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COD FRACTIONATION OF PULP AND PAPER MILL WASTEWATERS

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ABSTRACT

Silja Mustonen: COD fractionation of pulp and paper mill wastewaters
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Pulp and paper mill wastewaters contain typically high concentrations of organic material, which is measured as chemical oxygen demand (COD). The amount of organic material, among other environmentally harmful compounds, should be reduced from the wastewater before discharging. The activated sludge process can be used to remove mainly biodegradable organic material, which is measured as biological oxygen demand (BOD). In order to study the organic composition of different wastewaters and the removal of organic material in the wastewater treatment processes, COD fractionation can be carried out on the wastewater samples. In COD fractionation, COD is divided into different fractions according to the biodegradability and molecular size.

The first aim of this study was to investigate the organic composition of two wastewater streams (debarking and thermomechanical pulping (TMP)) and the influent and effluent of the activated sludge process from the pulp and paper mill in Finland. Another aim was to study the removal of COD fractions in the activated sludge process. Samples were taken from each sampling point both in winter and summer. One grab sample was taken in December, while three composite samples were taken during May and June. The organic composition was examined by the COD fractionation, for which the COD and respirometric BOD analyses were carried out. The removal of COD fractions in the activated sludge process was examined by comparing the results of COD fractionation of both the influent and effluent.

The largest fraction of both debarking and TMP wastewater was non-biodegradable soluble COD (nbsCOD) (35-62 %). Seasonal variations were observed in the debarking wastewater, as it contained over two times higher total COD in winter compared to summer. The influent of the activated sludge process contained mostly readily biodegradable COD (rbCOD) (39-62 %), while the effluent of the activated sludge process contained mostly nbsCOD (68-87 %). It was concluded that there have been slight variations in the efficiency of the activated sludge process to remove rbCOD at different sampling times, as in one effluent sample the rbCOD was lower (6 mg/l) and the rbCOD removal was higher (99.3 %) compared to the other effluent samples (10-11 mg/l and 98.7 %).

According to the results, the activated sludge process of the mill is able to efficiently remove rbCOD and achieve a low rbCOD in the effluent. Thus, adding new treatment processes to current wastewater treatment may not be necessary, since adjusting the operation of current activated sludge process can be sufficient to achieve low amounts of rbCOD in effluent. The results of COD fractionation can be utilized in modelling the activated sludge process, when examining the impact of different operation parameters on the process efficiency and determining the most appropriate process conditions. In the case that non-biodegradable COD (nbCOD) in effluent is required to reduce in the future, new treatment processes may be necessary to be investigated and introduced.

Keywords: pulp and paper mill, debarking wastewater, TMP wastewater, COD fractionation, activated sludge process

TIIVISTELMÄ

Silja Mustonen: Sellu- ja paperitehtaan jätevesien COD fraktiointi
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Sellu- ja paperiteollisuuden jätevedet sisältävät tyypillisesti suuria määriä orgaanista ainesta, jonka määrää mitataan kemiallisen hapenkulutuksen (chemical oxygen demand, COD) avulla. Muiden ympäristölle haitallisten yhdisteiden lisäksi, myös COD:n määrää jätevedessä tulee vähentää ennen jäteveden purkamista ympäristöön. Aktiivilieteprosessilla voidaan poistaa pääasiassa biologisesti hajoavaa COD:ta, jonka määrää mitataan biologisen hapenkulutuksen (biological oxygen demand, BOD) avulla. Jätevesinäytteille voidaan suorittaa COD fraktiointi, jotta saadaan tietoa eri jätevesien orgaanisesta koostumuksesta ja orgaanisen aineksen poistumisesta eri jätevedenpuhdistusprosesseissa. COD fraktioinnissa COD jaetaan fraktioihin biohajoavuuden ja molekyylikoon perusteella.

Työn tavoitteena oli tutkia Suomessa sijaitsevan sellu- ja paperitehtaan kuorimon ja kuumahierreprosessin (thermomechanical pulping, TMP) jätevesien sekä aktiivilieteprosessiin menevän (influentti) ja sieltä tulevan (effluentti) jäteveden orgaanista koostumusta. Työn toisena tavoitteena oli tutkia aktiivilieteprosessin kykyä poistaa eri COD fraktioita jätevedestä. Jokaisesta näytteenottopisteestä otettiin yksi kertanäyte joulukuussa ja kolme kokoomanäytettä touko- ja kesäkuun aikana. Orgaaninen koostumus määritettiin COD fraktioinnilla, jota varten jätevesinäytteille suoritettiin COD- ja BOD-analyysit. Eri COD fraktioiden poistumista aktiivilieteprosessissa tutkittiin vertaamalla aktiivilieteprosessin influentin ja effluentin COD fraktioinnin tuloksia keskenään.

Sekä kuorimon että TMP:n jätevesien suurin fraktio oli biohajoamaton liukoinen COD (non-biodegradable soluble COD, nbsCOD) (35-62 %). Kuorimon jätevedessä havaittiin vuodenaikaisvaihtelua, sillä COD:n määrä oli talvella yli kaksinkertainen verrattuna kesään. Aktiivilieteprosessin influentti sisälsi pääosin nopeasti biohajoavaa COD:ta (readily biodegradable COD, rbCOD) (39-62 %), kun taas aktiivilieteprosessin effluentti sisälsi pääasiassa nbsCOD:ta (68-87 %). Aktiivilieteprosessin tehokkuudessa poistaa rbCOD:ta havaittiin pieniä eroja eri näytteenottoaikoina, sillä yhdessä effluentin näytteessä sen määrä oli alhaisempi (6 mg/l) ja poistotehokkuus korkeampi (99.3 %) verrattuna muihin näytteisiin (10-11 mg/l ja 98.7 %).

Tulosten perusteella tutkittavan tehtaan aktiivilieteprosessi on kykenevä poistamaan tehokkaasti rbCOD:ta ja saavuttamaan matalia effluentin rbCOD:n pitoisuuksia. Näin ollen, uusien jätevedenpuhdistusprosessien käyttöönotto ei ole tällä hetkellä välttämätöntä, sillä säätämällä nykyisen aktiivilieteprosessin operointia voidaan saavuttaa riittävän alhaisia effluentin rbCOD:n pitoisuuksia. COD fraktioinnin tuloksia voidaan hyödyntää aktiivilieteprosessin mallinnuksessa, kun tutkitaan eri operointiparametrien vaikutusta prosessin tehokkuuteen ja pyritään määrittämään sopivimmat prosessiolosuhteet. Mikäli tiukentuvien jätevesimääräysten myötä biohajoamattoman COD:n määrää on vähennettävä tulevaisuudessa, uusien jätevedenkäsittelyprosessien käyttöönotto voi tulla aiheelliseksi.

Avainsanat: sellu- ja paperitehdas, kuorimon jätevesi, TMP:n jätevesi, COD fraktiointi, aktiivilieteprosessi

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CONTENTS

LIST OF SYMBOLS AND ABBREVIATIONS

AOP	advanced oxidation process
AOX	adsorbable organic halides
BAT	best available techniques
bCOD	biodegradable COD
BOD	biological oxygen demand
BOD_t	biological oxygen demand after time *t*
BOD_{tot}	total biological oxygen demand
COD	chemical oxygen demand
CTMP	chemi-thermomechanical pulping
DO	dissolved oxygen
EC	electrocoagulation
EO	electro-oxidation
F/M	food/micro-organisms
HRT	hydraulic retention time
k	reaction rate constant
MLSS	mixed liquor suspended solids
MLVSS	mixed liquor volatile suspended solids
NbCOD	non-biodegradable COD
NbpCOD	non-biodegradable particulate COD
NbsCOD	non-biodegradable soluble COD
RbCOD	readily biodegradable COD
SbCOD	slowly biodegradable COD
SRT	sludge residence time
SVI	sludge volume index
TMP	thermomechanical pulping
VOC	volatile organic compound

1. INTRODUCTION

A large amount of wastewater is generated in the pulp and paper industry due to a high water consumption in its various processes (Molina-Sánchez *et al.* 2018). Organic and inorganic material dissolves from the raw material in water during the pulp and paper making processes, and thus cause pollution load on generated wastewater. Although the chemical composition of wastewater depends on the raw material, the types of pulping and papermaking processes and the chemicals used, the pulp and paper industry wastewater contains typically high concentrations of organic material and suspended solids. Organic material is measured as chemical oxygen demand (COD), which amount is typically high in the pulp and paper industry wastewaters. (Francisco *et al.* 2014; Toczyłowska-Mamińska 2017) Biological oxygen demand (BOD) is part of the COD and it estimates the amount of biodegradable organic material (Tuteja *et al.* 2020, p. 7).

Wastewater treatment is necessary in order to prevent pollution of the environment, as polluted wastewater would cause harmful effects, such as the depletion of dissolved oxygen and toxic effects on fish, if discharged without treatment. In addition, wastewater treatment is carried out in order to meet the requirements set by laws and regulations. (Hubbe *et al.* 2016) The activated sludge process is commonly used in the treatment of the pulp and paper industry wastewater and it is based on the biodegradation of organic material by micro-organisms (Davis 2020; Singh & Tripathi 2020). Organic compounds have differences in their ability to biodegrade and thus COD can be divided into different fractions according to biodegradability and molecular size. For example, readily biodegradable COD (rbCOD) is the easiest fraction to biodegrade and it can be efficiently removed in the activated sludge process. (Baquero- Rodríguez *et al.* 2016)

Wastewater regulations and restrictions have been tightened and the discharge limits may become more stringent also in the future. The conventional treatment methods may need to be improved or supplemented by other techniques in the future to improve the effluent quality and meet stricter discharge limits. (Toczyłowska-Mamińska 2017) Before adding new techniques, current processes can be attempted to improve. For example, the activated sludge process has many operation parameters that affect the efficiency of the process and thus, adjusting the operation to be optimal, the process can be obtained more efficient (Hreiz *et al.* 2015).

The aim of this study is to investigate the COD of wastewaters from the pulp and paper mill in Finland. The samples were taken from two streams, debarking and thermomechanical pulping (TMP) wastewaters, and from the influent and effluent of the activated sludge process. The organic composition is examined by the COD fractionation, for which the COD and respirometric BOD analyses were carried out. Another aim is to study the removal of COD fractions in the activated sludge process, which is carried out by comparing the compositions of COD between the influent and effluent of the activated sludge process.

Chapters 2 and 3 cover the theoretical background. Chapter 2 focuses on the wastewater generation in pulp and paper making processes, the characteristics of pulp and paper industry wastewater and the regulations and restrictions on wastewater discharge. The organic composition of pulp and paper industry wastewaters and different wastewater treatment processes are covered in Chapter 3. Chapter 4 describes the materials and methods used in this study and the results are presented in Chapter 5. The results are discussed in Chapter 6 and finally the conclusions are summarized in Chapter 7.

2. WASTEWATER GENERATED IN THE PULP AND PAPER INDUSTRY

Pulp and paper industry consumes a large amount of water for its various processes. However, most of the water used is returned into the water bodies. (Bajpai 2017, p. 1, 40) In the early 20th century, water consumption was up to 200-1000 m^3 per ton of produced paper (Kamali *et al*. 2016). Over the last few decades, however, water consumption has been reduced significantly in the pulp and paper industry for both economic and ecological reasons (Jung & Kappen 2014). Due to water consumption, a large amount of wastewater is also discharged in the pulp and paper industry. Typically, the amount of wastewater discharged in a pulp and paper mill is ranging between 1.5 and 60 m^3 per ton of produced paper. Wastewater generated must be treated before discharging to aquatic environment in order to prevent environmental pollution. (Molina-Sánchez *et al*. 2018) There are regulations and restrictions for the pulp and paper industry which, for example, set limit values for the quality parameters of wastewater to be discharged (Hubbe *et al*. 2016).

2.1 Pulp and paper making processes

The main raw material of pulp and paper industry is wood, which consist of cellulose, hemicellulose and lignin. Lignin acts as a binding substance for the cellulose fibres. In addition, wood contains small amounts of extractives. (Shmulsky *et al.* 2019, p. 34, 45, 50) The manufacturing of paper is based on producing pulp from wood fibres. Various products, such as newspaper and packaging paper, are further produced from the pulp. (Karat 2013)

Pulp and paper making processes can be divided into the following steps: wood handling and debarking, pulping, bleaching and paper manufacturing (Karat 2013). Wood is debarked by using a debarking drum which can be either dry or wet. The dry debarking is based on a friction caused by wood logs rubbing against each other in the rotating drum. The wet debarking is enhanced by adding water to the drum. After debarking wood logs are chipped with a wood chipper. Formed chips are screened in order to isolate chips suitable for the pulping. (Fadrim 2011, p. 102, 107, 130)

Pulping is the process in which cellulose fibres are released from the wood material. There are several types of pulping processes and they can be divided into chemical and mechanical. In chemical pulping, chemicals and heat are used to dissolve the lignin and

release fibres. The most common chemical pulping process is kraft pulping in which the white liquor containing mainly sodium hydroxide and sodium sulfide is used. Other chemical pulping processes are, for example, acid sulfite and semichemical pulping. Sulfite pulping process uses aqueous sulfur dioxide and alkaline chemicals. Semichemical pulping utilizes both chemical and mechanical treatment. First the wood chips are digested chemically so that the bonds between fibres weaken and then the fibres are separated mechanically in a refiner. (Fadrim 2011, p. 191-192, 248-249)

Compared to sulphite pulping, kraft pulping can produce a stronger pulp at higher yield. On the other hand, sulphite pulp is easier to bleach for yielding high brightness. However, kraft pulping is a popular method, as it allows the use of many different wood species as raw material, produces strong pulp, and is an energy-efficient method. Semichemical pulps are generally used for producing corrugated board due to the high stiffness of the pulp. (Fadrim 2011, p. 202, 252, 295)

Mechanical pulping is based on abrasive grinding or refining with mechanical equipment to separate fibres from the wood material. In grinding, the wood logs are grinded into pulp using a revolving grindstone. When treating the wood chips, disk refiners are used for refining. In thermomechanical pulping (TMP) process, the wood chips are pretreated with steam heat before refining. Chemi-thermomechanical pulping (CTMP) process further involves pretreatment with alkaline chemical solution. Mechanical pulps are typically used to produce paper that requires high opacity and ink absorption, such as printing and writing paper. In addition, mechanical pulps can be used for producing paperboard, wallpaper and soft tissues. (Lönnberg 2009, p. 19, 22, 30, 248, 251)

Produced pulp can be bleached using bleaching chemicals to increase the brightness of the pulp. Bleached pulps are mainly used for producing writing papers, while unbleached pulps are suitable for producing, for example, linerboard and grocery bags. Chemical pulps are easier to bleach due to their lower lignin content. Mechanical and semichemical pulps contain high-lignin content, therefore bleaching is more difficult and requires a high dose of chemicals. The bleaching principles of mechanical and chemical pulps differ. The bleaching of chemical pulps is based on the lignin removal. When the mechanical pulp is bleached, the lignin is not removed, but its chromophoric groups are changed into a colourless form. (Lönnberg 2009, p. 362, 366; Fadrim 2011, p. 27)

A paper product is produced from the pulp in a paper machine. First step is stock preparation, in which, for example, fillers, chemicals and additives are added to the pulp. Components to be added depend on the type of paper product. Prepared stock is usually cleaned by deaeration and hydro-cyclones and screened before entering the headbox.

The headbox distributes the stock on the wire, where excess water is removed by gravity and vacuum boxes. Water is also removed in wet pressing, based on mechanical compression in the nip caused by two rolls. Remaining water is removed by a thermal process in the drying section. Dominant drying method is contact drying with steam heated cylinders. The next steps is calendaring, in which the thickness of the paper is reduced by pressing the sheet between the rolls. Finally, in order to achieve the properties of paper product, for example, for printing, coatings can be added before winding the paper product. (Paulapuro 2008, p. 142, 158, 254, 344; Karlsson 2010, p. 14; Rautiainen 2010, p. 14-15)

2.2 Water use and wastewater generation

The pulp and paper industry is one of the main industries using large amounts of water and generating significant amounts of wastewater in various processes (Mehmood *et al.* 2019). Pulp and paper mills with mechanical pulping generate typically 9-20 m^3 wastewater per ton of produced paper, while in chemical pulp and paper mills generation is usually 9-27 m^3 (Suhr *et al.* 2015). Water is needed for wood debarking, chipping, pulping, bleaching and papermaking. About 70 % of water taken in is consumed as process water, but in addition, water is used for cooling the machines and washing the equipment. (Kamali *et al.* 2016; Haq & Kalamdhad 2021, p. 211) The amounts of generated wastewater vary between different unit processes. For example, wastewater generation in the dry debarking is typically below 2 m^3 per air dry ton of produced pulp, whereas in the wet debarking, wastewater generation is approximately 5-10 m^3 higher. (Suhr *et al.* 2015)

The pulp and paper industry has significantly reduced the use of water over last few decades. Over the past 20 years the water use has reduced by a half and over the past 30 years by even 95 %. (Haq & Kalamdhad 2021, p. 211) One major means to reduce the water use has been the increasing of internal water recirculation at mills. The complete closure of water circuit is still limited, as it can cause corrosion, deposits and the deterioration of the quality of the final product due to the accumulation of contaminants in the process water. Some internal treatment processes are required if the quality of water is not sufficient for recycling. The level of water circuit closure depends on the type of final product. For example, brown paper grades do not require a water quality as high as white paper grades and thus, water circuits can be highly closed in the case of brown grades. (Hubbe *et al.* 2016) The recirculation of water affects the volume of discharged wastewater. In addition, the pulping and paper making process, the type of raw material and the amount of water used effects the wastewater amounts. (Zarkovic *et al.* 2011)

During the pulp and paper making processes organic and inorganic material dissolves from the raw material into the water. Dissolved organic material causes COD load on generated wastewater. Biodegradable organic material causes BOD load, which is part of COD. Similarly as the wastewater volumes, the pollution load depends on the pulp and paper making process, raw material, water use and water recirculation at mill. (Zarkovic *et al.* 2011) Although the volume and pollution load of wastewater depend on various factors and may differ, the pulping and bleaching processes can be considered the largest sources of polluted wastewater of all the pulp and paper making processes (Rintala & Puhakka 1994; Tewari *et al.* 2009).

2.3 The characteristics of wastewaters

The characteristics of wastewaters from the pulp and paper industry vary between various mills. The chemical composition of wastewater depends on the raw material and the types of pulping and papermaking processes in the mill. (Toczyłowska-Mamińska 2017) Typically, the pulp and paper industry wastewater contains high concentrations of organic material (measured as COD) and suspended solids (Francisco *et al.* 2014). In general, the organic compounds that are detected in wastewater are carbohydrates, extractives, lignin and low molecular weight compounds (Karat 2013).

The characterization of all organic compounds from the wastewater is difficult (Karat 2013). However, more than 250 different organic compounds have been identified in wastewater from the pulp and paper industry. For example, lignin, phenols, chlorides, furans and organic sulphur compounds are compounds that have been identified. (Toczyłowska-Mamińska 2017) Wastewater generated by different pulping and papermaking processes have different characteristics compared to each other. Main components of wastewater generated in each process are summarized in Figure 1.

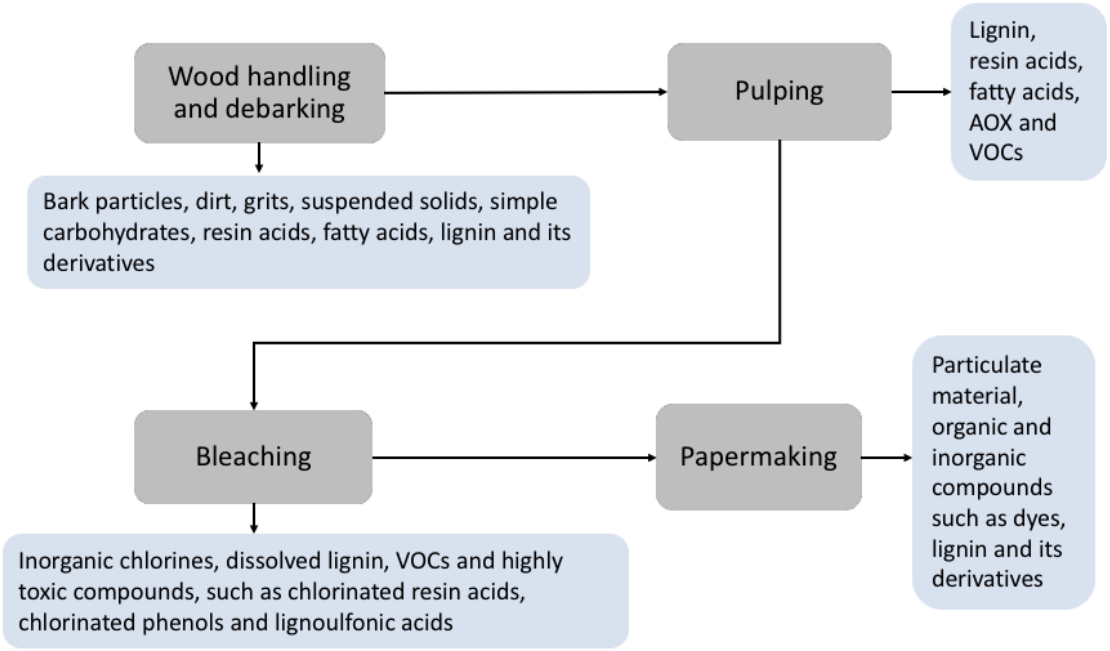

Figure 1. The typical characteristics of wastewaters from different pulp and paper making processes. The pulping and paper making method used affects which compounds the wastewater contains. (adapted from Patel *et al.* 2021) AOX=adsorbable organic halides, VOCs=volatile organic compounds

Wood handling and debarking generates wastewater that includes bark particles, grits, dirt, suspended solids and organic material (Patel et al. 2021). Some soluble compounds, such as simple carbohydrates, polymeric tannins and polar phenolic monomers, are released from the bark into the water (Field et al. 1988). Debarking wastewater contains also fatty acids, resin acids, lignin and its derivatives (Kindsigo & Kallas 2009).

Wastewater generated in the pulping has high lignin and lignin degradation products content. The lignin degradation products include catechol, vanillin, ferulic acid and phenolic compounds. (Toczyłowska-Mamińska 2017) In addition, wastewater from pulping usually contains resin acids, fatty acids, adsorbable organic halides (AOX) and volatile organic compounds (VOCs). Typically pulping wastewater contains high BOD and COD concentrations, as for example, in TMP wastewater the amount of COD can be 5600 mg/l and in CTMP wastewater up to 6000-9000 mg/l. The characteristics may differ between wastewaters from various pulping processes. (Pokhrel & Viraraghavan 2004)

Highly toxic compounds, such as chlorinated resin acids, chlorinated phenols and lignosulfonic acids, are formed during the bleaching process when chlorine reacts with lignin and other organic matter (Hubbe *et al.* 2016). Bleaching wastewater contains also AOX,

but with the replacement of chlorine by chlorine-free bleaching, AOX discharges have been significantly decreased (Leiviskä *et al.* 2008). In addition to the high amount of toxic compounds, wastewater generated in the bleaching process contains, for example, inorganic chlorines, dissolved lignin and VOCs (Pokhrel & Viraraghavan 2004). Wastewater from the papermaking contains particulate material and both organic and inorganic compounds, such as dyes (Patel *et al.* 2021). It also contains lignin and its derivatives due to the delignification processes during papermaking (Toczyłowska-Mamińska 2017). The COD load of papermaking wastewater is also caused by additives used (Suhr *et al.* 2015).

Wastewater from the pulp and paper making has a brown colour due to lignin and its derivatives contained in it. These compounds are hard to degrade due to their molecular structure with strong bonds. This causes challenge for the biological treatment of wastewater because non-biodegradable compounds, such as lignin, degrade slowly with conventional biological treatment processes. (Kreetachat *et al.* 2007; Mehmood *et al.* 2019) In addition to the brown colour of wastewater, lignin and its derivatives are one of the main causes of high COD and BOD values of wastewater from the pulp and paper industry (Hubbe *et al.* 2016).

2.4 Regulations and restrictions on wastewater discharge

Wastewater treatment is necessary in order to prevent the pollution of the environment. If wastewater would be discharged without treatment into the water bodies, it would cause harmful effects to the environment, such as toxic effects on fish, the depletion of dissolved oxygen and changes to temperatures, turbidity and colour in the recipient water bodies. In addition to protecting the environment, wastewater treatment is carried out in order to meet the requirements set by laws and regulations. (Hubbe *et al.* 2016)

In Finland, the Environmental Protection Act (527/2014) and Environmental Protection Decree (713/2014) are applied to the pulp and paper industry. They contain different obligations, one of which is applying for the environmental permit. The environmental permit defines the limit values for the wastewater discharged into the environment. The limit values are set, for example, for suspended solids and substances that have unfavourable effect on the oxygen balance of the water system. Substances (in the following, the term organic compounds will be used) effecting the oxygen balance are measurable with parameters BOD and COD. (Environmental Protection Act 2014; Environmental Protection Decree 2014)

Best available techniques (BAT) drawn up in accordance to Directive 2010/75/EU of the European Parliament and the Council on Industrial Emissions have to be taken into account by authority when drawing up discharge limits for the environmental permit. BAT-associated emission levels are minimum requirements that should not be exceeded under normal operating conditions of the mill. (Environmental Protection Act 2014) Discharge limit values for the environmental permit are set on a case-by-case basis based on both legal norms and local conditions (Silvo *et al.* 2009). As an example, Keskitalo & Leiviskä (2010) have reported the discharge limit of 45 000 kg COD/d for the bleached kraft pulp mill in Finland.

Wastewater regulations and restrictions have been tightened by limiting the toxicity and the amount of wastewater discharged. In order to meet tighter restrictions in the future, water consumption and the amount of wastewater could be reduced by increasing the internal water recirculation. To improve the quality of effluent and meet the discharge limits in the future, the conventional treatment methods need to be improved or supplemented with more efficient techniques. (Hubbe *et al.* 2016; Toczyłowska-Mamińska 2017)

3. ORGANIC COMPOSITION OF PULP AND PAPER INDUSTRY WASTEWATERS

The amount of organic compounds in wastewater is measured as COD and BOD. COD is the parameter used to reflect by measuring the amount of oxygen consumed for oxidizing organic material by a strong chemical oxidizing agent. (Davis 2020) Another parameter used to estimate the amount of organic material in wastewater is BOD. BOD test is based on measuring the amount of oxygen consumed by microorganisms to oxidize organic material contained in wastewater. More specifically, BOD value indicates the amount of biodegradable organic material in wastewater, as the degradation is based on the biological oxidation. (Hopcroft 2015, p. 42; Tuteja *et al.* 2020, p. 7)

3.1 COD fractions

COD value estimates the amount of organic compounds in wastewater but on its own it does not provide information about biodegradability. Understanding the biodegradability of compounds contained in wastewater is needed in the design of biological wastewater treatment, as it affects, for example, oxygen consumption and other dynamics of the activated sludge process. The biodegradability and fate of COD can be investigated by dividing the COD into different fractions. The total COD can be divided into two fractions: biodegradable (bCOD) and non-biodegradable COD (nbCOD). (Pluciennic-Koropczuk & Myszograj 2019) Hard COD and inert COD are also terms used for nbCOD (Kaindl & Liechti 2008; Guvenc *et al.* 2019). BCOD can be further divided into soluble readily biodegradable (rbCOD) and particulate slowly biodegradable COD (sbCOD). Even sbCOD is mainly considered a particulate matter, it in fact has been found to contain many different particle sizes from soluble to colloidal and larger particles. Also nbCOD can be further divided into two fractions: soluble non-biodegradable (nbsCOD) and particulate non-biodegradable COD (nbpCOD). (Orhon & Gokgör 1997; Pluciennik-Koropczuk & Myszograj 2019) COD fractions are presented in Figure 2.

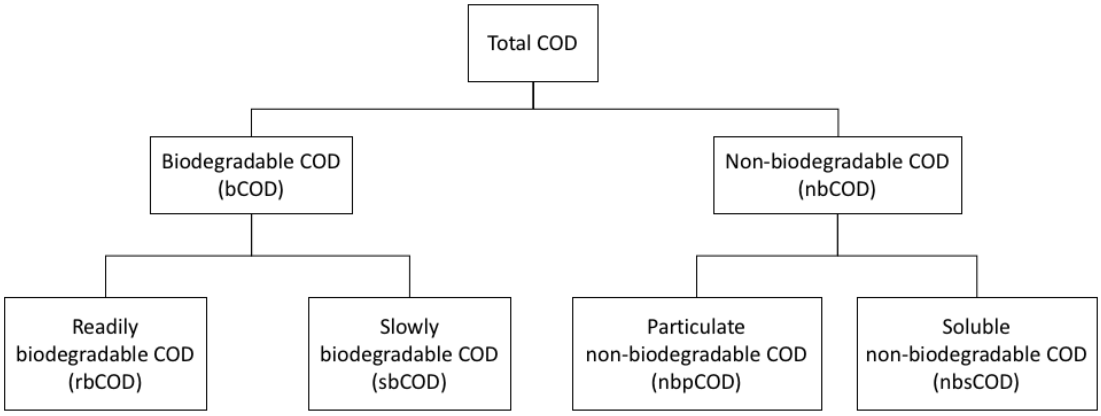

Figure 2. The total COD of wastewater can be divided into two fractions according to the biodegradability. Non-biodegradable COD is further divided according to molecular size and biodegradable COD is divided according to the rates of biodegradation. (adapted from Orhon & Gokgör 1997)

The fractionation of bCOD into rbCOD and sbCOD fractions is based on the bi-substrate model of Dold and Marais, in which the significant difference in the rates of biodegradation was shown between these fractions. The biodegradation of sbCOD is slower because it requires hydrolysis before being able to biodegrade. NbCOD differs from the above fractions in that it does not degrade during the biological treatment. (Orhon & Cokgör 1997) Both rbCOD and sbCOD can be further divided into two fractions (Figure 3).

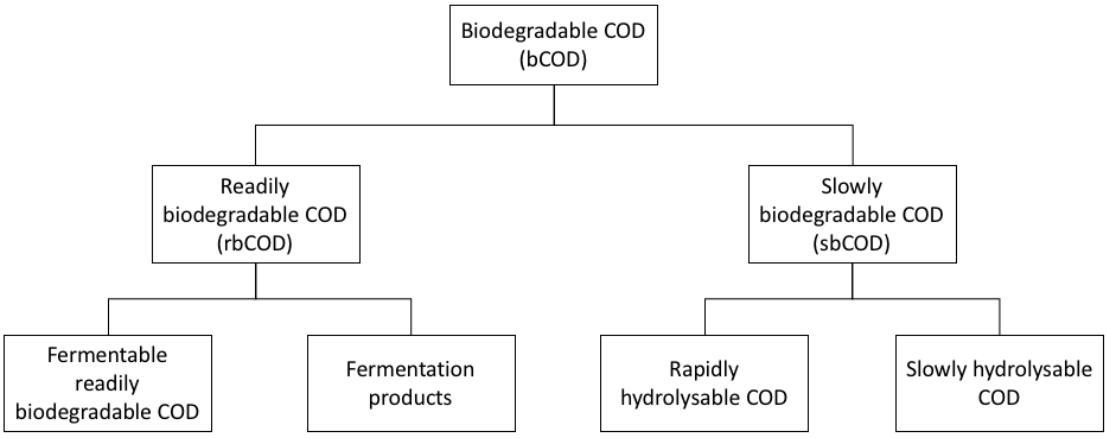

Figure 3. Readily biodegradable COD can be further divided into fermentable readily biodegradable COD and fermentation products. Slowly biodegradable COD is divided according to the rate of hydrolysis. (adapted from Orhon & Gokgör 1997)

RbCOD is divided into fermentable readily biodegradable COD and fermentation products. Fermentation products contain various compounds, but consist mainly of acetate. (Orhon & Cokgör 1997) In fermentation, microorganisms utilize organic compounds to produce energy under anaerobic conditions (Arora 2019, p. 202). SbCOD is divided into rapidly hydrolysable COD and slowly hydrolysable COD according to the rate of hydrolysis (Orhon & Cokgör 1997).

