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Development of advanced oxidation processes for the Finnish pulp and paper industry water treatment

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DEVELOPMENT OF ADVANCED OXIDATION PROCESSES FOR THE FINNISH PULP AND PAPER INDUSTRY WATER TREATMENT

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PREFACE

This dissertation focuses on developing advanced oxidation process (AOP) technologies for the Finnish pulp and paper industry water treatment.

During the last three decades, the AOP technologies have been developed as a pinnacle of chemical water treatment to face more tightening environmental limits. Whenever either pure coagulation & flocculation or/and biological technologies cannot reach the required environmental limits, then AOP technologies can be used.

This thesis reflects the author's experience, studies and work on water treatment topics since 1986.

From 1986 to 1992, the Metsä-Serla Lielahti CTMP mill focused on process and effluent water treatment, especially how to close the water loops and reduce the effluent volumes. Biological treatment started for Finnish pulp and paper in 1986, and Metsä-Serla Lielahti was the second to have one. The operational issues of this new biological treatment plant became the author's master's thesis work. After the master's thesis, the work continued by closing the water loops and looking for ways to reduce the effluent volumes and loadings through different water treatment technologies.

In 1992, the author was transferred to Metsä-Serla Corp R&D located at Kirkniemi, Finland, to continue with all five different Metsä-Serla plant water issues. Then, in 1994, the author joined Kemira Chemicals for the next 18 years, starting work worldwide with pulp and paper industry water issues and becoming the technical director for Kemira Corporate and VP of Kemira's Oulu Research Center. Most chemical water treatment methods became familiar at this time, including the AOPs.

The work has been continued at Metso Outotec, a worldwide mining technology provider. The author is responsible for developing and selling new, less water-consuming, more closed water loops and less polluting plants.

Please note that industrial R&D development differs significantly from an academic one. Whenever there is a new sales potential insight, most development information is kept secret until patents or patent families are public. Even after these restrictions on crucial products and processes, public information such as academic articles can be kept minimal. These restrictions create a time warp between what is old and new, when the innovation has been done and when it becomes public knowledge. Many of the AOP-focused developments were entirely new to the world when these presented studies started. These excuses can sometimes be seen as a lack of numerous references when general information on these applications was minimal at the time.

The practical outcome of studies presented in this dissertation has led to the following patents:

Year	Patent number	Subject
2003	FI 110683 Jansson K., Tuhkanen T., Korhonen S.	Patent on the utilisation of O_3+H_2O_2 as a biocide for paper machine water
2006	WO 2006/064084 Jansson K., Palonen H., Laine E.	Patent on the removal of manganese from raw waters with peracetic acid
2013	WO 2013/064484 Costa M., Jansson K., Saari K.	Patent on treating oily waters with peracetic acid
2013	EP 2 653 448 Öjstedt U., Garmstad R., Jansson K., Kolari M.	Patent for microbiological control with performic acid and UV
2014	US2014036733A Salonen J, Kolari M., Hesampour M., Jansson K.	Patent on preventing microbiological growth on membrane filtration by utilisation of performic acid
2017	US 9 617 170 Karpova T., Melin E., Vuori A., Ojstedt U, Gramstadt R., Jansson K., Kolari M.	Patent on controlling microbiological growth in water by using performic acid and UV
2018	US 9,970,919 FI 126240 Piironen M., Joensuu I., Ilmola P., Jansson K.	Patent on method and device for monitoring and controlling microbiological growth by utilisation of performic acid

I want to thank M.Sc. Ole Nickull, my first technology director at Metsä-Serla Lielahti CTMP Pulp Mill and many others from the site, probably taught me all I know about this industry. Besides, one should not forget my colleagues at Kemira – both the older and the more recent- in all the different R&D, applications, and sales positions, especially the Pulp and Paper WQM team and Tarmo Syväpuro, Juha Elmgren, and Seija Mäkinen. Finally, I would like to thank such long-time friends as M.Sc. Ole Nickull, M.Sc. Sakari Halttunen and Engineer Ossi Sippola for their considerable support and discussions concerning different water treatment methods.

At Åbo Akademi University, I would like to thank Professor Emeritus Kaj Fagervik for initiating this doctoral dissertation and utilising my studies in the pulp and paper industry, docent Jarl Ahlbeck for supporting and very inspiring discussions regarding pulp and paper environmental issues and history, Professor Margareta Björklund- Sänkiaho for focusing on the leading industrial drivers, and Professor Anders Brink for the very friendly, practical study that targeted the dissertation's hands-on orientation. Without his input, it would not have been completed.

I want to thank Professor Olli Dahl from Aalto University and Professor Tuula Tuhkanen from Jyväskylä University for their professional help on many topics.

Furthermore, I would like to thank my children, Carl and Frans and my wife, Niina, for providing the necessary leisure time during the years. Finally, I thank all my friends for their encouragement and peaceful moments of creativity, which are occasionally possible with a glass of good red wine.

Tammerfors September 2022

Kaj Jansson

ABSTRACT

Advanced oxidation processes (AOP) have been developed as a pinnacle of chemical water treatment to face the more tightening environmental limits during the last three decades. Whenever either pure coagulation & flocculation or/and biological technologies cannot reach the required environmental limits, then AOP technologies can be used.

This thesis presents four AOP methods to treat different pulp and paper water types.

The first study object is to enhance the conventional treatment COD_{cr} removal by placing the AOPs as a tertiary treatment step after the existing activated sludge process.

The second study focuses on reducing chemical and investment costs associated with the first study by placing the AOP before the activated sludge by modifying the difficult biodegradable matter to more readily biodegradable. The more biodegradable wastewater can then be removed more efficiently in the following activated sludge stage.

The third study uses AOP for more environmentally friendly and economical biocides used on paper machines for biological growth control, simultaneously reducing the recalcitrant compounds found in wastewater.

The fourth study aims at removing manganese from the incoming raw water using a new non-toxic, environmentally friendly oxidation method. This new environmentally friendly oxidation method can replace used recalcitrant compounds used in the pulp and paper process.

The presented AOP shows its ability to adapt and reach high removal efficiencies for COD_{Cr} and P_{tot} removal in cases known to be challenging to biological treatment only.

Suggestions for further AOP development include maximising the utilisation of the existing equipment and chemistries already at the site to lower the initial operational and capital expenses needed to obtain the suggested AOP. Simultaneously, simplifying the presented new AOP toward a more straightforward process with less process and required chemicals is preferred.

REFERAT

Avancerade Oxidation Processer (AOP) har utvecklats för den finska massa- och pappersindustrin under de senaste tre senaste decennierna för situationer då processer baserade på sedimentation, kemisk fällning och biologisk rening inte uppnår satta gränsvärden.

Finland fick sin första miljölagstiftning 1961. I lagstiftningen var fokus på reglering av avfallsvattenvolymen, på vattnets pH-värde samt på mängden suspenderade ämnen. I slutet av 1970-talet uppstod en diskussion kring behovet av nya begränsningar för att minska utsläppen av biologiskt nedbrytbara ämnen och fosfor. Dessa utsläpp orsakade kraftigt tillväxt av alger och annan mikroskopisk biomassa som i sin tur ledde till syrebrist i vattenströmmarna. De nya kraven ledde till byggande av biologiska reningsverk, vars design togs från kommunala reningsverk. Kort efter de första biologiska reningsverken hade tagits i bruk i mitten av 1980-talet upptäckte man att den förväntade BOD-reningen inte kunde uppnås. I slutet av 1980-talet trädde begräsningar på kemisk syreförbrukning (COD) och fosfor (P) i kraft. COD lämpar sig bättre än BOD för styrning av biologiska reningsverk då det kan analyseras snabbare och mer exakt. I slutet av 1980-talet började skogsindustrin sluta vattenkretsloppen för att minimera mängden avfallsvatten och på sätt minska på byggkostnaderna för reningsverken. I början av 1990-talet konstaterade man att de nya kraven på COD var mycket svårare att nå än de tidigare kraven på BOD. Så småningom blev det klart att en del av analyserade COD-värden inte var nedbrytbart i det biologiska reningsverket. För den här delen började den engelska termen hard COD användas. Den del av COD som inte bryts ner biologiskt består främst av långkedjiga organiska molekyler eller toxiska ämnen.

I denna avhandling presenteras fyra AOP-metoder för att behandla olika typer processvatten inom massa- och pappersindustrin. Gemensamt för AOP är in situ produktion av hydroxylradikaler. Fenton-processen är den mest kända AOP-tekniken. Fenton-processen grundar sig på användning av tvåvärt järn som metallkatalyt för att spjälka väteperoxid. I andra vanliga AOP används väteperoxid, ozon och UV bestrålning samt deras blandningar.

Den första studien använder den modifierade Fentons-processen för massa- och pappersavloppsvatten som ett tertiärt reningssteg förbättring av COD_{Cr}-reduktionen. I modifierade Fenton-metoden används betydligt större mängder järn som katalyt jämfört med den ursprungliga metoden för att kompensera för eventuell kelatering. Studierna utfördes i laboratorie- och pilotskala på industriella avloppsvatten. Resultaten visar på över 90 % reduktion i COD_{Cr} och P_{tot} då processen används som en tertiär behandlingsmetod för massa- och pappersavloppsvatten.

Den andra studien fokuserar på förbättring av BOD_7/COD_{Cr}-förhållandet i avloppsreningsverkets inloppsvatten genom användningen av O_3, H_2O_2 och den modifiera Fenton processen innan det biologiska reningssteget. Målet är att nå en högre COD_{Cr} reduktion sett till hela reningsverket. Studierna, som gjordes i laboratorie- och fullskala med 60°C vatten, visar en ökning i BOD_7/COD_{Cr} förhållandet från 0,3 upp till 0,9 då H_2O_2/O_3 användes i förhållande 1,5, och från 0,3 till 0,5 med den modifierade Fenton-processen. Den studerade metoden sänker kemikalie- och utrustningskostnader jämfört processen som undersöktes i den första studien.

I den tredje studien utvecklas en mindre skadlig AOP-baserad biocid för biologisk tillväxtkontroll i pappersmaskiner. Målet är inställt på att nå en deaktivering av de aeroba heterotroferna som överskrider 99 % med hjälp av AOP-tekniken. Olika doseringsförhållanden av H_2O_2 och O_3 användes för att generera hydroxylradikaler som hämmar den mikrobiologiska tillväxten. Studien visar att tillsatts av H_2O_2 i ozoneringsprocessen, i förhållandet 1:3, inaktiverar aeroba heterotrofa bakterier och jäst så att en reduktion 99 % kan uppnås.

I den fjärde studien undersöks alternativa och tekniskt enklare sätt att avlägsna Mn^{2+} från råvatten som används inom industrin. Processer baserade på högoxidativa föreningar och destillerad perättiksyra jämförs med processer baserade på $KMnO_4$ och HOCl. Resultat visar att en reduktion av på Mn^{2+} över 98 % kan nås. Resultaten visar också att pH-förändringar kan minimeras, vilket leder till inbesparing i kemikalier för pH-reglering. Resultaten visa även att användandet av en separat biocid kan vara onödig.

INSPIRING AOP PUBLICATIONS AND PATENTS

Related to Advanced Oxidation Processes, the following patents, conference and symposium articles are used:

1. Filho F., Costa M., Jansson K.; In-Situ Landfill Leachate Control by Chemical Application, *Singapore International Water Weeks 4*, 2-5 June, **2012.**
2. De Sá J., De Paula W., Kramer R., Jansson K.; Desinfix TM135 for Wastewater Treatment in Oil Refinery. *Singapore International Water Weeks 4*, 2-5 June, **2012**, Singapore.
3. Kukkonen J., Aitta E., Oinas P., Jansson K.; Compositions and processes for separating bitumen from oil sand ores, *Patent US 2101/0258477A1*, **2010**.
4. Jansson K., Palonen H., Laine E.; Treatment of pulp bleaching filtrate with Fenton´s technologies: *Advanced Oxidation Seminar*, Goslar, Germany, **2003**.
5. Jansson K., Palonen H.; Effect of pH and oxidation on sludge dewatering*., Proceedings of the 10th Gothenburg Symposium*, IWA publishing. June 17-19, **2002**.
6. Jansson K., Korhonen S., Tuhkanen T.; Cleaning of wastewater with ozone and peroxide, *Thomson Derwent*, **2002**.
7. Korhonen S., Laine E., Jansson K., and Tuhkanen T.; Advanced oxidation processes as a biocide in paper machine white water. *Chemical Water and Wastewater treatment VII, 10th Gothenburg Symposium*, IWA publishing, Gothenburg, Sweden, February 28 - March 2, **2001**.
8. Korhonen, S., Laine, E., Jansson, K., Palonen, H. and Tuhkanen, T; Ozone, Ozone + Hydrogen Peroxide and Hydrogen Peroxide as Biocides in Paper Machine White Water, *Proceedings of The Second European Workshop on Water, Air and Soil Treatment by Advanced Oxidation Technologies: Innovative and Commercial Applications. Ecole Supérieure d'Ingénieurs de Poitiers (ESIP)*, Université de Poitiers, France, 28.2. –2.3.**2001**.
9. Jansson K., Laine E., Korhonen S.; AOP treatment of an acidic pulp bleaching filtrate. *4th International conference on environmental impacts of the pulp and paper indust*ry, 133-136, Helsinki, Finland, 12-15 June, **2000.**

10. Jansson K., Wikberg H.; COD:n vähentäminen AOP-menetelmällä metsäteollisuuden jätevesistä. *Cactus technology program 109, TEKES*, NEI-FI-362. **1998.**
11. Tuhkanen T., Pessi M., Jansson K., Parén A., Laine E.; Comparison of different TiO_2 species for removal of organic matter from water and wastewater: *Conference Lausanne Switzerland*, 11-14.10.**1998**.
12. Jansson K.; FennoTriox, oxidative treatment system for pulp and paper waste waters, FINEXPO, Vancouver, Canada, **1997**.
13. Jansson K.; Kotimainen ratkaisu metsäteollisuuden vesistökuormitusongelmiin. *Kemia Kemi. Vol. 23(5),* 357-359. **1996.**

Patents

1. Jansson K., Tuhkanen T., Korhonen S.; Rening av bakvatten med ozon och peroxid, Patent, FI 110 683 B, **2003**.
2. Jansson K., Palonen H., Laine E., Ruohomäki K.; Process for removing manganese from water, Patent, WO2006/064084 A1, **2006**.
3. Kukkonen J., Aitta E., Oinas P., Jansson K., Nair M.; Compositions and processes for separation of bitumen from oil sand ore, Patent, US 2010/0258477 A1, CA2700692, **2010**.
4. Jansson K., Joensuu I., Piironen M., Sirviö J., Yrjänäinen T.; Method and system for treating chain treatment, Patent, BR 1120 1300 1498 -9 A2, **2012**.
5. Method for preventing microbial growth on filtration membrane, Patent, IL-233195, **2014.**
6. Costa M., Jansson K., Saari K., Method of treating oily waters, Patent, WO 2013/064484 A1, **2013.**
7. Jansson K., Joensuu I., Piironen M., Sirviö J, Yrjänäinen T.; Method and system for treating aqueous streams, Patent, CN103118755B, US 2013/015 3510 A1, **2013.**
8. Öjstedt U., Gramstad R., Jansson K., Kolari M.; Water Treatment, Patent. EP 2 653 448 A1, DK2653448T. **2013.**
9. Karpova T., Melin E., Vuori A., Öjstedt U., Garmstad R., Jansson K., Kolari M.; Water Treatment, Patent. US 9,617, 170 B2. **2017.**
10. Ilmola P., Jansson K., Joensuu I., Piironen M.; Method and device for monitoring and controlling the state of a process stream, Patent, US 9,970,919 B2. **2018.**

LIST OF ABBREVIATIONS AND DEFINITIONS

ADT
Air dry ton (cellulose pulp)

AOP
Advanced oxidation processes

AOT
Advanced oxidation technologies = same as AOP. However, used more commonly in the USA

AOX
Halogenated organic compounds

BAT
Best available techniques.

BCTMP
Bleached chemi-thermomechanical pulp

BOD
Biological oxygen demand

BOD is a measure of oxygen consumption of organic pollution in water. It is calculated either as BOD_5 or BOD_7, where the number describes how many days the incubation has taken. The BOD characterises the biological biodegradability and is closely related to the PV, as it describes this part of the COD_{Cr} that is more readily oxidised

$$PV\ (ppm\ O_2) = BOD_5(ppm\ O_2) * 1.5$$
$$PV\ (ppm\ KMnO_4) = BOD_5(ppm\ O_2) * 6$$

BREF
Best Available Techniques Reference Document

CFU
Colony-forming unit, used in microbiology to estimate the number of viable bacteria or fungal cells in a sample

COD
Chemical oxygen demand

COD_{Cr}
Chemical oxygen demand, oxidation with dichromate. Used for wastewater analysis

COD_{Mn}
Chemical oxygen demand, oxidation with $KMnO_4$. Used for raw water analysis

CAPEX
Capital expenditure, e.g., equipment investment costs

CTMP
Chemi-thermomechanical pulp

DAF
Dissolved Air Flotation

DIP
Deinking Pulp

ECF
Elementary Chlorine Free

EOP
Oxygen-peroxide delignification is a bleaching stage used in pulp manufacturing

FIM
Finnish Mark, the currency used in Finland from 1860 to 2002

HA
Humic acid

IED
Industrial Emissions Directive

IPPC
Integrated pollution prevention and control

KRAFT
Chemical Pulp made with the sulfate process

- Commonly applied chemical treatments of pulp and their symbols
- Chlorination (C): Elemental chlorine reacts with pulp in an acidic medium
- Alkaline extraction (E): Dissolution of the reaction product with NaOH
- Chlorine Dioxide (D): Chlorine Dioxide reacts with pulp in an acidic medium
- Oxygen (O): Molecular oxygen reacts with pulp in an alkaline medium at high pressure
- Hypochlorite (H): Hypochlorite reacts with pulp in an alkaline medium
- Peroxide (P): Peroxide reacts with pulp in an alkaline medium
- Ozone (Z): In this stage, the ozone reacts with pulp in an acidic medium
- Chelates (Q): Chelating stage
- Eo – extraction stage reinforced with oxygen
- Eop – extraction stage reinforced with oxygen and hydrogen peroxide
- X = enzymes stage
- Y = hydrosulfite stage
- Paa = peracetic acid stage
- Pp – pressurised hydrogen peroxide stage
- q – Semi-chelating stage (conducted in not ideal conditions)
- The numbers indicate similar bleaching stages, which can be several at one site.

Mw
Molecular weight

N_{tot}
Total nitrogen concentration analysed in the water

NOM
Natural organic matter

OPEX
Operating expenditure, e.g., operating costs such as energy, human resources, and chemistry as examples

PAM
Polyacrylamide

pH
The potential of hydrogen, a logarithmic scale of hydrogen-ion concentration gram atoms per litre

PEO
Polyethene oxide

P_{tot}
Total phosphorus concentration analysed in the water

Eh
Reference hydrogen electrode

SITRA
Suomen Itsenäisyyden Rahasto

SS
Suspended solids with a GF/A filter (10um)

TCF
Totally Chlorine Free

TMP
Thermo Mechanical Pulp

TOC
Total Organic Carbon

TABLE OF CONTENTS

1. INTRODUCTION

The pulp and paper industry is one of the largest industrial water polluters, discharging various liquid, colloidal, and solid wastes into the water streams. In addition, the industry generates significant volumes of wastewater for each metric ton of end product produced. These pollutants cause considerable pollution and eutrophication in the waterways, if not appropriately treated. These effluents contain compounds with high biochemical oxygen demand (BOD), chemical oxygen demand (COD), adsorbable organic halides (AOX), suspended solids (SS), fatty acids, tannins, resin acids, lignin and its derivatives, sulfur and sulfur compounds, and so on. Some of these pollutants are naturally occurring wood extractives, such as tannins, resin acids and lignin. Other pollutants are xenobiotic compounds formed during pulping and papermaking, such as chlorinated lignin, resin acids and phenols, dioxins and furans, making pulp and paper mill effluents challenging to treat by conventional methods such as chemical precipitation and biological treatment. Some of the pollutants listed above are recalcitrant to biological degradation and need a different treatment method to be removed (Purkait et al., 2019).

Advanced oxidation processes (AOP) have been developed for the Finnish pulp and paper industry over the past three decades to meet the tightened environmental limits when pure sedimentation, chemical precipitation and biological purification cannot reach the given environmental limit values.

Finland obtained its first Water Act in 1961 to regulate wastewater volume, pH, and suspended solids in pulp and paper discharges. When these new requirements came into force in the early 1970s, the industry met the emission requirements for suspended solids by applying sedimentation basins and existing dams. The neutral pH value could be easily controlled by dosing acids or bases before the outlet. In the late 1970s, discussions began about the need for new environmental restrictions to reduce biodegradable substances and phosphorus emissions. These emissions caused the strong growth of algae and other microscopic plants, leading to a lack of oxygen in the water streams. The new requirements led to biological treatment plant construction, whose design was taken from the municipal sector. Shortly after the first pulp and paper industry biological treatment plants had been put into operation in the mid-1980s, it was noticed that the expected BOD treatment requirements could not be met.

The entire biological treatment technology was new to the forest industry, which led to many new studies on its use and control. In addition, the forest industry's wastewater was much more concentrated and varied both quantitatively and qualitatively from municipal wastewater. The main thing was the control of the amount of incoming biological oxygen consumption (BOD) and the adjustment of its ratio to nitrogen (N) and phosphorus (P) while keeping the minimum dissolved oxygen levels in the aeration basin over 0.5 mg/L. The problem for accurate biological control was mainly in the BOD analysis, which took five (BOD_5) to seven (BOD_7) days to measure.

In the late 1980s, new environmental parameters with chemical oxygen demand (COD_{Cr}) and phosphorus (P) restrictions emerged. Especially with COD_{Cr}, which is a faster and more accurate method, it is better suited than BOD for controlling biological treatment plants. At the same time, the forest industry began to close the water cycle to minimise the amount of wastewater and save on the treatment plant's construction costs. In the early 1990s, it was noticed that the new given emission COD_{Cr} values were much more challenging to reach than the previously given BOD_7 values. It was soon observed that some of the analysed COD_{Cr} values are not degradable in the biological treatment plant. The part that could not be degraded began to be called hard chemical consumption (hard COD_{Cr}). The hard COD_{Cr} consists mainly of long-chain organic molecules or toxic substances for biology that do not have time to degrade under the given biological conditions.

During the 1990s, a number of research and development studies were initiated to improve COD_{Cr} purification and meet tighter environmental requirements. One of these studies was aimed at AOPs. Common to the AOPs is the in-situ production of hydroxyl radicals, known as the second strongest oxidant after fluorine. The most well-known AOP is Fenton's reagent, which uses a reagent consisting of a two-valent iron metal catalyst and hydrogen peroxide. Other well-known AOPs are based on hydrogen peroxide, ozone and UV radiation and their blends.

The author has been working with AOP technologies since 1992. Different chemical technologies, such as Fenton's modified Fenton's with both homogenous and heterogeneous catalysts, $H_2O_2+TiO_2$, $O_3+H_2O_2$, $UV+H_2O_2$, with H_2O_2, have been tested. Lately, from 2010 to 2020, electro-oxidation and electro Fenton's for mining industry applications have been studied.

2. OBJECTIVES AND SCOPE

The pulp and paper industry is one of the largest industrial water polluters, discharging various liquid, colloidal, and solid wastes into the water streams. In addition, the pulp and paper industry generates significant volumes of wastewater for each metric ton of end product produced. These pollutants cause considerable pollution and eutrophication in the waterways if not appropriately treated. Furthermore, these effluents contain compounds with, for example, high chemical oxygen demand (COD) that are partly recalcitrant to biological degradation and need a different treatment method to be removed.

This thesis aims to develop technologies based on AOPs to meet the tighter environmental limits given for the Finnish pulp and paper industry, following research based on AOP technologies. The presented research has extended over a relatively long time, and the methods presented have been developed to meet the then-current legislation and pulp and paper industry needs.

Chapter 6 discusses the modified Fenton's process used in pulp and paper wastewater as a tertiary treatment step to improve the COD_{Cr} reduction over an existing activated sludge plant. Discussions of the advantages and disadvantages of the modified Fenton's process, where a significantly higher catalyst dose is combined with hydrogen peroxide, are needed for the difficult-to-purify Kraft pulp wastewater.

Chapter 7 discusses decreasing the previously found modified Fenton's reagent's chemical dosing amounts and improving COD_{Cr} reduction over the existing activated biological treatment step. The scope is set to improve the effluent treatment plant inlet water's COD_{Cr} /BOD_7 ratio to enhance COD_{Cr} removal over the existing activated biological treatment plant without additional tertiary treatment steps.

Chapter 8 discusses developing a less hazardous AOP-based biocide for paper machines. The utilisation of catalytic metal-based AOP should be avoided and set as scope, as the process cannot tolerate soluble metals due to possible discolouring of the final product. The target is set to reach two orders of magnitude deactivation of the aerobic heterotrophs using AOP technologies. The AOP technologies rely on different dosage ratios of H_2O_2 and or O_3 to generate hydroxyl radicals that work as the microbiological control.

Chapter 9 discusses alternatives and more straightforward ways of removing the Mn^{2+} found in the raw inlet water to be treated. The existing oxidation, precipitation and microbiological control water treatment methods used in the Finnish pulp and paper industry are suggested to be simplified. As the scope, utilisation of new high oxidative compounds, the equilibrium and distilled peracetic acid are chosen against more common $KMnO_4$ and HOCl. Additional targets, such as readjusting the reaction pH and removing a separate biocide, are positive outcomes.

3. PULP AND PAPER WASTEWATERS

Before the foundation of the first university in Finland in 1640, paper usage in Finland was minimal. The first paper mill was established in 1667 in Tomasböle village in Pojo County. They used mainly linen, jute and cotton rag to produce handmade paper as raw material, and the production continued until 1713. However, this process could not significantly impact the residing water body. Only three paper mills existed in Finland before 1809. (Nikander et al. 1955) The current Finnish water judicial system dates back to medieval Swedish law. These early regulations were based on two parts: on the one hand, rights to use the water and, on the other hand, protecting harmful[2] waters from being mixed with natural waters. The 1734 Act already had many water management provisions that mainly focused on sawmills' sawdust that should not block the waterways. (Hallberg 2002, Hollo 2002)

After Sweden lost the war to Russia (1808–1809), Finland became a part of the Russian Empire (1809–1917). During that period, better raw materials were available, resulting in several new small paper mills starting their production just before the industrialisation of paper manufacturing. Still, the total number of Finnish handmade paper mills was only thirteen. (Kecskeméti 2007) In the 1900th century, the Nordic countries were known to be some of the poorest and most backward countries in Europe. (Blomström et al. 2002)

The next considerable leap in paper manufacturing in Finland was made when the first paper machine was installed at J.C. Frenkell's in 1842 in the City of Tampere. (Levlin 2008)

In 1857 and 1861, the saw industry was exempted from old laws that restricted the usage of steam-powered saws, leading to the fast growth of the forest industry. (Pekkala et al. 1933, Malm 1928) Finland's first mechanical wood grinding mill was established in Tampere in 1865. (Jalkanen 2008)

The 1734 Act was developed further in the 1868 Waterworks Regulation related to water distribution and utilities. Paragraph §15 forbade any material into the waterways that could raise the water levels and negatively affect the fairways or fishing waters. It was also forbidden for the sawmills to store sawdust close to the waterway to avoid being drawn into the waterways. (Hallberg 2002, Hollo 2002)

Due to the pulp market upswing during the French-German war in 1870-1871, the first integrated grinding pulp mill and paper mill was built in Valkeakoski to decrease the paper price by cutting the transport cost of pulp. (Malm 1928)

During the 1870s, fishing inspector E.J. Malmgren proposed an act forbidding industrial wastewater from being led into the waterways. The proposal led to the establishment of a committee to investigate the subject, which in 1875 resulted in more limited pollution restrictions than had initially been proposed. Thus, it was set that the mills sending their untreated wastewater into the waterways should not harm the fish. Additionally, it was suggested not to float unbarked wood logs and, in other ways, pollute the waterways. (Komitébetänkande 1875)

The first document relating to the birth of the Finnish Cellulose Industry took place on the 28th of September 1874 in St Petersburg, when Theodor Höffding submitted a patented proposal for a method to chemically dissolve wood for pulp production. The production, estimated to be 200-300t cellulose per year, started in February 1876 at the Nurmi Selluloosatehdas, which operated until 1880. The second caustic soda-based cellulose pulp mill started soon after in 1880 in Walkiakoski. The first Walkiakoski cellulose mill was based on the German Max Dresel patent, including cooker, circulation, and recovery units. The production capacity was estimated to be around 150t per year between 1881 and 1882. Later, in 1883, they purchased rights to the third Dresel cellulose cooking patent that included the spent liquor heating systems. In the autumn of 1884, C.F. Dahl started developing a new process where sodium carbonate alkali losses could be replaced with sodium sulphate. Sodium sulphate was cheaper than sodium carbonate and, at that time, regarded as a useless by-product of chlorine production. The utilisation of sodium sulphate resulted in smaller alkali losses, stronger fibre and better yield than with the soda process. The Walkiakoski company bought Dahl's new patent rights and upgraded the whole mill from soda-based to sulphate cellulose process.

After the upgrade and modernisation were done in autumn 1886, they could produce 800t per year and 2 300t per year cellulose after two years. The upgrade and modernisation resulted in considerably lower production costs and less polluting wastewaters per ton of pulp. Simultaneously, four new cellulose mills were built: Kuusankoski 1885, Nokia 1886, Kymi 1887, and Jämsänkoski 1888. All these new cellulose mills were based on the new sulphite process. (Cronström et al. 1968)

Later, the development of pulp-making from wood continued simultaneously with papermaking. The new industry was established along rivers and rapids to have access to free hydropower (Kuisma 1993).

The beginning of the Finnish Water Law Legislation could be said to have its origin in the 1888 Parliament, where it was proposed to renew the old main legal water acts. A new Committee was established in 1889 to investigate the subject, which resulted in the 1890s two new reports that divided the acts into three groups. These were acts related to making (1.) dikes and other water distributions, (2.) utilisation of water and (3.) suggestions for floating the forest products. (Hollo 2002)

In the early 1880s, the fishers stated that the new industry was causing a decrease in fish stocks. The reduction of fish stocks was thought to result from the pollution that caused oxygen lack, destroyed fish's gills, and ruined the spawning grounds. The pollution was stated to come from mining, chemical, textile, paper and cellulose, and other industries letting organic compounds into the waterways. Especially the chlorine and sulfuric acid originating from the cellulose industry were mentioned. As the committee set to renew the Water Law was not willing to investigate the fishing regulations, a new committee called Fiskerikomiten (The Fishing Committee) was established in December 1895 to investigate the reason for decreasing fish stocks and to make proposals for new fishing regulations, together with other measures that could benefit the country's fishing industry. (Kommitébetänkande 1898)

The committee gave its report in 1898 without making a conclusive proposal since the case owner had not completed the report. However, it stated that every strait or/and flowing water must be kept open and free from everything hindering the migratory fish in the king's veins. The regulation to keep openings in dams for migratory fish was set in 1868. Regulation on the protection of crayfish was set in 1875.

In 1890, these five cellulose mills reached 5 000t per year of cellulose production, and in 1900 eight mills were already producing 12 800t cellulose per year (Malm 1928, Cronström et al. 1968)

Development needs of society and health care arose in the City of Tampere after the strong growth of industrialisation and the population in the late 1900s. Around one-third of the Finnish labour force at that time worked for the industry. In the 1880s, the wells had been polluted with municipal and industrial waste, and epidemics were common. The mortality rate was higher than in other cities in Finland. The polluted wells led to the foundation of the city's Medical Board, which started to solve both the water supply and wastewater drainage problems. (Juuti et al. 2004)

The primary pulp and paper pollution, at that time, was related to off-gases from different process stages that were led directly to the air. Water pollution from cellulose mills was mainly related to fine fibre emission, and some residual chlorine and caustic originating from the bleaching steps could be found closer to the mill waste pipe. (Malm 1928)

By 1902, the Finnish Water Rights Act had already contained explicit general bans based on a permission system. The Water Works Act in the past inadequately regulated closing, modification, and anti-pollution measures, while its current form focused on water resources management. (Hallberg 2002, Hollo 2002)

One of the first examples of avoiding possible upcoming socio-political issues was building a new sulphate mill in Kotka in 1905 by W. Gutzeit & Co. As the people were already familiar with the earlier started Halla Sulphate Pulp Mill (1905) nauseating odours, W. Gutzeit sought solutions even before he was granted permission by the city to build one. He turned to the German Weissenfield Sulfate Pulp Mill that was claimed to be odourless and described the owners as both technological and economical, the best in the world. The Weissenfield mill had developed a new pulp cooker that developed less odour. After several discussions and travels to Weissenfield with health authorities from Kotka and Helsinki, Guitzeit was granted building permission in late 1905. (Huhtanen 1996).

In 1907-1908, five additional new sulphate pulp mills were built. The reasoning behind why so many new sulphate-based processes were built was better energy economy and chemical recovery. Four new sulphite-based mills were built, two in 1910 and two in 1914. The total capacity of the Finnish cellulose industry had grown from 1900 18 400t per year to 100 000t per year in 1910. (Cronström et al. 1968)

In 1908, a national committee called the Sulfatisellu Komitea (Sulphate Committee) was established to review the environmental problems caused by the new sulphate mills[1]. The investigation targeted whether the new sulphate process endangered health by air emissions and affected the fish breading near the mill's locations. Also, suggestions and how these could be avoided were expected. As a result, air emissions were mainly caused by organic sulphur species, which were the primary problem. The smell from these mills could be detected over a distance of 40km under favourable conditions and was accused of causing headaches and nausea to some people, whereas water pollution was of secondary importance. The water problems were mainly related to fine fibre material sedimentation in the bays close to the mills, affecting fish reproduction negatively, and in some cases, the material was also expected to clog fish gills. At this time, the effective distances of the pollution were relatively short, typically much less than 500m from the discharge point. Investigations conducted at European sulphate pulp mills sought technologies to mitigate the pollution. Air pollution could be reduced with an enlarged off-gas condenser that could better capture the harmful gases. Water pollution originated from fine fibre emissions and could easily be reduced by installing sedimentation tanks. The committee also suggested activities to mitigate the harm caused to human health, protect the mill's neighbours from harmful effects, and give possible compensation for the dangerous operation. Also, it was suggested to provide the Senate authority to close mills if they were causing substantial harm to the common interest.

However, the improved capture of spent liquor steams with effective condensers was not effective enough to remove all residual nauseating odours and turpentines, as the final option was to release these condensation waters to the recipient waters. Water pollution was more related to sulphite pulp manufacturing, as the sulphate process could recycle most of the chemicals. Still, emissions of fine fibres in the recipients were a problem for both processes. A suggestion was made to install sedimentation tanks to reduce the fine fibre emission from the mills. (Komiteamietintö 1909)

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[1] Only the sulphate process has/had the problem with smelling gases.

On November 18th, 1909, the Industry Board asked for a second opinion from Tekniska Föreningen i Finland to review the proposals given by Sulfatisellukomitea (Tekniska Föreningen i Finland 1909).

These suggestions were depressed by the Finnish-speaking technology society in 1910. They claimed that the weak point of the committee's suggestion was the subordination of industries' technological subjects to local authorities. Also, it made them depend on people's judgement and gave decision-making power to people who did not even have the context to understand the processes. Additionally, they stressed that it was essential to develop a uniform technical regulation for methods that could be used to mitigate the environmental pollution problems caused by the sulphate pulp mills. Therefore, the society suggested forming a separate technological committee to establish and develop these regulations[2]. (Tekniska Föreningen i Finland 1910)

The raw tall oil recovery was started at three different mills in Finland in 1911. A couple of years later, the distillation of tall raw oil into more value-added products for paint, lacquer, ink, and later for mining, pharmaceutical, and glue-plastic industries started. On average, the tail oil recovery was 40kg/ton of pine per pulp at W. Gutzeit & Co Kotka mill from 1912 to 1913. Distillation of methanol had also started in 1912 at three different mills. However, the raw turpentine was the most essential first by-product from the Finnish sulphate pulp mills. (Stenlund et al. 1983)

Before the first World War (WWI), a very strong forest industry had already been established in Finland with around 600 sawmills, three plywood mills, 17 chemical pulp mills and 25 paper mills (Luonsi 1987).

During WWI, the cellulose capacity was growing fast due to the higher demand caused by the Waldhofmill capacity loss in Estland, which was burned down by the Russians on the 20th of August 1915, besides some other smaller mills in the area. The increased cellulose production capacity increased exports mainly to Russia (the primary market) and later to Germany and England. (Malm 1928, Rantakari 1944)

On the 6th of December 1917, Finland was declared an independent country. In the autumn of 1918, the Finnish government met the big

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[2] Later came available in 2000 in the BREF documents.

cellulose producers to discuss possibilities of manufacturing sulphite spirit for the engines due to the high prices of motor petrol. The upcoming need to manufacture sulphite spirit led to the direct building of production processes that could produce sulphite spirit from the spent liquors. It was considered essential to the country with the additional benefit that the raw material existence was plentiful. However, the government cancelled the contract already in 1919 due to possible abuse of the produced sulphite spirit. (Malm 1928, Cronström et al. 1968)

One of the first steps towards more environmentally sound processes was taken in 1920 when the first alcohol manufacturing processes were adapted to use sugars from the sulphite pulp spent liquor (Paasonen 2011).

In 1927, four new mills were built: Johannes, Läskelä and Lievestuore Sulphite Pulp Mill and Kemi Sulphate Pulp Mill. (Finska Cellulosaföreningen 1928)

The first mills started in the 1930s with their water protection committees that voluntarily measured and collected data about the waterway's conditions. The voluntary measurements and data collections were done even when there was no requirement from governmental protection agencies or legal authorities (Murto 1966).

In the autumn of 1938, the Finnish Cellulose Union had foreseen the possibilities of the upcoming war and set up a technology committee to review the possibilities of rapidly increasing production of sulphite spirit in case fuel import to Finland became worse. However, after the start of WWII in September 1939, Finland had challenges in shipping the cellulose through the Baltic Sea. In December, Läskelä, Pitkäranta, and Johannes mills were stopped, whereas Enso barely continued the production. As a result, the total production fell by 40%. (Finska Cellulosaföreningen 1939)

In 1939, the Hällfors Committee published a proposal for a new Water Rights Act with extensive justifications. Due to the wartime condition of World War II (WW II) and the critical feedback from the higher juridical levels, the Hällfors committee's proposal was buried for the time being. (Hollo 2002)

With the Winter War peace, Finland lost 390 000t or 20.4% of the total pre-war cellulose capacity. In 1940, the capacity had decreased from 1939 642 000t to 307 700t (Finska Cellulosaföreningen 1941)[3]

In June 1941, Finland was at war again and continued the wartime economy until the end of 1944. (Rantakari 1944)

The wartime economy by-product from sulphite cellulose was of great value. As a result, three lubricant factories were established to produce sulphite spirit, raw turpentine and liquid resin. (Finska Cellulosaföreningen 1943, Cronström et al. 1968).

The production capacities of cellulose started to grow quickly after WWII. In 1944, it was 434 000t, 1945 492 000t, 1946 739 000t and in 1947 954 000t despite the lack of basically everything during the two years after the war. (Finska Cellulosaföreningen 1945)

First, in 1948, production rose to 1 000 000t or only 2/3 of the pre-war levels. Regarding technology, it was 10-15 years behind its time. However, the efficiency of the mills improved considerably when raw materials and production goods started to flow into the country.

By the late 1940s, the quality of Finland's water bodies had started to decline. The need for water pollution control and legislation was described by the specialist journal *Kunnallistekniikka*, which was driven by the oxygen depletion in many water bodies, such as the three main rivers Vuoksi, Kymi and Kokemäenjoki, serving the industry and the communities that had become a health risk while also reducing the fish stock. (Makkonen et al. 1947)

First, after the Water Act was put into force in 1962, the pulp and paper industry faced a new chapter when water emissions needed to be treated. Firstly, the focus was on effluent volumes and amounts of suspended solids sent to the recipients. Second, the industry needed to build

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[3] Finland lost with the Winter War peace Enso-Gutzeit Sulphite and Sulphate Pulp Mill in Enso, Hackman & Co Sulphite mill Johannes, Oy Läskelä Ab (Kymmene Ab) in Lääskelä, Pitkäranta Oy Sulphate Pulp Mill in Pitkäranta, Oy Waldhof Ab in Käskisalmi and The Wiborg Wood Company's small Sulphite Pulp Mill in Suojärvi. The total loss was 390 000 t or 20,4% of the total pre-war cellulose capacity.

sedimentation ponds and clarifiers to remove residual fibres from the emissions.

By the beginning of the 1970s, Finland and the rest of the Western world realised the importance of environmental protection, which appeared in general discussions and newspapers. As a result, new environmental limits on amounts of biological oxygen demand (BOD_7) were placed in the mid-1980s as new parameters, and the industry needed to add biological treatment stages, secondary sedimentation clarifiers and sludge treatment to reach the new requested limits. Simultaneously, chemical like coagulants and flocculants was applied to improve the existing treatment whenever needed.

In the late 1980s, the industry started closing the water loops to avoid extra capital expenditure (CAPEX) costs related to higher-than-needed wastewater treatment plant flows.

The pressure to minimise the environmental load arising from the pulp and paper mills significantly increased in the 1990s. There have been several driving forces behind this development, such as growing environmental concerns, tighter legislation, and a better understanding of how to control emissions when processing raw wood-based fibre materials. (Dahl et al. 2008). By the mid-1990s, new technologies were sought to deal with tighter environmental limits based on BOD_7, COD_{Cr} and P_{tot}. Especially the recalcitrant COD started to become of interest.

3.1. Typical composition of pulp and paper wastewaters

This section describes pulp and paper wastewater composition. The introduced concepts and measurements of water qualities are for understanding the difficulties of developing new treatment methods. It is necessary to understand what compounds the existing treatments can remove from the waters and what compounds they cannot remove.

The pulp and paper wastewaters contain high concentrations of mainly organic compounds, causing biochemical oxygen demand (BOD) and chemical oxygen demand (COD). The highly coloured black-brown filtrates and wastewater streams consist mainly of chromophoric compounds originating from the wood extractives, lignin derivatives and organochlorine compounds, many of which are recalcitrant. These recalcitrant compounds are known as non-biodegradable and persist in the environment. The compounds are very stable and chemically inert due to substitutions with halogen, nitro, and sulfonate groups. However, some of these compounds are insoluble in water and highly toxic or cause highly toxic degradation products. (Ahn et al. 2009, Dahlman et al. 1995, Franta et al. 1994, Freire 2003, Kamali et al. 2015, Karrasch et al. 2006, Kovacs et al. 2002, McKague et al. 1996, Muna et al. 2011, Pokhrel et al. 2004, Sinclair 1990, Uğurlu et al.2008, Zhao et al. 2014). *Table 1* shows the origins of typical pollutants found in pulp and paper process steps.

Table 1. Origins of primary pollutants in pulp and paper process (after Ahn et al. 2009)

Wood preparation	Digester house	Pulp washing	Pulp bleaching	Papermaking
SS, BOD, dirt, grit, fibre.	BOD, COD, AOX, VOC.	High pH, BOD, COD, SS, brown colour.	Lignin, carbohydrate, colour, COD, AOX, VOC, chlorate, dioxins, furans, chlorophenols	Particular waste, organic compounds, inorganic dyes, COD, acetone

The cellulosic plant materials consist of three main components. These are cellulose, hemicellulose, and lignin. Different wood parts need to be removed to obtain the targeted pulp properties depending on the targeted pulp qualities. In many cases, pure cellulose is the most sought-after one. Typically, the hemicellulose and lignin should be removed when the target is higher strength and has whiter pulp qualities. Removing more hemicellulose and lignin from the pulp corresponds to a lower yield.

However, lower yield means more organics in the water phase, and if not used, collected, or otherwise treated, they will end up as emissions. *Table 2* summarises the different yields of pulp processes and their main applications. The higher the yield is, the smaller part of the processed wood is dissolved in the water, and the probability of these dissolved compounds ending up in the waste stream is lower. For example, the sulfite process has the lowest yield, showing that most of the lost yield is dissolved in the process waters, from where some parts end up in the wastewaters to be treated. The opposite is the GW process, which has the highest yield of the presented process, resulting in more minor water emissions.

Table 2. Example of different pulp yields and uses, Biermann C. 1997.

Process	Yield%	Uses
Sulfite	40-45	Dissolved pulp, tissue, paper pulp, speciality pulp
Kraft (sulphate)	45-55	Kraft paper, tissue, paper pulp
BCTMP	90-94	Board strength, diapers
TMP	93-95	Newsprint and paperboards
GW	95-97	Newsprint and paperboards

Water contamination originates from various process stages such as debarking, pulping, screening, pulp washing, bleaching, paper machine, and coating processes.

From the very start, Finland's pulp and paper industry noticed the benefits of raw material recovery from different filtrates and the possibilities to avoid unnecessary pollution of the environment. This methodology simultaneously improved their economy but also reduced emissions.

Figure 1 presents the most common solids liquid technologies starting from 2 mm coarse particles removal with screens down to the 10 nm particle removal with ultrafiltration (Fawell et al. 2017)

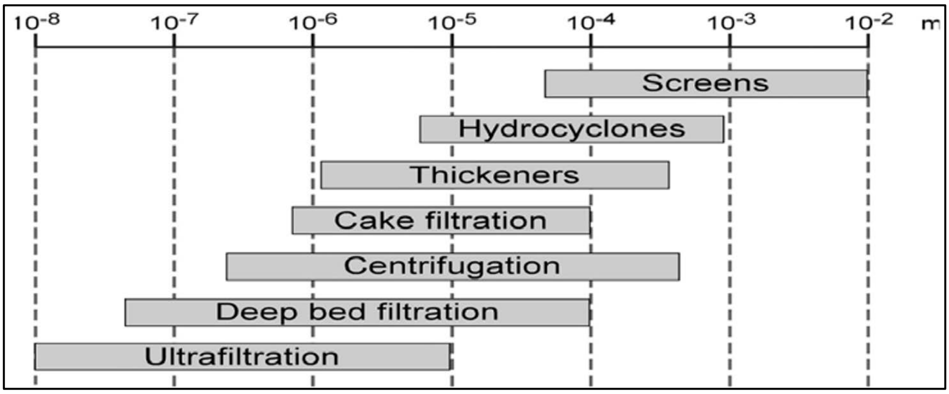

Figure 1: Most common solid-liquid separation technologies (Fawell et al. 2017).

Figure 2 shows typical treatment methods related to impurities and sizes found in pulp and paper industry wastewaters, together with the most current treatment technologies. For example, it is challenging to remove pure soluble particles when using only chemical methods such as polymers and coagulants. Ion exchange, meanwhile, can remove pure soluble ions but requires suspended and colloidal-free inlet water.

The reverse osmosis membranes (RO) and evaporation technologies are used down to desalination levels. Thus, the challenge is related to these processes' capital expenditure (CAPEX) & operational expenditures (OPEX).

A combination of biological treatment and sedimentation is generally found everywhere in Finland. The limits of biological treatment are several. It needs considerable space, takes weeks to a month to start operating, and needs a stable inlet feed.

Perhaps the most common way to treat highly contaminated filtrates in chemical pulping is by evaporation. Evaporation is a high capital expenditure (CAPEX) & operational expenditures (OPEX) value technology, but contrary to membrane technology, it has better runnability[4] for this kind of water.

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[4] Evaporators do not clog as easily as membranes do

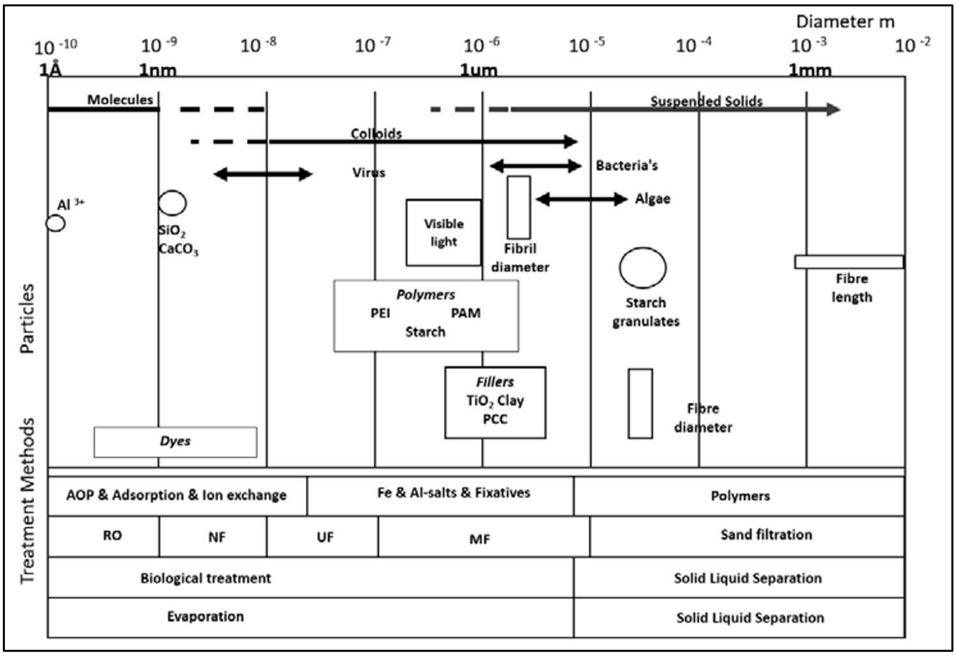

Figure 2: Typical impurities in pulp and paper, along with the most common treatment methods.

The slow biodegradation of some of the pulp and paper waters may be caused by compounds not recognised as a nutrient source for biological treatment. These features make the biological treatment insufficient for removing these compounds and lead to a search for new treatment technologies to comply with the new tightening environmental limits often expressed as COD_{Cr} instead of BOD_7.

The first method to characterise water has been to separate soluble COD from the total sample by letting the sample settle in a cylindrical settling column for two hours and then taking the supernatant for further testing. Other methods are based on filtering samples through a Whatman GF/C filter to separate the soluble (filtered) sample from the rest. (Cabera 2017, Dold et al. 1980, Ekama et al. 1986, Henze 1992, Orhon et al. 1994, Orhon et al. 1997)

A new own particle fractioning method was developed. This method utilised centrifugal filters with preselected cut-off molecular sizes to improve our knowledge of the substances found in different pulp and paper processes. This molecular size cut-off allows plotting molecular size distribution against COD_{Cr} measurements between each stage, *Figure 3* and *Figure 4*. These figures show apparent differences between pulp and paper process wastewaters. It shows that the CTMP process releases the highest amounts of COD_{Cr} in the colloidal area and the proper soluble areas. The minor COD_{Cr} discharge originates from fine paper production, where only fibre and fillers are present.

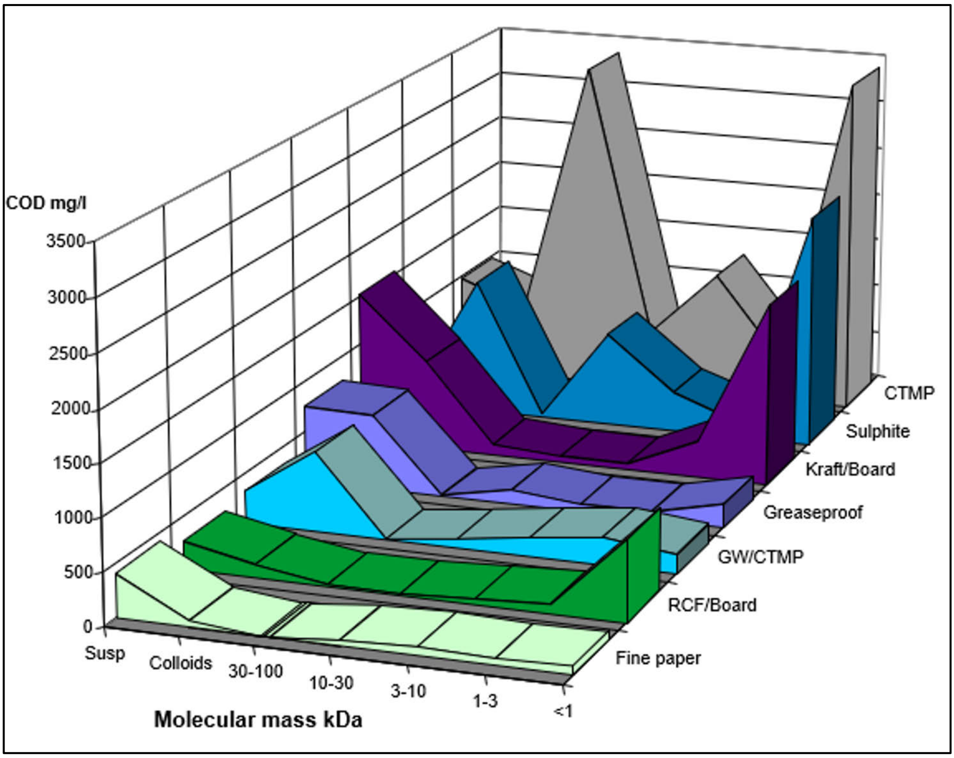

Figure 3: The COD_{Cr} mg/L versus the molecular weight in different fractions for pulp and paper effluent types. (Gytel et al. 2000)

Analysing the spaces between the different filter cut-offs made it possible to identify the main groups of impurities in pulp mill waters, *Figure 4*. Carbohydrates, especially the low molecular weight COD_{Cr}, basically sugars, top the total relative amount.

Figure 5 shows the COD_{Cr} removal efficiency of given treatment methods on pulp mill effluent effectiveness on the low molecular molecules such as carbohydrates. The chemical treatment is more effective in the colloidal range where extractives and lignins are present. The combined treatment has the most significant positive effect.

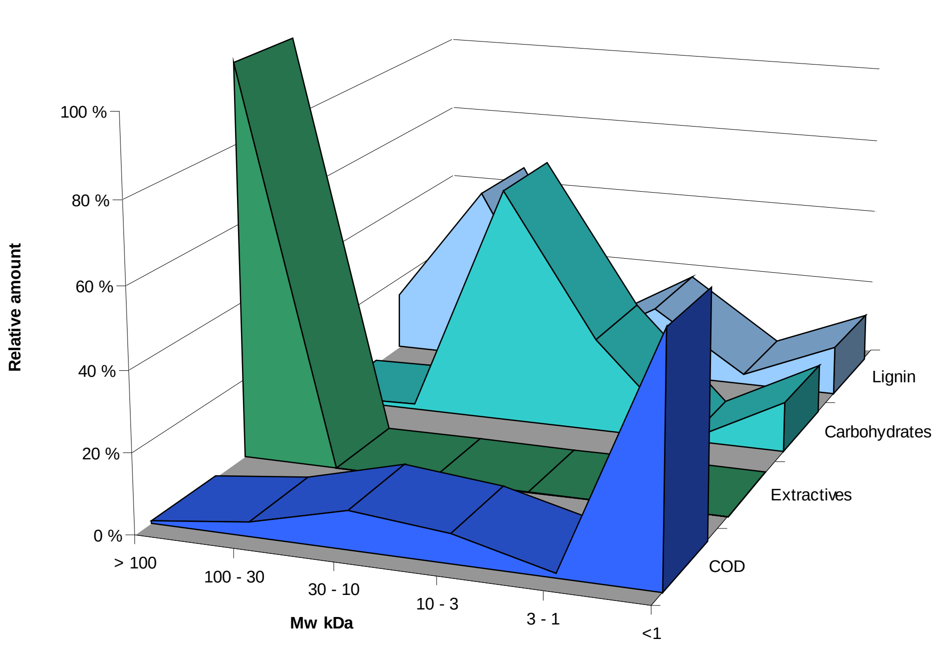

Figure 4: The different bleached pulp composition versus the molecular weight. (Gytel et al. 2000)

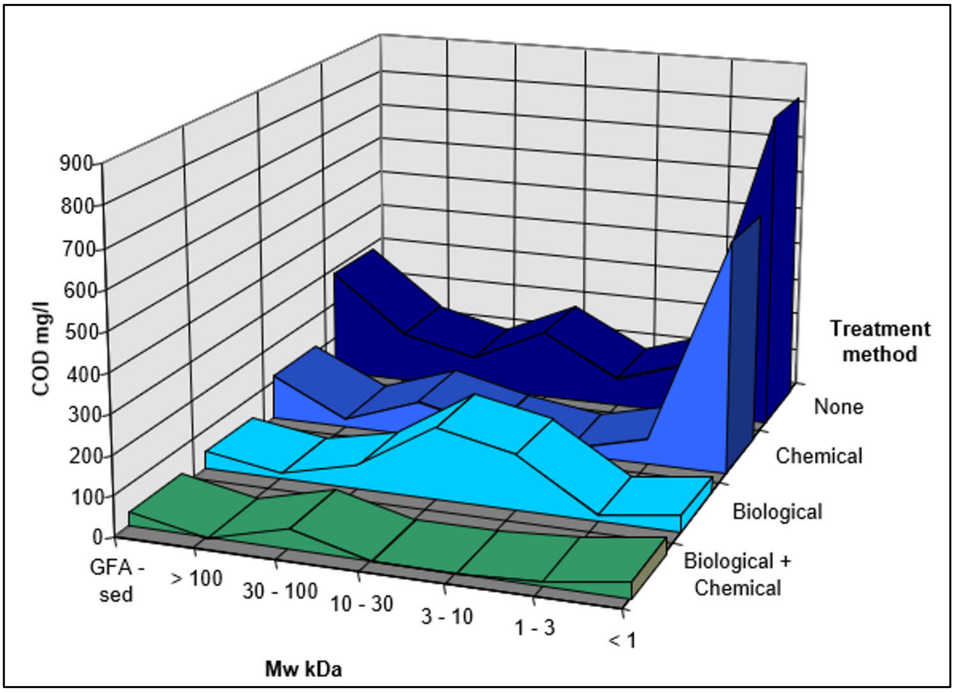

Figure 5: Different effluent treatment methods impact on bleached pulp effluent molecular distribution. (Gytel et al. 2000)

Figure 6 shows the benefits of modified AOPs (in this case, the FennoTriox system) over the normal coagulation to decrease the COD of bleached pulp mill effluent over a wide molecular size. These clearly show the benefit of combined coagulation and oxidation against traditional coagulants such as AVR[5]. (Gytel et al. 2000)

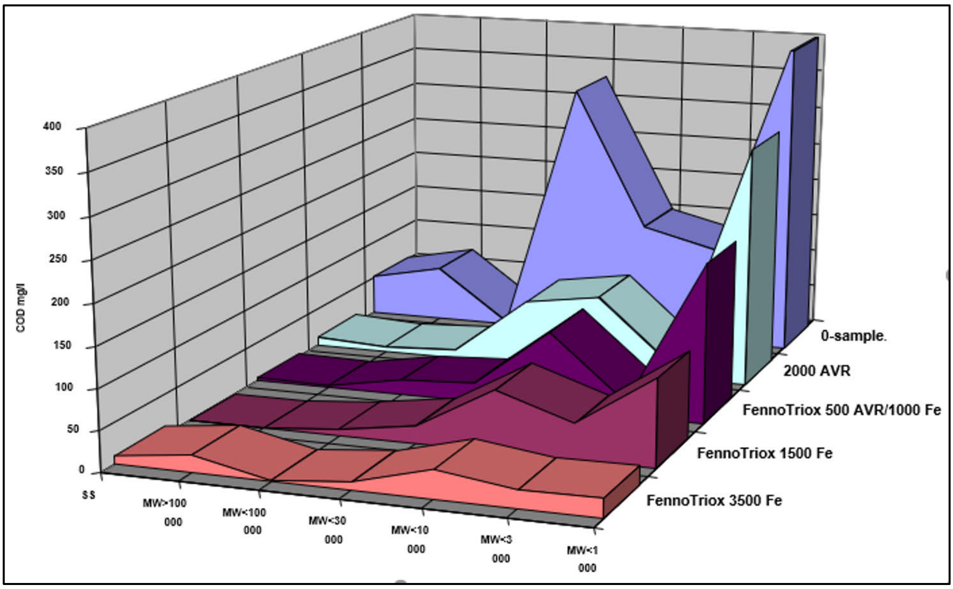

Figure 6: Effect of different chemical treatment methods on bleached pulp effluent. (Gytel et al. 2000)

3.2. Differences between BOD, COD and TOC

The degradable and non-degradable carbon needs to be understood correctly to understand why AOPs have been selected to remove these compounds from the waters. To select the correct treatment methods, information on organic strength or the organic load of the water is necessary. Three different measures of organic load are available, and they all have their benefits and weaknesses. (Boyles 1997, Lee et al. 2016)

The most used method to determine the biodegradable carbon is the 5- or the 7-day BOD (BOD_5 or BOD_7). The BOD measures the oxygen uptake over a 5- or 7-day period consumed by a small number of bacteria confined in the dark bottle containing the water to be analysed. During this time, the biodegradable organic carbon is taken up by the bacteria. This oxygen

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[5] AVR is a product name used by Kemira for a coagulant containing both aluminium and iron

uptake corresponds to decreased dissolved oxygen in the measurement bottle. This biodegradable carbon is expressed in oxygen units per ml. Initially, the test was introduced to measure the oxygen depletion in receiving waters caused by the residual degradable carbon in the different effluent. However, its primary value is regulating the composition of effluents from the treatment water. For process management, where knowledge of the influent's organic loading is required, BOD is of limited value because of the extended analysis time required to make the measurement.

The COD analysis is a fast and straightforward analytical method to measure the amount of oxidisable material in the water. The water sample is heated in strong sulphuric acid containing potassium dichromate. In the following reactions, oxidised carbon is determined by the amount of dichromate used up in the reaction. The result is expressed in units of oxygen rather than carbon. However, its weakness is that the recalcitrant organic carbon compounds that are not biologically oxidisable are included in the value obtained.

Conversely, some aromatic compounds, including benzene, toluene, and pyridines, which bacteria can break down, are only partly oxidised in the COD procedure. Thus, the COD value will overestimate the carbon the activated sludge treatment process can remove. Nevertheless, it is the most used system today for process management, as the analysis only takes 2 hours and can thereby be used for process control.

The Total Organic Carbon (TOC) is analytically straightforward to measure. It involves oxidation by combustion at very high temperatures and measurement of the resultant CO_2. However, TOC values include stable organic carbon compounds that cannot be broken down biologically. Therefore, TOC is the most accurate and fastest method of these three analyses.

The values obtained for BOD are consistently lower than those for COD, because activated sludge bacteria cannot degrade some of the compounds oxidised chemically in the COD test. Some of the carbon removed during the BOD test is not oxidised but ends up in new bacterial biomass. This means the BOD measures only the biodegradable carbon oxidised by the bacteria and can be removed in the biological wastewater treatment plant.

The ratio of BOD/COD will depend on the composition of the wastewater. For pulp and paper wastewaters, the ratio is around 0.3-0.6. However, for effluent leaving the treatment plant, it is closer to 0.2-0.3. The lower ratio results from readily biodegradable organic carbon removal during biological treatment, especially for chemical pulp manufacturing, leaving behind compounds not broken down by the bacteria. Thereby, it is called 'Hard' or "recalcitrant" COD or BOD.

The time course for removing the organic carbon varies with the activated sludge bacteria's ability to digest it. Small molecular weight compounds will start to be removed from the sewage immediately after it has entered the activated sludge tanks. Their removal may be completed in 1–2 hours. Meanwhile, the higher molecular weight compounds will take several hours to be degraded and removed. Some other compounds are more recalcitrant and may still be present after several days.

The net result is that larger, complex organic carbon molecules may not be degraded because the treatment time (hydraulic retention time) is not sufficiently long. Therefore, they will pass out in the effluent. To summarise, organic carbon's description in waters is shown in *Figure 7* (Gray 2004).

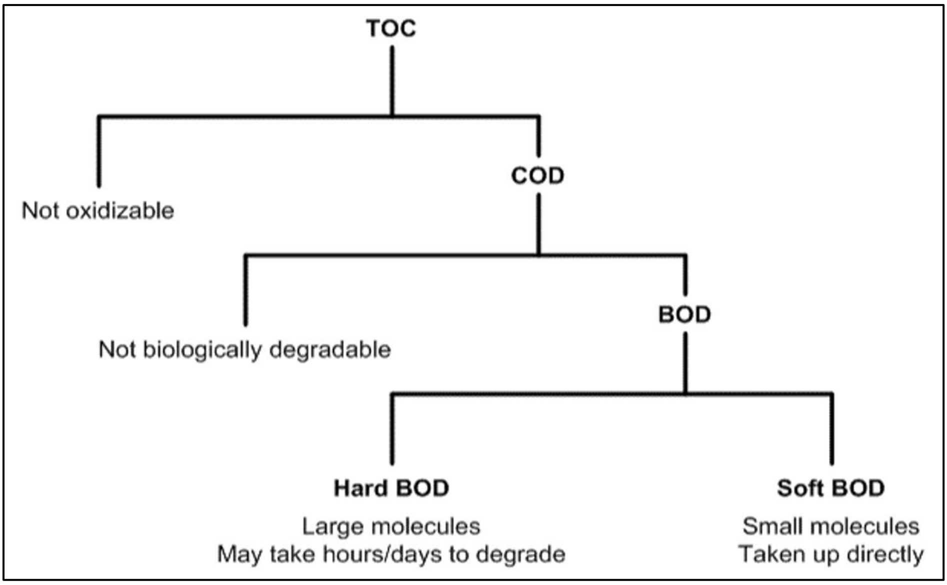

Figure 7: Relationship between the organic carbon fractions in wastewaters (Gray 2004)

4. DEVELOPMENT OF LEGISLATION AND TECHNOLOGIES

This section presents the background and development of AOP systems for pulp and paper industry water treatment. It follows the Finnish pulp and paper environmental development, actions and legislation progress from 1962 to 2020.

When the Finnish Water Act entered into force in 1962 with the first fundamental set of environmental limits based on wastewater flows, pH and Suspended Solids (SS), these environmental limits could be reached with sedimentation basins, ponds and tanks. In the late 1970s and early 1980s, the environmental limit focused on removing organics (BOD) present in wastewater. Reaching these new BOD levels, adapting biological treatment processes to existing treatment plants became necessary. By the late 1980s, new environmental parameters such as COD were given to improve the treated water qualities. These new limits resulted in many cases of adding chemical treatment steps to the existing treatment plants. However, even if the BOD removal rates over 95% were reached after the mid-1990s, the COD removal rates lagged behind often in the 60-80% range. Therefore, the industry sought alternative technological methods to improve COD removal rates. AOP was one of these technologies that saw its development in the early 1990s for the Finnish pulp and paper industry.

4.1. The 1960s and 1970s: First Water Act

In 1962, the new Water Act (Oikeusministeriö 282/1962) came into force with associated law settings, enabling the authorities to set legal requirements and time schedules for compliance with the industries polluting the lake and river waters. In addition, new legislation was brought into force to enhance the development of environmental protection. These legislation limits came with an acceptable level of suspended material in the wastewater that could be discharged (typically 4 to 2.5%). Furthermore, ground-based sedimentation basins were built to capture the fibre emissions before the water was discharged to the recipient.

An interesting development during this time was the collection and reuse of fibres from the bottom of rivers and lakes. Oy Keskuslaboratorio Ab showed that fibres suspended for decades in the sediments exhibited only minor changes. Many companies, such as Sunila Oy and the Imatra mill[6], started to utilise these reusable fibres. Pumping fibres from lake sediment lasted until the beginning of the 1970s as long as there was an economic benefit. (Hynninen 2009)

By the beginning of the 1970s, Finland and the rest of the Western world realised the importance of environmental protection, which appeared in general discussions and newspapers. Although, according to Luonsi (1987), the studies and works done within the pulp and paper industry in the previous decades on capturing the value of the suspended solids recovered from the lake sediments, the focus was set on reducing the overall suspended solid emissions by applying sedimentation to basins.

In January 1977, the Finnish government formed a Sulphite Committee to review the current diminishing Sulphite cellulose production capacities in Finland and its impact on the national welfare. *Table 3* and

Table 4 estimated the investment needs for the Sulphite cellulose industry from 1970 to 1980 with both production and environmental needs. The presented estimated investments are related to process development needed to improve sulphite production's cost competitiveness and continuation. The environmental investments included only those not focused on improving the cost competitiveness or the production continuation. Neither did these include maintenance and repair costs. (Komiteamietintö 1978)

Table 3. The estimated environmental and mill investments 1970-1980, MFIM (Komiteamietintö 1978)

Year	Production	Environmental	Total
Before 1980	191	105	296
1980s	289-344	46	335-390

Table 4. Estimated investment of Finnish Pulp and Paper 1972-1985, MFIM (Komiteamietintö 1978)

Parameter	1972	1980	1985
SS t/d	750	200	-
BOD_7 tO_2/d	1 300	650	400

In 1978, 71 primary sedimentation basins were used at 43 mill sites. Later, some were converted into aerated lagoons to capture soluble organic loadings. The sediment basins' design was mainly copied from the USA, where municipal treatment plants already used similar round-shaped sedimentation basins. (Hynninen 2012)

The first experience of the aerated lagoons was that the efficient removal of the BOD_7, on average, was 55–70%. Still, there was significant difficulty removing SS and sensitivity to annual temperature variations that affected the organic removal. Additionally, the process cultivated poor sedimentation bacteria, which could easily cause a 1-1.5g/l SS load to the recipient water. This handicap resulted in examining an activated sludge process that could remove both the BOD_7 and the SS more efficiently. (Hynninen 2012)

Because of the increasing public pressure on the pulp and paper industry's environmental emissions, SITRA created, in the late 1970s, a research program called "Industrial Effluents" (TESI 1978-1980). This research program focused on enhancing the technological knowledge of water treatment and suggesting new environmental limits for the 1980s. As a sub-target, it was stressed that the amount of Finnish technology used in water treatment should be raised. Some of the topics studied in this research program are shown in *Table 5*. (SITRA 1981)

Table 5. Some of the main topics studied in the Industrial Effluent program TESI 1978 – 1980 (SITRA 1981)

How to decrease the environmental loadings of a Finnish integrated mechanical / paper mill
The enhancement of the Finnish pulp and paper mill's primary sedimentation basins performance
The utilisation of biological treatment technologies in the Finnish chemical pulp mills

This research program resulted in new information regarding the upcoming biological treatment type plants and their dimensions. From a technical point of view, it was realised that the suspended solids and organic components could be removed very efficiently using biological processes – but phosphorous removal was still a problem. (Ruonala 1993)

One of the significant outcomes of this research program recommended more stable wastewater flows to enhance the operation of the sedimentation basins (Saunamäki 1980).

4.2. The 1980s: Technologies to comply with BOD

By the end of the 1970s, a new step was taken by focusing on the organic removal of the pulp and paper effluents and adapting activated sludge treatment plants to the newly commissioned primary sedimentation basins. Additionally, the environmental impact of sulfite pulp processes and chlorine-based bleaching later led to the shutdown of specific processes or changes in the bleaching sequences.

New biological treatment plants emerged in the mid-1980s with new water emission parameters. The first significant beneficial changes in the pollution levels began to be seen in local rivers and lakes. Many mills had their old effluent limit revised to tighter ones, including the new BOD_7 and P_{tot} limits.

Many activated sludge designs were copied from existing municipal treatment sites abroad. However, there was little understanding of the changes required to make these processes function in a pulp and paper industry where typical effluent concentrations were 10-20 times higher than in municipal wastewater. In addition, the inlet wastewater load and quality variations occurred over hours instead of days. These quality variations caused high variations in the Food to Microbes (F/M) ration[7], followed quickly by a lack of oxygen and nutrient due to bulking sludge[8].

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[7] F/M or Food to Microbes ration describes how much food (BOD_7) kg is given for each kg of Microbes (MLSS) found in the biological stage.

[8] Bulking sludge indicates a state of activated sludge treatment, where the bio sludge is raising up to the surface instead of sedimentating to the bottom of the secondary sedimentation basin.

These new limits on reducing the soluble organic loadings (BOD_7) forced the industry to build and operate biological treatment plants[9]. However, new operational challenges emerged with the biological treatment plants, such as the phosphorous loadings caused by the additional nutrients needed to operate the biological processes. Simultaneously, the development of new control strategies for the operation of the new WWTP was set.

In general, this adaptation of biological treatment plants consumed more resources than predicted in the 1970s. As a result, much new research was directed to learning how to operate the new biological effluent treatment plants unfamiliar to the industry.

New water treatment technologies emerge to comply with the tightening environmental limits and hope of new technology sales from the water technology companies.

The main legal focus was set on developing the Water Act and new environmental emissions limits. However, during the same period, the public pressure to close the Sulphite Pulp Mills increased due to their high-water emission levels. As a result, new emissions targets of BOD_7 and total phosphorus (P_{tot}) as mg/L were given in 1985-87.

The first equalisation and emergency basins started to emerge at Kraft mills (Joutseno Pulp Oy, Metsä-Botnia Oy in Äänekoski, Oy W. Schauman. Pietarsaari). Their design parameters were set to around five hours of effluent flow volumes. At the Joutseno mill, the basins included an emergency basin with a retention time of 7 hours, mainly meant for the bleaching filtrates (Luonsi 1987).

New environmental parameters and limits emerged in the late 1980s and early 1990s with the addition of COD_{Cr}, SS, and P_{tot}. Practically, this transfer was challenging as BOD_7 is probably the correct parameter to follow the soluble organic removal over a biological process. COD_{Cr} is an even larger clump measurement that includes the values of organic suspended solids, the reductive, and even some of the oxidative chemistry present in the water. Typically, the proportion of $COD_{Cr,tot}/BOD_7$ for pulp paper untreated waters is around 2.2 to 2.7. After the biological treatment, the typical amount of BOD_7 removed was approximately 99%.

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[9] Mainly activated sludge treatment plants.

Generally, only around 75% of COD_{Cr} could be removed from Kraft mill effluents. Metsä-Botnia Äänekoski's new Kraft mill was the first one to be given COD_{Cr} permits.

After commissioning the first activated sludge treatment plants in the mid-1980s, it became clear that something was wrong with the biological process due to the higher-than-expected residual BOD_7, SS, and P_{tot} values in the emissions. A large part of this problem was low secondary sedimentation efficiency, which led to high amounts of suspended particles in the effluents. However, because most of these suspended particles consisted of biological sludge, it also resulted in higher BOD_7 and P_{tot} values in the emissions.

Furthermore, seasonal variations still affect the biological process and the emission limits. It had been noticed that, from October to the following April, the performance of the biological process was challenging. This challenging operation was caused by the seasonal increase in the wood's sugar content, which stretched the limits of the effluent treatment plant, especially the oxygen supply. (Jansson 1992)

Also, the challenges of controlling phosphorous emissions continued. The main problem was that bacteria needed phosphorous to grow and clean the water. However, when the bacteria die, they release phosphorus into the water. Consequently, this made it very difficult to know precisely which part of phosphorous was being measured in the emission and how to control it. For example, did a direct overdose of phosphorus cause it, or was it just a result of decomposed bacteria?

The main issues with these early-activated treatment plants were the insufficient aeration capacities and an uneven oxygen distribution into the basin. This uneven oxygen distribution caused oxygen-free zones that led to anoxic or anaerobic conditions that enhanced filamentous bacteria growth. The oxygen-free zones caused bulking sludge that resulted in biomass runoff to the recipient lake, thus increasing the levels of SS, BOD_7, and P_{tot} in the effluent

By the end of the 1980s, a new research and development program called MEBITE (1988-91) was suggested by Prof. Pertti Hynninen and DI Sakari Halttunen (Tampere University of Technology) to improve the operation and controllability of the new, but poorly running, activated sludge treatment plants.

In the late 1980s, the industry realised that these new effluent treatment plants were costly to build and operate. For this reason, they started focusing more on closed water loop processes. One of the main learning points was not to mix different water qualities. Instead, process waters were to be reused. This closed water loop thinking became the most vital industry driver in the 1990s to reduce pollution to watercourses.

Overall, during the 1980s, environmental technological development made considerable progress. Simultaneously, the public pressure was decreasing with the improved situation of waterways.

In the early 1980s, two forest industry firms, Enso-Gutzeit and Tampella invested considerably into developing anaerobic treatment processes for the pulp and paper industry's wastewaters. Tampella developed the first methane-producing anaerobic treatment process TAMAN for the Inkerois paper mill. The design parameters were 75% BOD_7, removal with a 16 h retention time, and a BOD_7 load of 2 kg/m^3. The operational expenses were estimated to be around 0.4 MFIM per annum, only one-tenth of an activated sludge treatment plant's costs. Still, the investment costs were around the same for activated sludge ~ 21.5 million FIM in 1984. The development was unsuccessful because of operational issues originating from uneven BOD7 loads. (Luonsi 1987)

Some of the products developed during the '80s were the multistage anaerobic processes developed by Tampella (TAMAN) and Enso-Gutzeit. Enso-Gutzeit was also very active in developing new treatment methods, such as the Enso-HUFO packaged biofilter, Enso-Biox, developed to treat odours from condensed waters using a filter made of bark. They also developed a wastewater treatment concept for bleaching filtrate treatment to remove adsorbable organic halogens (AOX) with combined anaerobic-aerobic stages. To improve the aeration efficiency for the activated sludge, Outokumpu produced new submerged OKI-85 aerators. First, equalisation basins emerged to stabilise the inlet feed to the biological treatment plant. (Hynninen 1998)

To comply with tighter environmental permits, pulp and paper companies started looking for alternative manufacturing processes. These new processes significantly affected the mill's environmental performance and economic parameters. Some figures describing the new CTMP process's economic benefits over a sulphate pulp mill (KRAFT) are shown in *Table 6*. Of significant importance is the difference in CAPEX and OPEX on the benefits of BCTMP over Kraft mill. Due to the non-existing chemical recirculation included in the CTMP mill, the effluent BOD_7 load is much higher. It, thus, needs a larger biological treatment plant than Kraft mills with the same production capacity.

Table 6. Comparison of BCTMP and bleached Kraft mill in Western Canada with a capacity of 750 ADT aspen (Sharman 1989).

Item	Unit	BCTMP	KRAFT
Yield	%	90	50
Personnel	Number	100	300
Energy needed	kWh/ADT	3000	750
Water usage	m^3/ADT	20-25	50-60
Effluent BOD_7	kg/t-pulp	60-80	20-30
Operating costs	USD/ADT	300	360
Capital costs	USD million	200-220	550-600

4.3. The 1990s: Technologies to comply with COD

The Water Act law was changed in 1990 (Oikeusministeriö 308/1990) so that the Water Court ordered the inspection review of the application to be held only in significant cases. After the prolonged public pressure, the last sulfite mills in Finland, Metsä-Serla Mänttä and UPM-Kymmene Rauma, were closed in 1991.

The following R&D focus of the pulp and paper industry was the SYTYKE[10] program (1990-1993). The program resulted in only a slight decrease in pulp and paper industry emissions. The needs and the possible closing of water circuits were troublesome in 19 different study cases. (Ruonala 1993)

The challenge in phosphorous emissions recognised in the late 1980s continued over the turn of the decade. One of the first development issues during 1985-1990 was concern about the biological treatment itself, as researchers tried to analyse what was occurring in the aeration basin by observing the type of living organisms present. From these observations, it was then possible to determine whether there was a lack of phosphorus or oxygen or whether the problem was that the incoming wastewater load was too high. The fundamental change in the philosophy of nutrient

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[10] SYTYKE Project aimed on reducing the Pulp & Paper industry emission to water and utilisation of waste. The program cost was around 20 million FIM (Palo 1992)

control occurred when constant nutrient feed was replaced by adjustment of daily dosages.

The phosphorous in wastewaters originated mainly from the wood and added nutrients, and the nitrogen came mainly from the process chemicals. Also, it was observed that it is difficult to lower the residual phosphorus concentration once it has reached residual levels of 2 to 3 mg/L, even by closing the phosphoric acid dosage completely. This lack of understanding led to studies on how much phosphorous could be stored in biological treatment plants' bacteria. (Jansson et al. 1994)

Two chemical treatment ideas were developed to control the outlet phosphorus. The first idea was derived from the municipal sector. This control involved the simultaneous precipitation of phosphorous with coagulation by ferrous sulfite. The ferrous sulfate is dosed directly into the aeration basin with the idea of finding the overdosed soluble phosphorus and precipitating it into the sludge. Unfortunately, this ferrous sulfate dosing did not work as expected, probably because too much soluble phosphorus was removed. A second idea relied on using a tertiary treatment step with a chemical dosing with either aluminium and or iron-based coagulants that could decrease to the level of 0.1 mg P_{tot}/l.

Kemira started the FennoTriox concept (modified AOP) development in the early 1990s as a tertiary treatment step to polish the residual COD_{Cr} and P_{tot} after the biological treatment step. The main idea of this system was to utilise the famous Fenton's reaction originally developed by H. Fenton (1894). This process uses $HO^{\bullet}$ radicals to oxidise sturdy molecules with aromatic rings, such as phenols.

The first actual membrane tests started in the Finnish pulp and paper industry at Metsä-Serla Kirknemi in 1992 by testing the suitability of ultrafiltration (UF) and nanofiltration (NF) membranes for the paper machine's white water cleaning. After the first mass balance studies and calculations were made in the late 1980s and early 1990s, they indicated where the most significant effluent loads in the mills originated from the pulp mills and not the paper machines. After this, the focus was placed on the primary sources of the impurities. The logical reasoning behind it was that it is simpler and cheaper to clean impurities at the source than after being mixed with other compounds in a vast effluent treatment plant. Moreover, building a big effluent treatment plant to take care of diluted concentrations does not make sense from an investment perspective when they could be treated in high concentrations in a smaller specified treatment step.

The amendment in 1993 (Oikeusministeriö 87/1993) targeted to adjust it as a part of the National Legislation towards the European Legislation. Altogether, 13 water-related directives and four environmental directives were put into force. In compliance with the directives also came a case-specific decision-making process and new fixed emission limits.

Changes in the Water Act (Oikeusministeriö 653/1993) included water protection precaution procedures that were based on the authorisation rule. It allowed some better precaution procedures to be developed.

The Water Act (Oikeusministeriö 471/1995) included the European Communities Council Directive 91/676 / EEC guidelines protecting waters from nitrates originating from agriculture farming. Thus, this Water Act might have been the first indication of N limits entering the pulp and paper industry later in the 1990s.

Changes in the Water Act in 1995 (Oikeusministeriö 1347/1995) regarding the European Economic Area Agreement, linked to the authorisation provisions, were amended to meet the European Union requirements, which later meant the adaptation of EU environmental limits for the pulp and paper industry.

The largest BOD_7 or COD_{Cr} kg/h source in the pulp and paper industry originated from the bleaching stages – especially if alkaline oxidative bleaching (O_2, H_2O_2) was used. The alkaline conditions and oxidative surroundings are very effective in dissolving extractives from the wood. Depending on the wood type and the process used, the extractives are one large impurity flow in the process. Problems start when the water circuit closure reaches the extractive's solubility level and starts to precipitate on screens, filters, and equipment surfaces, causing runnability problems. These typically lead to paper brakes on the paper machine and final product quality issues. (Opedal 2011)

In the mid-1990s, a new internal water cleaning concept called NetFloc was developed. The Netfloc concept focused on removing extractives that were the most significant COD_{Cr}-load causing impurities from the chemical pulp making. The main drivers for developing the NetFloc system came from the effluent treatment plants with limited capacity to handle the increasing loads (COD_{Cr} and flow) and the mill's unwillingness to invest in costly WWTP upgrades. For example, suppose the extractives are not removed before entering the treatment plant. In that case, they will flow through the effluent treatment plant, increasing the SS (and COD_{Cr}) in the outlet and decreasing the oxygen transfer in the aeration basin.

The NetFloc focus was to remove extractives and non-process elements (NPE) from process waters in paper and pulp production. In the NetFloc system, a high molecular weight polyethene oxide (PEO) or polyacrylamide (PAM) water solution was added to the selected filtrate. In the actual application, a PEO or PAM water solution was prepared in a polymer-dissolving unit and dosed directly into the filtrate pipe coming from the pulp washing stage. The final operation included separating resin sludge from the filtrate with a Dissolved Air Flotation (DAF) unit, vortex cleaner, or a bow screen.

The alternative solution was to reuse the water by directly removing the harmful compounds in the process. By cleaning some of the typical first washing stage filtrates and reusing them, it was possible to save around 5-15 m^3/t of the pulp water. Besides, removing the extractives could improve the process's runnability and the product's final quality. The resin sludge was usually burned in the bark boiler directly or after dewatering in a press, to generate additional energy[11].

Removal efficiencies of more than 90% have been documented for extractives and heavy metal ions in pilot tests and mill trials for different pulp and paper processes. Even a COD_{Cr} reduction of more than 40% has been reported. (Jansson et al. 1996 a, b,c,d, 2001a,b).

The addition of the Water Act 1996 (Oikeusministeriö 1105/1996) gave specific small water bodies provisions to protect water from changing and enhance the protection of small streams.

Discussion regarding whether Totally Chlorine Free (TCF) or Elementary Chlorine Free (ECF) bleaching in Kraft processes was more environmentally friendly emerged in the late 1990s. Some of the reasons behind these discussions were the possible formation of absorbable organic halogen (AOX) compounds and the relatively high price of ClO_2

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[11] Already with 9% dry solids content of the extractive sludge it was possible to react break even energy value due to the close energy value of crude oil

used in the ECF process. In 1990, approximately 94% of the bleached pulp was produced by chlorine bleaching. However, most of it was replaced with ClO_2 in all Nordic countries by 1994. It was a more environmentally friendly and safe bleaching chemical. TCF bleaching uses whitening agents that do not contain chlorides, such as hydrogen peroxide (H_2O_2) and sodium hydrosulfite (NaHS). (Popp et al., 2011)

When chlorine dioxide (ClO_2) was produced onsite at the mill, its limited capacity soon became, in many places, a bottleneck. The limited $ClO_{2\ \text{production}}$ caused a reduction of process capacity at the beginning of the bleaching process and prolonged the brown side cooking, with an additional oxygen stage to reach the needed delignification. New EOP (alkaline H_2O_2 delignification) stages were also introduced to enhance the alkaline bleaching results. In addition, the process waters became very dirty with the increased recycling of process water in chemical pulp manufacturing. Thus, the effect of pulp washing became less effective. These dirty processes waters created the need to develop the NetFloc concept for cleaning these filtrates. With the NetFloc concept, the process water reuse could be increased from 5 to 15 m^3/t-pulp, and the overall freshwater usage similarly decreased.

As the ECF process was reengineered, it eventually became the primary bleaching method. Today, it accounts for over 75% of the world's bleached pulp production. Overall, it is accepted that TCF and ECF discharges cannot be separated for environmental reasons. ECF generally produces higher molecular weight compounds in wastewater than TCF bleaching.

The third extensive R&D program was called CACTUS[12] (1996-1999), which focused on minimal water usage in paper mills, closed loops, and minor environmental emissions into the air, soil, and water. Some topics were designed to decrease raw water usage utilisation without jeopardising the final product quality. Other targets were energy efficiency, better usage of chemicals, cleaner processes, and better stability. The results created an increase in expertise, new products, and services. CACTUS was also the last extensive environmentally focused program where all the Finnish pulp and paper industries participated. (Komppa et al. 2000)

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[12] CACTUS program aimed on low water using paper manufacturing. The full R&D program cost was around 52.6 million. (Komppa et al. 2000)

The development of controlling the activated sludge and the whole WWTP efficiency brought Dissolved Air Flotation (DAF) technology development, mainly as internal paper machine white water kidneys, and later as a tertiary treatment step. At UPM Jämsänkoski, the new Russian-originating electrocoagulation-based technology was tested to treat different waters. New evaporators, called Zedivap (Zero Effluent Discharge Evaporator), based on Mechanical Vapor Recompression (MVR) and Multiple Effect Evaporation (MEE), were developed by Ahlström. A new type of MVR evaporator with a polymeric heat transfer surface that claimed to offer superior resistance to the effects of scaling, fouling, and precipitation in closed water loops, was developed by Hadwaco. VTT developed new enzymes to disintegrate extractives for easier removal by the biological treatment plant. The company Certus[13] introduced a new ceramic membrane with an ultrasound cleaning mechanism. Metso developed ceramic disk filters, capturing material larger than the 1-2um particle size. Meanwhile, Kemira developed AOPs, and new process monitoring and control system for automatic chemical dosing.

The target of new processes such as the AOPs was to remove mainly the organics from the waters. This technology originated mainly from the USA. These new AOPs utilised UV + H_2O_2 and O_3 systems to destroy organics present in waters.

Even if the main design problems were solved mainly by the MEBITE program, the P_{tot} emission remained a problem (Hynninen 2009). Therefore, several new technologies were developed to improve COD_{Cr} reduction and meet the latest environmental limits. Further treatment steps after activated sludge treatment were introduced as a polishing step or tertiary treatment step. It consisted of a chemical treatment step followed by a solid/liquid separation process such as the DAF-or ordinary sedimentation unit.

The tertiary treatment steps were still regarded as polishing and the last rescue steps for the mill if something goes wrong with their WWTP. However, noticeable decreases in the emissions were achieved wherever it was in use because of these actions.

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[13] Continues today with the new name of Sofifilter

To overcome the tightening environmental limits, Metsä-Serla Kirkniemi built the first tertiary treatment plant (1997) with a chemical addition ensuring the required COD_{Cr}, and P_{tot} limits could be reached.

In the late 1990s, the effluent treatment plants had grown into large and complicated processes to meet the requested emission levels. As a result, new equalisation basins, emergency basins, and selector basins were developed and installed at many sites to equalise the inlet quality and quantity flows to the biological stages. At the same time, Finland's environmental administration started sharing and discussing typical pulp and paper environmental issues with other Nordic countries, such as Sweden and Norway. The discussions included emission limits and technologies to reach these targets. This work was later found to have prepared good foundations for the EU-coordinated European Integrated Pollution Prevention and Control (IPPC), set up in 1997, to organise information exchange between the member states and the industries. Simultaneously, the Best Available Techniques (BAT) with associated monitoring was developed.

4.4. The 2000s: Technologies to comply with recalcitrant COD

The new IPPC-based directives were put into force in 2001, with the target to be reviewed every 6th year. (European Commission 2001)

The idea of the IPPC was to create standard regulations for the entire European pulp and paper industry and suggest how to reach these levels with BAT technologies. The production type and the age of the mill in question gave the primary emission limits. The local environmental agents could then adjust or fine-tune the emission limits according to the recipient's ability to receive such a stream. The new environmental parameters were changed from mg/L concentration to kg of emission/t product produced. (Saarinen et al., 2014)

The IPPC developed reference documents called the Best Reference Documents (BREF) to describe which technological paths some mills have taken to reach these new environmental targets. The reference document for the pulp and paper industry was divided into the following processes, with process details described to minimise the wastewater generated. The main processes are listed in*Table 7*. (European Commission, 2001)

Table 7. The main pulp and paper processes are listed in the BREFs (European Commission, 2001)

Kraft pulping
Sulfite pulping
Mechanical pulping and Chemi-mechanical pulping
Recycled fibre processing
Papermaking and related processes

Table 8 presents some of the BAT technologies for the Kraft mills to reach the lower emissions targets.

Table 8. Examples of leading BREF technologies for Kraft Mills (European Commission, 2001)

Dry debarking of wood
Increased delignification before the bleach plant by extended or modified cooking and additional oxygen stages
Highly efficient brown stock washing and closed-cycle brown stock screening
Elementary chlorine-free (ECF) bleaching with low AOX or chlorine-free bleaching
Recycling of some, mainly alkaline process water from the bleach plant
Effective spill monitoring, containment, and recovery systems
Stripping and reuse of the condenses from the evaporation plant
Sufficient capacity of the spent liquor evaporation plant and the boiler to cope with additional liquor and dry solids if necessary
Collection and reuse of clean cooling waters
For prevention of unnecessary loading and occasional upsets in the external effluent treatment process due to spending liquors and dirty condensates, sufficiently large buffer tanks for storage are considered necessary
In addition to process-integrated measures, primary and biological treatment are considered BAT for Kraft pulp mills.

Table 9 contains the suggested emission levels as kg/tADT-pulp, which could be reached if such a process was implemented.

Table 9. The IPPC suggestions for the pulp and paper industry directives. Note that integrated mills are calculated from pulp production and paper making according to the product mix (European Commission 2001).

Production type	COD kg/ADT	BOD kg/ADT	TSS kg/ADT	AOX kg/ADT	Total N kg/ADT	total P kg/ADT	Flow m^3/ADT
Bleached Kraft Pulp	8-23	0.3-1.5	0.5-1.5	<0.25	0.1-0.25	0.01-0.03	30-50
Unbleached Kraft Pulp	5-10	0.2-0.7	0.3-1.0	-	0.15-0.2	0.005-0.02	15-25
Bleached sulphite Pulp	20-30	1-2	1-2	-	0.2-0.5	0.02-0.05	40-55
CTMP pulp	10-20	0.5-1	0.5-1	-	0.1-0.2	0.005-0.01	15-20
Integrated mechanical Pulp and Paper mill	2.5	0.2-0.5	0.2-0.5	<0.01	0.04-0.1	0.004-0.01	12-20
Non-DIP RCF paper	0.5-1.5	<0.05-0.15	0.05-0.15		0.02-0.05	0.002-0.005	<7
DIP RCF	2-4	0.05-0.2	0.1-0.3		0.05-0.1	0.005-0.001	8-15
RCF tissue	2.0-4.0	0.05-0.4	0.1-0.4		0.05-0.25	0.005-0.15	8-25
Uncoated fine paper	0.5-2	0.15-0.25	0.2-0.4	<0.005	0.05-0.2	0.003-0.01	10-15
Coated paper	0.5-1.5	0.15-0.25	0.2-0.4	<0.005	0.05-0.2	0.003-0.01	10-15
Tissue	0.4-1.5	0.15-0.4	0.2-0.4	<0.005	0.05-0.25	0.003-0.015	10-25

Simultaneously, the Water Act was also revised with changes mainly made of administrative and technical nature towards EU legislation IPPC & IED. (Oikeusministeriö 689/2000, 121/2001, 1030/2003, 1062/2004, 1301/2004, 732/2005, 386/2009)

For example, following the new BREF recommendation and process water cleaning developments gathered from Lielahti BCTMP Pulp Mill in the 1990s, the Metsä Botnia Joutseno BCTMP could close their water loops in 2005. The water loops were closed by sending CTMP plug screw washing filtrates to the Kraft mill recovery boiler to generate additional energy, recover cooking chemistry and produce high-quality water for reuse, *Figure 8*.

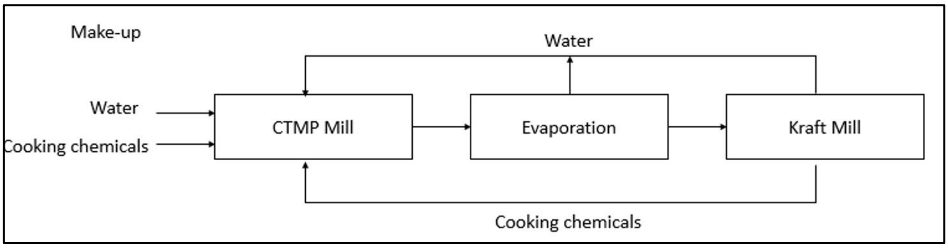

Figure 8. The basic layout of the Joutseno BCTMP and Kraft Mills shared water and cooking chemistry process (Nickull 2013).

Returning the condensate to the CTMP mill led to an almost entirely closed water circuit with only 1-2 m^3/t-pulp makeup water needed and no corrosion risk [14]. As a result, the BCTMP Pulp was made more environmentally friendly (a zero-emission CTMP mill) and at a lower cost than previously possible[15]. (Ojanperä 2005).

In early 2000, improved computer calculation, process modelling, and simulations emerged for mills to reach water efficiency targets and recognise possible process problems before they were actualised. The BALAS ®[16] calculations emphasised the importance of proper raw water treatment on the number of impurities entering the mill. These impurities could be hundreds of kg per day in a typical 200 000 t/a to 500 000 t/a capacity mill, causing an increase in the chemical costs, wear on the machinery, and decreased final product quality.

In other countries, mainly in Europe, many deinking and RCF mills needed to decrease their water usage by recirculating 10-20% of their final wastewater in either the pulp mill or the paper machine. These waters had to be chemically treated to remove excess Pt_{ot} and COD_{Cr} and reduce the main processes' bio growth potential. Recycling more than 20% of the wastewater back to the process would have increased the accumulation

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[14] First attempts to fully close the water loops of a CTMP plant resulted in sever scaling and corrosion of the plant. (Great Slave Lakes CTMP, Canada)

[15] For this work, DI Ole Nickull, PhD Maija Pitkänen, DI Marko Pekkola, Eng Isto Nikamaa and DI Kai Vikman of Metsä-Serla were awarded the Annual Inventor Price of Finland in 2005. (Ojanperä 2005)

[16] VTT BALAS ® is a steady-state simulation package for chemical processes with emphasis on pulp and paper, food processing and biochemical processes.

of hard COD_{Cr}, biological growth, scaling, and depositions in the system. An alternative was to recycle the pure Deinking Pulp (DIP) sludge treatment filtrate that did not have these problems. However, the soluble matter in recycled DIP water contained inks that caused pulp colourisation problems.

To overcome many of these challenges, and instead of optimising a single process, several companies started looking at cooperation with other technology suppliers to enhance their process by physical, chemical, and biological means, thereby improving the complete technology offer.

Changes in landfill legislation inside the EU (European Communities 1999) caused sludge treatment, handling, and placement to be developed. The biosludge volumes increased, making dewatering even more challenging to treat with the available sludge treatment equipment. Mills, with their own landfills, had to close these areas and recondition them into green places. The idea behind the new IPPC directive was to decrease the output of organic sludge and inhibit its placement in landfills by increasing the dumping costs. Mills started to consider the possibility of disposing of the sludge by incineration. The challenges were to get biosludge dryness up to 35-40% levels to reach the required breakeven dryness.

AOP treatment, the modified Fenton's process, was reported to improve bio sludge dewatering speed, which nearly doubled in the 30s with a $10kgH_2O_2$/t-biosludge dosage (Jansson et al. 2003).

Soon after the FennoTriox system had been developed, a new focus was put on avoiding the low pH needed for the FennoTriox to work. Also, methods for avoiding possible problems caused by the soluble catalyst (e.g., iron) were developed. As the focus was placed on the internal loops, there was an interest in cleaning the filtrates at the location where they emerged and reusing them as soon as possible somewhere else in the process. The FennoTriox system's disadvantage was that the multi-component system using H_2O_2, Fe, pH, and a polymer needed to be controlled simultaneously. Removal of the formed sludge was done with a DAF unit. Results of COD_{Cr} removal > 90% and SS, P_{tot} removal > 99% were obtained. The main disadvantage of the FennoTriox concept was the low operating pH of 4. The needed low reaction pH meant considerable financial cost by first reducing the pH and increasing it again before sending the cleaned water to the recipient.

4.5. The 2010s: The challenges of water treatment technologies

In 2010, the new decade started with a slow recovery from the financial crisis of 2008, which resulted in a prolonged recession. As a result, the focus was now on the energy-water nexus as a global megatrend. With the low paper price, alternative income sources again started to emerge in the form of energy production with anaerobic treatment. One of the leaders in this field was the Dutch Paques Company, responsible for many successful anaerobic installations in Europe. The idea behind producing biogas (methane) was either to use it inside mills for heating or electricity generation or to sell it as pressurised gas for city buses. A significant driver of this development was the anaerobic biological treatment plant's considerably smaller operational costs than an aerobic one. In addition, some pulp and paper industries proposed capturing all organic waste streams and turning them into biogas.

Many pulp and paper mills are expected to have new tighter environmental limits, especially regarding COD_{Cr} reduction. Also, some additional parameters, such as $SO_{4,}$ have been discussed but not realized for the Finnish pulp and paper industry. Therefore, the AOP described in more detail in the following chapter has a real opportunity to remove, destroy, or modify soluble organics compounds that are toxic or non-biodegradable for conventional biological treatment systems.

The new Industrial Emissions Directive (IED, C) contained the BAT reference documents adopted under the Industrial Pollution and Prevention Control (IPPC Directive 2008/1/EC) and the IED. Therefore, for BREFs adopted under the IED, the BAT conclusions were also adopted according to the IED.

The improvement to the existing treatment plants focused on utilising membrane bioreactors (MBR) instead of activated sludge processes. These benefited from a much smaller physical footprint and guaranteed a suspended solids-free effluent. The disadvantages of MBRs are their higher energy requirement, which is around two times higher than for the activated sludge, and the high investment costs. A newer MBR generation is the submerged anaerobic membrane bioreactors (SAnMBR), combining the benefits of aerobic MBR good filtrate with anaerobic digestion biogas production and high operation temperature to cope with the temperature of the high temperature of the wastewaters and lower sludge generation. (Gao et al. 2011, Kamali et al. 2015, Gao et al. 2016)

Nevertheless, some familiar fundamental problems were still to be overcome, such as controlling the soluble nitrogen and phosphorus without a chemical polishing step. Nevertheless, the sensitivity of anaerobic versus aerobic will most probably keep the aerobic processes running, at least on a smaller scale.

Other membrane systems started to be seen in the raw water treatment process, such as ultrafiltration (UF) and the manufacturing of demineralised water for the power plant with reverse osmosis (RO) membranes. However, the main drawback of membrane technology, especially with RO, is the high concentrate volume generated. A typical RO plant has a permeate flow of around 60-70%, meaning 40-30% of the flow is diluted concentrate.

5. ADVANCED OXIDATION PROCESSES

This chapter reviews the historical development of advanced oxidation processes (AOP) systems since the discovery of Fenton's reagent in 1886. This background explains why the AOP processes have been selected and studied to treat some pulp and paper waters. The AOP or advanced oxidation technologies (AOT) are treatment methods mainly designed to remove organic materials from water and wastewater through oxidation reactions with hydroxyl radicals ($OH^•$). In most treatment applications, this term usually refers to a subset of chemical processes that mainly employ ozone (O_3), hydrogen peroxide (H_2O_2), catalytic hydrogen peroxide, or UV light. Meanwhile, Fenton's reagent is a catalytic oxidation process to generate hydroxyl radicals in situ. This section follows the development of some AOP toward today's new methods and applications.

5.1. Background

Due to its strong oxidation properties, hydrogen peroxide has been used for a long time in water treatment and industrial applications. For example, the pulp and paper industry widely uses hydrogen peroxide for pulp bleaching and some water treatment. However, the hydrogen peroxide oxidation potential, 1.80 and 0.87 V at pH 0 and 14, is not strong enough by itself to break the phenolic/aromatic compounds found as recalcitrant COD_{Cr} in the pulp and paper industry effluents (Degussa Corporation 1997).

In water treatment, hydrogen peroxide utilisation can result in four types of reactions, i.e., water redox reactions, peroxide group transfers, decomposition into oxygen gas (O_2), and additional compound formation. Hydrogen peroxide has its optimum stability in acidic conditions and cold temperatures. On the other hand, the decomposition of H_2O_2 is favourable under alkaline conditions and is substantially accelerated by the presence of some metallic impurities such as iron, copper, manganese, nickel and chromium. (Snell et al. 1971).

Some of these oxidative and reductive reactions are listed below. In *Reactions 1-4*, the H_2O_2 works as an oxidant, and in *Reactions 5-8* as a reductant. Sulphuric acid is used in *Reactions 3* to reach the optimal acidic reaction pH 3-4. (Schumb et al. 1955)

$$H_2SO_3 + H_2O_2 \rightarrow H_2SO_4 + H_2O \tag{1}$$

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O \tag{2}$$

$$2FeSO_4 + H_2O_2 \xrightarrow{H_2SO_4} Fe_2(SO_4)_3 + 2H_2O \tag{3}$$

$$2KI + H_2O_2 \rightarrow 2KOH + I_2 \tag{4}$$

$$Ag_2O + H_2O_2 \rightarrow 2Ag + H_2O + O_2 \tag{5}$$

$$2KMnO_4 + H_2O_2 \rightarrow 2MnO_2 + 2KOH + 2O_2 \tag{6}$$

$$Cl_2 + H_2O_2 \rightarrow 2HCl + O_2 \tag{7}$$

$$MnO_2 + H_2O_2 \rightarrow MnSO_4 + 2H_2O + O_3 \tag{8}$$

With metal catalysts, hydrogen peroxide may generate a wide variety of free radicals and other reactive species that can transform or decompose organic chemicals in the water.

Of these radicals, the OH$^{\bullet}$–radical is known to be one of the strongest known oxidants, *Table 10.* The OH$^{\bullet}$–radical is capable of non-selective oxidation with a very high reaction speed of 10^9 M^{-1} s^{-1}.

Table 10. Relative oxidisation power of different oxidative compounds to chlorine (Nyer et al. 1999)

Relative Oxidation Power (Cl=1.0)	
Fluorine	*2.23*
Hydorxyl Radical	*2.06*
Atomic oxygen (singlet)	*1.78*
Ozone	*1.52*
Hyrdogen Peroxide	*1.24*
Perhydroxyl Radical	*1.17*
Permanganate	*1.15*
Hypobromous Acid	*1.10*
Hypoiodous Acid	*1.07*
Chlorine	*1.00*
Bromine	*0.80*
Hydrogen Peroxide	*0.64*
Iodine	*0.54*
Oxygen	*0.29*

Figure 9 shows general AOP methods capable of producing hydroxyl radicals. The most common is the catalytic oxidative such as the Fenton's reagent. The other mainstream AOPs are based on $UV/H_2O_2/O_3$.

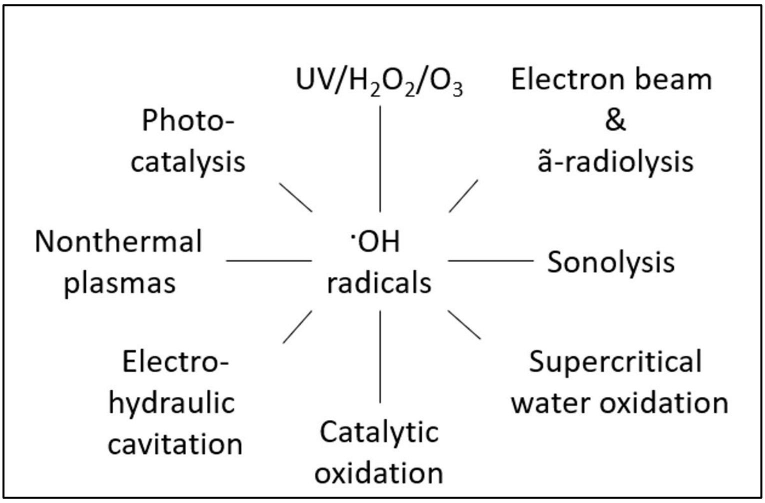

Figure 9. Different AOP ways of producing OH• radicals.

Fenton’s process is a known method to produce the hydroxyl radical in water treatment. Fenton’s process consists of at least four stages: (1) pH adjustment, (2) oxidation reaction, (3) neutralisation and (4) coagulation-precipitation, where the last one is related to $Fe(OH)_3(s)$ generation.

H. J. Fenton did the first report on using Fenton's reactions to oxidise tartaric acid with ferrous salt and H_2O_2 under mildly acidic conditions of pH 3-5. This reaction initiated a powerful oxidation process that caused the liquid to turn to delicate violet colour. This colour change was first thought to originate from sodic or potassic ferrate formation. (Fenton 1894).

In 1929, it was proposed that hydroxyl radicals were generated in the iron-catalysed decompositions of hydrogen peroxide. In 1931, Haber et al. suggested the hydroxyl radical mechanism in a paper for the first time. They suggested that the OH• could be produced by one-electron reduction of H_2O_2 by $HO_2^{\bullet}$ and that OH• could abstract hydrogen from a carbon-hydrogen bond and initiate a radical chain reaction. In 1932, Haber et al. suggested the generation of OH• one-electron reduction of H_2O_2 by Fe^{2+} (Haber et al. 1932, Haber et al.1934, Weiss 1935). For this reason, *Reaction 9* is often called Fenton’s reaction or the classical Fenton’s reaction, although Fenton never wrote it (Hofer 2001). It should be noted that the oxidation of organics was never addressed by Haber et al. The reaction kinetics, *k,* for *Reaction 9* is estimated by Rigg et al. 1974.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \ OH^- \ + OH^{\bullet} \qquad (9)$$
$$k \approx 70 \ mol^{-1} \ s^{-1}$$

In 1949, it was suggested that $OH^{\bullet}$ from *Reaction 9* adds to the carbon double bond and can initiate a polymerisation reaction (Baxendale et al. 1946). The *Reactions 10-13* initially suggested involved in Fenton's reactions by Haber and Weiss were later modified in 1951 by Barb et al. (Barb et al. 1951, Pignatello 1992, Walling et al. 1974). The reaction kinetics, *k*, for *Reactions 10 and 13* are suggested by Buxton et al. 1954 and *Reactions 11 and 12* by Bielski et al. 1985.

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + \ H_2O \qquad (10)$$
$$k\text{=}3.3\text{x}10^{7} \ mol^{-1} \ s^{-1} \text{ at pH=3}$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + \ HO_2 \ + H^+ \qquad (11)$$
$$k\text{=}1.2\text{x}10^{6} \ mol^{-1} \ s^{-1} \text{ at pH=3}$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + \ HO_2^- \qquad (12)$$
$$k\text{=}1.3\text{x}10^{6} \ mol^{-1} \ s^{-1} \text{ at pH=3}$$

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + \ OH^- \qquad (13)$$
$$k \approx 3{,}2 \text{ x}10^{8} \ mol^{-1} \ s^{-1}$$

Reaction 9 in the chain reaction serves as the chain initiation step, and *Reactions 12* and *13* as termination steps. Thus, the *Reaction* cycle *9-10-11* forms the chain reaction that is the site of O_2 evolution. (Kremer 1999).

Two decades later, Walling presented further evidence of hydroxyl radical involvement in the oxidation of organic compounds by the Fenton’s reagent *Reaction 14* (Bossman et al. 1998). The kinetic constant, *k*, is given by Walling et al. 1971.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO^{\bullet} + \ HO^- \qquad (14)$$
$$k\text{=}1\text{-}2\text{x}10^{-2} \ mol^{-1} \ s^{-1}$$

(14

It should be noted that *Reaction 14* is about 6000 times slower than *Reaction 9*. *Figure 10* shows the inefficiencies of the Fe^{3+} and Fe^{2+} reaction cycle, as an outcome of *Reactions 9 and 14*, that lead to the accumulation of Fe^{3+} and $Fe(OH)_3$ in the system (Song et al. 2006, Martinez-Huitle et al. 2016). The conventional Fenton reaction is shown in, *Figure 10* (Melin et al. 2016, Salgado et al. 2017).

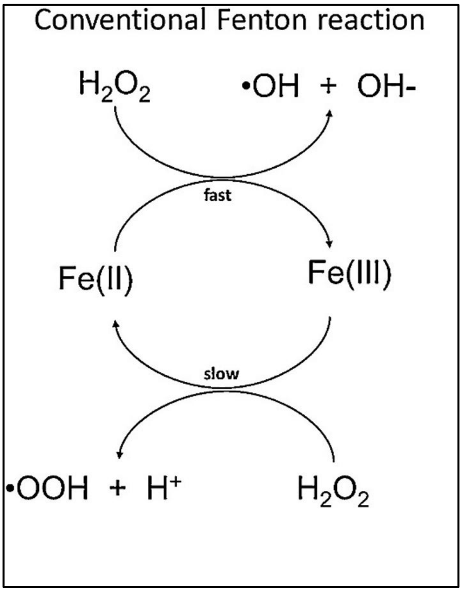

Figure 10. Conventional Fenton's reaction mechanism

Today, more than 20 chemical reactions have been identified for Fenton's reagent (Duesterberg et al. 2008, Pliego et al. 2015).

Hydroxyl radicals can oxidise organics (RH) by abstracting protons producing organic radials ($R^\bullet$) that are highly reactive and can be further oxidised, *Reaction 15.* (Venkatadri et al. 1993, Walling et al. 1971, Lin et al. 1997)

$$RH + HO^\bullet \rightarrow H_2O + R^\bullet \rightarrow further\ oxidation \qquad (15)$$

If concentrations of the AOP reactants are not limited, the organics can be completely converted to CO_2, water and substituted organic and inorganic salts if the treatment is continued (Neyens et al. 2003).

The addition of metal ions such as iron, copper or chromium has been shown to increase the efficiency of H_2O_2 to form hydroxyl radicals. Other metals, such as cobalt (2^+) and nickel (2^+), can be used at a lower oxidation state (Neurd et al. 2001). Therefore, Fenton's reaction can also involve several other metals (M^{n+}), cations, and a similar reaction may be characterised as *Reaction 16* (Prousek et al. 1995).

$$M^{n+} + H_2O_2 \rightarrow M^{(n+1)+} + OH^- + HO^{\bullet} \tag{16}$$

In the 1990s, a substantial acceleration of *Reaction 14* was noticed when a Fenton's process was photo-assisted. The photo-Fenton generated much faster $HO^{\bullet}$ and higher degree oxidation of organic material than ordinary dark Fenton. In addition, the photo Fenton efficiency increases when irradiated with wavelengths below 580nm due to the light adsorption of Fe^{3+} in organic ligand (L) complexes generated by *Reaction 14* to be reduced to Fe^{2+} and generation of extra $HO^{\bullet}$ and enabling the iron cycle to restart, *Reaction 17.* However, this method was not successfully utilized in the dark and turbid pulp and paper wastewater treatment.

$$Fe^{3+} L_n + h\vartheta \rightarrow Fe^{2+} L_{n-1} + L^{\bullet}_{ox} \tag{17}$$

The pH affects the Fe speciation strongly and, therefore, the solubility of iron in water, establishing the optimum Fenton or photo-Fenton reaction at a pH ≤ 3. The three iron (II) species found in the water as a function of the pH are $Fe(H_2O)_6^{2+}$ or Fe^{2+} that are predominant in acidic conditions, $Fe(H_2O)_4(OH)_2$ at alkaline conditions, and $Fe(H_2O)_5(OH)^+$ and $FeOH^+$ when pH is lower than 5. (Hem et al. 1959)

However, the speciation of iron (III) differs from iron (II), and in strongly acidic solutions, the main species is the hexaaquo ion, $Fe(H_2O)_6$. When pH increases, the hydrolysis of $Fe(H_2O)_6^{3+}$ occurs depending on several parameters, including the ionic strength and the total iron concentration. Consequently, this ion precipitates as amorphous ferric oxyhydroxide ($FeO(OH)$), which is considerably less active. Therefore, the reaction of ferrous ion and H_2O_2 will lead to iron precipitation when Fe(III) oxyhydroxides are formed when pH is higher than 3, *Figure 11*.

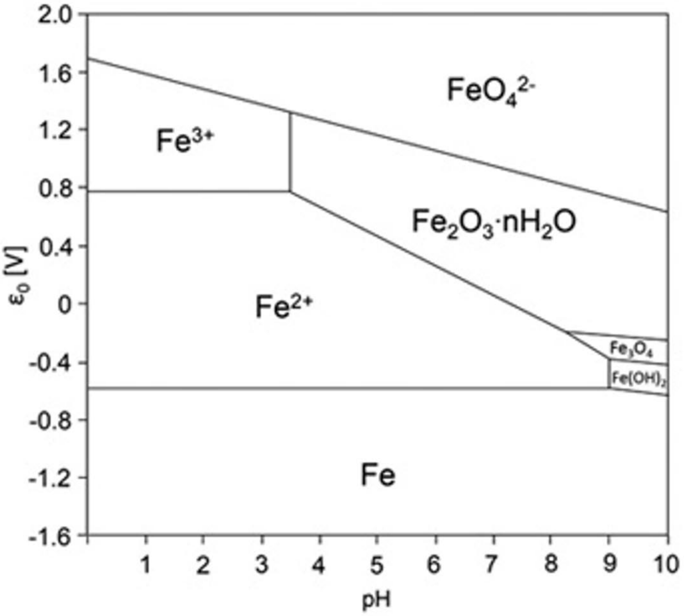

Figure 11. Iron Pourbaix diagram. (Modified from Beverskoog et al. 1996)

Iron ions and Fenton's process are negatively affected by several inorganic chemical compounds in the water. These inorganic chemical compounds mainly produce iron precipitation, scavenging of radicals, and or less reactive Fe complexes. Some hydroxyl radical scavenging compounds are carbonates (CO_3^{2-}) and bicarbonates (HCO_3^-). These anions may react with $HO^\bullet$, scavenging it and reducing their ability to oxidize the target pollutants. Therefore, treatment of any water with AOP in the presence of CO_3^{2-} will directly compete with the oxidation by $HO^\bullet$, *Reactions 18-19.* (Polo-Lopez et al. 2018)

$$HO^\cdot + HCO_3^- \rightarrow CO_3^- + H_2O \tag{18}$$
$$HO^\cdot + CO_3^{2-} \rightarrow CO_3^- + H_2O \tag{19}$$

Phosphate ions have been shown to have a critical and detrimental role during Fenton's reaction because they react with iron and are coprecipitated as stable complexes at neutral and acidic conditions and scavenge hydroxyl radicals. In addition, other anions present in the natural waters, including sulfates, nitrates, and chlorides, may also react with iron and H_2O_2, limiting Fenton's capability to oxidize organic chemical and biological pollutants. (Polo-Lopez et al. 2018)

5.2. Applications of AOP in the pulp and paper industry

Different compounds are formed and naturally found in the untreated pulp and paper wastewaters depending on the type of process, raw material, and chemical used. Most typical compounds found in high concentration levels are SS, extractives, fatty acids, lignin, tannins, and derivates resulting in high BOD and COD. Some of these naturally occurring compounds can be easily removed by biological processes. (Area et al. 1998, Ali et al. 2001). However,, some of these substances are recalcitrant to biological processes and toxic to aquatic life. The bleaching processes can also, in some cases, form bioaccumulated compounds or, depending on the Kraft bleaching process, even some compounds such as dioxins and furans (EU IPPC 2001, Karrasch et al. 2006, Kovacs et al. 2002)

Conventional treatment methods such as biological, thermal, and physicochemical treatment methods, including adsorption, flocculation, coagulation, extraction, and membrane technologies, are often insufficient to remove all compounds found in the pulp and paper waters. For this reason, advanced treatment systems have been sought to reduce refractory organic compounds to meet the increasingly stringent discharge limits. (Scott et al. 1995, 1996, 1997, Wardman et al. 1996, Marco et al. 1997, Karimi et al. 2009, Kim et al. 2011)

If concentrations of the AOP reactants are not limited, the organics can be completely converted to CO_2, water and substituted organic and inorganic salts if the treatment is continued, or partial mineralisation to transform them into a more biodegradable form (Neyens et al. 2003). In addition, utilising AOP as a pre-treatment method in front of an existing biological treatment plant is seen as an advantage, if there is available treatment space left in the following treatment step to enhance the overall COD_{Cr} removal rate.

TiO_2-photocatalysis, used by Pérez et al. 2001, resulted in 50% COD_{Cr} mineralisation and total removal of colour and phenols from a cellulose ECF effluent. Also, Pérez et al. 2002 and Torres et al. 2003 used Fenton and photo-Fenton with radiation from a black-light fluorescent lamp, xenon lamp, and solar light irradiation to successfully degrade the organic content of a Kraft pulp mill bleaching effluent and a conventional cellulose bleaching effluent.

The use of ozone or ozone/UV to treat real effluents has been studied by Amat et al. 2003. They found that the COD decrease depended on the fatty acids/phenol ratio. The respirometric studies showed increased BOD in effluents subjected to mild oxidation, while a BOD decrease was observed under stronger conditions.

The study made by Eskelinen et al. 2010 shows that using Fenton and photo-Fenton will achieve a higher biodegradation rate than using TiO_2photocatalysis. In addition, the Fenton and photo-Fenton treatment cost less than using photocatalysts to treat pulp and paper mills' bleaching effluents.

Most studies published after 2010 focus on combining AOP with other technologies, especially biological and membrane technologies, to overcome specific problems when using single treatment technologies. (Rostam et al. 2020, Dogan E. et al. 2021, Nidheesh P., et al. 2021)

The utilisation of ozone and TiO_2-photocatalysis and their combinations with biological treatment (MBR) to close the water loops in a recycled paper mill and kraft mill was studied by Merayo et al. 2013. They found 2.4 g O_3/L ozone treatment to be the most effective, reducing the COD by about 60% for the Kraft mill effluent at pH 7. The photocatalytic treatment reduced the COD by 20-30% for both types of effluents. Additionally, the recycled paper mill showed a higher biodegradability after the AOP treatment. When ozone was used as a pretreatment step before the biological treatment, the COD reduction over the effluent treatment plant reached 90%.

Combining oxidation processes and electricity is another option to maximise the treatment efficiency of pulp and paper industry wastewaters. Amongst the electrochemical advanced oxidation processes (EAOPs), anodic oxidation (AO) methods have attracted significant attention over recent years for reducing toxic and recalcitrant compounds from highly polluted and complex wastewaters (El-Ghenymy et al. 2015). This process generates highly reactive hydroxyl radicals at the anode surface (Me), according to *Reaction 20* (Panizza et al. 2009):

$$Me + H_2O \rightarrow Me(\cdot OH) + H^+ + e^- \qquad (20)$$

Anodic oxidation (AO) is a chemical-free technology in which various materials such as platinum, graphite, doped and undoped PbO_2, and boron-doped diamond (BDD) electrodes can be used as anodes. Salazar et al. 2015, treated acidic and alkaline bleaching effluent from a hardwood-based Kraft pulp mill by an AO-H_2O_2 process containing an air diffusion cathode and dimensionally stable anodes[17] (DSA)-RuO_2 or BDD anode with a constant cell voltage of 2 to 12 V. The study showed the BDD anode to have a much better performance in the mineralisation of the recalcitrant organics compounds when compared to the DSA-RuO_2 anode. A 75% TOC removal and 65% alkaline reduction were achieved using nine hours of reaction time for acid effluents.

Using three-dimensional electrode reactors is another possible solution to enhance the degradation of acidified reed pulp black liquor. Both types of direct electrolysis based on anodic oxidation and indirect electrolysis based on microcell mechanism achieved a TOC removal rate of 35.57%. (Xiong et al. 2003, Li et al. 2013, Gedam et al. 2014, Jung et al. 2015)

Some recent studies have also been successfully applied using the nano-scale catalyst for wet air oxidation of pulp and paper wastewaters. Anushree et al. 2015 investigated catalytic wet air oxidation using NiO-CeO_2 nano-catalyst, prepared via a co-precipitation process. The results showed 62% COD_{Cr} and 75% colour removal at mild operational conditions of 90 °C and 1 atm. Using 1 g/L $Ce_{0.4}Fe_{0.6}O_2$ mixed oxides as a catalyst at pH 4 and a reaction time of 2 h resulted in 74% COD and 82% colour removal. The catalyst could be used three times without significantly reducing catalytic performance.

Erhardt et al. 2021 studied the utilisation of nano zero-valent iron (nZVI) and H_2O_2 to degrade pulp and paper industry effluent adsorbable organohalogens (AOX). In their work, two different agitation processes were also mechanical, and ultrasound was compared with process

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[17] Mixed metal oxide (MMO) electrodes with high conductivity and corrosion resistance for use as anodes in electrolysis.

variables such as time, p, nZVI, and H_2O_2 concentration. Results show a higher AOX reduction with a higher nZVI concentration. Furthermore, the optimal combination of variables with mechanical agitation was found in the ratio of nZVI:H_2O_2 as 2:5, reaction time 1 h, pH 2.7 with an 85% degradation of AOX.

Dogan et al. 2021 studied the utilisation of Fenton and photo-Fenton processes integrated with submerged ultrafiltration to treat pulp and paper industry wastewater. The experimental work examined the benefits of hybrid Fenton and photo-Fenton, with UVC_{254} and UVA_{365} radiation, with the UF system treating raw wastewater from the pulp and paper industry by membrane oxidation reactor (MOR). Their optimised results showed a 91% COD reduction.

Combined electrocoagulation and UV-based sulfate radical oxidation processes for treating pulp and paper wastewater were studied by Jaafarzadeh et al. 2016. In this work, the UV/oxidant system followed electrocoagulation to remove organic compounds from pulp and paper wastewater. Under optimum conditions (existing pH, time = 33.7min and current density = 5.55mA/cm^2), about 61% COD_{Cr} removal was achieved over the electrocoagulation. After electrocoagulation, the effluent was treated with UV/persulfate and UV/peroxymonosulfate. The results showed that UV/persulfate had the best performance at the existing pH of 8.2, while UV/peroxymonosulfate required a reaction pH of 4.0 to provide the best efficiency. Using the electrocoagulation process only was found not as effective in improving the biodegradability (BOD_5/COD ratio) of the wastewater, whereas, combining the electrocoagulation and UV/oxidant could significantly increase the biodegradability. In addition, solar irradiation was tested as an alternative for UV sources, and the related results exhibited negligible efficiency.

5.3. Applications of AOP in other industries

Fenton’s reaction was first applied in wastewater treatment in 1950 at the Massachusetts Institute of Technology as a disinfectant (Schumb et al. 1995). However, the first application of Fenton’s reactions as an oxidative process for destroying hazardous organic compounds in water was made in the middle of the 1960s (Huang et al. 1993, Neyens et al. 2003)

In environmental applications, catalytic AOPs have proven particularly useful in degrading and detoxifying organic contaminants (Balcioglu et al. 2001, Bhatkhande et al. 2002, Neyens et al. 2003, Gonze et al. 2003, Sarria et al. 2004, García-Montaño et al. 2006a). In the early 1990s, the expansion of hydrogen peroxide for environmental applications in soil treatment using catalyst and chemistry approaches deviated from traditional applications of Fenton's reagent usage in the industry. Early publications by Watts et al. 1990, Pignatello 1992, Watts 1992, Pignatello et al. 1994, and others began to explore the roles of soil mineralogy and different chemical amendments on hydrogen peroxide effectiveness.

The application of AOP to disinfect water, i.e., to inactivate waterborne pathogens, was initiated in the 2000s. The first demonstration capacity of photo-Fenton to disinfect water was reported by Rincón et al. in 2006. Since then, other pathogens, chemical and biological parameters related to iron chemistry, and the treatment efficiency in several types of surface waters have been investigated.

With the growth of the environmental industry, iron-catalysed hydrogen peroxide was adapted to site remediation and has been used for over 40 years as an oxidant to treat contaminated soil and groundwater. However, applications utilising these oxidants in-situ result in dramatically more complex chemistry than only generating hydroxyl radicals, as presented in *Reaction 9*. In addition, many other catalysts and radicals that are not present in the classical Fenton process have been found to play a significant role in contaminant degradation reactions when hydrogen peroxide is applied in situ.

The AOPs have received increasing attention from researchers worldwide, especially during the last decade. The related processes were frequently reported to be among the most appropriate water treatment technologies to remove natural organic material from different water sources and mitigate the formation of disinfection by-products (DBPs). These AOPs typically include UV and or ozone-based applications, different Fenton processes, and various heterogeneous catalytic and photocatalytic oxidative processes. In addition, other non-conventional AOPs such as ultrasonication, ionising radiation, plasma, and electro-oxidation technologies are also reported. (Sillanpää et al. 2019)

Among some new AOPs are the so-called electrochemical advanced oxidation processes (EAOPs) that are reported to be used for various synthetic and natural wastewaters: The EAOPs can be divided into five key methods, anodic oxidation (AO), anodic oxidation with electrogenerated H_2O_2 (AO-H_2O_2), electro-Fenton (EF), photoelectro-Fenton (PEF) and solar photoelectro-Fenton (SPEF), alone and in combination with other methods like biological treatment, electrocoagulation, coagulation and membrane filtration processes. (Moreira et al. 2017)

Several AOPs are being applied in real-case scenarios to treat drinking water supplies, especially UV, Fenton, and O_3-based processes. Nonetheless, the main issues for a broader application of AOP methods remain the technological complications and economic viability. In general, the widely used processes for the treatment of potable water sources are separation and purification technologies, including (micro, ultra, and nano) membrane filtration (Guo et al. 2010, Pendergast et al. 2011, Metsämuuronen et al. 2014), reverse or forward osmosis (Malaeb et al. 2011, Chun et al. 2016), adsorption technique (Bhatnagar et al. 2017) and/or coagulation (Matilainen et al. 2010, Keeley et al. 2016). In order to improve the overall efficiency of water treatment facilities, combining two or more of those technologies was proven to be a viable option. These integrated water treatment processes include the combination of AOPs with membrane filtration, adsorption and coagulation, and biodegradation (Ang et al. 2015).

In membrane-based technologies, the drinking water supply is generally pre-treated with micro or ultrafiltration membranes before applying nanofiltration or reverse osmosis. Such an approach is necessary because membrane fouling by humic substances significantly lowers ultrafiltration efficiency to remove natural organic matter (NOM) from water (Sutzkover-Gutman et al. 2010), hence the need to reduce the fraction of NOM before applying the more sensitive nanofiltration membranes (fouling wise). In membrane-based integration scenarios, the application of AOPs, prior to or after the membrane filtration, helped to improve the quality of the treated water one hand and reduced the occurrence of the fouling phenomenon on the other hand (Gao et al. 2011, Jeong et al. 2014, Winter et al. 2016).

In this context, Pramanik et al. 2016 investigated and compared the influence of O_3 and UV/H_2O_2 as pre-treatment of a drinking water supply before its purification using an ultrafiltration membrane. In addition, the evolution of organic fouling was also monitored. The main related results showed that high molecular weight organic compounds (e.g., proteins and polysaccharides) contributed to 90% of the total fouling phenomenon. Furthermore, applying these AOPs as pre-treatments reduced the foulants content (i.e., degradation of high Mw organics), which helped improve the membrane flux (61% for UV/H_2O_2 and 43% for O_3).

Another option to combine AOPs and membranes that is increasingly gaining interest is the development of photocatalytic membrane reactors (PMR) (Huang et al. 2008, Song et al. 2012, Mozia et al. 2015, Molinari et al. 2017). In water treatment applications, this integrated process is based on combining photocatalytic oxidation and submerged membranes. The former helps mitigate the fouling phenomenon by degrading organic compounds present in the waters, whereas the latter helps separate the suspended photocatalysts via filtration. For the specific case of photocatalytic degradation, adsorption takes another dimension as it occurs alongside the photocatalytic activity of semiconductors such as TiO_2 (Reddy et al. 2015) and ZnO (Oskoei et al. 2016)._Those single or hybrid photocatalyst adsorbents generally combine high adsorption capabilities and high photocatalytic activities (Yoneyama et al., 2000, Upadhyay et al. 2014)

The other possible integration scenario involves the combination of AOPs with the adsorption technique. This method includes the combination of catalytic ozonation and charcoals. In a related study, the applicability of heterogeneous catalytic ozonation with bone charcoal to remove humic acid (HA) substances was assessed in comparison with other oxidation and advanced oxidation processes, including H_2O_2, O_3, O_3/H_2O_2, and O_3/H_2O_2/bone charcoal (Mortazavi et al. 2010). The results showed that, under various pH conditions, adding the charcoal catalyst in the ozonation process helped increase the HA degradation rates by 1.5 times more than the single ozonation. Furthermore, under various temperatures, the reaction of the catalytic ozonation of HA was also efficient, which makes the studied process applicable for the degradative removal of humic substances from water. Similar studies made with AOP and adsorbents for removing NOM from drinking water supplies have been successfully applied (Yan et al. 2010, Trang et al. 2014, Naghizadeh et al. 2015, Naghizadeh 2016, Omorogie et al. 2016). Other absorbents and photocatalytic compounds used in different studies are Cu_2O nanocrystals (Jing et al. 2014) and TiO_2-ZrO_2 (Khan et al. 2015). In addition, other improved and combined adsorption and photocatalytic activities for the removal of NOM (specifically HA) were reported for different hybrid photocatalysts such as the TiO_2/AC (Lim et al. 2011, Xue et al. 2011), TiO2/coconut shell powder (Kim et al. 2016), TiO_2/zeolite (Liu et al. 2014) and ZnO-TiO_2/bamboo charcoal (Wang et al. 2013b, Wang et al. 2013a).

Integrated AOP technologies also include a combination of AOPs with coagulation. For both integrated processes, AOPs are generally applied as a pretreatment step for improved coagulation or biodegradation (Uyguner et al. 2007). In this configuration, the oxidative degradation of NOM is the key factor conditioning the efficiency of the subsequent coagulation or biodegradation stages. Thus, based on the characteristics of the initial NOM content and the specifically applied AOP, various intermediate compounds with modified features are then available for further treatments. At this point, the structural, molecular, and chemical modifications will substantially impact the choice of coagulants, the doses to be applied, and other operating conditions, mainly pH (Rodríguez et al. 2012, Ayekoe et al. 2017). In addition, the application of coagulation after AOPs was also reported to be an advantageous additional stage to remove DBPs formed during the oxidation process (Selcuk et al. 2007, Sillanpää et al., 2014). The issue is less complicated for improved biodegradation because most studies report the transformation of high Mw hydrophobic compounds, including humic-, fulvic- and protein-like substances, into more biodegradable low Mw hydrophilic compounds (Sallanko et al. 2013, Liao et al. 2017).

6. OBJECTIVE 1: MODIFIED FENTON'S PROCESS FOR WASTEWATER

This section focuses on finding a chemical way to improve COD reduction and significantly improve the hard COD removal over a biological treatment plant in chemical pulp mill wastewaters to reach new and tighter environmental limits.

In the author´s early laboratory tests, the author recognized that the original Fenton reagent with only catalytic amounts of catalyst metals did not work for pulp and paper waters. One possible reason it did not work originated from pulp mill bleaching sections where residual chelating agents such as ethylenediaminetetracetic acid (ETPA) and diethyleneaminepentacetic acid (DTPA) were used to capture metal ions such as iron. These chelating agents are used to inactivate metal ions found in process waters that cause H_2O_2 decomposition in the bleaching stage and form hydroxyl radicals that may cause fibre damage, reducing the final product's value. (Jones et al. 2002)

The study scope is set to develop a more robust Fenton's reagent to cope with these organically strong wastewaters where the original Fenton's reagent is less effective. Fenton´s reagent has been reported to remove or oxidize difficult to biodegradable organic molecules.

6.1. Introduction

Different compounds are formed and naturally found in untreated pulp and paper wastewaters depending on the type of process, raw material, and chemical used. Most typical compounds found in high concentration levels are SS, extractives, fatty acids, lignin, tannins, and derivates resulting in high BOD and COD. Some of these naturally occurring compounds can be easily removed by biological processes. (Area et al. 1998, Ali et al. 2001). However, some of these substances are recalcitrant to biological processes and toxic to aquatic life. The bleaching processes can also, in some cases, form bioaccumulated compounds or, depending on the Kraft bleaching process, even some compounds such as dioxins and furans (EU IPPC 2001, Karrasch et al. 2006, Kovacs et al. 2002)

The activated sludge process was reported to remove only 68% of the initial COD load of 12 000 mg/L, and similar values were found for NSSC pulping effluent with 14 200 mg/L initial effluents (Meza et al. 2010). In addition, only 31% COD removal of Kraft mill effluent by activated sludge process was reached (Larrea et al. 1989), whereas an Upflow Anaerobic Sludge Blanket (USAB) reactor reached 80-86% without recirculation and 75-78% with circulation (Buzzini et al. 2006, Thompson et al. 2001).

Fenton's reagent is known for its easily scalable removal rate, fast reaction times, and effectiveness in treating effluents from chemical, petrochemical, textile, and other industries (Steber et al 1986, Bowers et al. 1989, Bidga 1995, Adams et al. 1996, Pulgarín et al. 1996, García et al. 2001, Muñoz et al. 2006, Lapertot et al. 2006, Diyaúddeen et al. 2011, Martinez-Huitle et al. 2009, Oller et al. 2010, Lal et al. 2017, Ribero et al. 2020).

In the late 1980s and the early 1990s, the water regulations for the Finnish paper industry became tighter, and especially COD_{Cr} and P_{tot} reduction was targeted. (Länsi-Suomen Vesioikeus, 1995). As a result, new treatment methods to remove soluble organic compounds that are either toxic or non-biodegradable over traditional chemicals (chemical coagulation and flocculation) and biological methods were continuously investigated to enhance COD_{Cr} reduction and meet the requested environmental limits.

Pulp and paper mills use chelating agents to capture and inhibit soluble metal ions from decomposing valuable bleaching chemicals such as hydrogen peroxide. Some of the active chelating agents and wood-originated molecules could be found in the wastewaters, hindering catalytic reactions. These chelating agents are known not to be degradable in the biological treatment plant and become one source for the recalcitrant COD (Sillanpää et al. 1995). Other compounds of interest are the adsorbable organic halogens (AOX), mainly in the form of chlorinated high-molecular-mass (>1000 Da) lignin-derived material. (Lindström et al. 1981, Berry et al. 1993, Dahlman et al. 1993, Savolainen et al. 1993)

A new modified Fenton's reaction treatment based on coagulation and oxidation, FennoTriox, was developed based on Saunamäki's 1992 study to overcome the challenges of a chelated catalyst. This treatment was designed as a final stage of effluent treatment to reduce the H_2O_2 and iron salts' operational costs, *Figure 12*.

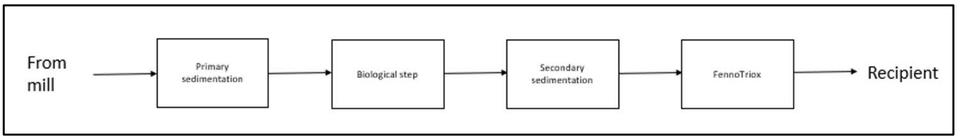

Figure 12. The placement of the FennoTriox step as a polishing step in the pulp and paper effluent treatment step.

Different compounds are found and formed in the untreated pulp and paper wastewaters depending on the type of process, raw material, and chemical used. These compounds contribute to high concentrations of BOD, COD, SS, extractives, fatty acids, lignin, tannins, and derivates in pulp and paper wastewaters. Some of these compounds are naturally occurring and easy to remove by biological processes. (Area et al. 1998, Ali et al. 2001) However, some of these substances are recalcitrant to biological processes and toxic to aquatic life. The Kraft bleaching stages can also, in some cases, form bioaccumulated compounds or even some compounds such as dioxins and furans (Karrasch et al. 2006, Kovacs et al. 2002, EU IPPC 2001)

Conventional treatment methods such as biological, thermal, and physicochemical treatment methods, including adsorption, flocculation, coagulation, extraction, and membrane technologies, are often insufficient to remove all of these compounds. For this reason, advanced treatment systems have been sought to reduce refractory organic compounds to meet the increasingly stringent discharge limits. (Scott et al. 1995, Wardman et al. 1996, Marco et al. 1997, Karimi et al. 2009, Kim et al. 2011)

Lucas's et al. 2012 study compared pulp mill wastewater treatment with tertiary treatment with Fenton (Fe^{2+}/ H_2O_2) and solar photo-Fenton ($Fe^{2+}/ H_2O_2/UV$) processes in a pilot plant scale. The study resulted in DOC mineralisation, COD, and total polyphenol removal exceeding 90%, thereby reaching the set environmental limits. In addition, the impact of the flocculation-Fenton oxidation and sand filter process on anaerobic and aerobic pre-treated papermaking effluent was studied by Wang et al. 2012. The study of Wang et al. shows a 93% reduction in COD.

Additionally, Shi et al. 2013 studied a full-scale Fenton/flocculation process for a pulp and paper mill placed as a tertiary treatment step after the biological process from January to December 2011. The study focused on wastewater from a pulp and paper mill producing containerboard paper, corrugated paper, and wood pulp. The production raw materials consisted mainly of wood chips and wastepaper. The study focus was on the relation of H_2O_2, waste acid (8% $FeSO_4$), $Al_2(SO_4)_3$, polyacrylamide (PAM), and CaO dosages on COD removal efficiency from the wastewater. The study used H_2O_2 and waste acid for the Fenton process over a 25 min reaction time. The Fenton-treated water was sedimented in a 30 min lamella unit with the help of $Al_2(SO_4)_3$, CaO, and PAM flocculation before being sent to the receiving water body. The results show that dosages of H_2O_2, waste acid, $Al_2(SO_4)_3$, and CaO increased with influent COD load, but PAM had no significant change. The molar ratio of H_2O_2/Fe^{2+} was about 1.0 to 2.0. As a result, the treated effluent COD dropped from 400-300 mg/L to 65-100 mg/L and SS 20-30 mg/L, respectively, and met the discharge limits set for pulp and paper industry effluents.

A study on the performance of a Fenton's reaction on an industrial scale to remove phenols from the pulp and paper industry wastewaters was made by Skoronsk et al. 2015. The overall phenol removal efficiency reached over 99.7%, demonstrating that combining biological and Fenton processes is a promising method for removing calcitrant contaminants.

$FeCl_3$ pre-treated pulp mill effluent subjected to Fenton-like oxidation was studied by Lal et al. 2017. Residual dissolved iron from the pre-treatment step and H_2O_2 were utilized as catalysts and oxidants, respectively, while the initial wastewater pH was 4.0 (unadjusted). As a result, maximum lignin and total organic carbon (TOC) removals of 85% and 48% could be achieved within a 2 h reaction. Moreover, adding radical scavenger tertiary butyl alcohol and chloroform significantly reduced TOC removal.

Grötzner et al. 2018 studied Brazilian Chemical Thermal Mechanical Pulping (CTMP) wastewaters. The CTMP process generates effluent with a high concentration of organic matter that is difficult to treat biologically. The study evaluated the efficiency of combining physicochemical pre-treatment by coagulation-flocculation-sedimentation (CFS) process and Fenton to treat the effluent. The treatment with CFS showed better results in removing solids and Fenton in removing recalcitrant compounds such as lignin. Combining CFS and Fenton to treat the CTMP effluent resulted in 95% TOC removal efficiency, 61% for COD, and 76% for lignin contents.

Similar to Wang et al., He et al. 2019 studied the effect of Fentons reaction on a traditional two-stage biochemical treatment process from papermaking wastewater that does not meet the given environmental COD discharge limit. The study uses Fenton oxidation technology to treat effluent from a secondary sedimentation vessel overflow. The optimum Fenton parameters that resulted in the highest COD reduction were the H_2O_2 dosage of 6.54 mmol/L, $FeSO_4{\cdot}7H_2O$ 200 mg/L, pH=3, a reaction time of 1.5 h, and a 3-ppm dosage of polyacrylamide. The COD of the treated water was under 50 mg/L resulting in a 75.4% reduction. After the Fenton treatment, the effluent met the first grade of the Chinese wastewater discharge standard.

The Fenton process was used by Kumar et al. 2019, to treat the pulp and paper industry wastewater in India. The lignin is mainly responsible for the high COD found in pulp and paper wastewater. Their study focused on three independent variables COD: H_2O_2, H_2O_2: $Fe^{2+,}$ and time. The results show a maximum 94% COD removal at the optimised value of COD: H_2O_2 at 0.165, H_2O_2:Fe^{2+} at 0.0165, and a reaction time of 115 min.

Yu et al. 2020 studied full-scale deinking wastewater treatment. Their results indicated that coagulation and flocculation used as a pre-treatment process was a preferred option for SS removal. The semi-extended aeration system for COD and BOD_5 removal delivered excellent performance. The Fenton reactions could efficiently remove the wastewater's residual and barely biodegradable pollutants. The COD, BOD_5, and SS total removal efficiencies achieved were 94%, 90%, and 99%, respectively. Their results show that Fenton’s process applied as a tertiary process in deinking wastewater treatment can efficiently remove recalcitrant pollutants and show reliable performance for effluent.

6.2. Methods and materials

The wastewaters used for the on-site laboratory and pilot-scale experiments originate from a Finnish Kraft mill, an integrated Kraft mill, and a paper mill. The wastewater samples are collected from the effluent treatment plant primary sedimentation and secondary sedimentation stage overflows *Figure 12*. The untreated primary sedimentation overflow referred to untreated water samples, and activated sludge treatment referred to biologically treated water.

The laboratory and pilot tests were conducted at the site to avoid changes in water quality caused by biological activities and temperature changes. The individual sample sizes used are 10-20L and should be used within two hours from sampling.

6.2.1 Test equipment and chemicals

A Kemira Flocculator was used as a jar test for the Fentons reaction study in the laboratory. This equipment consists of six 1 L jar glasses where every single jar can individually be controlled in terms of mixing speed, mixing time, and sedimentation time. The chemicals used for pH control were 1M H_2SO_4 or 1M NaOH. The Hydrogen peroxide was Kemira Chemical's technical grade of 50% H_2O_2, and Kemira Kemwater's technical grade ferrosulphate containing 17.5% ferrous iron. In addition, 2 mg/L of Kemira Fennopol K1384, a low cationic high molecular weight polyacrylamide, was used for flocculation. Before being used, the dry Fennopol K1384 flocculant was diluted to a 0.2% liquid concentration.

6.2.2 Analytical methods

The analysis was done right after the laboratory and pilot tests sampling. The following analysis was made pH, Oxidation-Reduction Potential (ORP), Turbidity (NTU), COD_{Cr}, N_{tot}, and P_{tot}. Hach Test'N'tubes vials were used for COD_{Cr} analysis (High Range 20-1500 mg/L, article number 2125951), P_{tot} (range of 0.06-3.5 mg/L, article number 2742545), and N_{tot} (range of 0.5-25.0 mg/L, article number 2672245). The COD_{Cr} tubes were cooked for two hours at 120 °C before measurement in a Hach 45600 COD reactor. These fast tube analyses and the untreated turbidity measurements were measured with a Hach DR-2010 portable spectrophotometer. The Adsorbable Organic Halides (AOX) and Chloro Phenols (CP) analyses were sent to Keskuslaboratorio (KCL) for analysis according to Finnish Standard Method SFS-EN 1485 and SFS-EN 12673.

6.2.3 The modified Fenton's tests

A pH of 4 was used for the Fenton's reaction. First, a false test was conducted by adding the needed amount of ferrous sulfate followed by H_2O_2 under fast mixing and pH correction to reach the targeted reaction pH by adding the requested amounts of H_2SO_4 or NaOH. Afterwards, when the pH control reactants volumes were known, the real test was done by reversing the dosing sequence by starting with the needed amount of pH control reagent, followed by ferrous and H_2O_2 dosing to reach the targeted reaction pH of 4 directly. A mixing speed of 400 rpm for 30 s was used for the H_2SO_4, COP, and H_2O_2 peroxide addition. For polymer addition, a mixing speed of 40 rpm for 15 min was used to build up the particles formed after the Fenton stage. Finally, a 30 min sedimentation time was used before sampling the clear supernatant.

For the pilot test, a containerized water treatment pilot unit was used. The unit is built around a 100 L mixing reactor, a 500 L mixing reactor, and a second 500 L mixing reactor, followed by a Krofta 4 - dissolved air flotation unit as the last unit in the process. The DAF unit's function is to separate the formed iron sludge from the treated water by the generated microbubbles that attach to the formed flocs. Additionally, four chemical tanks with a mixing device for acid, polymer, and precipitation chemicals are fitted in the container. The unit includes pH-control and turbidity measuring fitted in the inlet tank and DAF-treated water for process control. The flow through the process is 4 m^3/h. The incoming water is taken to the unit via a submersible pump from the secondary sedimentation unit overflow.

The difference between the modified Fenton's and the original Fenton's reagent was the addition of iron in a much higher dosage than the catalytic amount needed for various pulp and paper effluents. Using a higher iron coagulant dose resulted in the coagulation of possible iron-chelating or hydroxyl radical scavengers that reduced the operational costs related to higher H_2O_2 dosages. Thus, this method improved the cost performance of the modified Fenton's process when treating wastewater with high organic concentrations. The FennoTriox applied for Kraft, and integrated Kraft was mainly used with the following chemical dosages, *Table 11*.

Table 11. Typical dosage levels of the FennoTriox systems (Jansson 1996a).

Parameter	Dosage
Incoming COD_{Cr}, vs $FeSO_4*7H_2O$	1:1 e.g., 2000 mg/L COD_{Cr}, in: 2000 mg/L $FeSO_4*7H_2O$
H_2O_2	10% of iron
H_2SO_4	to reduce pH
pH (the reaction pH)	4
Dosage of high molecular low cationic polymer just to the inlet of the solid/liquid separation unit	2 mg/L
To readjust the pH to acceptable emission levels	$Ca(OH)_2$ or NaOH

The modified Fenton's process flow diagram is shown in *Figure 13*. First, the ferrous solution is dosed to the effluent stream before adding the right amount of either acid or alkaline solution. After the H_2O_2 dosing, the pH in the reactor is at the desired level. After the reaction tank, the polymer is added just at the inlet of dissolved air flotation, where the created sludge is removed from the top, and the purified water is taken out close to the bottom.

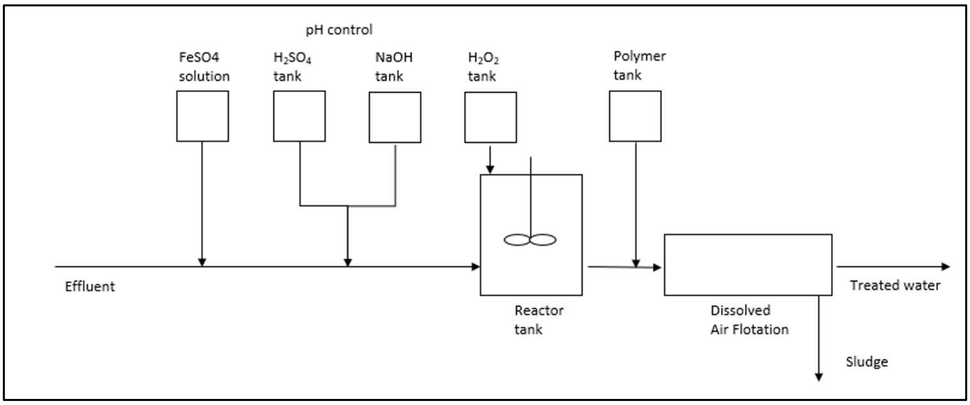

Figure 13. Basic flow diagram of the modified Fenton's x system in the 1990s (Jansson 1996a).

6.3. Results and discussion

Table 12 to *14* show results gathered from s pilot tests made from 1990 to 1996 at three Finnish pulp and paper mill sites.

Table 12 shows results achieved from Bleached birch Kraft mill treatment with modified Fenton. A high 92% reduction for COD_{Cr}, AOX 88%, chlorophenols (CP) 92% and P_{tot} 98%. Especially the high COD_{Cr} reduction indicates a good hard COD_{Cr} removal. The high 85% N_{tot} reduction from treating bleached birch Kraft mill effluent is partly expected to originate from residual chelating agents' adsorption into the formed iron sludge. (Jansson 1996a)

Table 12. Bleached birch Kraft mill effluent (Jansson 1996)

Process stage	COD_{Cr} mg/L	AOX mg/L	CP mg/L	N_{tot} mg/L	P_{tot} mg/L
Before activated sludge	910	12.9	0.060	4.35	1.82
After Activated sludge	460	10.4	0.048	4.20	0.95
After FennoTriox	70	1.6	0.026	0.64	0.03
Reduction%	92	88	92	85	98

Table 13 presents pilot test results from an integrated Kraft and paper mill effluent treatment with modified Fenton's process. The COD_{Cr}, AOX, N_{tot}, and P_{tot} reduction levels of 91%, 85%, 87%, and 97% are similar to the bleached birch Kraft mill effluent treatment results.

For paper mill effluent treatments, the COD_{Cr}, N_{tot}, and P_{tot} reductions are good but not as high as for the bleached birch Kraft and the integrated Kraft and papermill, *Table 14*. The reduction levels seem to be around 10% lower than in the presented Kraft mill effluents. Reasons for lower reduction levels are unknown but likely caused by unoptimised chemical dosing.

Table 13. Integrated Kraft and paper mill effluent (Jansson 1996).

Process stage	COD_{Cr} mg/L	AOX mg/L	Colour Pt mg/L	N_{tot} mg/L	P_{tot} mg/L
Before activated sludge	740	10.8	750	2.75	1.05
After Activated sludge	467	8.9	755	2.64	0.44
After FennoTriox	69	1.6	59	0.34	0.03
Reduction%	91	85	92	87	97

Table 14. Paper mill effluent (Jansson 1996).

Process stage	COD_{Cr} mg/L	SS mg/L	Color Pt mg/L	N_{tot} mg/L	P_{tot} mg/L
After Activated sludge	122	46	83	3.4	0.28
After FennoTriox	31	7	4	1.3.	0.03
Reduction%	75	85	95	62	89

The 92 to 75% high COD_{Cr} removal efficiency indicates that the modified Fenton's process is an effective chemical method to improve the hard COD_{Cr} removal after a biological treatment plant for various pulp and paper wastewaters. In addition, this improved hard COD removal means that Fenton's process can be used as a tertiary treatment step to reach new and tighter environmental limits, *Table 15*.

Table 15. Chemical pulp mill wastewater COD_{Cr} treatment removal efficiencies (Jansson 1996)

Method	COD_{Cr} reduction%
Chemical	30-50%
Biological	50-75%
Chemical + Biological	60-85%
Chemical + Biological +AOP	>90%

The over 90% high COD_{Cr} reduction removal efficiencies results are in line when using modified Fenton's process as a tertiary treatment step for pulp and paper industry wastewaters reported by Lucas et al. 2012, Wang et al. 2012, Skoronski et 2015, Grötzner et al. 2018, Kumar et al. 2019, Yu et al. 2020. The high COD_{Cr} removal efficiencies are based on the removal of difficult-to-degrade compounds present in the pulp and paper industry wastewaters like lignin, phenolic and oil compounds. In addition, the reduction of acute wastewater toxicity on *Daphnia Magna* after treatment with Fenton's process was reported by Grötzner et al. 2018, which supports the removal of recalcitrant COD_{Cr}, like toxic phenolic compound, from the wastewaters.

Grötzner et al. also noted the importance of using an additional iron dose prior to H_2O_2 in the Fenton's process to coagulate, remove, and reduce the possible hydroxyl radical scavengers present in the wastewater to be treated. For example, the results of Lal et al. 2017 showed that adding radical the scavenger's tertiary butyl alcohol and chloroform before the Fenton's process reduced the TOC removal significantly.

Several factors limit the generalizability of the study results. First, the modified Fenton process is challenging to optimise due to four control parameters. These parameters are reaction pH, iron, H_2O_2, and polymer dosages. Shi's et al. 2013 study showed that following the continuously changing inlet wastewater quality is essential to control the process. The wastewater quality, such as incoming water SS, COD_{Cr}, pH and redox, directly affects the used reagent dose, thereby generating hydroxyl radicals. Therefore, especially to minimize the H_2O_2 dosages, the water to be treated should be SS and colloidal-free and focus only on oxidizing the soluble compounds.

Shi et al.2013 and Kumar et al. 2019 reported optimum pH:H_2O_2: Fe doses and reaction times to treat specific pulp and paper mills wastewaters. These three reports utilise the Fenton process as a tertiary treatment step. However, only general dosage rates can be given as all pulp and paper industries use different process combinations, raw materials, chemicals, dosages, and processing times.

Further research is needed to keep the modified Fenton's process parameters, such as pH and redox (ORP), stable in a pilot or full-scale pulp and paper operation where the inlet water qualities are fast-changing. The real challenge is ensuring the generation of hydroxyl radicals and how to ensure the oxidation potential is high enough even to expect the presence of hydroxyl radicals in the treatment step. In addition, understanding how the measured redox (ORP) measurement relates to Eh and or rH-value is crucial for the optimised Fenton's process.

6.4. Conclusions

The modified Fenton's method is shown to be an effective tertiary treatment method for various pulp and paper wastewaters. Especially the COD_{Cr} and P_{tot} reductions were shown to be over 90% for Kraft mill and integrated Kraft and paper mill wastewaters. In addition, a slightly lower but still excellent COD_{Cr} removal of 75% and P_{tot} removal of 89% is achieved for paper mill wastewater treatment. Fenton's process used as a tertiary treatment stage increases the COD_{Cr}, AOX, P_{tot} and N_{tot} removal over an existing activated sludge treatment, making it easier for the Kraft, integrated Kraft and papermills to reach the sticker environmental limits.

Results show that higher amounts of ferrous ions are advantageous for Fenton's process in these specific cases. In addition, the extra-formed ferric coagulates impurities and further increases the removal of organic compounds, thus improving the overall runnability of the process.

Compared with the ordinary Fenton's reagent, the modified Fenton's reagent has some advantages such as less sensitivity for metal complexing, high COD_{Cr} and P_{tot} removal rate in very turbid waters, better runnability, simple operation, rapid degradation and organics mineralisation. In addition, the higher iron dosage used in the modified Fenton process shows a better reduction efficiency by coagulating possible residual chelating agents or hydroxyl radical scavengers from the wastewater before the H_2O_2 dosage. Additionally, the reagents used for modifying Fenton's process are readily available and familiar to the pulp and paper industry. The modified Fenton's also works for high wastewater flows typically found in pulp and paper. These flows can be measured from hundreds to thousands of m^3/h.

However, the modified Fenton's main disadvantage is the narrow operational pH of 3 to 4 and the amount of sludge generated.

7. OBJECTIVE 2: ADJUSTMENT OF WASTEWATER BOD_7/COD_{Cr} RATIO

This study targets using modified Fenton's processes before the existing activated sludge treatment plant and decreasing the oxidative chemical cost by modifying the wastewater BOD_7/COD_{Cr} ratio instead of targeting maximal COD_{Cr} removal. In the previous study, the modified Fenton's process is placed after activated sludge treatment as a polishing step for additional COD_{Cr} and P_{tot} removal. The investment cost (CAPEX) in the previous study consists mainly of adding oxidation reactors, chemical dosing and solid-liquid separation equipment needed for the process to work. The operational cost (OPEX) consists of necessary oxidation- and pH-control chemicals to reach the targeted oxidation environment and Fenton's reaction pH 4.

The present study uses acidic pulp bleaching filtrate to decrease the OPEX related to oxidation chemical and pH regulation. Moreover, additional CAPEX investments are avoided using the wastewater pipe leading down to the wastewater treatment plant as a reactor. The wastewater treatment plant existing primary sedimentation is used for the solid-liquid separation unit. The AOP studied are Fe^{2+}/H_2O_2, O_3/H_2O_2, O_3/UV and H_2O_2/UV to enhance the BOD_7/COD_{Cr} ratio for acidic pulp bleaching filtrate. If successfully enhancing the BOD_7/COD_{Cr} ration of the filtrate, the following biological treatment stage will have a better COD_{Cr} removal rate.

7.1. Introduction

Chemical oxidation for complete mineralisation is generally expensive because the oxidation intermediates formed during treatment tend to be more and more resistant to their complete chemical degradation, and they all consume energy (radiation, ozone, etc.) and chemical reagents (catalysts and oxidisers), which increase with treatment time (Muñoz et al. 2005). One alternative is to apply these chemical oxidation processes as a pre-treatment step to convert the initially persistent organic compounds into more biodegradable intermediates, which would afterwards be treated in a biological oxidation process with a considerably lower cost (Kearney et al. 1988, Haberl et al. 1991, Heinzle et al. 1992, Hu et al. 1994, Kiwi et al. 1994, Reyes et al. 1998, Mantzavinos et al. 1999, Pulgarín et al. 1999, Parra et al. 2000, Beltrán-Heredia et al. 2001, Sarria et al. 2003).

Studies have shown that the biodegradability of a waste stream changes when subjected to prior chemical oxidation (Gilbert 1983, Watt et al. 1985, Mohammed et al. 1992). The primary role of the chemical pre-treatment is partial oxidation of the biologically persistent part to produce biodegradable reaction intermediates. Therefore, the mineralisation percentage should be minimal during the pre-treatment stage to avoid unnecessary expenditure of chemicals and energy, thereby lowering the operating cost. Practical examples of sequential chemical and biological oxidation treatment have been previously reviewed by Scott et al. 1995, 1997, Jeworski et al. 2000, Sarria et al. 2002, Mantzavinos et al. 2004, Tabrizi et al. 2005, Augugliaro et al. 2006, Ikehata et al. 2006 and Gaya et al. 2008.

AOPs are based on the generation of highly active hydroxyl radicals and their intermediates. Therefore, AOPs are most widely applied when normally difficult-to-decompose compounds are present in the water. Destruction of organic compounds, such as phenols and chlorinated organic compounds, is an illustrative example of utilising AOPs. However, a total demineralisation of organic contaminants by AOP is not usually cost-effectively or chemically reasonable under ambient conditions (p and T). Thus, AOP treatment is applied mainly to decompose, e.g., toxic to less toxic products, or make the effluent more biodegradable by breaking up larger organic molecules into smaller ones. (Tuhkanen et al. 1994, Hunter 1996, Francoisse et al. 1996, McGrane 1996, Park 1999)

The full-scale implementation of conventional oxidation for pulp and paper waters is not economically feasible due to the high energy and chemical requirements for the complete degradation of recalcitrant compounds (Khalaj et al. 2018). Hence, advanced oxidation processes that convert the recalcitrant compounds into more biodegradable substances are considered promising alternatives in the existing pulp and paper wastewater treatment technologies. (Ginni et al. 2014, Neoh et al. 2016)

The drawbacks of using the modified Fenton’s process as a tertiary treatment method for pulp and paper effluents are additional equipment needs, high reagent cost and high sludge volumes. Therefore, to avoid these drawbacks, the focus has been set on process simplification and more effective reagent consumption by utilising the AOPs as a pre-treatment method before a biological treatment step to enhance COD_{Cr} removal.

This study aims to determine if the simplified AOPs can remove the hard COD_{Cr} and improve the biodegradability of pulp and paper wastewaters. For example, can the investment cost be reduced by utilising the existing wastewater pipeline leading to the treatment plant as a reactor? In addition, can the wastewater treatment plant's preliminary sedimentation basin be used as part of the process? Similarly, can the operational cost be reduced, especially the costs of the Fenton's reagent, utilising existing acidic wastewater in a pulp mill for pH control? Lastly, can the hard COD_{Cr} removal target be reached by modifying the inlet wastewater BOD_7/COD_{Cr} to improve biodegradability and reduce sludge generated by the modified Fenton process when used as a tertiary treatment? If successful, the non-biodegradable COD_{Cr} is removed in the following biological treatment plant.

7.2. Methods and materials

7.2.1 The utilised process

Figure 14 shows the process flow diagram for an existing bleached Kraft mill wastewater treatment. The process flow starts where three different waste streams are collected. Then, the reagents are mixed with these waste streams and sent into the wastewater pipeline that acts as a reactor. Then the reaction-generated solids could be removed in the primary sedimentation basin. Next, the modified BOD_7/COD_{Cr} stream flows to the activated sludge biological stage, where bacteria can remove the newly formed biodegradable organics. After the biological stage, the treated water flows to the secondary sedimentation basin from the biological stage, where the bacteria are removed and partly returned to the beginning of the biological stage. The treated water then flows to the recipient water stream.

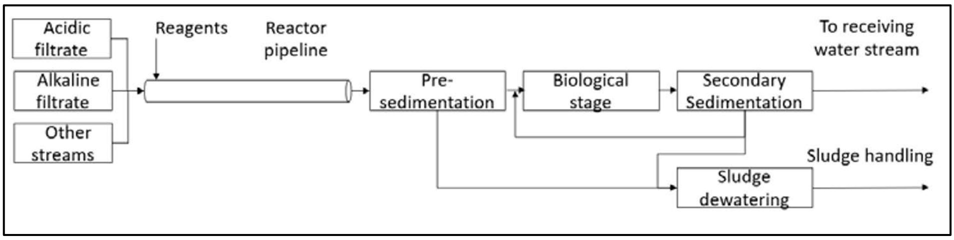

Figure 14. The studied process flow diagram for a typical pulp mill effluent treatment plant with the suggested incorporated reagent dosing and utilisation of the inlet pipeline as a reactor.

In the present study, the tests were made with the acidic pulp bleaching filtrate and AOP based on Fe^{2+}/H_2O_2 as a reference system against O_3/H_2O_2, O_3/UV, and H_2O_2/UV.

7.2.2 Acid filtrate sample

The acidic pulp bleaching filtrate (D0 filtrate) sample to be oxidated was taken from the softwood pulp mill process with a bleaching sequence D0-O/O-D1-E(P)-D2. The D refers to the ClO_2 stage, and the number indicates the ClO_2 stage counted from pulp stock. Similar, O-stage refers to oxygen bleaching, E for the alkaline and P for the peroxide stage. The temperature in this bleaching stage is 65 °C. The analysis of three different batches of the filtrate is shown in *Table 16*. The tests of the present study were done by oxidising filtrate D2.

Table 16. Analysis of three D0 filtrates (Laine et al. 2003).

	D0	D1	D2
pH	3.4	3.0	3.1
COD_{Cr}, mg/L	820	940	1210
TOC, mg/L	360	400	520
BOD_7, mg/L	na	na	350

na: not analysed

7.2.3. Chemicals

Hydrogen peroxide used was Kemira Chemical's technical grade 50% H_2O_2, Kemira Kemwater's technical grade ferrous sulphate containing 17.5% ferrous iron. Ozone was generated from oxygen gas with a

Herrman-ozone generator. 1 M NaOH was used for pH regulation. Sigma's Catalase C-30 (EC 1.11.1.6) was used to destroy residual hydrogen peroxide from the solution to avoid possible analysis errors caused by residual H_2O_2 in the COD_{Crr} analysis.

7.2.4. Analytical methods

COD_{Cr} was analysed with DrLange Cuvette Tests LCK114 and LCK014, TOC Shimadzu TOC-5000A apparatus and BOD_7 with standard SFS 5508. The residual hydrogen peroxide was detected with a strip test, Baker Strips Peroxide. The molecular weight (Mw) distribution was determined by HPLC using a TSK-GEL G3000SW column and UV-VIS detector. The molecular weight distribution of the treated effluents was compared to untreated water. Thus, no absolute values but only comparative molecular weight distributions were obtained with the present method. The method can detect molecules with a molecular weight not less than approximately 100. Thus, the share of the smallest (undetected) molecules can be evaluated by comparing the amount of organics shown in Mw diagrams to the respective COD_{Cr} values.

7.2.5 Experimental

In the oxidation tests with hydrogen peroxide and ozone, the pH of the filtrate was increased to 7 with 1 M NaOH. Hydrogen peroxide was dosed to the heated solution, and ozone was added so that the mass ratio of hydrogen peroxide/ozone was 0.5-1.5. The dosages of hydrogen peroxide were 1.9 and 3.8 g/1 100% H_2O_2, equal to 0.75 and 1.5 theoretical amounts needed to oxidise the COD_{Cr} completely. The reaction temperature of 60 °C was used for the oxidation tests. After the oxidation tests were conducted, the residual hydrogen peroxide was decomposed with Catalase C-30 enzyme, and COD_{Cr}, TOC, BOD_7, and the molecular weight distribution were analysed. BOD_7/COD_{Cr} ratio was calculated and used as an indicator of the biodegradability of the water.

Oxidation tests with hydrogen peroxide and ferrous iron catalyst were carried out by adding 20 mg/1 Fe^{2+} and 0.38-3.8 g/1 100% hydrogen peroxide into the heated filtrate. The hydrogen peroxide dosages correspond to the 0.15-1.5 of the theoretical amount needed to oxidise the COD_{Cr} completely. A reaction temperature of 60 °C was used. In addition, some comparative tests were carried out at room temperature, 24 °C. After the desired reaction time, 60 min for the tests at 60 °C and 90 min for the tests at room temperature, the samples were treated and analysed after hydrogen peroxide/ozone treatment.

7.3. Results and discussion

The test parameters and results of the oxidation tests are shown in *Table 17* and *Table 18*. *Table 17* reveals 18 to 48% COD_{Cr} and 13 to 40% TOC reductions obtained with hydrogen peroxide/ozone oxidation while BOD_7 increases or remains at the initial level. The BOD_7/C COD_{Cr} ratio increased in all oxidation experiments, i.e., the share of the biodegradable organic compounds increases during oxidation. The more effective the oxidation is, the higher the impact on BOD_7/ COD_{Cr} ratio. Ozone alone also increases the share of biodegradable compounds, but the combination of hydrogen peroxide and ozone is much more efficient. With ozone alone, the ratio BOD_7/COD_{Cr} increases from 0.3 to 0.4, while with hydrogen peroxide/ozone (equal amount of ozone, H_2O_2/O_3 1.5), the ratio is as high as 0.9. This increase in biodegradability of other waste streams when subjected to prior chemical oxidation is in line with previously reported studies (Gilbert 1983, Watt et al. 1985, Mohammed et al. 1992).

A similar trend in the COD_{Cr} and TOC-reductions is observed when using ferrous iron ions as a catalyst for hydrogen peroxide oxidation at 60 °C. 23-37% of COD_{Cr}, and max. 20% of TOC is removed, and the BOD/ COD_{Cr}, ratio increases from the initial 0.3 to 0.4-0.5.

Table 17. Conditions and COD_{Cr}, TOC, and BOD_7 reductions in the oxidation of DO 3 filtrates at 60 °C, 60min. (Laine et al. 2003)

H_2O_2 g/L	O_3 g/L	H_2O_2/O_3 g/g	Fe^{2+} mg/L	COD_{Cr} mg/L	COD_{Cr} red.%	TOC mg/L	TOC red.%	BOD_7 mg/L	BOD_7/COD_{Cr}
-	-	-	-	1210	-	520	-	350	0.3
1.9	0.95	1/0.5	-	990	18	450	13	370	0.4
1.9	1.9	1/1	-	870	28	440	15	340	0.4
1.9	2.8	1/1.5	-	800	34	400	23	360	0.5
3.8	1.9	1/0.5	-	860	29	430	17	440	0.5
3.8	3.8	1/1	-	710	41	360	31	**	-
3.8	5.7	1/1.5	-	620	48	310	40	570	0.9
0	5.7	-	-	780	35	390	25	330	0.4
0.38	-	-	20	930	23	na	-	na	-
0.63	-	-	20	850	30	430	17	na	-
1.3	-	-	20	760	37	na	-	na	-
1.9	-	-	20	780	36	410	21	300	0.4
3.8	-	-	20	820	32	430	17	380	0.5
1.9*	-	-	20	1060	12	510	2	370	0.3
3.8*	-	-	20	1010	17	500	4	400	0.4

*24 °C and 90 min, ** analysis failed, na: not analysed.

A comparison of the contents of the residual organic compounds in the filtrate based on COD_{Cr}, or TOC and Mw distribution, *Table 18*, indicates that the remaining COD_{Cr} and TOC share is 66% and 77% (hydrogen peroxide/ozone ratio 1/1.51 hydrogen peroxide dose 1.9 g/L), the share which is observed in Mw distribution is only 30% of the initial. Thus, it can be concluded that the sample contains organic compounds, which are not shown in the Mw analysis, their molecular weight is very low. This is in accordance with the increase of BOD_7/COD_{Cr} in this oxidation: the ratio is 0.5 instead of the original 0.3.

Table 18. The share of the residual organic compound after oxidation of DO 3 filtrates at 60 °C, 60min (Laine et al. 2003)

H_2O_2 g/L	O_3 g/L	H_2O_2/O_3 g/g	Fe^{2+} mg/L	COD_{Cr} %	TOC %	BOD_7/COD_{Cr}	M_w %
-	-	-	-	-	-	0.3	-
1.9	0.95	1/0.5	-	82	87	0.4	65
1.9	1.9	1/1	-	72	85	0.4	50
1.9	2.8	1/1.5	-	66	77	0.5	30
3.8	1.9	1/0.5	-	71	83	0.5	50
3.8	3.8	1/1	-	59	69	-	25
3.8	5.7	1/1.5	-	52	60	0.9	20
0	5.7	-	-	65	75	0.4	50
1.9	-	-	20	64	79	0.4	60
3.8	-	-	20	68	83	0.5	45
1.9*	-	-	20	88	98	0.3	85
3.8*	-	-	20	83	96	0.4	90

*24 °C and 90 min, na: not analysed

The effect of temperature on removing organic compounds by oxidation is evident. After oxidation with H_2O_2/Fe^{2+} at room temperature, the COD_{Cr} and TOC-reductions remain at the level of 12 and 2%, respectively. At 60 °C, the reductions are 36% for COD_{Cr} and 21% for TOC. The filtrate biodegradability, measured as BOD_7/COD_{Cr} ratio, increases almost as much as at a higher temperature, where BOD_7/COD_{Cr} ratios are 0.4 to 0.5 at 60 °C and 0.3 to 0.4 at room temperature. However, the share of the smallest (undetectable) molecules is lower than after oxidation at a higher temperature.

There is no bigger difference between the hydrogen peroxide/ozone method and the ferrous ion catalysed hydrogen peroxide method in removing organic compounds and decomposing COD_{Cr} to BOD_7 at 60 °C. In this specific case (acid bleaching effluent), the application of ferrous ion catalysis is advantageous because no additional pH control is needed for the Fenton's process of oxidation reactions. In addition, the formed ferric ion may be utilised afterwards by elevating pH to such a level that ferric sulphate coagulates impurities and further increases the removal of organic compounds.

Similar tests, which show comparable results in the presented study, aiming to decrease incoming BOD_7/COD_{Cr} ratio and improve biodegradability, have later been reported to accomplish when using O_3 as pre-ozonation Kraft mill effluent (Bijan et al. 2005). Bijan et al. reported a 21% COD_{Cr}, 16% TOC removal and 13% BOD_5 increase. In addition, biodegradability increased from 5% to 50%. Bierbaum et al. 2009, studied two different paper mill effluents. They reported that the pre-ozonation increased for the first wastewater BOD_7/COD_{Cr} ratio from 0.06 to 0.24 and the second mill from 0.02 to 0.14.

The results indicate that the presented AOPs used as a pre-oxidation step is a new way to convert the recalcitrant compounds found in acidic pulp bleaching filtrate into more biodegradable substances. In addition, the increased BOD_7/COD_{Cr} ratio improves the overall biological treatment step COD_{Cr} removal.

This study shows that the simplified AOP can modify the alkaline pulp mill wastewater BOD_7/COD_{Cr} ration, thus making it easier to remove in the biological treatment step with higher COD_{Cr} and hard COD_{Cr} removal ration. This finding of improving the biodegradability of acid pulp mill wastewater from BOD_7/COD_{Cr} from 0.3 to 0.9 is in line with results found in municipal and other industries described by Kearney et al. 1988, Haberl et al. 1991, Heinzle et al. 1992, Hu et al. 1994, Kiwi et al. 1994, Reyes et al. 1998, Mantzavinos et al. 1999, Pulgarín et al. 1999, Parra et al. 2000, Beltrán-Heredia et al. 2001 and Sarria et al. 2003.

7.4. Conclusions

The results indicate that oxidation of the acid pulp mill effluent at 60 °C with hydrogen peroxide combined with ozone or with a ferrous ion catalyst significantly decreases the content of organic compounds. Close to 50% COD_{Cr} and 40% TOC reductions were obtained in the presented tests. In addition, the biodegradability of the filtrate increased during the AOP treatment. The share of the biodegradable material measured as the BOD_7/COD_{Cr} ratio increased from 30% to 90% after the most efficient oxidation treatment. The ferrous ion-catalysed hydrogen peroxide treatment at room temperature decomposed organic compounds to more biodegradable ones, even if the removal of organic compounds remained low. The benefit of ozone is its capability to oxidise organic compounds without a catalyst, but it is clearly shown that the combination of ozone and hydrogen peroxide is more efficient than ozone alone.

The apparent limitation for any Fenton’s process is the low reaction pH of 3-4, which will be an obstacle for mills with a plentiful amount of carbonates in the water to be treated. These carbonates are typically found in a paper mill, deinking, and some board mill waters from paper filler. However, the efficiency of this process should be tested on other pulp and paper effluents, especially for streams with high organic concentrations with low biodegradabilities, like debarking and H_2O_2 bleaching effluents.

8. OBJECTIVE 3: GREEN BIOCIDES

This study aims to find a less harmful biocide made with AOP methods without metal catalysts. The environmental authorities and industries have requested to move towards safer-to-use compounds. The scope is to use different O_3/H_2O_2 rations and dosages to achieve a 99% reduction in microbiological growth in the paper machine white waters. The chemical types of anti-slime agents are organic sulphur, bromine and quaternary ammonium compounds, aldehydes and some chlorine-based like NaOCl and ClO_2.

8.1. Introduction

Paper mills' operation would be virtually impossible without chemicals to control the biological or slime formation. The desirable biocides or slimicides characteristics are high toxicity and slow biodegradability, which attract regulatory attention. There would be less regulatory agency concern with a slimicide derived from a natural product that would be easily biodegradable. (Horn et al. 2007)

A paper mill provides a favourable environment for the growth of microorganisms (Klahre et al. 1996, Hassler et al. 2007, Robertson 2009). Microorganisms can enter in uncontrolled quantities with the process water, materials, additives and through the air. As water is available, biologically degradable material is plentiful, and the operating temperature is between 30 °C and 45 °C to support mesotrophic organisms, which encounter a variety of habitat, from fully aerobic to fully anaerobic, thus allowing for high biodiversity (Lahtinen et al. 2006). Given these circumstances, it is unsurprising that excessive microbial growth results. Microbial problems in papermaking have been experienced and documented for decades, and the expansion of production plants has provided more space and opportunities for microbial growth (Beckwith 1931, Appling 1955).

In principle, biofouling processes in a paper mill are the same as those typical of a wastewater treatment plant. The microorganisms form films and flocs, utilising organic carbon by converting it into metabolic products and new biomass. In a wastewater treatment plant, this is the desired process which eliminates carbon from water while generating activated sludge. Thus, the same process occurs in a paper mill but constitutes biofouling (Flemming 2002). The primary countermeasure is the application of biocides to control microbial growth, a process commonly termed disinfection (Simons et al. 2005, Schrijver et al. 2006).

Biocides are of utmost importance technically and economically for the paper industry to control the slime formation in paper machines. It has been estimated that under some circumstances, slime deposits can be responsible for up to 70% of all breaks, blockages and pump failures in pulp and paper mills. (Safade 1988)

Biocides are routinely used for slime deposit control in paper mills and are directed against living organisms without restriction to only targeted organisms. This implies that they also inevitably can harm the health of non-targeted organisms such as humans or animals. Biocides contain highly hazardous substances potentially harmful to the skin and can cause cancer or damage the DNA, reproductive or immune system. They can also have endocrine-disrupting effects, impairing the hormonal system with long-lasting harmful consequences. For these reasons, green biocides are desirable (Knight et al. 2002, Arai et al. 2009, Timothy et al. 2004, Rycroft et al. 1980, Hahn et al. 2005, Olea et al. 2002). An additional problem may be caused by their physicochemical properties that accumulate biocide in the fibres and affect the final product quality. However, little information is available on biocides in pulp and paper-mill white water and effluents because of the complexity of the white water matrix. (Lacrote et al. 2003).

Due to their hazardous properties, standard biocides are highly regulated substances worldwide. The regulatory considerations profoundly affect the pulp and paper industry, most notably in the United States, Canada, and Western Europe. The European Union Biocidal Products Directive went into effect in 2000, eventually removing many products from the market that did not pass a regulatory round-up or producers decided not to submit them for approval. (Tereskonova et al. 2004, Whalqvist J. 2007)

Many biocides currently in use necessitate safety precautions, and they contribute to the burden of undesired substances in wastewater, subject to the European Union biocide guidelines (Directive 98/8/EC, Directive 2010/72/EU, EU Regulation No 528/2012).

This study focused on the efficiency of ozone, ozone/hydrogen peroxide, and hydrogen peroxide treatments for microbiological control of paper machine white water. First, the efficiency of tested treatments was evaluated by considering the inactivation of aerobic heterotrophic bacteria, yeasts, and moulds because they were found in paper products. Besides, the effects of treatments on total organic material ($COD_{Cr\ tot}$), dissolved organic material ($COD_{Cr,\ sol}$), and water pH were measured.

8.2. Green biocides

Any substance, especially a bactericide or fungicide that kills or retards the growth of microorganisms and is considered to inflict minimal or no harm to the environment, is called green biocide. The most crucial industrial requirement for biocides is that they must be cost-effective, effective against a broad spectrum of microorganisms, and compatible with the application with no interference with other additives. However, the interest in these green biocides means that these need to meet new additional demands such as low toxicity, environmentally acceptable, safe and easy to handle and store, effective, and fast active. (Choudray 1998)

As the pulp and paper industry is going towards more closed water loops with minor freshwater usage, the need for better biocide systems is rising. More closed water loops with higher temperatures, availability of primary food sources, and micronutrients lead to higher bacteria counts in the paper machine white waters causing paper defects and paper machine runnability issues if not taken care of. However, many commonly used biocides have some adverse environmental effects. Together with strengthened legislation concerning biocide types and usage, these adverse environmental effects lead to more environmentally friendly biocide development. (Korhonen et al. 2001)

For example, hydrogen peroxide is used for disinfection purposes in medical applications, as a preservative in consumer goods, and slimicide in cooling water systems. Hydrogen peroxide is effective against bacteria, bacterial spores, viruses, and fungal species, but a long contact time is needed to achieve sterility. (Payne 1988)

Historically, most ozone treatment studies on pulp and paper mill effluents have focused on removing colour, odour, COD_{Cr}, BOD_7, lignins and tannins, chlorinated organics, resin, fatty acids and toxicity. (Coburn et al. 1984, Mohammed et al. 1984, Sozanska et al. 1991, Saunamäki et al. 1992, Beulker et al. 1993, Hostachy et al. 1993, Munter et al. 1993, Murphy et al. 1993, Pérez-Rey et al. 1993, Boyden et al. 1996, Mao et al. 1995, Möbius et al. 1996, Roy-Arcand et al. 1996, Zhou et al. 1996, Oeller et al. 1996, Nerud et al. 2001)

Ozone can be used for the microbiological control of recycled process waters. In addition, ozone is an effective antimicrobial agent in various applications. (Langlais et al. 1991, Masten et al. 1994, Filippi 1997, Paraskeva et al. 1999, Laari et al. 2001, Polo-López et al. 2018, Gorito et al. 2021)

In an aqueous solution, various compounds can react with ozone in two ways: 1) directly with the molecular ozone or 2) indirectly with the free radical species formed when molecular ozone decomposes. Hydroxyl radicals ($HO^{\bullet}$) are the main secondary oxidants produced from decomposed ozone. Hydroxyl radicals are stronger oxidising agents than ozone and are the most reactive oxidants used in water treatment ($E° = +3.06$ V) (Parsons et al. 2004). Reactions of hydroxyl radicals with organic compounds are nonselective, and those radicals can attack almost any organic substance. (Langlais et al. 1991)

In the paper machine environment, both the initial concentration (for example, 10^5 CFU/ml) and the acceptable residual level of microorganisms (for example, 10^3 CFU/ml) are much higher than in drinking water treatment. When the number of microorganisms related to the volume of water is high, the short-living free radicals come into contact with microorganisms at a satisfactory frequency. Despite their short half-life, free radicals are oxidants powerful enough to damage bacteria, bacterial spores, viruses, algae, and fungal species.

The presence of hydrogen peroxide initiates the chain decomposition of ozone with the formation of hydroxyl radicals. Hydrogen peroxide reacts with ozone in its deprotonated form (HO^{2-}). In ultra-pure water, the formation of hydroxyl radicals can be presented as *Reactions 21-26* (Staehelin et al. 1982, Bühler et al. 1984):

$$H_2O_2 + H_2O \rightleftharpoons HO_2^- + H_3O^+ \qquad (21)$$

$$HO_2^- + O_3 \rightarrow HO^{\cdot} + {}^{\cdot}O_2^- + O_2 \qquad (22)$$

$${}^{\cdot}O_2^- + O_3 \rightarrow {}^{\cdot}O_3^- + O_2 \qquad (23)$$

$${}^{\cdot}O_3^- + H^+ \rightarrow {}^{\cdot}HO_3 \qquad (24)$$

$${}^{\cdot}HO_3 \rightarrow HO^{\cdot} + O_2 \qquad (25)$$

with the net equation:

$$H_2O_2 + 2O_3 \rightleftharpoons 2HO^{\cdot} + 3O_2 \qquad (26)$$

According to the stoichiometry above, the theoretical optimum molar ratio of hydrogen peroxide to ozone, which can maximise hydroxyl radicals, is 1:2 mol. However, in reality, the chain decomposition of ozone is a complex reaction system with many affecting variables (Gray 2014). EPA 1999 has found the optimal ratio for drinking water application to be H_2O_2:O_3 ≤ 0.3 (w/w) (≈1:2 mol/mol).

The actual yield of hydroxyl radicals may differ significantly from the theoretical amount in ultra-pure water. Besides the H_2O_2:O_3 ratio, the maximum amount of radical production depends on the pH, ozone concentration, contact time, and water composition, such as trace metals (Glaze et al. 1987). Therefore, the optimum dose ratio must be determined for a specific oxidation application, especially in the case of dirty water, such as paper machine white water.

8.3. Methods and materials

Experiments were conducted in a semi-batch bubble column reactor (water volume 17 L; i.d. 11.0 cm; height 200 cm). Tests were carried out at the temperature predominant in the actual process, about 45 °C. A thermal mantle around the column controlled the temperature. The column was filled with the water sample, and the ozone-containing gas (Q = 10 L/min, O_3 concentration = 7 500 ppm) was continuously added at the bottom of the column through a ceramic diffuser. Ozone was generated with a Pacific Technology G-22 generator from pure dry air. Ozone concentration in the gas phase was measured with a Dasibi 1008 UV analyser from the influent and effluent gas stream. The water was circulated through a measurement chamber for dissolved ozone measurement and then recycled back to the column. Ozone concentration in the water phase was determined with an Orbisphere 3600 analyser. Both analysers were connected to a computer, calculating the total ozone that reacted with the sample water. Thus, the ozone values given in the results are always the consumed doses.

White water[18] used in the experiments was obtained from a newsprint machine, which uses thermomechanical pulp, Kraft pulp, groundwood

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[18] Papermakers use the term" white water" when referring to the process water present in a paper machine system. The white appearance gives evidence to the presence of various suspended materials like fibre and fillers.

pulp, and deinked pulp as raw materials. The samples were cloudy filtrate from fibre recovery (disc filter), *Figure 15*.

Table 19 summarises the laboratory analysis of the fibre recovery cloudy filtrate quality.

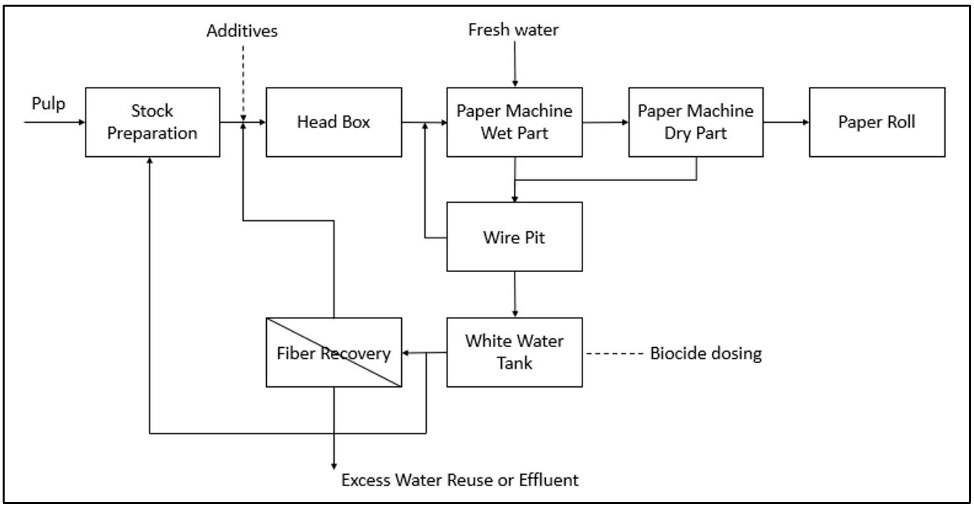

Figure 15. Paper machine water circuit showing the place for biocide. The sampling point is in the fibre recovery cloudy filtrate.

Table 19. Laboratory analysis of the water samples

Parameter	Cloudy Filtrate
COD_{Cr}, mg/L	1 500 – 2 000
pH	0.95
Aerobic heterotrophic Bacteria, CFU/ml	$1.5 \times 10^3 – 1.5 \times 10^4$
Yeast and Mould Count, CFU/ml	$1.0 \times 10^2 – 2.0 \times 10^3$
Reuse	Dilution of pulp

During the O_3/H_2O_2 treatment process, H_2O_2 was added to the water through a valve at the column face. The molar ratio between H_2O_2-feed and incoming O_3 was 1:4, 1:3, 1:2 (the stoichiometrical optimum), 1:1, and 3:2 mol. To achieve similar H_2O_2 experiments in each treatment, they were conducted with the same equipment and procedure, except that incoming gas contained no ozone. The column was filled with the sample water, and clean air was added through the diffuser to ensure the mixing effect (Q = 10 L/min). Hydrogen peroxide was added in the same dilutions and at the same rate as in the O_3/H_2O_2 treatments. The water samples for chemical and microbiological analyses were taken at the same intervals as in the O_3/H_2O_2 treatments.

Aerobic heterotrophic bacteria were enumerated by the spread plate method (Cleceri et al. 2005). Samples and their dilutions were cultured on 3M™ Petrifilm™ Aerobic Count Plates (Jordano et al. 1999). The plates were incubated at 30 °C for 72 ± 3 h in an aerobic environment. Yeasts and moulds were cultivated on 3M™ Petrifilm™, Yeast and Mold Count Plates, and the plates were incubated at 25 °C for 72 ± 3 h in an aerobic environment. The following were considered among the physical-chemical parameters that might be affected by tested treatments: pH, residual peroxide concentration, total $COD_{Cr,tot}$ concentration, and dissolved $COD_{Cr,sol}$ concentration. The pH and water temperature were measured with a WTW Type 320 pH meter during the experiments. The concentration of total residual peroxides was measured by iodometric titration in the presence of ammonium molybdate. To calculate the dosages of hydrogen peroxide and the other peroxides, the water sample was treated with catalase Sigma C-30 (Sigma Chemical Co, USA) and titrated as mentioned. The organic material was determined as COD in water samples by oxidation with dichromate in closed tubes (COD_{Cr}). For dissolved $COD_{Cr,sol}$ determination, the water samples were filtered through a 0.45 μm membrane before oxidation. Detailed procedures are given in Standard Methods (Cleceri et al. 2005).

The effect of the addition of H_2O_2 on the efficiency of the ozonation process was quantified by measuring the consumed amount of ozone needed to reach a 2-log, i.e., 99-99.8% reduction of the aerobic heterotrophic bacteria, yeasts, and moulds.

8.4. Results and discussion

Figure 16 shows an average ozone dose of 60 mg/L was required for a 2-log inactivation of the aerobic heterotrophic bacteria in the cloudy filtrate whose initial heterotrophic bacteria $1.5\times10^3 - 1.5\times10^4$ CFU/ml and COD_{Cr} 1500 – 2000 mg/L. The used ozone and hydrogen peroxide doses and the times required to achieve a 99 to 99.8% aerobic bacteria inactivation are shown in *Table 20*.

Table 20. The ozone and hydrogen peroxide doses and exposure times required for a 2-log, i.e., 99-99.8% *inactivation of aerobic heterotrophic bacteria.*

Input ration of hydrogen peroxide / ozone (mol/mol)	Added H_2O_2 mg/L	Consumed O_3 mg/L	Time min
O_3 only	0	60	10
H_2O_2:O_3 = 1:4	7	35	5
H_2O_2:O_3 = 1:3	7	25	4
H_2O_2:O_3 = 1:2	7	15	2
H_2O_2:O_3 = 1:1	15	15	2
H_2O_2:O_3 = 3:2	20	15	2
H_2O_2 only	15	0	6

Studies conducted by Korhonen et al. 2000, showed ozone dosage of 18 to 26 mgO_3/L is needed for 80% removal of aerobic heterotrophic bacteria in paper machine recycled white water save-all cloudy filtrate with initial COD_{Cr} 800 to 1900 mg/L. When Korhonen et al. 2000 increased the ozone dosage to 32 to 76 mgO_3/L, a 99% aerobic heterotrophic bacteria removal rate could be achieved. They also found that adding H_2O_2 decreased the required amount of ozone. When the molar ratio between H_2O_2-feed and incoming ozone was 1:4 mol and 1:3 mol, a 2-log inactivation of the aerobic heterotrophic bacteria was achieved by a consumed ozone dose of 35 mg/L and 25 mg/L, respectively. When H_2O_2:O_3–ratio was the theoretical optimum of 1:2 mol, the same inactivation level required an ozone dose of 15 mg/L. Higher H_2O_2:O_3-ratio showed no improvement in the inactivation. In the H_2O_2 treatment, a pure hydrogen peroxide dose of 15 mg/L was sufficient for a 2-log inactivation of the aerobic heterotrophs, regardless of the dosage's rate and the additive's concentration. Based on these findings, a more plausible explanation for a smaller ozone dose of 18 to 26 mg/L to achieve the 99% reduction of aerobic heterotrophic bacteria can be caused by the initial lower COD_{Cr} found in this cloudy filtrate, where other compounds do not consume as much as the ozone. This finding is in line with Glaze et al. 1987 who showed that the maximum amount of radical production depends on the pH, ozone concentration, contact time, and water composition, such as trace metals.

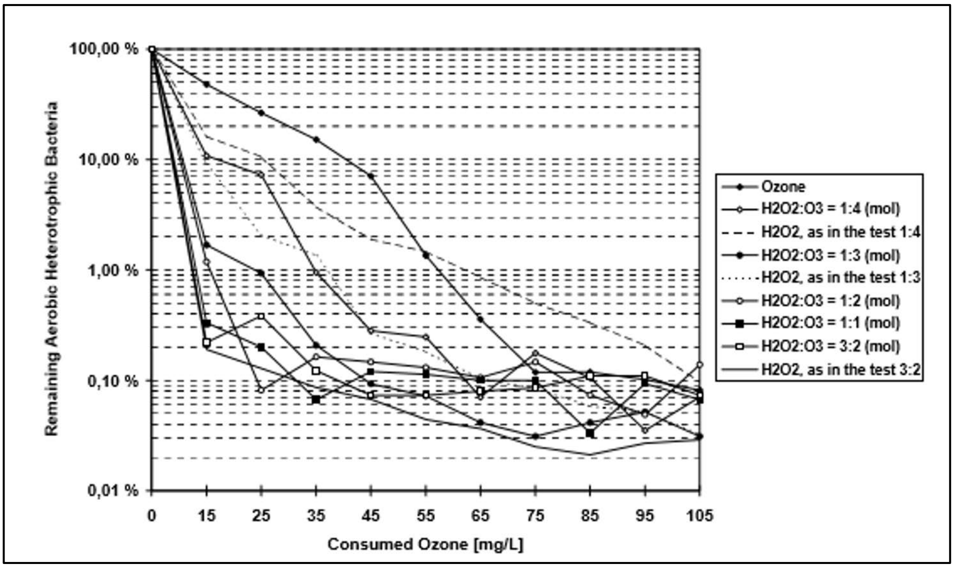

Figure 16. Effects of O_3, O_3/H_2O_2 and H_2O_2 treatments on the aerobic heterotrophic bacteria where 10% corresponds to 1-log, and 1% log 2-log remaining.

Yeasts and moulds were more resistant to treatments than aerobic heterotrophic bacteria. A 2-log removal was not achieved by an ozone dose of 105 mg/L when the initial yeast and mould count was 1.0×10^2 – 2.0×10^3 CFU/ml, *Figure 17* and *Table 21*. Among tested treatment methods, only the combination of O_3/H_2O_2 gave a 2-log (100x) inactivation. Then the ozone dose of 60 - 80 mg/L and H_2O_2: O_3 ratio 1:4 (mol) was adequate.

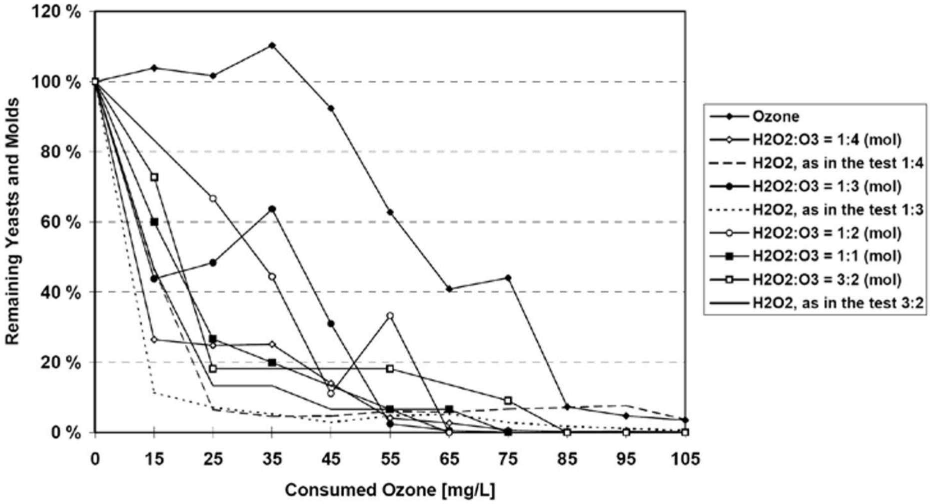

Figure 17. Effects of O_3, O_3/H_2O_2 and H_2O_2 treatments on yeasts and moulds.

Table 21. The ozone and hydrogen peroxide doses and exposure times required for a 2-log (100x) inactivation of yeast and moulds.

Input ration of hydrogen peroxide / ozone (mol)	Added H_2O_2 mg/L	Consumed O_3 mg/L	Time min
O_3 only	0	>105	>20
H_2O_2:O_3 = 1:4	16	75	13
H_2O_2:O_3 = 1:3	18	65	11
H_2O_2:O_3 = 1:2	32	60	11
H_2O_2:O_3 = 1:1	81	70	13
H_2O_2:O_3 = 3:2	136	80	14
H_2O_2 only	>75	0	14

Hydrogen peroxide and ozone are often readily available in a modern, combined pulp and paper plant because they are used as delignification and bleaching chemicals in ECF and TCF bleaching. The combined investment and operating costs of ozonation amount to US$ 1.5 per kg O_3 produced. The price of hydrogen peroxide used was US$ 0.5 per kg, 100% H_2O_2. The costs of O_3/H_2O_2, and especially H_2O_2, treatments to inactivate the aerobic heterotrophs were competitive with other biocides, *Table 22*.

Table 22. Cost estimation for a 2-log removal (99-99.8%) of aerobic heterotrophic bacteria and yeast and mould count in newsprint machine white water by ozone/hydrogen peroxide and hydrogen peroxide treatments. The cost is presented according to the 2001 value.

Treatment	Aerobic Heterophilic Bacteria Costs US$ per m^3 of water treated	Yeast and Mould Count Costs US$ per m^3 of water treated
O_3 only	0.09	>0.16
$H_2O_2:O_3$ = 1:4	0.06	0.12
$H_2O_2:O_3$ = 1:3	0.04	0.11
$H_2O_2:O_3$ = 1:2	0.03	0.11
$H_2O_2:O_3$ = 1:1	0.03	0.15
$H_2O_2:O_3$ = 3:2	0.03	0.19
H_2O_2 only	0.01	>0.04

The experiments were continued until the ozone dose was 105 mg/L, which is relatively low compared to the organic material concentration in that water. With that ozone dose, the removal of organic material measured as total COD_{Cr} was lower than 10% and dissolved COD_{Cr} was about 5%. The decrease in pH caused by forming organic acids was lower than 1.0 units. With the ozone and hydrogen peroxide doses sufficient for a 2-log inactivation of the aerobic heterotrophic bacteria, the removal of total COD_{Cr} was about 5%, dissolved COD_{Cr} ±0%, and the decrease of pH was lower than 0.5 units. The effect of such a pH drop on the runnability depends on the process (neutral or acidic), and it is easily adjustable with pH chemicals.

Ozone reacted rapidly, and no dissolved ozone was detected during experiments. However, immediately after the experiments, a residual concentration of peroxides was present in the water. The total amount of residual peroxides depended on the dose of added hydrogen peroxide. Part of the residual was in the form of H_2O_2, and the part contained other peroxides. The exact concentrations of the residual hydrogen peroxide and the other peroxides could not be measured with the catalase treatment and titration method because of the interference from some unidentified oxidising compounds in the sample water.

Compared to ozone alone treatment, the supported formation of hydroxyl radicals by H_2O_2 addition improved the antimicrobial effectiveness. It reduced the required ozone dose and decreased the time needed for the treatment. Due to the difference in ozone and hydrogen peroxide costs, the optimal H_2O_2:O_3 ratio must be determined for each water system with different specifications and demands for the water's microbiological quality, as described by Glaze et al. 1987.

Furthermore, the oxygen dissolved in water from the ozone-containing gas and formed from the reactions between O_3 and H_2O_2 supports the aerobic conditions in the white water system. This reduces the biocorrosion caused by anaerobic bacteria. However, the lack of residual ozone concentration makes these treatments insufficient to control microbiological growth over the entire white water recirculation system.

8.5. Conclusions

The results indicate that ozone, ozone/hydrogen peroxide, and hydrogen peroxide are effective methods for inactivating aerobic heterotrophic bacteria in paper machine white waters. The studied AOP methods are suitable for local control of microbiological problems in the paper machine white water tank. Furthermore, these AOP methods will decrease the dosage of chemically more stable biocides used for longer biological growth control.

All tested treatments were more effective against aerobic heterotrophic bacteria than against yeasts and moulds. However, yeasts and moulds were more resistant to treatments than aerobic heterotrophic bacteria. A 2-log removal was not achieved by an ozone dose of 105 mg/L when the initial yeast and mould count was 1.0×10^2 to 2.0×10^3 CFU/ml. Among tested treatment methods, only the combination of O_3/H_2O_2 gave a 2-log (100x) inactivation. Then the ozone dose of 60 - 80 mg/L and H_2O_2:O_3 ratio 1:4 (mol) was adequate.

The microbiologically effective ozone doses against organic and inorganic pollutants used in paper machine white water were very low. This meant that ozone could react rapidly, and no residual ozone was dissolved in the water. Therefore, there should not be any corrosion problems caused by residual ozone in full-scale applications.

9. OBJECTIVE 4: MANGANESE REMOVAL FROM RAW WATER

This study aims to find an alternative oxidative chemical to remove manganese (Mn) from the raw waters before letting it into the pulp and paper processes.

The main adverse effect of soluble manganese in industrial water is related to discolouration and growth of iron- and manganese-oxidising bacteria in water mains and pulp bleaching that can lead to a general deterioration of the quality of the water distributed.

9.1. Introduction

The pulp industry has made several changes in the paper pulp bleaching process to minimize environmental impacts during the last decades. Some of the current processes are chlorine-free, giving preference to oxygen-based oxidants such as ozone, hydrogen peroxide, molecular oxygen and peracids (Ni et al. 2000).

Hydrogen peroxide is widely used as a bleaching agent in paper manufacture. However, the presence of transition metals, such as iron (Fe), manganese (Mn) and copper (Cu), affects the efficiency of the oxidizing agent because they catalyse the degradation of hydrogen peroxide. These metals are found as impurities originating from raw water, chemicals used in bleaching, washing water, and wood. Therefore, controlling these transition metals is critical to minimising hydrogen peroxide degradation and maximising bleaching efficiency (Wuorimaa et al. 2006).

Other typical problems caused by manganese are clogging the washing screens, consuming bleaching chemicals, and dispersing agents (Riddick et al. 1958, Islam et al. 2010).

Various physical, chemical, and biological processes can remove Mn from surface water sources (Brandhuber et al. 2013, Civardi et al. 2015). However, this study focuses on chemical oxidation methods for Mn removal.

The traditional way to remove Mn from raw water is to utilise coagulation and flocculation to remove the organics, humic acids, iron, and part of the bacteria in a solid-liquid separation step. However, the soluble manganese needs to be oxidised from the natural II oxidation state to IV before being able to remove at elevated pH around 9.3-9.5. Typical strong oxidants used are NaClO, $KMnO_4$ and O_3. The Mn(II) is oxidized to insoluble Mn(III) and or Mn (IV) forms for removal in particulate form. (Tobiason et al. 2016). However, hydrogen peroxide (H_2O_2) alone is shown ineffective for Mn(II) oxidation (Knocke et al. 1987, Knocke et al. 1991).

Hereafter, the formed metal hydroxide particle can be removed by sand filtration. After the sand filter, the pH is decreased to neutral before entering the clean process water tank, where additional biocide is dosed. A finished water Mn concentration below 0.02 mg/L is a common treatment goal for preventing aesthetic and operational problems associated with manganese. Historically, the United States Environmental Protection Agency (USEPA) has not established an enforceable health-based standard for the allowable Mn concentration in drinking water. Instead, the USEPA publishes a non-enforceable secondary maximum contaminant level of 0.05 mg/L. (Tobiason et al. 2016). In 2020, the European Parliament revised drinking water quality paraments meant for human consumption setting the manganese limit to 50 ug/L. (Directive (EU) 2020/2184)

However, discovering undesirable by-products when certain oxidants are used in treatment has impacted physical-chemical Mn removal methods. Also, the existing raw water treatment processes with Mn removal and additional biocide control of the treated water, with all of the necessary chemistries needed, are seen as complicated. Therefore, the scope of the study is set to develop an AOP method based on the utilisation of peracetic acid, known for its oxidation capabilities and biocidic power, to remove the Mn and simultaneously work as a biocide. *Figure 18* shows a typical flow diagram of conventional raw water treatment for cleaning river and lake waters containing an Mn removal step in sand filtration.

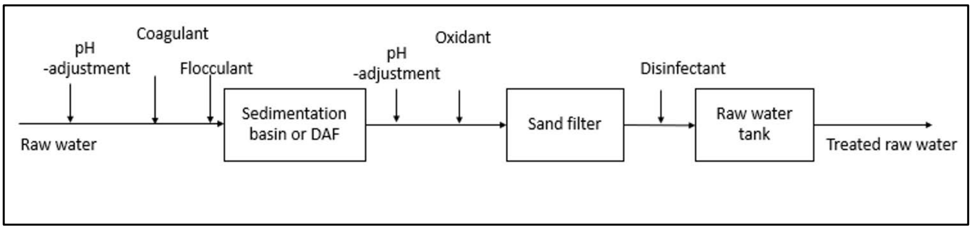

Figure 18. The layout of a typical freshwater treatment process, with manganese removal step by oxidation before the sand filtration.

Peracetic acid (PAA, $CH_3C(O)OOH$) is a strong oxidant and bleaching agent and is widely used in food processing, medical, textile, pulp and paper industries (Kitis et al. 2004). PAA has a high oxidation potential (1.96 V), which is surpassed only by ozone (2.01 V) and hydroxyl radicals (2.80 V) of the commonly used oxidisers (Awad et al. 2004).

The radicals previously reported generated by PAA exist in the form of $OH\cdot$, $CH_3C(=O)O\cdot$, $CH_3C(=O)OO\cdot$, $CH_3\cdot$ and $CH_3OH\cdot$ (Zhang et al. 2017, Rokhina et al. 2010, Waclawek et al. 2017, Bianchi et al. 2002, Cai et al. 2017, Luukkanen et al. 2017).

Compared with methods based on ozone and UV, the usage of PAA is simpler to implement and cheaper to use. More importantly, PAA disinfection generates much less harmful disinfection by-products (DBPs) than chlorine disinfectants and, thus, has been used as an alternative to chlorine disinfection in full-scale wastewater treatment plants in Europe (Luukkonen et al. 2014)

Some added oxidants and biocides typically leave a new anion in the treated water. Some of these anions, especially the Cl^- will cause corrosion issues and should be avoided. The number of traditional biocides and the additional pH control needed for Mn removal could be eliminated using organic oxidants such as peracetic acid (PAA). Utilising PAA with the high oxidative power leads to oxidation of Mn(II) to Mn(IV) at lower pH than the traditional methods, with the additional benefits of working as an effective biocide. This study uses NaOCl and $KMnO_4$ as reference oxidation chemicals to PAA. Two different types of PAA are used, distilled PAA (dPAA) and equilibrium PAA (ePAA), *Table* 26. Oxidants and parameters *used in the study.*

9.2. Materials and methods

The raw water for the study was collected from three locations in Finland, namely the Cities of Rauma, Vaasa, and Kempele. All three cases are located along the west coast of Finland. The first sample from the City of Rauma is taken before conventional raw water treatment for industrial use, where manganese is a problem. After the conventional cleaning with iron coagulants, the second surface water sample was taken from The City of Vaasa. Finally, the last sample consisting of surface and groundwater was taken from the City of Kempele before any treatment. *Table 23* shows the quality parameters of these waters. The City of Kempele water shows the highest values in Fe 1.526 mg/L and Mn 0.592 mg/L, followed by Vaasa, respectively 0.360 mg/L and 0.507 mg/L and Rauma 0.321 mg/L and 0.359 mg/L.

Conversely, the highest $KMnO_4$ value describing organic contaminants present in the water is in Rauma at 77.4 mg/L, Kempele at 21 mg/L and Vaasa at 14 mg/L. These high values are expected to consume most of the used oxidizer dose available for oxidation of Mn(II) to Mn (IV), especially if used before the coagulant, thus expected to impact negatively on the manganese removal efficiency. Also, the very different water pH should be noted.

Table 23. Analysis results for the three untreated water samples used in this study.

Parameter		Rauma	Vaasa	Kempele
pH		6.2	5.2	7.5
Conductivity,	µS/cm	221	186	369
Turbidity	NTU	8.6	1.2	7.0
$KMnO_4$-value	mg/L	77.4	14	21
TOC	mg/L	15	36	7
COD_{Cr}	mg/L	20	17	30
Mn	mg/L	0.356	0.507	0.592
Mn, filtered	mg/L	0.309	0.28	0.549
Fe	mg/L	0.321	0.360	1.526
Fe, filtered	mg/L		0.032	0.025
Alkalinity	mmol/l	0.14	0.03	2.66

Two different process setups are used to treat the three different raw water samples. The first process consists of the primary coagulation step to reduce the organic load before oxidation. This process will lower the amount of oxidant used; therefore, the OPEX will also be lower, *Figure 19*.

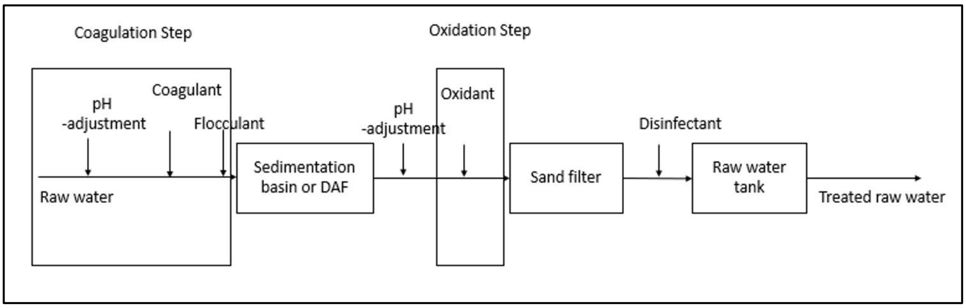

Figure 19. First process flow diagram with oxidative treatment after the coagulation step

In the second process, the oxidation step is placed before the coagulation step for possible enhanced coagulation, *Figure 20*. This process aims to open up some neutral charge organic molecules to generate targeted molecules charged sites. Afterwards, the coagulation step will be much more effective in organic removal.

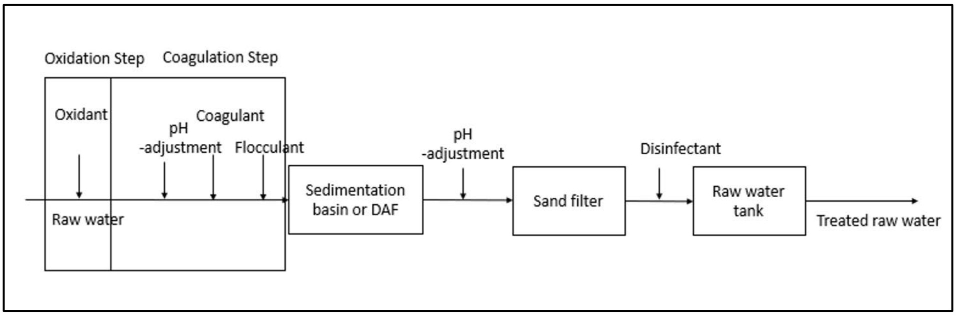

Figure 20. Second process flow diagram with oxidative treatment before the coagulation step.

The effect of oxidising agents on the removal of manganese was tested. Tests were done in 1-litre batches with a miniflocculator. Then manganese was added to the water to achieve a 0.15 mg/L level. Afterwards, the water was coagulated either using poly aluminium chloride (PAX-18) or ferric sulfate (PIX-322). The selected oxidants were added before or after the coagulant. Finally, the manganese concentration was analysed from the water after filtration.

When using ferric sulphate, the reaction pH was kept between 4.4 and 5.0. Furthermore, when poly aluminium chloride was used, the reaction pH was kept between 5.6 and 6.2. A detailed description of the test procedure is listed below. The coagulation procedure when the oxidant was added before the coagulant dosage was as follows, *Table 24,* and added after the coagulant, *Table 25. Table 26* shows the types of oxidants used in the test and a 5 min delay time before adding coagulant in a specific test with dPAA.

Table 24. The coagulant procedure when the oxidant was added before the coagulant.

Rapid mixing:	400 rpm, 30 s
- First rapid mixing	oxidant addition
- Second rapid mixing	pH adjustment so that after the addition of coagulant, the pH is about 6.0 when poly aluminium chloride (PAX-18) was used as a coagulant, and about 4.5, when ferric sulfate (PIX-322) was used as a coagulant
- Third rapid mixing	coagulant addition
- Slow mixing:	30 min 30 rpm
- Sedimentation	30 min
- Filtration	Whatman GF/A filter

Table 25. The coagulation procedure when the oxidant was added after the coagulant.

Rapid mixing:	400 rpm, 30 s
- First rapid mixing	pH adjustment so that after the addition of coagulant, the pH is about 6.0 when poly aluminium chloride (PAX-18) was used as a coagulant, and about 4.5, when ferric sulfate (PIX-322) was used as coagulant oxidant addition
- Second rapid mixing	coagulant addition
- Slow mixing:	30 min 30 rpm
- Decantation	500 ml
- Oxidant addition to the supernatant	
- Sedimentation 15 min	
- Filtration	Whatman GF/A filter

Table 26. Oxidants and parameters used in the study.

Oxidants used
- ePAA = equilibrium peracetic acid (aqueous solution containing about 13% by weight peracetic acid, 22% by weight acetic acid and 15% by weight hydrogen peroxide)
- dPAA = distilled peracetic acid (aqueous solution containing about 40% by weight peracetic acid, 1% by weight hydrogen peroxide and 2% by weight acetic acid)
- H_2O_2 = hydrogen peroxide
- NaClO = sodium hypochlorite (as a reference)
A 5 min delay time at high pH was used before the coagulant addition is made (dPAA).

9.3. Results and discussion

The studies using water from Rauma focused on the effect of oxidants when used before or after coagulation made by either ferric sulphate or poly aluminium chloride at different pHs. *Table 27* shows the results of the different oxidants (ePAA, dPAA, and NaClO) and the type of coagulants used oxidant (ferric sulfate (PIX-322) and poly aluminium chloride (PAX-18) on manganese removal. After coagulation with 50 mg/L ferric sulfate, the manganese concentration was reduced by 37% to 0.094 mg/l. Similar results were achieved with a 30.7 mg/L dose of poly aluminium chloride that reduced the manganese concentration by 37% to 0.095 mg/l. Both oxidants, ePAA and dPAA, were able to oxidise and remove manganese by 50% from 0.150 mg/L to 0.075 mg/L levels when ferric sulphate was used for pre-or-post coagulation. However, lower residual manganese levels of below 0.0043 mg/L were achieved when ePAA/dPAA was added after the coagulation with ferric sulphate. Apparently, the high $KMnO_4$ level of 77.4 mg/L in the water consumes more oxidants if the oxidant is added before the coagulant. This leads to a lower removal degree of manganese. Also, the precipitation of the organic matrix releases Mn for easier oxidation.

A 5 min delay before 50 mg/L ferric sulphate addition increased the manganese reduction considerably to 0.032 mg/L level or 78% reduction, indicating that a longer oxidation time than 30 min is preferred. However, additional results also show that ePAA could only slightly reduce the manganese levels by 26%, from 0.150 to 0.110 mg/L. This is probably caused by ePAA not being capable of having enough oxidation power or a lack of oxidation time to oxidize the manganese (II) when poly aluminium chloride coagulant was added after the oxidant, as Knocke's et al. 1987 results predicted for utilisation of hydrogen peroxide. If the addition point was before the coagulant, a higher dose of dPAA effectively removed manganese to a 0.010 mg/L level with a 97% efficiency. However, if the reference oxidant, NaClO, was added before the coagulant, it could not remove manganese and stay at the same levels as ePAA. If ePAA was added after coagulation with poly aluminium chloride, it could remove manganese by 27% removal efficiency to 0.110 mg/l. A higher dose of 8 mg/L dPAA was more effective than ePAA, reducing manganese by 97% efficiency to 0.010 mg/L. NaClO efficiency on manganese removal was on the same level as ePAA, around 26%.

For studies made with Rauma water, it was found that iron pre-treatment was necessary to achieve high manganese removal rates of 97% with dPAA, which was also the only effective oxidant. However, it should be noted that the treatment with dPAA was effective only in pH-neutral or slightly alkaline conditions. Other interesting remarks were that ePAA or NaClO did not work as well as dPAA and that manganese could be precipitated with a high amount of iron without using PAA. Other interesting results show that ePAA did not work, and manganese could be precipitated to a level of 0.094 mg/L with a high amount of iron without using either dPAA or ePAA.

The studies using water from Vaasa focused on the effect of oxidants $KMnO_4$ and dPAA on manganese removal, as shown in

Table 28. Here, the pH was adjusted to 8.5 with 0.1-M NaOH in tests 2 to 5, and the oxidant was added right after. In test 5, $KMnO_4$ was used as a reference oxidant.

Table 28 shows that dPAA can remove Mn to level 0.02 mg/l or less at pH 7 to 6.9 compared to the reference oxidant $KMnO_4$ at pH 8.2. This demonstrates dPAA possibilities to oxidize Mn(II) to Mn(IV) at neutral or slightly alkaline pH without additional pH control, contra to when $KMnO_4$ is used as an oxidant. Furthermore, the removal efficiency of both oxidisers for their optimised pH was over 93%.

Table 27. Effects of coagulants in the tests. The addition of oxidant was before or after the coagulation. "pH after 5 min" refers to coagulation pH registered 5 min after the beginning of slow mixing. The dose of ePAA or dPAA is calculated based on active substance, i.e., 100% PAA.

	Oxidant	Dose, ppm	pH after 5 min	Mn, mg/L
Initial + Mn	-	-	6.4	0.150
PIX-322, 50 mg/L	-	-	4.5	0.094
Coagulant after oxidant	ePAA	2	4.4	0.075
	ePAA	8	4.5	0.087
	dPAA	2.3	4.8	0.076
	dPAA	8	4.8	0.075
	dPAA[*]	2.3	4.4	0.032
Coagulant before oxidant	ePAA	2	4.5	0.039
	ePAA	8	4.4	0.043
	dPAA	2.3	4.5	0.042
	dPAA	8	4.4	0.043
Initial + Mn			6.7	0.150
PAX-18, 30.7 mg/L			6.0	0.095
Coagulant after oxidant	ePAA	2	6.1	0.110
	ePAA	8	5.9	0.110
	dPAA	2.3	5.6	0.095
	dPAA	8	5.8	0.010
	NaClO	2	5.8	0.095
	NaClO	8	6.0	0.092
Coagulant before oxidant	ePAA	2	6.2	0.080
	ePAA	8	6.2	0.081
	dPAA	2.3	6.1	0.080
	dPAA	8	6.1	0.049
	NaClO	2	6.1	0.081
	NaClO	8	6.0	0.077

[*] *5 min delay time before the coagulant was added.*

Table 28. Effect of oxidants (dPAA and $KMnO_4$) on manganese removal. pH was adjusted to 8.5 with 0.1-M NaOH in the tests 2-5. Oxidant was added after pH adjustment. The dose of dPAA is calculated based on active substance, i.e., as 100% PAA.

Test	$KMnO_4$, Mn, mg/L 30 min	dPAA mg/L	pH 3 min	pH 10 min	pH 30 min	Mn mg/L 10min
1	-	-	5.9	-	-	0.28
2	<0.02	5	7.0	6.9	6.9	<0.02
3	<0.02	1	7.8	7.6	7.4	<0.025
4	<0.05	0.5	8.0	7.7	7.5	<0.05
5	0.6	-	8.2	8.1	-	0.02

**$KMnO_4$ used as reference oxidative treatment*

The dPAA is shown to be capable of reaching a similar or slightly higher manganese reduction of 97% than the reference oxidant $KMnO_4$. However, dPAA can reach high removal efficiency at neutral or slightly alkaline pH versus $KMnO_4$, which needs a higher pH. The high manganese removal efficiency indicates that dPAA can be used without additional pH adjustment or reduced pH control compared to $KMnO_4$.

The third surface water sample was from a river close to the City of Kempele in western Finland. The composition of the water sample is shown in *Table 23*.

Table 29 and *Table 30* show how dPAA is more effective than combinations of H_2O_2 or ePAA in slightly alkaline pH conditions without the iron sulfate as pre-treatment. The 5 mg/L dPAA can remove the manganese by 97% from 0.498 mg/L to 0.02 mg/L level, contra when H_2O_2 is mixed with dPAA, thus mimicking utilisation of ePAA. However, when 1.5 mg/L H_2O_2 is mixed with 5 mg/L dPAA, it reduces the manganese levels by 4% from 0.498 mg/L to 0.478, ruining the results achieved by dPAA dosage only. The low removal might indicate manganese activity due to the presence of manganese ions with different oxidation states in the presence of H_2O_2 (Knocke et al. 1987). Similar effects might be behind the similar poor performance related to ePAA, which consists of 15% by weight of hydrogen peroxide.

Increasing the dPAA dosage to 10 mg/L seems to drop the manganese removal slightly for unclear reasons. However, similar to the addition of H_2O_2 to dPAA addition of ePAA does not improve manganese removal. In addition, the table shows how fast the manganese concentration is dropping from 0.498 to 0.02 mg/L when using 5 ppm dPAA at pH 8.5.

Table 29. Effect of oxidants dPAA and H_2O_2 on manganese removal at pH 8.5.

dPAA mg/L	H_2O_2 mg/L	pH	Redox mV	Mn mg/L
0		8.5	240	0.498
5	0	8.5	260	0.020
5	1.5	8.5	200	0.478
10	0	8.5	400	0.029
10	1.5	8.5	230	0.481

Table 30. Effect of oxidants dPAA and ePAA on manganese removal at pH 8.5.

dPAA mg/L	ePAA mg/L	pH	Redox mV	Mn mg/L
0		8.5	240	0.498
5	0	8.5	260	0.020
5	1	8.5	260	0.130
5	10	8.6	270	0.469
5	50	8.5	260	0.476
10	0	8.5	400	0.029
10	1	8.4	350	0.026
10	10	8.6	275	0.464
10	50	8.5	275	0.474

The results show the dPAA capability of oxidising and removing Mn at normal or slightly alkaline pH from 0.498 mg/L to levels below 0.02 mg/L and reaching the set target below 0.05 mg/L set for drinking water application (EU 2020), and reaching the level of 0.02 mg/L set by many industries. The lower effects of ePAA on manganese oxidation and thus causing less effective removal are thought to be caused by a lower amount of active PAA contra dPAA and partly due to H_2O_2 included in the product that is not effective in manganese removal (Knocke et al. 1987). The results support the study hypothesis that dPAA can replace typical oxidants used for Mn removal to levels like when using NaClO and $KMnO_4$. Furthermore, with the knowledge of the PAA biocidal effect (Luukkanen et al. 2017), it can be expected when using dPAA for Mn removal at neutral or slightly alkaline pH to work as a biocide, thus simplifying the existing raw water treatment chemistries.

Based on the gathered results, it is suggested to use the dPAA after the coagulation stage to avoid non-selective oxidation of other compounds found in the untreated water and, thus, decrease the needed dPAA dosage. Furthermore, the study shows that when using dPAA for Mn removal in raw water treatment, it is possible to run the process step at normal pH, thus removing the need to increase the pH to 9.5 as in conventional treatment with either NaOCl or $KMnO_4$. More importantly, PAA disinfection generates much less harmful disinfection by-products (DBPs) than chlorine disinfectants. However, some added oxidants and biocides typically leave a new anion in the treated water. Some of these anions, especially the $Cl^{-,}$ will cause corrosion issues and should be avoided, as reported by Luukkanen et al. 2017.

Furthermore, after the Mn oxidation and removal, the additional benefits come from residual dPAA, which can work as a biocide to prevent further bio growth in the cleaned water. These two benefits simplify the raw water treatment operation with fewer steps and reduce the number of chemicals used. Therefore, further research is suggested to focus on dPAA online dosage control, both in Mn removal and residual biocidal efficiency.

9.4. Conclusion

The new method using dPAA for Mn removal has been demonstrated to be very effective. Very high Mn removal efficiency (> 98%) from levels 0.473 ppm to 0.008 ppm at pH 8.5 has been achieved, clearly showing its possibilities in these tasks and reaching similar levels or even better than the reference chemicals NaClO and $KMnO_4$. Additionally, the dPAA can also become one of the industry's new green chemicals so much searched for. However, the ePAA containing 15 weight-% H_2O_2 could not reduce the Mn levels to similar levels as dPAA.

10. SYNTHESIS

This section discusses the thesis title “Development of advanced oxidation processes for the Finnish pulp and paper industry water treatment” and how the studied AOP methods match this topic. The AOPs are based on the generation of highly active hydroxyl radicals and their intermediates. Therefore, AOPs are most widely applied when normally difficult-to-decompose compounds are present in the water. Destruction of organic compounds, such as phenols and chlorinated organic compounds, is an illustrative example of utilising AOPs in the pulp and paper industry. However, a total demineralisation of organic contaminants by AOP is not usually cost-effectively or chemically reasonable under ambient conditions (p and T). Thus, AOP treatment is applied mainly to decompose, e.g., toxic to less toxic products, or make the effluent more biodegradable by breaking up larger organic molecules into smaller ones. (Tuhkanen et al. 1994, Hunter 1996, Francoisse et al. 1996, McGrane 1996, Park 1999)

10.1. Discussion

The studies in the thesis show that the selected AOPs can reach the set targets. In all studied cases, utilisation of the selected AOP has generated new information and methods focused on use in the pulp and paper industry. Furthermore, the selected AOP processes have successfully reached the set target when applied as a post or pre-wastewater treatment, green biocide and removal of Mn from raw water entering the mill.

The modified Fenton’s method, presented in Objective 1, resulting in high COD and hard COD removal rates for the pulp and paper industry, is similar to general Fenton’s and AOP results found and discussed in the literature used in other industries (Lucas et al. 2012, Wang et al. 2012, Shi et al. 2013, Skoronski et al. 2015, Grötzner et al. 2018, Wang et al., He et al. 2019, Kumar et al. 2019, Yu et al. 2020). However, the application area and dosing methods in the pulp and paper industry are new and have better runnability due to higher iron dosage. Nevertheless, the high COD removal rates, widely studied and reported, make it a suitable alternative post-treatment method to reach stricter environmental limits. However, the operation window of modified Fenton’s is limited to pH 3 to 4, which in some cases with high carbonate concentration will make it ineffective and very costly. Also, the multicomponent system and sludge generation with additional equipment investments make it less attractive.

Regarding improved biodegradability with AOP pre-treated Kraft mill effluent, presented in Objective 2, the results show similar effectiveness in converting the initially persistent organic compounds into more biodegradable intermediates. The improved biodegradability wastewater would then be treated in a biological stage with a considerably lower operational cost and higher COD removal rate, as described for other applications (Gilbert 1983, Watt et al. 1985, Kearney et al. 1988, Haberl et al. 1991, Mohammed et al. 1992, Heinzle et al. 1992, Hu et al. 1994, Kiwi et al. 1994, Reyes et al. 1998, Mantzavinos et al. 1999, Pulgarín et al. 1996, Parra et al. 2000, Beltrán-Heredia et al. 2001, Sarria et al. 2003). Practical examples of sequential chemical and biological oxidation treatment have been previously reviewed by Scott et al. 1995, 1996, 1997, Jeworski et al. 2000, Sarria et al. 2002, Mantzavinos et al. 2004, Tabrizi et al. 2005, Augugliaro et al. 2006, Ikehata et al. 2006 and Gaya et al. 2008. These studies have shown that the biodegradability of a waste stream changes when subjected to prior chemical oxidation. The study findings align with results showing the role of the chemical pre-treatment for partial oxidation of the biologically persistent part to produce biodegradable intermediates. Therefore, the mineralisation percentage should be minimal during the pre-treatment stage to avoid unnecessary expenditure of chemicals and energy, thereby lowering the operating cost. Additionally, using the acidic wastewater, residual H_2O_2 from the bleaching section, wastewater pipeline as reactor, and primary sedimentation basin as solid/liquid separation vessels reduces the capital investment needed for the process. The method limitations are multi-component systems and sludge created due to higher organic loading than in waters after the biological treatment. However, the easiness of utilising this approach is valid for today's pulp and paper industry to improve COD removal by utilising existing equipment and residual chemistries found in the waters to be treated.

Reviewing results from the study with green biocides, presented in Objective 3, shows how O_3/H_2O_2 1:3 molar ratio can remove 99% of the bacteria from paper machine white waters and, thus, become the sought-after green biocide. Similar effectiveness and reduction levels have been reported by Korhonen et al. 2000 when using O_3 only. Ozone has been reported to be used for the microbiological control of recycled process waters and is an effective antimicrobial agent in various applications

(Langlais et al. 1991, Masten et al. 1994, Filippi 1997, Paraskeva et al. 1999, Laari et al. 2001, Polo-López et al. 2018, Gorito et al. 2021). However, the results show that combining O_3/H_2O_2 is more effective than ozone alone in removing bacteria, yeast and moulds from the paper machine white waters. The benefit of the combination of O_3/H_2O_2 is the need for a smaller O_3 generator than using ozone only. H_2O_2 is a general bleaching chemical found in most integrated paper mills, thus lowering the need for additional chemical containers and storage. Ozone can also be found as a bleaching chemical at some integrated TCF mills. However, the O_3/H_2O_2 system has several challenges. As a two-component system, it is more complicated to use than a single-component system. Also, a gas and liquid combination has its own safety challenges that need to be approved before being accepted for use. Furthermore using hydroxyl radicals to kill bacteria is fast and effective but needs a conventional biocide to control the whole system's growth rates. A combination of these drawbacks affects the utilisation of this method negatively.

The effects of using ePAA and dPAA to oxidize Mn(II) to Mn(IV) and remove it from Finnish raw waters were studied in Objective 4. As reference oxidants, NaOCl and KMnO4 were used. The outcome of this study shows the dPAA removed Mn over 97% from raw water, thus reaching the set targets for the study and reaching similar or better results than the reference oxidants $KMnO_4$, NaOCl and H_2O_2. Moreover, the benefits of being able to oxidize the Mn(II) to higher valences and thus create particles for easy solid-liquid removal at neutral pH saves on chemistries and simplifies the operation by using only one chemical for the oxidation and as a biocide instead of two or three. For these reasons, this is a real alternative for the pulp and paper mills with high Mn concentrations in the raw water.

A general comment for the AOP is that chemical oxidation for complete mineralisation is generally expensive, because the oxidation intermediates formed during treatment tend to be more and more resistant to their complete chemical degradation. They consume energy (UV radiation, ozone, etc.) and chemical reagents (catalysts and oxidisers), increasing with treatment time. Also, as a general development suggestion, future research should focus on online control for AOP to keep the operational cost down and effectiveness high in variable water qualities and quantities.

10.2. Conclusions and recommendations

In general, the effluent treatment plants designed during the 1980s and 1990s have difficulties reaching new lower COD_{Cr} limits, which they were not originally designed to meet.

These design limits have opened possibilities for new treatment technologies, such as the AOP, to remove soluble organics that are either toxic or non-biodegradable for conventional biological and chemical treatment processes.

Firstly, the results gathered with the modified Fenton's reagent have shown excellent COD_{Cr} and P_{tot} removal rates of over 90% when used as a tertiary treatment method for pulp and paper wastewaters.

Secondly, the wastewater BOD/COD ratio adjustment shows that it is possible to decrease the chemical dosing by slight oxidation where the long-chain hard COD_{Cr} is partly decomposed to a more biodegradable form that can be removed in the following biological treatment process. For example, oxidation of the acid pulp mill effluent at 60 °C with hydrogen peroxide combined with ozone or ferrous ion catalyst improves the biodegradability from the original BOD_7/COD_{Cr} from 0.4 to 0.9.

Thirdly, the development of non-metallic AOP systems as a new green biocide has also proven to work. For example, a combination of ozone/hydrogen peroxide (O_3/H_2O_2) can efficiently inactivate aerobic heterotrophic bacteria, yeasts, and moulds found in newsprint machine white water by 2-log (99.9%).

As the fourth study shows, removing Mn from natural water sources can be done with one chemical compound component, such as the peracetic acid and achieving additional benefits in the systems by simplifying the process steps and reducing additional chemistries.

The studies show that the original Fenton's and modified Fenton's processes are effective COD removal and BOD/COD ration modifier methods. However, it has found its limitations in the narrow acidic pH of 3 to 4 that many processes cannot reach for technological or economic reasons. Also, the disadvantages in some of the applications are the utilisation of iron catalyst and sludge formation in some modified Fenton's processes. However, when looking at the removal efficiency, the combined coagulation followed by hydroxyl radical reactions is, in many cases, is a winner concept when treating effluents with high COD_{Cr} values.

In some cases, utilising metal ligands can avoid pH adjustment to trigger the hydroxyl radical reactions. However, these applications are seldom seen in today's marketplace.

Reactions, where catalytic metals have been replaced with radiation catalysts such as UV, are the most common in water treatment. However, the drawback of using visible UV light has been the fast absorption of UV light in contaminated waters. For these reasons, these applications are found primarily within clean waters, such as potable and raw water applications.

The newly developed AOP treatment process has shown its ability to adapt and reach high removal efficiencies for COD_{Cr} and P removal in cases known to be challenging to reach with biological treatment only. Furthermore, studies presented in the dissertation have increased the understanding of the academic task and helped develop AOPs toward sellable products with patents.

As a recommendation for further studies, the theoretical focus should also be set to reduce costs and simplify AOP treatment's operational parameters and conditions from CAPEX and OPEX perspectives. These suggested methods should come closer to accepted treatment costs. Depending on the water quality to be treated, a more significant focus on the pre-treatment method should lower the following AOP CAPEX and OPEX.

11. REFERENCES

1. Ahn J., Lim M.; Characteristics of Wastewater from the Pulp and Paper Industry and its Biological Treatment Technologies, *J. of Korean Inst. of Resources Recycling, Vol. 18, No. 2*, 16-29, **2009.**
2. Adams C., Spitzer S., Cowan R.; Biodegradation of non-ionic surfactants and effects of oxidative pre-treatment, *J Environ Eng, Vol. 122*, 477–83. **1996**.
3. Ali M., Sreekrishnan T.R; Aquatic toxicity from pulp and paper mill effluents: a review, *Advances in Environmental Research, Vol. 5*, 175-196, **2011.**
4. Amat A., Arqués A., Beneyto H., García A., Miranda M., Seguí S.; Ozonisation coupled with biological degradation for treatment of phenolic pollutants: a mechanistically based study, *Chemosphere, Vol. 53*, 79–86, **2003**.
5. Ang W.L., Mohammad A.W., Hilal N., Leo C.P.; A review on the applicability of integrated/hybrid membrane processes in water treatment and desalination plants. *Desalination 363*, 2-18, **2015.**
6. Appling J.; Microbiology of pulp and paper. *TAPPI monograph series No. 15*. TAPPI Press, New York (NY), **1955.**
7. Arai T., Harino H., Ohji M., Langston W.; Ecotoxicology of Antifouling Biocides, *Springer, XVII*, 437, **2009.**
8. Area M.C., Valade J.L.; Revisión de los procesos de pulpado con acción química, El papel. *La revista papelera para Espeña y América Latina*, *Vol. 69*, 47-51, **1998.**
9. Augugliaro V., Litter M., Palmisano L., Soria J.; The combination of heterogeneous photocatalysis with chemical and physical operations: a tool for improving the photoprocess performance. *J Photochem Photobiol Vol.7*, 127–44, **2006.**
10. Ayekoe C.Y.P., Robert D., Lanciné D.G.; Combination of coagulation-flocculation and heterogeneous photocatalysis for improving the removal of humic substances in real treated water from Agbo River (Ivory-Coast), *Catal. Today Vol.281*, 2-13, **2017.**
11. Awad, M.I., Denggerile, A. and Ohsaka, T.; Electroreduction of Peroxyacetic Acid at Gold Electrode in Aqueous Media, *J. Electrochem. Soc., Vol. 151,* E358–E363. **2004.**
12. Balcioglu I., Arslan I., Sacan M.; Homogeneous and heterogeneous advanced oxidation of two commercial reactive dyes, *Environ Technol., Vol. 22,* 813–22. **2001**.
13. Barb W.G., Baxendale J.H., George P., Hargrave K.R.; *Trans Faraday Soc., Vol. 47,* 462-500, **1951.**

14. Baxendale J.H., Evans M.G., Park G.S.; *Trans. Faraday Soc., Vol. 42*, 155-169, **1946.**
15. Beltrán-Heredia J., Torregrosa J., García J., Domínguez J.R., Tierno J.C; Degradation of olive mill wastewater by the combination of Fenton's reagent and ozonation processes with an aerobic biological treatment, *Water Sci Technol Vol. 44*, 103-108, **2001.**
16. Berry R.M., Luthe C.E., Voss R.H., Wrist P.E., Axegård P., Gellerstedt G., Lindblad P.O. and Pöpke I.; The effects of recent changes in bleached softwood kraft mill technology on organochlorine emissions: An international perspective, Jameel H. (ed.), *Bleaching, Vol. 2,* TAPPI Press, Atlanta, GA, USA, 759-769, **1993.**
17. Beulker S., Jekel, M.; Ozonation and precipitation for treatment of bleachery effluents from pulp mills, *Ozone Sci. Engng*, *Vol.15*, 361-370, **1993**.
18. Bhatkhande D., Pangarkar V., Beenackers A.; Photocatalytic degradation for environmental applications: a review, *J Chem Technol Biotechnol Vol. 77,*102–16, **2002.**
19. Bhatnagar A., Sillanpaa M.; Removal of natural organic matter (NOM) and its constituents from water by adsorption - a review, *Chemosphere Vol.166*, 497-510, **2017.**
20. Beckwith T.; The bacteriology of pulp slime, *J Bacteriol Vol. 22*, 15–22, **1931.**
21. Bianchini R., Calucci I., Lubello C., Pinzino C.; Intermediate free radicals in the oxidation of wastewaters, *Res. Chem. Intermediat. Vol.28*, 247-256, **2002.**
22. Bigda R.J.; Consider Fenton's Chemistry for Wastewater Treatment, *Chemical Engineering Progress, Vol. 91*, 62-66, **1995.**
23. Bielski B.H.J., Cabelli D.E., