Adt	25
Costs(+) & profit(-), eur/kg COD removed	
Daily	0.07
Annual	26

Aerobic treatment	
Power demand	
Power, kWh/d	5965
Cost, e/d	435
Sludge formation	
Sludge t/d	37,6
Disposal eur/d	3040
Nutrient demand (+) or purification need (-)	
N, kg/d	3012
P, kg/d	605
Urea and phosphoric acid costs	
Urea, eur/d	24.9
Phosphoric acid, eur/d	9.4
Purification efficiency / Effluent quality	
COD removal %	85
Effluent	
COD, kg/d	22882
COD, kg/Adt	38
Costs(+) & profit(-), eur/kg COD removed	
Daily	0.03
Annual	9.6

Anaerobic treatment	
Power demand	
Power, kWh/d	3886
Cost, e/d	284
Biogas / Methane production	
Methane, m3/d	21509
Biogas, m3/d	33091
Biogas, kWh/d	340102
Biogas, MWh/d	340
Profit, e/d	8673
Nutrient demand (+) or purification need (-)	
N, kg/d	1070
P, kg/d	216
Urea and phosphoric acid costs	
Urea, eur/d	8.8
Phosphoric acid, eur/d	3.4
Purification efficiency / Effluent quality	
COD removal %	60
TOC removal %	45
Effluent	
COD, kg/d	61019
COD, kg/Adt	100
Costs(+) & profit(-), eur/kg COD removed	
Daily	-0.09
Annual	-32

The anaerobic treatment alone can not reach the BAT-limits, but it could be possible to combine the anaerobic treatment with aerobic treatment. This combination of two techniques would utilize the high methane potential in the water and decrease the formation of excess sludge in the aerobic treatment. The combination is presented in figure 20. Some calculations for the factors and COD are also calculated into the figure.

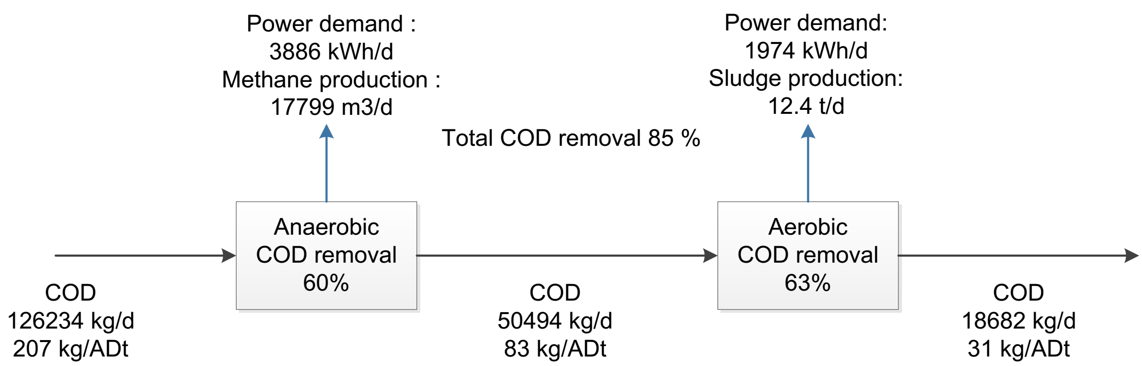


Figure 20 Combination of anaerobic and aerobic treatment for aspen CTMP wastewater.

From table XXVII and figure 20 it can be concluded, that if the water would be treated only with aerobic treatment, is would produce 31.1 ton of sludge per day, and when treated with the combination, it produces only 12.4 ton of sludge daily. The decrease in the sludge formation is noticeable and has a great effect on the operating expenses.

If some tertiary treatment would be added after these two treatments, the excess COD could be removed to reach smaller COD for discharged effluent. Most likely the BAT-limits would be reached.

6.5 Summary

Literature search showed that the connection between process parameters and wastewater characteristics is obvious. The chemical dosing, used chemicals and refining for example affects to the amount of COD, but also in general to the wastewater quality. The used raw materials seems also to have some influences, but the main difference between softwood and hardwood CTMP wastewaters comes from different kind of chemical treatment. There is very little information available from the connections between process parameters and wastewater characteristics. It would have been good to get some data about the connections, so these could have been added into the excel tool which was created during the thesis, but this would need deeper examination of the processes, trial runs at the mills and more laboratory analysis.

Every treatment method has its pros and cons. The selection of “the best” method can vary, depending on the perspective where it is considered. If selection is based on the most pure effluent, meaning that the discharges into the environment are as low as possible, evaporation is the best solution. Also, with membrane filtration, using reverse osmosis, the effluent is very pure. The environmental impacts can be minimized, when using these methods, since the condensate can be recycled and the concentrate is often incinerated. However, evaporation is not usually economical. The power demand is so high, 17 kWh/t H_2O, that it should carefully be considered, if this is the method to be chosen. On the other hand, the countries where hardwood CTMP is most likely produced; the price of electricity can also be much lower when compared to Finland. So the evaporation might not be so expensive alternative and can compete with biological methods. For example in Canada, where evaporation is used at one CTMP plant, the price of electricity for large industrial plants at 2017 was around 0.05 CA$ (Hydro Quebec, 2017), which is about 0.03 € (rate of exchange 28.6.2018 1 EUR = 1.54 CAD).

Biological methods then, offer a lot more economical solutions. When the selection is based on economical evaluation, the ranking for the best method would be anaerobic and then aerobic treatment. Anaerobic method is very tempting, since the CTMP wastewater has a high methane potential. The methane production and profits from utilizing or selling it further, moves the costs/kg COD removed value to the positive side. Also, using fuel made from waste decreases the demand for fossil fuels, which is good. From the economical point of view, the second best option is the aerobic treatment.

In general, the selection is based on the combination of the purification efficiency and the economic analysis. Anaerobic treatment alone can not reach the purification level requirements, but offers benefits from the methane production. Aerobic treatment then, has quite good purification efficiency for the CTMP wastewaters and can compete in economics, so it is a good option. Aerobic treatment is also the most certain method. The purification and operations are quite stable and guaranteed. Compared to anaerobic treatment, which is very sensitive for changes, the aerobic method is more secure option. Table XXVIII summarizes the benefits and challenges of evaluated methods.

Table XXVIII Wastewater treatment method comparison.

Method	Benefits	Challenges
Evaporation	– zero liquid discharge – chemical recovery – suitable for most waters without big problems – no impact for aquatic environment	– fouling and deposit formation – high investment costs – high energy demand – equipment needs quite a lot of space near the CTMP plant – recycling water may affect to the product quality – may increase the air pollution load
Aerobic treatment	– efficient reduction of COD and TSS – can reach the current discharge regulations – does not affect to the product quality (no recycling to the process)	– lot of sludge formed – may have long-term impacts in environment – does not treat EDTA&DTPA – extractives are inhibitors
Anaerobic treatment	– less energy needed – lower addition of nutrients(vs. aerobic) – less sludge formation (vs. aerobic) – methane production – does not affect to the product quality (no recycling to the process)	– inefficiency because of the inhibiting compounds in the effluent – sensitive for changes in the process conditions – long start-up time – odour formation – need for further treatment(aerobic) – may have long-term impacts in environment

There are few possible process options presented in chapters 6.1-6.3 for different cases. These options are collected into table XXIX, where possible treatment methods are marked with green signs and not suitable, or at least methods with more difficulties, with red signs.

To be noticed, evaporation is evaluated not to be beneficial for any softwood CTMP waters due to high amount of energy needed in evaporation. With softwood wastewaters, which have lower COD load, there are biological methods that can be combined or enhanced, and still it will most likely be more economical than using evaporation. For hardwood CTMP waters, the evaporation is considered to be an option, since the COD load can be so high.

Table XXIX Possible treatment methods for different cases.

Case	Evaporation	Aerobic	Anaerobic	Anaerobic + aerobic
1 : total flow	×	✓	×	✓
1 : streams treated separately	-	-	-	✓
2 : total flow	×	✓	×	✓
2 : streams treated separately	-	-	-	✓ + tertiary treatment
3 : Hardwood	× (✓)	✓ + tertiary treatment	×	✓ + tertiary treatment

7. Conclusions

The purpose of this thesis was to evaluate the suitability of evaporation, aerobic treatment and anaerobic treatment for the purification of CTMP wastewaters. The CTMP wastewaters characteristics were determined both based on literature and with laboratory analysis. An excel tool was created to give rough estimate of the different treatment method's operating expenses. With these operating expenses, the methods were compared.

The literature survey showed, that CTMP wastewaters have a high COD load and contains toxic components, which makes it hard to handle. Main compounds to be noticed are extractives, hydrogen peroxide residuals and sulphur compounds. Some non-biodegradable chemicals are also used in the process, EDTA and DTPA for example, which might cause some problems in the future, if their discharges into environment will be restricted.

In the experimental part of the work, wastewater analyses were done for CTMP wastewaters from two different mills. With these analyses, the wastewater could be better identified. To compare the different treatment methods, and to connect the wastewater characteristics to the selection of the best method, excel tool was created to evaluate the operating expenses of the different treatment methods.

On the ground of the excel results, seems that evaporation is too expensive option. Biological methods, together or alone, would suit to treat CTMP wastewaters, if high amounts of inhibitors are not found. Since with the biological methods the quality requirements can not always be reached, physicochemical treatments for tertiary or primary treatments have to be considered. The literature search showed that a lot of research has been done in this area and there are several possible methods to be used to solve the problems in CTMP wastewater treatment. Membrane filtration, adsorption and oxidation are for example methods, that have been used to treat CTMP wastewaters. Most likely, these methods will become more general in the future, since it is assumed that the environmental requirements will tighten. This master's thesis includes only the typical secondary treatment methods, aerobic and anaerobic treatment and evaporation.

As a final conclusion, it seems that the aerobic method is, at least for now, the best solution to treat the wastewaters from CTMP mills among the studied methods. It is the most guaranteed and stable, economical and most often the purification requirements can be reached with this method. The excel tool results show, that every case should still be well examined and methods compared, since there are variations between the processes and wastewaters, and different kind of possibilities for the treatment process to be selected.

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