3.2 COD in pulp and paper industry wastewaters

High concentration of COD is typical for the wastewater from the pulp and paper industry. During the different pulp and paper making processes, various compounds end up to wastewater and some of them increase the amount of COD in wastewater. (Singh & Singh 2019, p. 15-18) According to Choi *et al.* (2017), the pulp and paper industry wastewaters contain a high amount of nbCOD, specifically nbsCOD. In the study of El-Fadel *et al.* (2012), the total COD of the pulp and paper mill wastewater was composed of 34 % of sbCOD, 33 % of nbsCOD, 28 % of rbCOD and 5 % of nbpCOD.

RbCOD in pulp and paper industry wastewater consists of soluble compounds, such as volatile fatty acids, alcohols, amino acids and simple carbohydrates, whereas sbCOD consists mainly of particulate organic matter. The nbsCOD consists of lignin and its derivatives as well as aromatic compounds. Aromatic compounds can end up in the pulp and paper industry wastewater, for example, from chemical dyes with aromatic or heterocyclic ring structures. (Orhon & Gokgör 1997; Choi *et al.* 2017) In addition, additives used during papermaking can contain non-biodegradable compounds that cause the nbCOD load on effluent (Suhr *et al.* 2015). In the study of Herold-Majumdar *et al.* (2021), 27 different low molecular weight compounds were detected from the fraction of nbCOD of the wastewater from eucalyptus using pulp and paper mill. These consisted of the following types of compounds: 46 % aromatics, 36 % acids, 14 % alcohols and 4 % other compounds (Herold-Majumdar *et al.* 2021).

The amounts of COD differ between wastewaters from different unit processes. For example, according to Pokhrel & Viraraghavan (2004), wastewater from the TMP process can contain 5600 mg/l of COD, while the amount of COD in wastewater from CTMP process can be even 9000 mg/l. There are also differences in the composition of COD between different wastewater fractions. Typical amounts of COD as well as the compounds mainly contained in COD are presented in Table 1.

Table 1. Reported amounts and the composition of COD of pulp and paper industry wastewaters

Wastewater fraction	Total COD (mg/l)	Main compounds in COD
Debarking and chipping	1275[1] 2508-3684[2] 7000[3]	Tannins[8,9] Lignin[9] Carbohydrates[8] Monomeric phenols[8] Resin acids[8]
TMP	5600[4] 2475[5] 3512[6]	Lignin[8] Carbohydrates[8] Extractives[8] Acids[8]
CTMP	7300[7] 6000-9000[4]	Lignin[8] Polysaccharides[8] Organic acids[8]
Pulp bleaching	3680[1]	Chlorinated lignin polymers[8] Methanol[8] Carbohydrates[8] Volatile fatty acids[8]
Papermaking	1116[1] 953[4]	nr

[1]Singh & Singh 2019, [2]Tuhkanen & Merta 2005, [3]Saunamäki & Savolainen 1999, [4]Pokhrel & Viraraghavan 2004, [5]Jahren *et al.* 2002, [6]Haavisto *et al.* 2019, [7]Ashrafi *et al.* 2015, [8]Rintala & Puhakka 1994, [9]Leiviskä *et al.* 2012, nr=not reported

The compounds in COD vary between different wastewater fractions (Table 1). For example, debarking wastewater contains tannins that are not usually present in other wastewater fractions. On the other hand, all wastewater fractions contain lignin. (Rintala & Puhakka 1994; Leiviskä *et al.* 2012) The organic composition of the pulp and paper industry wastewater does not always remain the same, since it may have seasonal variations depending on changes in the chemical composition of the wood. Widsten *et al.* (2003) investigated the effect of seasonal variations on the organic composition of

wastewaters from the pulp and paper mill in Finland and reported, that the COD load was higher in winter than in summer. They noted that the variation was caused by carbohydrates contained in the wood, the amount of which was clearly higher in winter. According to their study, the concentrations of lignin and lignan have no clear season-dependency.

Seasonal variations were also investigated in the study of Saunamäki & Savolainen (1999), in which the organic loads of debarking wastewaters in Finland were studied. They reported that the COD load of debarking wastewater can be two to three times higher in winter compared to summer. It is because in winter the trees used as raw material are frozen, thus the logs need to be defrozen using hot water. Due to the hot water, more compounds are extracted from the wood into the water which causes the increase in the concentration of pollutants. (Saunamäki & Savolainen 1999) According to Hart (2009), there is a clear difference in the ability of wood to debark between winter and summer, causing a higher bark content to the following process stages during winter.

3.3 Effect of wastewater treatment on COD

The amount of COD and other harmful substances is reduced by wastewater treatment prior to discharging it into the environment. Wastewater treatment is composed of various unit processes which can be based on mechanical, chemical or biological methods. Conventional treatment methods in the pulp and paper industry are usually primary clarification and activated sludge process, but there can also be some other methods included for more efficient pollutant removal. Additional treatment methods can be for example, anaerobic treatment processes, electrochemical methods, advanced oxidation processes (AOPs) and enzymatic treatment processes. Instead of adding new technologies, improvements in the treatment results may be achieved by adjusting the operation parameters of the activated sludge process. (Hubbe *et al.* 2016)

3.3.1 Conventional wastewater treatment processes

The conventional wastewater treatment in pulp and paper industry generally consists of mechanical treatment based on sedimentation in the primary clarifier, and biological treatment done with activated sludge process containing the aeration basin and the secondary clarifier (Singh & Tripathi 2020). There can also be an equalizing basin between the primary clarifier and the aeration basin. The aforementioned treatment processes and the effect of unit processes on COD fractions are shown in Figure 4.

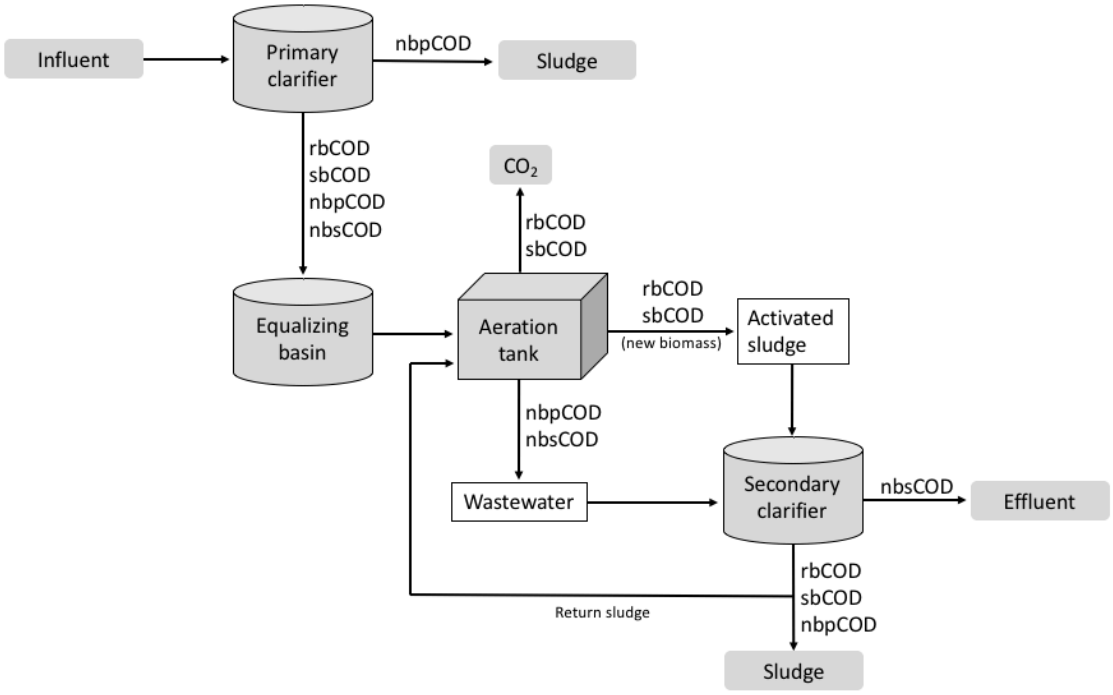

Figure 4. Typical fate of COD fractions in the wastewater treatment processes. Primary clarifier removes mainly nbpCOD, while the activated sludge process removes mostly bCOD consisting of both rbCOD and sbCOD.

In the primary clarifier the removal of particles is based on sedimentation. The basic idea of the sedimentation is that the particles with a higher density compared to water settle to the bottom of the basin due to gravity. (Stuetz 2009, p. 48) Material removed with sedimentation includes bark particles, wood fibres, and fillers (Pokhrel & Viraraghavan 2004). According to Thompson *et al.* (2001), the sedimentation can remove more than 80 % of suspended solids. In the study of Mehmood *et al.* (2019), sedimentation as a primary treatment achieved a COD removal of 14.5 %. Before the biological treatment, there may be an equalizing basin. The objective of the basin is to equalize fluctuations both in water flow and organic load, and thus improve the performance of the biological treatment. (Mikola 2013)

In biological treatment, dissolved and colloidal organic material is reduced by microorganisms that consume these organic compounds as sustenance. Biological treatment can also remove some other substances, such as suspended solids. (Stuetz 2009, p. 119-220) In the activated sludge process, microorganisms grow by utilizing organic compounds under aerobic conditions in the aeration basin, into which air is injected in order to provide oxygen to the microorganisms. During the process, microorganisms flocculate and form an active biomass called activated sludge. (Davis 2020) The activated sludge

process includes biochemical reactions that end up either transforming organic material into smaller molecules or mineralizing them completely into water and carbon dioxide. Part of the bCOD is converted into new biomass. (Tchobanoglous *et al.* 2003, p. 548) The biodegradation requires the presence of certain nutrients (mainly phosphorus and nitrogen), therefore if the wastewater does not contain enough of them, they need to be added to it (Hubbe *et al.* 2016).

The final stage of the activated sludge process takes place in the secondary clarifiers, where the sludge is separated from the effluent. The separation is based on the sedimentation during which the sludge is settled by gravity and then collected from the bottom of the clarifier. (Jenkins & Wanner 2014, p. 171) Part of the collected sludge is removed and some returned to the aeration basin. Clarified water is discharged. (Stuetz 2009, p. 132) The activated sludge process can also include nutrient removal, but in the pulp and paper industry, there is typically only need for the removal of organic material due to which a conventional activated sludge process is adequate (Keskitalo & Leiviskä 2010).

Barañao & Hall (2004) investigated the proportions of COD fractions in the influent of the activated sludge process. The influent was from the pulp and paper mill and pre-treated in the primary clarifier. According to the results they obtained, 49 % of the total COD was rbCOD, 30 % sbCOD, 14 % nbsCOD and 7 % nbpCOD. A high amount of bCOD is reduced during the activated sludge process but there is a difference in the biodegrading rate between the rbCOD and sbCOD (Orhon & Cokgör 1997). RbCOD can be transported immediately to cells and oxidized into biomass, while sbCOD requires hydrolysis before being used by microorganisms. Hydrolysis is needed due to the particulate form that prevents it from entering as such through the cell wall. During hydrolysis, sbCOD is converted into readily biodegradable form. The amount of nbpCOD is also decreased during the activated sludge process as it accumulates in the activated sludge and is removed from the plant through the sludge waste stream. (Orhon & Gokgör 1997; Baquero-Rodríguez *et al.* 2016)

NbCOD in wastewater is formed not only in the pulp and paper making processes but also during the biological treatment, in the form of residual microbial products formed during substrate utilization (Orhon & Okutman 2003). Therefore, it should be noted that the nbCOD of effluent consist of nbCOD from both wood and microbial products. According to the study of Roppola *et al.* (2009), a high amount of new metabolic products can be generated during the biodegradation process. Furthermore, they found out that oxygen is not only consumed for the mineralisation of biodegradable COD, but also for the formation of residual microbial products. Microbial products consist of soluble organic

compounds, such as proteins, polysaccharides, nuclein acids, organic acids and amino acids that are released during the metabolism of microorganisms (Barker & Stuckey 1999).

In Finland, the activated sludge process has been utilized in the pulp and paper industry since 1984 and used specifically for the removal of organic material (Junna & Ruonala 1991). Sivard *et al.* (2007) reported, that with the activated sludge process, 90 % BOD and 60 % COD removal can be achieved for wastewater from a pulp and paper mill, where softwood and hardwood were used as raw material. In the study of Leiviskä *et al.* (2008), more than 95 % of BOD_7 and 60-70 % of COD were reduced by the activated sludge process from wastewater of a pulp and paper mill in, where the raw materials used were softwood, hardwood and sawmill chips. Keskitalo & Leiviskä (2010) investigated the characteristics of wastewater from a bleached kraft pulp mill in Finland and reported, that the amount of COD in the effluent after primary sedimentation and aerobic activated sludge process was 541 mg/l and BOD_7 was 14 mg/l.

In the study of Choi *et al.* (2017), the treated effluent of the pulp and paper mill consisted mainly of nbsCOD, which accounted for approximately 80 % of the total COD. NbpCOD accounted for 14 % and the smallest fraction was bCOD, which was only 6 % of the total COD and was mainly composed of sbCOD. The effluent from the pulp and paper mill to be discharge still contains, for example, lignin, resin acids, chlorinated phenols and AOX (Kumar *et al.* 2020, p. 1). Although the biologically treated effluent is mainly composed of nbsCOD, it can also contain some particulate COD, which is released from a secondary sludge when the process operation is incomplete (Henze *et al.* 2008, p. 61). Deflocculation can be caused, for example, by too high dissolved oxygen (DO) level in the aeration basin that breaks the flocs due to turbulence or old sludge caused by too low food/microorganism ratio (F/M ratio) combined with too high sludge residence time (SRT) (Comas *et al.* 2003).

3.3.2 The effect of operation parameters on the efficiency of the activated sludge process

The operation parameters, such as mixed liquor suspended solids (MLSS), sludge residence time (SRT) and the amount of nutrients and oxygen affect the treatment efficiency of the activated sludge process. Due to strictening environmental regulations, improvements in the operation of the process may be necessary. As there are various operation parameters needed to be determined and optimized, the process optimization can be challenging and arduous. In addition, there is also a desire to minimize the operating

costs, which causes an additional challenge in the operating and designing of the activated sludge process. (Hreiz *et al.* 2015)

MLSS is the parameter reflecting the amount of suspended solids in the aeration tank. MLSS can be determined by filtering known volume of the sample and weighing it after drying at 105 °C. MLSS can contain both organic and inorganic material. The organic part of suspended solids can be estimated using the parameter mixed liquor volatile suspended solids (MLVSS). MLVSS is measured by burning dried sludge at 550 °C. The concentration of MLVSS affects the efficiency of the aeration process, as the more microorganisms are available, the more organic material is utilized by them. However, the value of MLSS should not get too high, because in that case the amount of oxygen and the capacity of secondary settling will become limiting factors in the process. (Gray 2004, p. 477-478)

SRT (or sludge age) is the parameter affecting the characteristics of flocs formed during the activated sludge process. SRT can be determined by dividing the amount of sludge solids in the tank by the rate of sludge loss from the system, using equation (1)

$$SRT = \frac{V \cdot X}{(Q_w \cdot X_w + Q_e \cdot X_e)}, \quad (1)$$

where V is the volume of basin, X is the MLSS, Q_w is the rate of sludge wastage, X_w is the MLSS in the waste sludge, Q_e is the discharge rate of effluent and X_e is the suspended solid concentration in effluent. SRT can be used to estimate the sludge activity. If SRT is lower than 0.5 d, the sludge growth rate can be considered high and SRT more than 5 d indicates low growth rate. SRT affects the settleability of sludge, so if it is more than 6 d or less than 3 d, the settleability is reduced. SRT can be adjusted by changing the rate of sludge removal. (Gray 2004, p. 478)

Hydraulic retention time (HRT) reflects the time in which the wastewater passes through the process (Sperling 2007, p.2). HRT has an effect on the efficiency of the activated sludge process, as too short HRT in the aeration tank may cause the deterioration of BOD removal. If HRT is too short, flocs do not have enough time to stabilise and thus to provide free adsorption sites for further material (suspended, colloidal and ionic) that tends to adhere to the floc. (Gray 2004, p. 469-470) Barr *et al.* (1996) studied the effects of HRT and SRT on the performance of activated sludge process. They reported, that in case of bleached kraft mill effluent, HRT had more effect on BOD removal than SRT. In their study, HRT was varied between 4 h and 12 h and SRT between 5 d and 15 d. With longer HRT, a clear improvement in BOD removal was achieved, while longer SRT had no significant effect.

F/M ratio is also an important parameter, which describes the amount of substrate (BOD) supplied per unit biomass in the reactor within one day and it is expressed as kg BOD/ kg MLVSS·d. A high F/M ratio indicates that there is more substrate offered than microorganisms are able to use, which causes a larger amount of substrate in the effluent. If F/M ratio is low enough, microorganisms can consume all the organic material from the wastewater and start using their own organic cell material as well. The sludge age has an effect on the F/M ratio, because when the sludge age is high, the F/M ratio is usually low. On the other hand, a decrease in the sludge age causes an increase in the F/M ratio. (Sperling 2007, p. 3)

Sludge settling is a critical factor affecting the efficiency of the process and therefore the quality of the effluent. Settleability can be described by sludge volume index (SVI) which can be determined with a 30-minute settling test. SVI can be calculated by dividing the volume of settled sludge obtained from the test by MLSS. If SVI value is high (over 150 ml/g), it may indicate bulking of sludge, which can cause problems with sludge separation. Bulking can be caused by the excess growth of filamentous bacteria, the cause of which may be, for example, low concentration of DO, too low or high temperatures or lack of nutrients. In addition to filamentous bulking, some microorganisms can produce huge amounts of extracellular material and cause sludge bulking. Operation parameters, such as long SRT and low F/M ratio can also be reasons for bulking and thus the formation of flocs with poor settleability. (Kõrgmaa *et al.* 2019)

The concentration of DO is important aspect to consider when operating the activated sludge process (Thompson *et al.* 2001). Oxygen is required for both organic material degradation and endogenous respiration, due which it can be considered an important factor affecting the performance of the process (Keskitalo & Leiviskä (2010). Keskitalo & Leiviskä (2010) studied the modelling of activated sludge process and in the mill under investigation, DO concentration was between 3-6 mg/l. According to them, DO concentration of 1.5-3.0 mg/l can be considered sufficient and concentrations above 4 mg/l do not cause a significant improvement in the treatment. Because low DO can cause the growth of filamentous bacteria, resulting in sludge bulking, it is important to achieve a sufficiently high DO concentration (Hreiz *et al.* 2015). On the other hand, it should be noted that high DO causes increased energy costs and lower sludge quality (Pittoors *et al.* 2014).

As discussed earlier, the amount of nutrients should also be taken into account. The main nutrients required for the metabolic processes of microorganisms are nitrogen and phosphorus. If there are not sufficient amount of nutrients in the influent, they need to be added to the activated sludge process. (Balakrishnan *et al.* 2021) Industrial wastewaters

usually contain carbon compounds, due which only nitrogen and phosphorus need to be added. The sludge with a good settleability can be achieved dosing nutrients in BOD:N:P ratio of 100:5:1 to prevent sludge bulking caused by nutrient deficiency. (Eikelboom 2000, p. 110; Guo *et al.* 2014) According to Gray (2004), optimal nutrient balance for heterotrophic activity can be obtained with BOD:N:P ratio of 100:6:1, which means 0.03-0.06 kg nitrogen and 0.007-0.01 kg phosphorus is required per kg BOD.

3.3.3 Other treatment methods for the removal of COD

The conventional treatment technologies require improvements or supplementation with new techniques in order to meet tighter environmental restrictions in the future (Toczyłowska-Mamińska 2017). The need to enhance the treatment efficiency is particularly related to non-biodegradable organic compounds such as lignin and its derivatives, since their removal is low when treated with the conventional treatment technologies (Hou *et al.* 2020). Other treatment methods that could be used for enhanced COD removal include chemical precipitation, electrochemical treatment, such as electrocoagulation (EC) and electro-oxidation (EO), enzymatic treatment and AOPs.

Chemical precipitation is an available technology to efficiently remove COD from pulp and paper industry wastewaters. It is based on the addition of precipitation chemicals, such as alum, ferric chloride or polyaluminium chloride to wastewater, which results in the precipitation of dissolved material into a solid form. (Wang *et al.* 2005, p. 141; Chaudhari *et al.* 2010)

Over the past few decades, the interest of using electrochemical technologies for enhanced COD removal has been increased (Soloman *et al.* 2009). Electrocoagulation and electro-oxidation are examples of electrochemical methods. In these methods, electricity is utilized to remove contaminants from water. In the electrocoagulation, metal anode oxidizes, releasing metal ions that form metal hydroxides. Metal hydroxides adhere to the particles in the water and together they form flocs that settle to the bottom by sedimentation. In the electro-oxidation, contaminants are removed by oxidation. Oxidation can occur either directly at the surface of the electrode or indirectly in the solution by the oxidants generated into it on the electrode. In the direct oxidation, hydroxyl radicals are formed at the anode and contaminants are oxidized. If chloride is present during the anodic oxidation, chlorine and hypochlorite are generated and they act as oxidizing agents for indirect oxidation. (Asfaha *et al.* 2021)

Enzymatic treatment using oxidoreductases has the potential to reduce COD, especially nbCOD, from pulp and paper industry wastewaters. The method is based on oxidoreductases, which are enzymes capable of catalysing oxidation-reduction reactions. Fungal oxidoreductases, such as peroxidases, haloperoxidases and laccases, have ligninolytic activity, due which there are interest for utilizing them in wastewater treatment. However, using them on the industrial scale has still some limitations due to availability of commercial products and the conditions of industrial processes that are usually not optimal for enzymes. (Herold-Majumdar *et al.* 2021)

AOPs include various available processes, such as ozonation, Fenton process and different oxidizing species combined with catalysts or UV light. These processes are based on the formation of free hydroxyl radical (HO·), which acts as a powerful oxidizing agent. In ozonation, oxidation can occur both indirectly producing hydroxyl radical or directly reacting with dissolved compounds. In Fenton process, the hydroxyl radical is generated due to the reaction between ferric or ferrous ions and hydrogen peroxide. (Hubbe *et al.* 2016)

All of these technologies for enhanced COD removal have both advantages and disadvantages, which are associated with, for example, energy consumption, process operation and the use of chemicals. The advantages and disadvantages are shown in Table 2, which also summarizes the effectiveness of COD removal achieved in different studies.

Table 2. Selected wastewater treatment methods for enhanced COD removal of pulp and paper industry wastewaters

Method	COD removal (%)	Advantages	Disadvantages
Chemical precipitation	67[1] 91[2]	Easy operation[13] Low capital costs[13]	The use of chemicals[13] Sludge production[13]
Electrochemical treatment	55[3] (EC) 77[4] (EC) 82[5] (EC) 97[6] (EO) 87[7] (EO)	No need for chemicals.[14, 15] Easy operation.[14, 16] All types of organics can be removed and the biodegradability of wastewater is also improved.[17]	Electrodes need to be replaced regularly.[20] The consumption of electricity may cause high costs.[20, 16]
Oxidoreductases	82[8] (Bleaching wastewater) 78[9]	Short retention times[18]	The conditions of industrial processes can be too heavy for enzymatic application.[18]
AOPs	35-60 (Ozone)[10] 65-75 (Fenton)[11] 92 (UV/H_2O_2)[12]	The recalcitrant compounds are converted to a more biodegradable form[19]	High energy consumption[11] The use of chemicals[11]

[1]Qadir & Chhipa 2017, [2]Ahmad *et al.* 2008, [3]Soloman *et al.* 2009, [4]Khansorthong & Hunsom 2009, [5]Kumat & Sharma 2019, [6]El-Ashtoukhy *et al.* 2009, [7]Asha *et al.* 2014, [8]Pedroza *et al.* 2007, [9]Raj *et al.* 2014, [10]Bierbaum & Öeller 2009, [11]Hermosilla *et al.* 2015, [12]Ahmed *et al.* 2009, [13]Wang *et al.* 2005, [14]Asfaha *et al.* 2021, [15]Särkkä *et al.* 2015, [16]Anglada *et al.* 2009, [17]Sen 2015, [18]Herold-Majumdar *et al.* 2021, [19]Kamali *et al.* 2019, [20]Kabdaşli *et al.* 2012, EC=electrocoagulation, EO=electro-oxidation, AOP=advanced oxidation processes

4. MATERIALS AND METHODS

4.1 Wastewater sampling

This study examined wastewater samples obtained from a pulp and paper mill in Finland. Two sampling periods were applied. The first one was carried out on the 16th of December 2021, when grab samples were taken simultaneously from two wastewater streams (debarking and TMP) and from the influent and effluent of the activated sludge process (Figure 5). The samples are named according to the sampling week as follows: debarking W50, TMP W50, influent W50 and effluent W50.

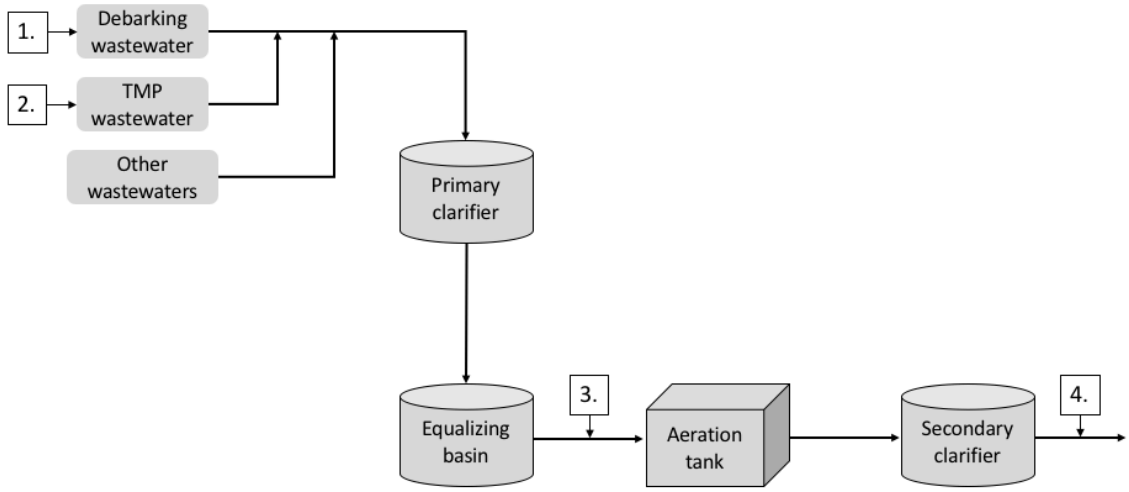

Figure 5. Samples were taken from debarking wastewater (1), TMP wastewater (2), influent to activated sludge process (3) and effluent (4). Other wastewaters include other industrial wastewaters and reject waters from sludge dewatering.

The second sampling period was carried out during May and June. Composite samples were taken once a week from debarking wastewater, TMP wastewater and both the influent and effluent of the activated sludge process (Figure 5). A total of three manual composite samples were taken from both debarking and TMP wastewater. Debarking wastewater samples were taken during weeks 21-23 (named as debarking W21, W22 and W23), while TMP wastewater samples were taken during weeks 22-24 (named as TMP W22, W23 and W24). Manual composite samples were carried out by taking manually three grab samples every two hours (between 9:00 and 15:00) and combining them into a composite sample.

A total of three composite samples were taken once a week from both the influent and effluent of the activated sludge process during weeks 23-25 (named as influent W23, W24 and W25 and effluent W23, W24 and W25). The samples were taken with composite samplers (HACH AS950, Figure 6), which took grab samples every four hours and 40 minutes during 24 hours and combined them into a composite sample. The volume of one grab sample was one litre and the total volume of the composite sample was six litres. The HRT of activated sludge process was 24 h, due which the sampling of effluent was started approximately 24 h after starting the influent sampling. After sampling, the samples were stored at 4°C for up to 2 days before processing them in the laboratory.

Figure 6. The HACH AS950 composite sampler pumped grab samples to the sample container placed in the refrigerator to obtain a composite sample from one day.

4.2 Fractionation of wastewater samples

The samples were fractionated into original and soluble fractions prior to analysis. The fractionation was carried out according to the molecular size by filtration. Original samples were the samples as such, and the soluble samples were prepared filtering original samples through filter cloth and then through 1.6 µm GF/A filters (Whatman) and finally through 0.45 µm syringe filter (Chromafil Xtra Pet-45/20).

COD and respirometric BOD analyses were carried out for all the original and soluble samples. The samples were analysed immediately after fractionation or frozen for later analysis.

4.3 Analytical methods

4.3.1 COD

COD analyses were done using the dichromate method according to SFS 5504 standard (1988). The principle of the method is to boil the sample for 2 hours with sulfuric acid, mercury sulfate, silver sulfate and potassium dichromate and finally titrate the sample with ferrous ammonium sulphate solution. COD was calculated by equation (2)

$$COD = \frac{8000 \cdot C_{Fe} \cdot (V_3 - V_4)}{V_5}, \quad (2)$$

where 8000 is the convert factory, C_{Fe} is the concentration of ferrous ammonium sulphate solution, V_3 is the average volume of ferrous ammonium sulphate solution used for blank, V_4 is the volume of ferrous ammonium sulphate solution used for the sample and V_5 is the volume of the sample. C_{Fe} was calculated by equation (3)

$$C_{Fe} = \frac{6 \cdot 0.04 \cdot V_1}{V_2} = \frac{0.24 \cdot V_1}{V_2}, \quad (3)$$

where 0.04 is the concentration of dichromate solution (mol/l) and 6 is used as coefficient because 1 mol of dichromate is equivalent to 6 moles of ferrous ammonium sulphate, V_1 is the volume of dichromate solution and V_2 is the volume of ferrous ammonium sulphate solution used for the titration of unheated blank sample. (SFS 5400 1988)

4.3.2 Respirometric BOD analyses

Respirometric BOD analyses were performed using OxiTop measuring system (WTW), which measures oxygen demand (mg/l). The measurement of oxygen demand is based on detecting the change in pressure. (WTW n.d.) Prior to analysis the samples were

diluted based on the estimated BOD_5 value of the sample and the fact that the measured BOD_5 value of the diluted sample should be between 100-200 mg/l. The samples were diluted with dilution water which was prepared adding 1 ml saline solutions (0.29 M phosphate buffer solution, 0.09 M $MgSO_4 \cdot 7H_2O$, 0.25 M $CaCl_2$ and 0.9 mM $FeCl_3 \cdot 7H_2O$) in 1000 ml MQ water and aerating for 1 hour. After aeration, the solution was let stand for 1 hour, after which 5 ml activated sludge from wastewater treatment plant of pulp and paper mill was added to the solution to achieve a sufficient amount of microorganisms for the process. Activated sludge was aerated for 1 day and settled before the analysis.

The volume of diluted samples were 300 ml and 6 drops of NHT 600 nitrification inhibitor (allylthiourea 8.6 mM) was added into it. Using an overflow flask, 250 ml of diluted samples were added into the BOD bottles and magnetic stirrers were also added. A blank sample was prepared by adding only 250 ml of dilution water into the BOD bottle. Rubber stoppers with two sodium hydroxide tablets were added on the top of the bottles. OxiTop sensors were screwed onto the bottles and the bottles were connected to the OxiTop measuring system. The bottles were placed in the thermostat cabinet at 20 °C on a stirring platform and incubated for 20 days.

OxiTop measurement is based on measuring the change in pressure. Microorganisms utilize oxygen and convert it to carbon dioxide. Because the volume of one mol of oxygen and one mol of carbon dioxide are equal, the change in pressure is not observed. For this reason, sodium hydroxide tablets were placed on the rubber stoppers, which react with the generated carbon dioxide and form sodium carbonate. The release of sodium carbonate causes the change in pressure, which is detected by the sensor. After the BOD run, it is possible to draw BOD curves and determine BOD values at different time points, for example BOD_7 and BOD_{20}. (WTW n.d.) BOD values were calculated by equation (4)

$$BOD_x = \frac{\left(BOD_d - BOD_0 \cdot \frac{V_d}{300}\right)}{\frac{V_s}{300}}, \tag{4}$$

where BOD_x is the BOD of the undiluted sample, BOD_d is the BOD of the diluted sample BOD_0 is the BOD of the blank sample, V_d is the volume of dilution water in the dilution and V_s is the volume of sample in the dilution.

The reaction rate of BOD degradation was estimated using the results of the respirometric BOD analysis. The kinetics of BOD degradation can be described by equation (5)

$$BOD_t = BOD_{tot} \cdot \left(1 - e^{-k \cdot t}\right), \tag{5}$$

where BOD_t is biochemical oxygen demand after time t, BOD_{tot} is total biochemical oxygen demand and k is the reaction rate constant of BOD degradation. (Pluciennik-Koropczuk & Myszograj 2019) The values of k and BOD_{tot} can be determined by various methods. The method used in this study was the least square method based on fitting the curve through the data points of BOD measurement, so that the sum of the squares of the residuals is at a minimum. Equations (6) and (7) were used to calculate the values of a and b, which were used to calculate the values of k and BOD_{tot} according to equations (9) and (10). The value of y′ used in equations (6) and (7) was calculated by equation (8).

$$na + b\sum y - \sum y' = 0, \tag{6}$$

$$a\sum y + b\sum y^2 - \sum yy' = 0, \tag{7}$$

$$y' = \frac{y_{n+1} - y_{n-1}}{2\Delta t}, \tag{8}$$

$$k = -\mathrm{b}, \tag{9}$$

$$BOD_{tot} = -\frac{a}{b}, \tag{10}$$

In the equations above, n is the number of data points and y is BOD at time t. (Tchobanoglous *et al.* 2003, p. 88-89)

4.4 Calculations

4.4.1 Biodegradability of wastewater

The biodegradability of the wastewater samples was estimated both by determining rising rates of BOD curves and the COD/BOD_5 ratios of the samples. The rising rates were estimated by determining the reaction rate constants of BOD degradation according to equations 6-9 presented in section 4.3.2. The rising rates were determined to estimate how fast BOD is degraded. The higher the reaction rate constant is, the greater proportion of bCOD in the sample can be considered rbCOD (Kreetachat *et al.* 2007).

The estimation of biodegradability utilizing the COD/BOD_5 ratio of the sample was carried out based on the guidelines of Pluciennic-Koropczuk & Myszograj (2019). If COD/BOD_5 ratio is less than 2.5, the wastewater can be considered prone to biodegradation. Wastewater can be considered easily biodegradable when the ratio is less than 2.0. When the ratio is greater than 2.5, wastewater has a high content of nbCOD and can be

considered slowly biodegradable. If the ratio is greater than 5.0, wastewater can be considered resistant to biodegradation.

4.4.2 COD fractions

Results obtained from the COD and BOD analyses were used to calculate the concentrations of COD fractions for each sample using equations shown in Table 3.

Table 3. Equations for the determination of COD fractions

COD fraction	Equation
bCOD	BOD_{20} of original sample
rbCOD	BOD_{7} of original sample
sbCOD	$\mathrm{bCOD} - \mathrm{rbCOD}$
nbCOD	COD of original sample $-\ \mathrm{bCOD}$
nbsCOD	COD of soluble sample $-\ \mathrm{BOD}_{20}$ of soluble sample
nbpCOD	$\mathrm{nbCOD} - \mathrm{nbsCOD}$

bCOD = biodegradable COD, rbCOD = readily biodegradable COD, sbCOD = slowly biodegradable COD, nbCOD = non-biodegradable COD, nbsCOD = non-biodegradable soluble COD, nbpCOD = non-biodegradable particulate COD

4.4.3 COD and BOD_7 loads

The COD and BOD_7 loads were calculated for the debarking and TMP wastewaters as well as the influent and effluent of the activated sludge process. The loads were calculated by multiplying the concentration of the sample by the flow rate of the wastewater. The averages of 24 hour flow rates were used as the flow rates.

The loads of the debarking and TMP wastewaters were compared to the loads of the activated sludge process influent in order to determine the proportions of loads caused by debarking and TMP wastewaters to the process. The debarking and TMP wastewater loads were compared to the influent samples taken on the same day. Thus, the proportions are rough estimates, as the delay of the debarking and TMP wastewaters to the activated sludge process is approximately 22 hour, which was not taken into account in the calculations.

5. RESULTS

5.1 Debarking and TMP wastewater streams

5.1.1 The biodegradability of COD

The biodegradability of COD was assessed using the results of respirometric BOD analyses (Appendix A). The BOD_{20} corresponds to the bCOD in the sample. The debarking W50 had the highest BOD_{20}, up to 2200 mg/l. The debarking W21-23 had the BOD_{20} in the range of 1100-1200 mg/l. The biodegradability of the COD was estimated using BOD curves (Figure 7) and their reaction rate constants (Appendix C).

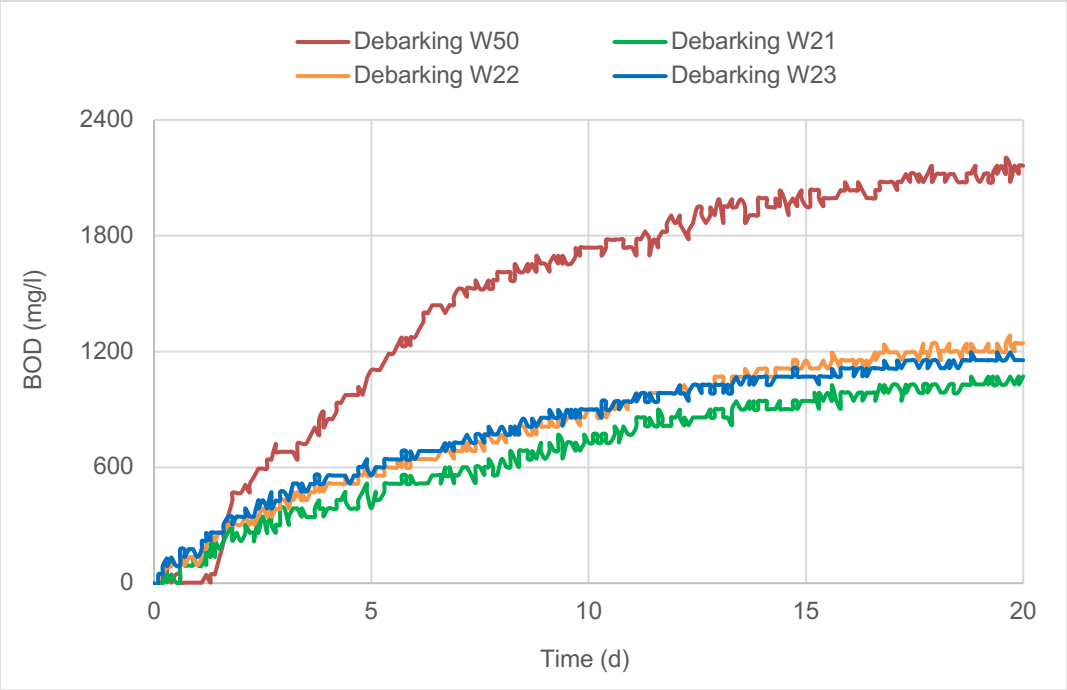

Figure 7. BOD curves of each original debarking wastewater sample

The BOD curve of the debarking W50 rose the fastest, as its reaction rate constant was the highest (0.17). Based on the reaction rate constant, this sample can be considered to contain a higher proportion of rbCOD of total bCOD compared to the other debarking wastewater samples. The debarking W21 had the lowest reaction rate constant (0.09) and thus can be assumed to contain the lowest proportion of rbCOD. The reaction rate constants of the debarking W22 and W23 were quite similar (0.11 and 0.12).

The TMP W23 had the highest BOD_{20}, up to 2000 mg/l. The TMP W50, W22 and W24 had the BOD_{20} values in the range of 1600-1800 mg/l. The biodegradability of the COD was estimated using BOD curves (Figure 8) and their reaction rate constants (Appendix C).

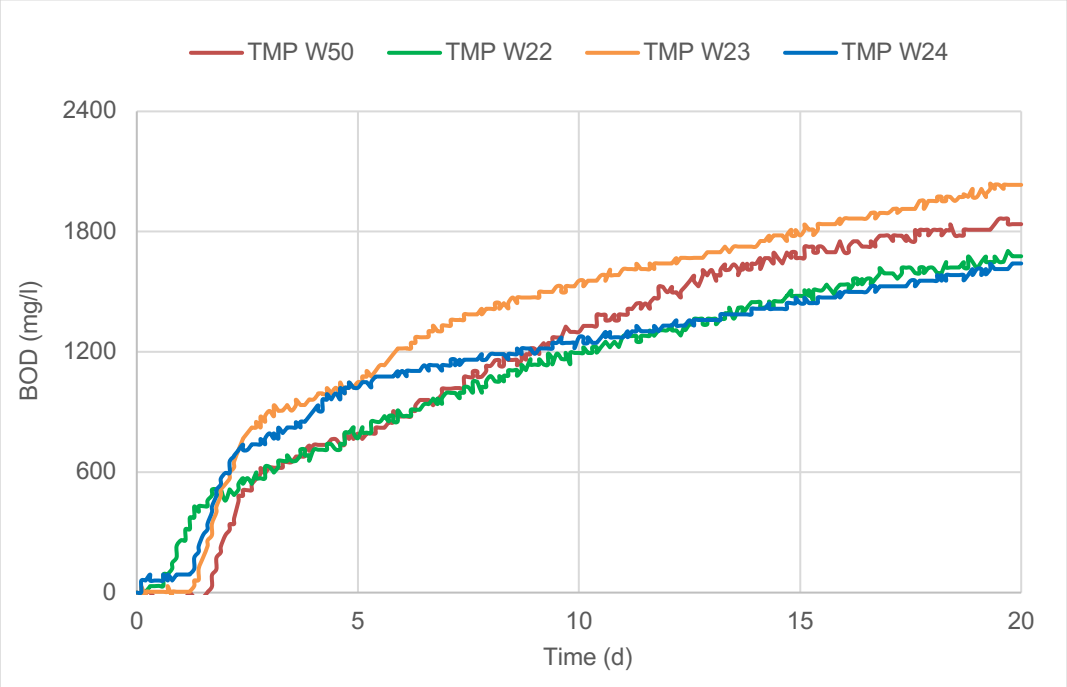

Figure 8. BOD curves of each original TMP wastewater sample

The BOD curve of the TMP W24 had the highest reaction rate constant (0.21) and thus rose the fastest. Based on the BOD curves and their reaction rate constants, this sample can be considered to contain a higher proportion of rbCOD of total bCOD compared to the other TMP wastewater samples. The TMP W23 had a lower reaction rate constant (0.16), while the TMP W50 and W22 had the lowest (0.10 and 0.11) and can be considered to contain the lowest proportion of rbCOD of total bCOD.

The BOD curves of the debarking wastewater samples had the reaction rate constants in the range of 0.09-0.17, while in TMP wastewater samples they were between 0.10-0.21. Comparing the reaction rate constants, it was observed that the debarking and TMP wastewaters had the reaction rate constants almost in the same range, but in one TMP sample it was clearly higher and thus it can be considered to contain a higher proportion of rbCOD of total bCOD compared to the debarking wastewater samples.

The biodegradability of the debarking and TMP wastewater samples were also estimated by determining the COD/BOD_5 ratios (Table 4). The values used for calculations are presented in Appendix A.

Table 4. Total COD and COD/BOD_5 ratios of the original debarking and TMP wastewater samples

Sampling week	Debarking wastewater		TMP wastewater	
	COD (mg/l)	COD/BOD_5 ratio	COD (mg/l)	COD/BOD_5 ratio
W50	5800	5.3	4800	6.0
W21	2600	6.8	ns	ns
W22	2800	4.9	3600	4.6
W23	2600	4.7	3600	3.5
W24	ns	ns	4300	4.2

ns=no sample

The debarking W21 had the highest COD/BOD_5 ratio (6.8) and thus can be considered the hardest to biodegrade. This conclusion is supported by the BOD curves, as this sample had the lowest reaction rate constant. The debarking W22 and W23 had the COD/BOD_5 ratio in the range of 2.5-5.0 and thus they can be considered to be slowly biodegradable. The debarking W50 had the COD/BOD_5 ratio slightly over 5.0 and thus can be considered hard to biodegrade. However, the COD/BOD_5 ratios were quite similar between the debarking W50, W22 and W23, therefore major differences in their biodegradabilities are not considered.

The TMP W22, W23 and W24 had the COD/BOD_5 ratios in the range of 2.5-5.0 and thus they can be considered slowly biodegradable. The COD/BOD_5 ratio of the TMP W50 was 6.0 and thus it can be considered slightly harder to biodegrade. Comparing the COD/BOD_5 ratios of the debarking and TMP wastewater samples, it was observed that they were in the same range. Thus, it was concluded that the biodegradabilities of the debarking and TMP wastewater are generally quite similar.

5.1.2 COD fractionation

The COD fractionation was carried out to all debarking and TMP wastewater samples and the results are shown in Figures 9 and 10. In addition, the exact amounts of each fraction are summarized in Appendix A.

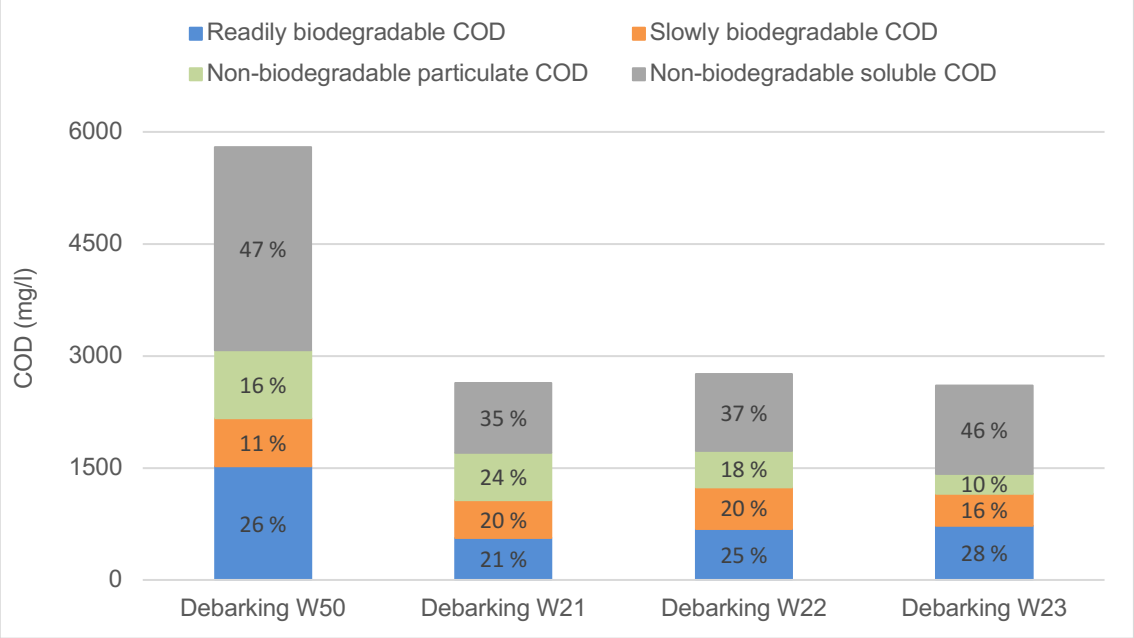

Figure 9. The composition of COD in the debarking wastewater samples

The debarking W50 contained considerably the highest total COD, which was up to 5800 mg/l (Figure 9). The debarking W21, W22 and W23 had the amount of total COD in the range of 2600-2800 mg/l, therefore the differences were small between these samples. It was observed that the rbCOD was quite same in the debarking W21, W22 and W23, as they were in the range of 560-730 mg/l (21-28 %). A significant difference was observed in the debarking W50, where the rbCOD was up to 1500 mg/l (26 %). Although the rbCOD was higher in the debarking W50, the proportion of rbCOD was in the same range in all samples (21-28 %).

There were no major differences in the sbCOD between different debarking wastewater samples, as they were in the range of 430-640 mg/l (11-20 %). Slightly larger differences were observed in the amounts of nbpCOD, which were in the range of 270-910 mg/l (10-24 %). There were significant differences in the nbsCOD, as the highest amount was up to 2700 mg/l (47 %) in the debarking W50 and the debarking W21, W22 and W23 contained nbsCOD in the range of 940-1200 mg/l (35-47 %).

Differences were observed in the amounts of total COD in different TMP wastewater samples (Figure 10). The TMP W50 contained the highest total COD (4800 mg/l), while the lowest total COD was obtained for the TMP W22 (3600 mg/l).

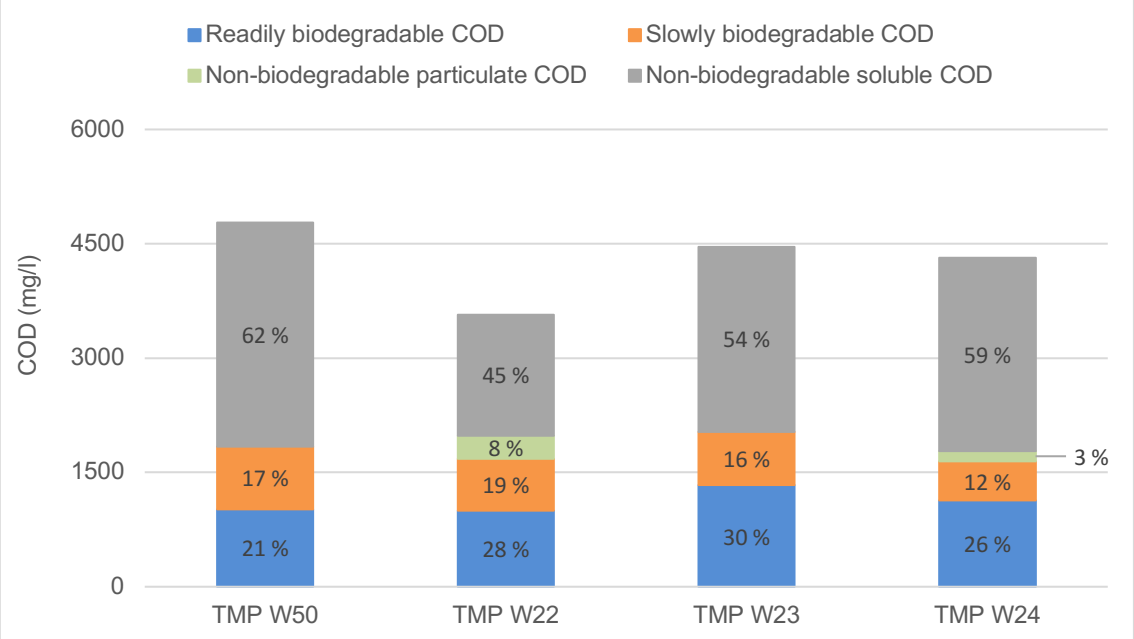

Figure 10. The composition of COD in the TMP wastewater samples

The largest fraction of each TMP sample was nbsCOD, which was in the range of 1600-2900 mg/l (45-62 %). The rbCOD was in the range of 1000-1300 mg/l (21-30 %) and it was the second largest fraction in each sample. The second smallest fraction in each sample was sbCOD, which was in the range of 510-820 mg/l (12-19 %). The smallest fraction in each sample was nbpCOD which was in the range of 0-300 mg/l (0-8 %).

5.2 The influent of the activated sludge process

5.2.1 The biodegradability of COD

The biodegradability of COD was assessed using the results of respirometric BOD analyses (Appendix B). The influent W50 had the highest BOD_{20} up to 1500 mg/l. The influent W23-W25 had the BOD_{20} values in the range of 1200-1400 mg/l. The biodegradability of the COD was estimated using BOD curves (Figure 11) and their reaction rate constants (Appendix C).

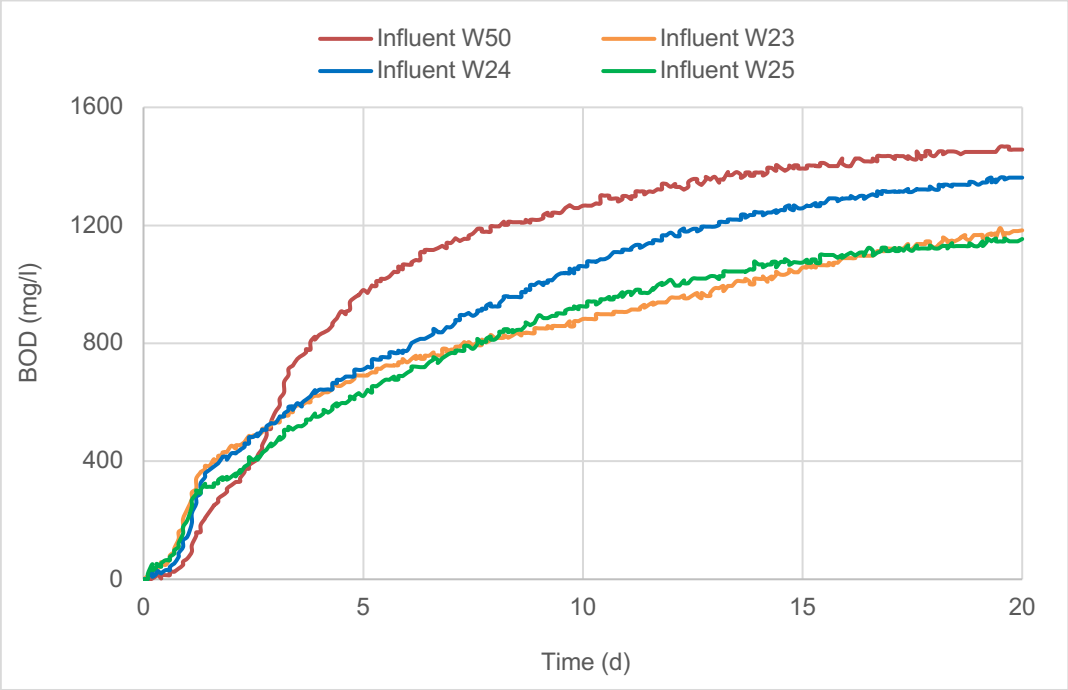

Figure 11. BOD curves of each original influent sample

The BOD curve of the influent W50 rose the fastest, as the reaction rate constant was the highest (0.18). This lead to the conclusion that the sample contained a higher proportion of rbCOD of total bCOD compared to the other influent samples. The reaction rate constants of the influent W24 and W25 were the lowest (both 0.15) and the constant of the influent W23 was only slightly higher (0.17). According to these results, the influent W24 and W25 can be considered to contain the lowest proportions of rbCOD. However, the differences in the reaction rate constants were not significant, due which the proportions of rbCOD can be assumed to be quite similar between the influent samples.

The biodegradability of the influent samples were also estimated by determining COD/BOD_5 ratios (Table 5). The values used for calculations are presented in Appendix B.

Table 5. Total COD and COD/BOD_5 ratios of the original influent samples

Sample	COD (mg/l)	COD/BOD_5 ratio
Influent W50	1800	1.9
Influent W23	2000	2.9
Influent W24	2000	2.8
Influent W25	1600	2.6

The influent W50 had the lowest COD/BOD_5 ratio (1.9) and is considered prone to biodegradation. This is in line with the conclusions obtained from the estimation of BOD curves, as this sample had the highest reaction rate constant. The influent W23, W24 and W25 had the COD/BOD_5 ratios between 2.5-5.0 and can be considered slowly biodegradable. The COD/BOD_5 ratios of W23, W24 and W25 were fairly similar (in the range of 2.6-2.9), therefore no significant differences are considered in their biodegradabilities,

5.2.2 COD fractionation

The COD fractionation was carried out to all influent samples and the results are shown in Figure 12. In addition, the exact amounts of each fraction are summarized in Appendix B.

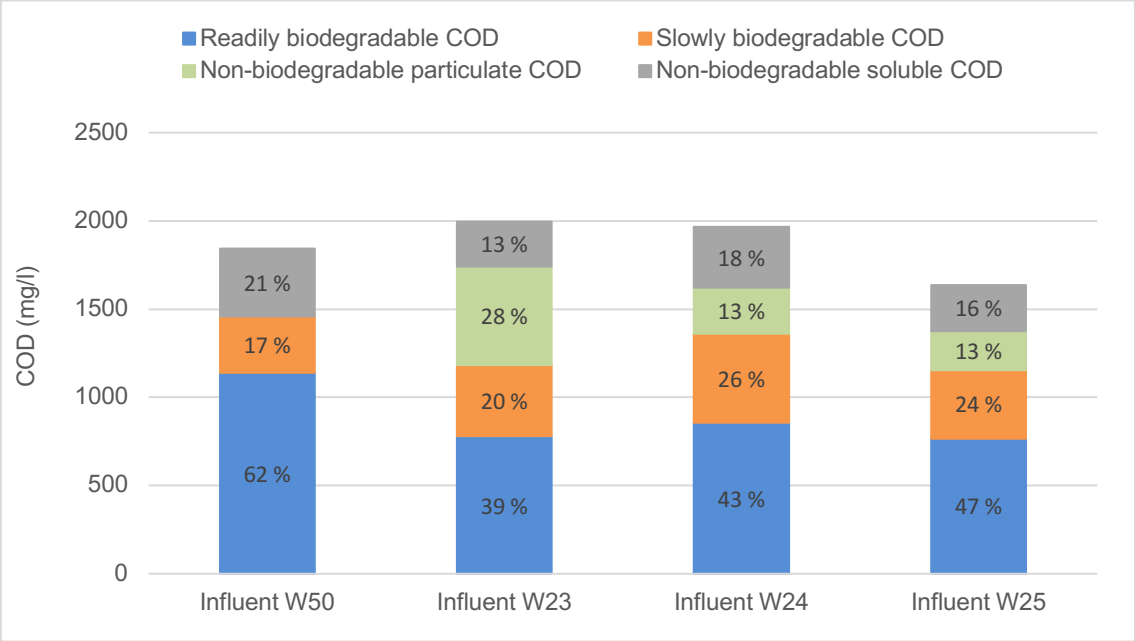

Figure 12. The composition of COD in the influent samples

Total COD varied between different influent samples (Figure 12). The lowest total COD was 1600 mg/l and the highest was 2000 mg/l. The rbCOD was quite the same in all the influent samples varying between 770-860 mg/l (39-47 %), except in the influent W50, in which the rbCOD was up to 1100 mg/l (62 %). There were not significant differences in the sbCOD between different influent samples, as it was in the range of 320-510 mg/l (17-26%). Also, the nbsCOD did not vary much, as it was in the range of 250-390 mg/l (13-21 %). Significant differences were observed in the amounts of nbpCOD between different influent samples. The influent W50 contained no nbpCOD, while the influent W23 contained up to 560 mg/l (28 %) nbpCOD. The amounts of nbpCOD in the influent W24 and W25 were in the same range, being 260 mg/l (13 %) and 220 mg/l (13 %).

5.3 The effluent of the activated sludge process

5.3.1 The biodegradability of COD

The biodegradability of COD was assessed using the results of respirometric BOD analyses (Appendix B). The highest BOD_{20} value of the effluent samples was 61 mg/l and it was obtained for the effluent W50. The BOD_{20} in other effluent samples were in the range of 14-25 mg/l. The biodegradability of the COD was estimated using BOD curves (Figure 13) and their reaction rate constants (Appendix C).

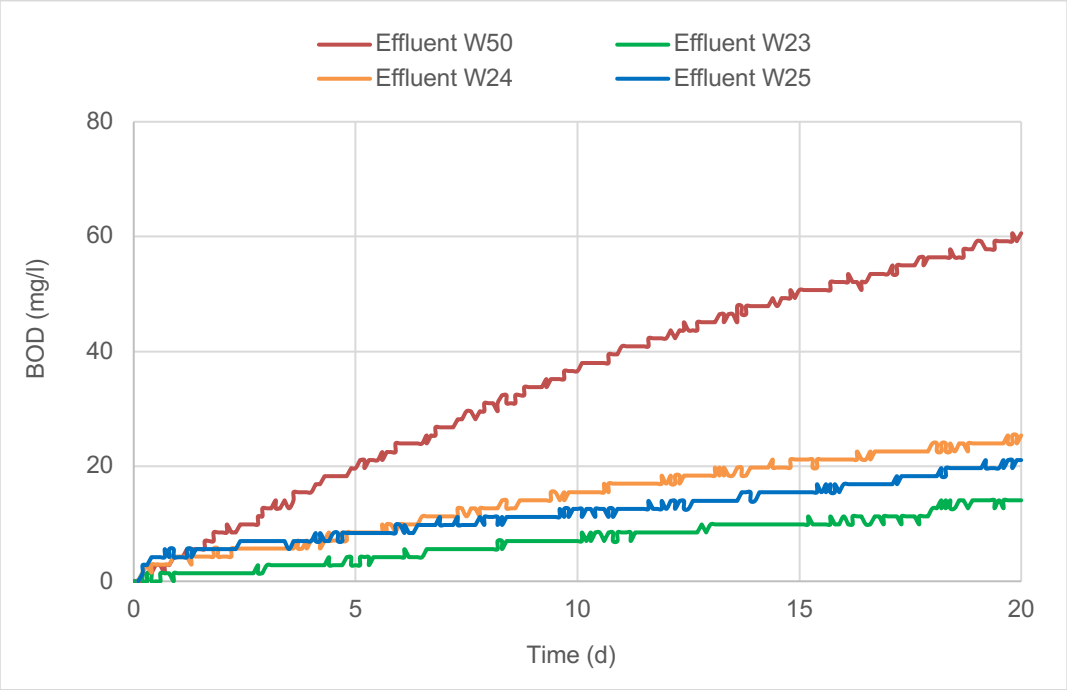

Figure 13. BOD curves of each original effluent sample

The BOD curve of the effluent W23 rose slowest, as the reaction rate constant was the lowest (0.00). Based on the reaction rate constants, this sample can be considered to contain the lowest proportion of rbCOD of total bCOD. The effluent W50 had the highest reaction rate constant (0.04) and thus can be assumed to contain the highest proportion of rbCOD of total bCOD. The reaction rate constants of the effluent W24 and W25 were only slightly lower (both 0.03)

More information about the biodegradability of the effluent samples was obtained by determining the COD/BOD_5 ratios (Table 6). The values used for calculations are presented in Appendix B.

Table 6. Total COD and COD/BOD_5 ratios of the original effluent samples

Sample	COD (mg/l)	COD/BOD_5 ratio
Effluent W50	240	12.3
Effluent W23	190	67.9
Effluent W24	200	23.2
Effluent W25	170	20.0

Based on the COD/BOD_5 ratios, all effluent samples can be assumed to be incapable to biodegrade and thus are considered to contain mostly nbCOD. The effluent W23 had significantly the highest COD/BOD_5 ratio (up to 67.9) and thus can be considered the most hardly biodegradable. This is in line with the results obtained from the estimation of COD curves, as the effluent W23 had the lowest reaction rate constant. The COD/BOD_5 ratios of the effluent W24 and W25 were quite similar (20.0 and 23.2), while the effluent W50 had the lowest ratio (12.3) and thus can be considered the most easily biodegradable.

5.3.2 COD fractionation

The COD fractionation was carried out to all effluent samples and the results are presented in Figure 14. The exact amounts of each fraction are summarized in Appendix B.

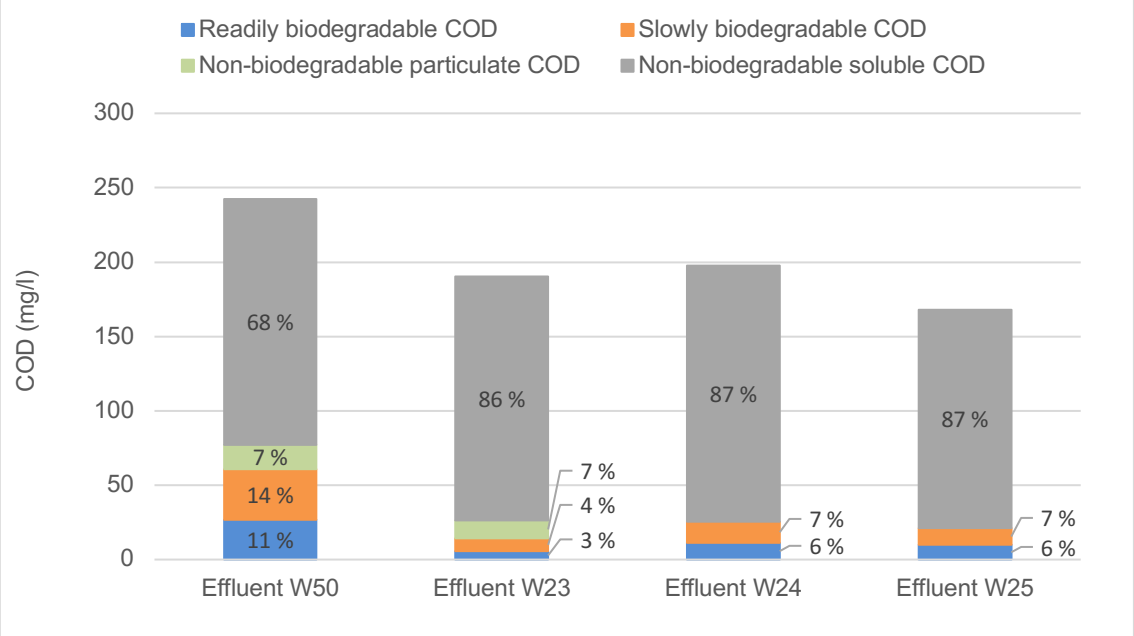

Figure 14. The composition of COD in the effluent samples

The amounts of total COD varied between different effluent samples (Figure 14). The lowest total COD was 170 mg/ and the highest was up to 240 mg/l. The largest fraction in each effluent sample was nbsCOD. The nbsCOD had slight differences between the effluent samples, as they were in the range of 150-170 mg/l (68-87 %). There were also slight differences in the nbpCOD, as they were in the range of 0-17 mg/l (0-7 %). Both rbCOD and sbCOD had slight variations between different effluent samples, as the

rbCOD was in the range of 6-27 mg/l (3-11 %) and the sbCOD was in the range of 9-34 mg/l (4-14 %). The clearest differences were observed in the effluent W50, in which the rbCOD and sbCOD were clearly higher compared to the other effluent samples.

5.4 The removal of COD fractions in the activated sludge process

The efficiency of the activated sludge process was estimated by determining the removal of each COD fraction achieved in the activated sludge process. The removals were calculated using the amounts of COD fractions in the influent and effluent composite samples from weeks 23-25 (Appendix B). The removals (%) of COD fractions are presented in Table 7.

Table 7. The removals of total COD and COD fractions (%) achieved in the activated sludge process. Absolute removals are presented in parentheses.

Sample	COD (%)	rbCOD (%)	sbCOD (%)	nbpCOD (%)	nbsCOD (%)
Week 23	90.5 (1806 mg/l)	99.3 (773 mg/l)	97.9 (396 mg/l)	97.8 (546 mg/l)	35.7 (91 mg/l)
Week 24	90.0 (1771 mg/l)	98.7 (844 mg/l)	97.2 (493 mg/l)	100.0 (259 mg/l)	50.5 (175 mg/l)
Week 25	89.7 (1469 mg/l)	98.7 (757 mg/l)	97.1 (375 mg/l)	100.0 (220 mg/l)	44.2 (116 mg/l)

There were slight differences in the removals of total COD and COD fractions between different weeks. The highest total COD removal was obtained on week 23 (90.5 %) and the lowest on week 25 (89.7 %). There were slight variations in the removals of nbpCOD and nbsCOD between different weeks. The removals of nbpCOD were 100 % on weeks 24 and 25, while on week 23 the removal was 97.8 %. The removals of nbsCOD were in the range of 35.7-50.5 %.

Activated sludge process should effectively remove rbCOD and on week 23 it has been removed efficiently, up to 99.3 %. On weeks 24 and 25, the removals were slightly lower (98.7 %). Due to tightening wastewater regulations and discharge limits, attention should be paid to the rbCOD (BOD_7) in effluent, as there may also be stricter discharge limits on its quantity in the future. On week 23, the rbCOD in the effluent was only 6 mg/l, while on weeks 24 and 25 it was higher (10 mg/l and 11 mg/l).

The removals of sbCOD were quite similar between weeks 23-25, but on week 23 it was slightly higher. However, the amounts of sbCOD in the effluent samples were in the range of 9-14 mg/l, therefore significant differences were not observed. In conclusion, the activated sludge process has been the most effective on week 23, as the removals of both rbCOD and sbCOD were the highest compared to the results of weeks 24 and 25.

5.5 COD and BOD_7 loads

5.5.1 The influent of the activated sludge process

The COD and BOD_7 values (Appendix B) and the flow rates of the influent samples (Appendix D) were used to calculate COD and BOD_7 loads to the activated sludge process (Table 8).

Table 8. The flow rates of the influent and the COD and BOD_7 loads to the activated sludge process

Sample	Flow rate (m^3/d)	COD load (t/d)	BOD_7 load (t/d)
Influent W23	19000	39	15
Influent W24	21000	42	18
Influent W25	20000	33	15

Based on the results, the influent W24 caused significantly the highest COD and BOD_7 loads to the activated sludge process (42 t/d and 18 t/d). There were large variations in the COD loads of the influent to the activated sludge process, as they were in the range of 33-42 t/d. Smaller differences were in the BOD_7 loads, as they were in the range of 15-18 t/d. Large variations in the loads of the influent must be taken into account in the operation of the activated sludge process. Calculated COD and BOD_7 loads of the influent can be utilized when examining factors affecting the efficiency of the activated sludge process. The values of the COD fractions (Appendix B) were used to calculate COD fraction loads to the activated sludge process (Table 9).

Table 9. The COD fraction loads to the activated sludge process

Sample	rbCOD (t/d)	sbCOD (t/d)	nbpCOD (t/d)	nbsCOD (t/d)
Influent W23	15	7.9	11	4.9
Influent W24	18	11	5.5	7.4
Influent W25	15	7.8	4.4	5.3

Although the influent W24 had significantly the highest COD load to the activated sludge process, it did not have the highest nbpCOD load, as the highest nbpCOD was obtained for the influent W23 (11 t/d). However, the influent W24 had the highest rbCOD, sbCOD and nbsCOD loads (18 t/d, 11 t/d and 7.4 t/d). The COD fraction loads of the influent can be used to determine the proportions of COD fraction loads caused by different wastewater streams of the total loads to the activated sludge process.

5.5.2 Debarking and TMP wastewaters

The COD and BOD_7 values (Appendix A) and the flow rates of debarking (W21, W22 and W23) and TMP (W22 and W24) wastewaters (Appendix D) were used to calculate COD and BOD_7 loads to the wastewater treatment (Table 10).

Table 10. The COD and BOD_7 loads and the flow rates of debarking wastewater

Sample	Flow rate (m^3/d)	COD load (kg/d)	BOD_7 load (kg/d)
Debarking W21	1400	3800	790
Debarking W22	1500	4000	1000
Debarking W23	1400	3700	1000
TMP W22	1200	4200	1200
TMP W24	1700	7200	1900

Differences were observed in the COD loads between both debarking wastewater samples (3700-4000 kg/d) and TMP wastewater samples (4200-7200 kg/d). The debarking wastewater samples had also lower BOD_7 loads (790-1000 kg/d) compared to the TMP wastewater samples (1200-1900 kg/d). Calculated COD and BOD_7 loads can be used to

determine the effect of debarking and TMP wastewater streams on the total load entering the wastewater treatment processes. The proportions of the debarking and TMP wastewater COD loads of the total COD loads entering the primary clarifier were calculated (Table 11). Calculations were carried out using the COD loads of the primary clarifier influent obtained from the data of the mill (Appendix E).

Table 11. The proportions of the debarking wastewater COD loads of the total COD loads entering the primary clarifier

Sample	The proportion of COD of total COD load (%)
Debarking W21	5.8
Debarking W22	5.5
Debarking W23	7.3
TMP W22	5.7
TMP W24	7.7

The proportions of the debarking and TMP wastewater COD loads of the total COD loads entering the primary clarifier were quite similar (in the range of 5.5-7.7 %). In order to determine which wastewater streams cause the highest COD loads, all wastewater streams of the mill should be investigated and the proportions of their COD loads of total COD load should be determined. In addition, by carrying out the COD fractionation to all wastewater streams and the influent of primary clarifier, COD fraction loads could be determined and their proportions of total COD fraction loads entering the primary clarifier could be calculated.

The proportions of the debarking and TMP wastewater COD and COD fraction loads of the total loads entering the activated sludge process were calculated (Table 12). Calculations were carried out using the COD and COD fraction loads of the activated sludge process influent obtained in this study.

Table 12. The proportions of the debarking and TMP wastewater COD and COD fraction loads of the total loads entering the activated sludge process

Sample	COD (%)	rbCOD (%)	sbCOD (%)	nbpCOD (%)	nbsCOD (%)
Debarking W23	9.5	6.8	7.7	3.5	33.7
TMP W24	17.2	10.4	7.9	4.3	57.2

On week 24, the TMP wastewater caused 17.2 % of the total COD load entering the activated sludge process, while on week 23, the debarking wastewater caused 9.5 % of the total COD load. The proportions of the debarking and TMP wastewater rbCOD, sbCOD and nbpCOD loads were in the range of 3.5-10.4 %, while the proportions of the nbsCOD were up to 33.7-57.2 %. It should be noted that the proportions (Table 12) are estimates, as the COD removals in the primary clarifier were not taken into account. However, the primary clarifier removes particulate material (nbpCOD and sbCOD), therefore the proportions of the rbCOD and nbsCOD can be considered to be close to correct. The proportions of sbCOD and nbpCOD were low (less than 7.9 %) and their actual proportions can be assumed to be even lower. However, based on the results obtained in this study, both debarking and TMP wastewater cause a significant proportion of total nbsCOD load entering the activated sludge process.

5.5.3 The effluent of the activated sludge process

The environmental permit of the mill set limit values for COD and BOD_7 loads to be discharged. The COD and BOD_7 values (Appendix B) and the flow rates of the effluent samples (Appendix D) were used to calculate COD and BOD_7 loads that were discharged (Table 13).

Table 13. Flow rates of effluent and COD and BOD_7 loads to be discharged

Sample	Flow rate (m^3/d)	COD load (kg/d)	BOD_7 load (kg/d)
Effluent W23	20000	3700	110
Effluent W24	23000	4500	260
Effluent W25	17000	2800	160

Differences were observed in COD and BOD_7 loads between different effluent samples. Both COD and BOD_7 loads were the highest in the effluent W24. It was also observed that the lowest BOD_7 load was in the effluent W23, but the lowest COD load was in the effluent W25. Thus, it was considered that the proportion of rbCOD (BOD_7) is lower in the effluent W23 than in the effluent W25. The COD and BOD_7 loads obtained in this study can be compared with the current limit values of the mill under investigation and see if the results are within the limit values.

6. DISCUSSION

6.1 Debarking and TMP wastewaters

It was observed that the debarking wastewaters taken in May and June contained lower total COD (in the range of 2600-2800 mg/l) compared to the TMP wastewaters (3600-4500 mg/l). However, the debarking wastewater taken in December contained a significantly higher total COD (5800 mg/l), while the TMP wastewater taken in December had the total COD in the same range with the samples taken in June (4800 mg/l). The higher total COD in the debarking W50 may be due to seasonal variations, as in winter, frozen wood logs need to be defrozen using hot water, which causes more compounds to be extracted from the wood into the water and thus the total COD can be two to three times higher in winter than in summer (Saunamäki & Savolainen 1999).

Furthermore, trees contain a higher amount of carbohydrates in winter compared to summer, due which more carbohydrates are released from the wood into the water and thus the rbCOD in wastewater may be increased (Orhon & Gokgör 1997; Widsten *et al.* 2003). Higher rbCOD was observed in the debarking W50, although the proportion of rbCOD was in the same range in all debarking samples (21-28%). The debarking W50 also had significantly the highest nbsCOD. Lignin is one major compound in nbsCOD, but according to Widsten *et al.* (2003), lignin does not have clear season-dependency and thus a higher nbsCOD in winter is not considered to be caused by an increase in the amount of lignin in wood. In order to investigate the factors affecting the amounts of COD fractions at different seasons, samples taken in both summer and winter could be further analysed to determine the amounts of compounds they contain, such as lignin, carbohydrates and extractives.

However, it should be noted that only one sample was taken from each sampling point in December. In addition, samples taken in December were grab samples and do not provide as comprehensive picture as a composite sample. Thus, unusual results of grab samples may also be due to some exceptional situation in the pulp and paper making processes. In order to obtain more accurate information about seasonal variations, more samples should be taken both in winter and summer.

Differences were observed in the proportions of different COD fractions between the debarking and TMP wastewaters. The largest fraction of both wastewater streams was nbsCOD, but in the TMP wastewaters its proportions were clearly higher (debarking 35-47 %, TMP 45-62 %). It was also observed that the debarking wastewaters contained

higher proportions of nbpCOD (10-24 %), while in the TMP wastewaters its proportions were markedly lower (0-8 %). However, based on the COD fractionation, the biodegradability can be considered quite similar between the debarking and TMP wastewaters.

No literature studies were found on the COD composition of debarking and TMP wastewater, and therefore other research results supporting the results obtained in this study were not found. Thus, in order to obtain more information about the COD composition of these wastewater streams and to provide support for the results obtained in this study, more samples should be taken and analysed.

6.2 The efficiency of the activated sludge process

6.2.1 Influent characteristics

Differences were observed in the total COD between different influent samples, as they were in the range of 1600-2000 mg/l. Variations in the total COD of the influents of the activated sludge process can be caused by several different reasons, such as changes in pulp and paper making processes, seasonal variations in raw material and variations in the effectiveness of primary clarifier (Gernaey *et al.* 2001; Widsten *et al.* 2003; Antikainen *et al.* 2018). In addition, variations can be caused by the fact that, for example, during the break in the run of some pulp and paper making process, a certain wastewater stream does not enter the wastewater treatment plant in such large quantities.

The amount of sbCOD and nbsCOD were quite similar in all influent samples. However, the influent W50 had significantly higher rbCOD, which may be due to seasonal variations. Differences were also observed in the nbpCOD, as the influent W23 contained up to 560 mg/l (28 %) nbpCOD, while the other influent samples had nbpCOD in the range of 0-260 mg/l (0-13 %). One possible reason for the unusually high nbpCOD can be the incomplete operation of primary clarifier. Primary clarifier mainly removes nbpCOD from the wastewater, but for example, due to too short HRT, particulate material does not have enough time to attach to other solids and thus nbpCOD is not removed as much as a complete operation (Tchobanoglous *et al.* 2003, p. 407; Gray 2004, p. 470).

The high nbpCOD may also be due to some exceptional situation in the pulp and paper making processes or wastewater streams entering the wastewater treatment plant. For example, based on the results obtained in this study, debarking wastewater contains more nbpCOD than TMP wastewater, therefore if the amount of debarking wastewater entering the wastewater treatment plant increases, the nbpCOD may be higher in the influent. The proportion of the debarking W23 COD load of the total COD load entering

the primary clarifier was higher (7.3 %) compared to the debarking W21 and W22 (in the range of 5.5-5.8 %). Thus, the higher proportion of COD load on week 23 may be on one reason for the higher nbpCOD in the influent.

The COD fractions of the influent of activated sludge process obtained in this study were compared to the results obtained in the study of Barañao & Hall (2004) (Table 14). Barañao & Hall carried out the COD fractionation for the influent of activated sludge process, which was pre-treated in the primary clarifier. The wastewater investigated in their study was from the pulp and paper mill in Canada, where the raw material was softwood and the pulp was produced using the CTMP process.

Table 14. The proportions of COD fractions in the influent of activated sludge process obtained in this study and the study of Barañao & Hall (2004)

COD fraction	This study	The study of Barañao & Hall (2004)
rbCOD (%)	39-62	49
sbCOD (%)	17-26	30
nbpCOD (%)	0-28	7
nbsCOD (%)	13-21	14

In both studies, the rbCOD was the largest fraction (Table 14). In the study of Barañao & Hall (2004), the second largest fraction was sbCOD, while in this study it was the second largest fraction in two influent samples. In the study of Barañao & Hall, the smallest fraction was nbpCOD. In this study nbpCOD had significant variations, as in one influent sample it was the second largest fraction and in all other influent samples the smallest fraction. However, the results of COD fractionation are mainly similar and support each other. Small differences in the composition of COD may be due to the use of different pulping processes, as in the study of Barañao & Hall (2004), the mill produced pulp using the CTMP process, whereas in this study the wastewater was from the mill producing pulp using the TMP process.

6.2.2 Effluent characteristics

The amounts of total COD, rbCOD and sbCOD were clearly higher in the effluent W50 compared to the other effluent samples. Differences can be explained by the technical reasons that caused limitations on the operation of the activated sludge process and thus probably affected the efficiency of the process. The amounts of total COD also varied between different effluent samples taken in June (in the range of 170-200 mg/l). The total COD in the effluent depends on both the efficiency of the activated sludge process and the organic composition of the influent entering the process. For example, the more nbsCOD the influent contains, the greater amount of total COD is in the effluent, as nbsCOD is not removed in the activated sludge process (Baquero- Rodríguez *et al.* 2016).

There were differences both in the rbCOD and sbCOD between different effluent samples taken in June. The rbCOD was in the range of 6-11 mg/l (3-6 %) and the sbCOD in the range of 9-14 mg/l (4-7 %). Variations in the rbCOD and sbCOD can be caused by their variations in the influent, but also the efficiency of the activated sludge process, as it should remove both rbCOD and sbCOD. (Roppola *et al.* 2009; Baquero- Rodríguez *et al.* 2016). The nbpCOD in the effluent samples taken in June were in the range of 0-12 mg/l (0-7 %). The efficiency of the activated sludge process also affects nbpCOD in effluent, as for example, deflocculation can lead to the release of nbpCOD from secondary sludge and thus increase the nbpCOD in effluent. Deflocculation can be caused by, for example, too low amount of nutrients, too high DO level or old sludge. (Comas *et al.* 2003; Henze *et al.* 2008, p. 61)

The largest fraction in each effluent sample was nbsCOD. There were slight differences in the nbsCOD between the effluent samples, as they were in the range of 150-170 mg/l (68-87 %). The differences in the nbsCOD may be due to its differences in the influent, as nbsCOD is not reduced by the activated sludge process (Myszograj *et al.* 2017). However, in this study, there were no major differences in the nbsCOD between different effluent samples.

The fraction of nbsCOD in pulp and paper mill wastewater is mainly composed of lignin and its derivatives as well as aromatic compounds (Choi *et al.* 2017). In this study, the fraction of nbsCOD was the major fraction in all effluent samples and thus they are considered to contain a large amount of lignin, its derivatives and aromatic compounds. In order to ensure these assumptions and determine the exact organic composition of the effluent, the compounds contained in the effluent could be identified in the future, for example, by GC-FID/MS analysis according to Herold-Majumdar *et al.* (2021).

The COD fractions of the effluent of activated sludge process obtained in this study were compared to the results obtained in the study of Choi et al. (2017) (Table 15). Choi et al. (2017) investigated the proportions of each COD fraction in the treated effluent of the pulp and paper mill in Korea. In their study, raw material used, pulp and paper mill unit processes and wastewater treatment processes had not been reported.

Table 15. The proportions of COD fractions in the effluent of activated sludge process obtained in this study and the study of Choi *et al.* (2017)

COD fraction	This study	The study of Choi *et al.* (2017)
bCOD (%)	7-25	6
nbpCOD (%)	0-7	14
nbsCOD (%)	68-87	80

In both studies, the nbsCOD was the major fraction (68-87 % and 80 %). Choi *et al.* (2017) reported nbpCOD to be the second largest fraction, while in this study its proportion was smaller. In the study of Choi *et al.* (2017), the smallest fraction was bCOD and it was mainly composed of sbCOD. In this study, the proportion of bCOD was slightly higher with both rbCOD and sbCOD accounting for a significant proportion of bCOD. There can be many possible reasons for differences in the results, as in the study of Choi *et al*. (2017), both raw material, pulp and paper mill unit processes and wastewater treatment processes may differ from the mill investigated in this study, as they were not reported.

6.2.3 COD removal in the activated sludge process

The lowest removal of nbpCOD in the activated sludge process was obtained on week 23 (97.8 %), while on weeks 24 and 25 the removals were 100 %. A lower removal of nbpCOD may be due to the significantly higher nbpCOD in the influent, as on week 23 the nbpCOD was up to 560 mg/l and on weeks 24 and 25 it was in the range of 220-260 mg/l. A high nbpCOD may not have had enough time to attach to the flocs and thus its amount was left higher than on weeks 24 and 25. In addition to the nbpCOD in the influent of activated sludge process, nbpCOD in the effluent also depends on the efficiency of the activated sludge process. Thus, a low nbpCOD removal can be caused by, for example, deflocculation in the activated sludge process (Comas *et al.* 2003).

There were differences in the removals of rbCOD in the activated sludge process between different weeks. One possible reason to the lower removal of rbCOD on week 24 may be the higher BOD_7 (rbCOD) load of the influent to the activated sludge process, as on week 24 it was clearly higher (18 t/d) compared to the influents on weeks 23 and 25 (both 15 t/d). The activated sludge process was the most effective on week 23, as the removal of rbCOD was the highest (99.3 %) and the rbCOD in effluent was the lowest (6 mg/l). On weeks 24 and 25 the removal of rbCOD was lower (98.7 %) and the rbCOD was higher (in the range of 10-11 mg/l), therefore there may have been a need for improvement in the operation of the process at these sampling times. For example, too low amount of oxygen or nutrients can cause the deterioration of BOD removal, as microbes need enough of them (Balakrishnan *et al.* 2021). The lack of nutrients and too low oxygen concentration can also cause the bulking of sludge, which can lead to problems with sludge separation and settling (Kõrgmaa *et al.* 2019). The removal of BOD can also be reduced by too short HRT, if flocs does not have sufficient time to stabilized and provide free adsorption sites for further material to attach and flocculate (Gray 2004, p. 470).

In order to determine the reasons in the process operation for lower removal of rbCOD, the online data of operation parameters (i.a. HRT, MLVSS and the amounts of oxygen and nutrients) from these sampling times could be compared to the results obtained in this study. Furthermore, the results obtained in this study and the process operation data could be used to investigate the effect of operation on BOD removal through modelling. The effect of operation parameters could also be studied by treating influent samples with a laboratory-scale activated sludge process, varying operation parameters and comparing the results of BOD removal.

Based on the results, the activated sludge process of the mill is able to efficiently remove rbCOD. Thus, in order to achieve more efficient BOD_7 removal, adding new treatment processes may not be necessary, since adjusting the operation of the process can be sufficient. New treatment processes (e.g. chemical precipitation, AOPs or electrochemical technologies) may become necessary to investigate and introduce, if the nbCOD in the effluent is required to reduce in the future. In addition, the treatment of the debarking or TMP wastewater could be considered, as based on the results of this study, both the debarking and TMP wastewater account for a large proportion of nbCOD entering the wastewater treatment plant.

7. CONCLUSIONS

The aim of this study was to investigate the organic composition and biodegradability of the pulp and paper mill wastewaters and the removal of different COD fractions in the activated sludge process. The study examined two wastewater streams of the mill, debarking and TMP wastewaters as well as the influent and effluent of the activated sludge process.

Based on the results obtained in this study, it is concluded that the largest COD fraction of both debarking and TMP wastewater is nbsCOD. The biodegradability of these wastewater streams is concluded to be quite similar (COD/BOD_5 ratios in the range of 3.5-6.8). It is also concluded that in debarking wastewater the total COD can be over two times higher in winter compared to summer, while in TMP wastewater there is no season-dependency observed. A suggestion for further research is to conduct a larger study of the effect of season on the COD in debarking wastewater. In addition to COD fractionation, compound such as lignin, carbohydrates and extractives contained in debarking wastewater could be analysed to provide more accurate information on whether the season-dependency of some compound causes higher COD concentration in winter.

It is concluded that there may be variations in the proportions of COD fractions in the influent of the activated sludge process in different weeks and seasons. The largest variations are considered to occur in the proportions of nbpCOD (0-28 %). However, based on the results, it can be assumed that the largest COD fraction is usually rbCOD in the influent of the activated sludge process.

The effluent of the activated sludge process is concluded to contain mostly nbsCOD (68-86 %). It is assumed that there may be variations in the proportions of rbCOD, sbCOD and nbpCOD, depending on the efficiency of the activated sludge process and their variations in the influent. The activated sludge process efficiently removed rbCOD, as in one effluent sample the rbCOD was 6 mg/l (99.3 %) and in the other two effluent samples it was in the range of 10-11 mg/l (98.7 %). However, there have been slight variations in the efficiency of the activated sludge process at different sampling times.

Possible reasons for variations in the efficiency of the activated sludge process could be investigated in the future. For example, the results of COD fractionation of both the influent and effluent of activated sludge process obtained in this study can be utilized in modelling the activated sludge process and analysing the long term data, when examining

the impact of different operation parameters on the process efficiency and determining the most appropriate process conditions.

Based on the results of this study, the activated sludge process of the mill is able to efficiently remove rbCOD and achieve a low rbCOD in the effluent. Thus, adding new treatment processes to current wastewater treatment may not be necessary for achieving more efficient BOD_7 removal, since adjusting the operation of current activated sludge process can be sufficient to achieve low amounts of BOD_7 in effluent. In the case that the nbCOD in effluent is required to reduce in the future, new treatment processes (e.g. chemical precipitation, AOPs or electrochemical technologies) may be necessary to be investigated and introduced.

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APPENDIX A: BOD, COD AND COD FRACTIONATION RESULTS OF THE DEBARKING AND TMP WASTEWATER SAMPLES

Sample	BOD_5 (mg/l)	BOD_7 (mg/l)	BOD_{20} (mg/l)	COD (mg/l)
Debarking W50, original	1103.8	1523.8	2162.6	5795.8
Debarking W50, soluble	612.6	757.7	1264.2	3983.1
Debarking W21, original	387.9	558.9	1071.5	2641.2
Debarking W21, soluble	255.5	304.3	487.1	1422.2
Debarking W22, original	558.9	684.9	1242.5	2759.8
Debarking W22, soluble	176.6	226.2	428.5	1456.1
Debarking W23, original	558.9	726.9	1155.5	2607.4
Debarking W23, soluble	216.4	265.2	448.1	1633.9

Sample	BOD_5 (mg/l)	BOD_7 (mg/l)	BOD_{20} (mg/l)	COD (mg/l)
TMP W50, original	792.8	1016.8	1837.6	4776.5
TMP W50, soluble	775.6	1007.6	1075.2	4014.1
TMP W22, original	769.9	995.9	1677.5	3572.5
TMP W22, soluble	870.3	1062.3	1101.5	2692.1
TMP W23, original	1049.6	1331.6	2033.6	4461.0
TMP W23, soluble	631.2	855.2	1111.2	3538.6
TMP W24, original	1021.6	1133.6	1641.6	4317.5
TMP W24, soluble	559.2	695.2	1139.2	3674.1

Sample	RbCOD (mg/l)	SbCOD (mg/l)	NbpCOD (mg/l)	NbsCOD (mg/l)
Debarking W50	1523.8	638.8	914.3	2718.9
Debarking W21	558.9	512.6	634.7	935.1
Debarking W22	684.9	557.6	489.7	1027.6
Debarking W23	726.9	428.6	266.1	1185.8

Sample	RbCOD (mg/l)	SbCOD (mg/l)	NbpCOD (mg/l)	NbsCOD (mg/l)
TMP W50	1016.8	820.8	0.0	2938.9
TMP W22	995.9	681.6	304.4	1590.6
TMP W23	1331.6	702.0	0.0	2427.4
TMP W24	1133.6	508.0	141.0	2534.9

APPENDIX B: BOD, COD AND COD FRACTIONATION RESULTS OF THE INFLUENT AND EFFLUENT SAMPLES

Sample	BOD_5 (mg/l)	BOD_7 (mg/l)	BOD_{20} (mg/l)	COD (mg/l)
Influent W50, original	980.4	1140.4	1456.8	1842.1
Influent W50, soluble	651.6	751.6	1083.2	1468.5
Influent W23, original	690.8	778.6	1183.0	1995.6
Influent W23, soluble	569.9	649.9	981.3	1235.9
Influent W24, original	711.1	855.1	1361.7	1968.0
Influent W24, soluble	653.9	749.9	1093.3	1440.6
Influent W25, original	621.5	767.1	1153.7	1637.4
Influent W25, soluble	497.9	581.9	925.3	1188.7

Sample	BOD_5 (mg/l)	BOD_7 (mg/l)	BOD_{20} (mg/l)	COD (mg/l)
Effluent W50, original	19.7	26.8	60.6	242.5
Effluent W50, soluble	19.7	21.1	31.0	196.4
Effluent W23, original	2.8	5.6	14.1	190.1
Effluent W23, soluble	8.5	7.0	12.7	176.3
Effluent W24, original	8.5	11.3	25.4	197.4
Effluent W24, soluble	11.3	12.7	16.9	188.9
Effluent W25, original	8.4	9.8	21.1	168.1
Effluent W25, soluble	7.0	8.5	15.5	162.5

Sample	RbCOD (mg/l)	SbCOD (mg/l)	NbpCOD (mg/l)	NbsCOD (mg/l)
Influent W50	1140.4	316.4	0.0	385.3
Influent W23	778.6	404.4	558.0	254.6
Influent W24	855.1	506.6	259.0	347.3
Influent W25	767.1	386.6	220.3	263.4

Sample	RbCOD (mg/l)	SbCOD (mg/l)	NbpCOD (mg/l)	NbsCOD (mg/l)
Effluent W50	26.8	33.8	16.6	165.4
Effluent W23	5.6	8.5	12.4	163.6
Effluent W24	11.3	14.1	0.0	172.0
Effluent W25	9.8	11.3	0.0	147.0

APPENDIX C: REACTION RATE CONSTANTS

Sample	Reaction rate constant (*k*)
Debarking W50	0.17
Debarking W21	0.09
Debarking W22	0.11
Debarking W23	0.12
TMP W50	0.10
TMP W22	0.11
TMP W23	0.16
TMP W24	0.21

Sample	Reaction rate constant (*k*)
Influent W50	0.18
Influent W23	0.17
Influent W24	0.15
Influent W25	0.15
Effluent W50	0.04
Effluent W23	0.00
Effluent W24	0.03
Effluent W25	0.03

APPENDIX D: FLOW RATES

Sampling time of debarking wastewater	Flow rate of debarking wastewater (m^3/d)
Week 21 (25.5.)	1420.7
Week 22 (1.6.)	1464.7
Week 23 (7.6.)	1405.1

Sampling time of TMP wastewater	Flow rate of TMP wastewater (m^3/d)
Week 22 (1.6.)	1183.6
Week 24 (14.6.)	1677.7

Sampling time of influent to activated sludge process	Flow rate of influent to activated sludge process (m^3/d)
Week 23 (7.-8.6.)	19425.2
Week 24 (14.-15.6.)	21416.1
Week 25 (21.-22.6.)	20122.5

Sampling time of effluent from activated sludge process	Flow rate of effluent from activated sludge process (m^3/d)
Week 23 (8.-9.6.)	19455.4
Week 24 (15.-16.6.)	22955.2
Week 25 (22.-23.6.)	16685.8

APPENDIX E: COD LOADS OF INFLUENT TO PRIMARY CLARIFIER

Date	COD load of the influent to primary clarifier (t/d)
Week 21 (25.5.)	64.6
Week 22 (1.6.)	73.7
Week 23 (7.6.)	50.3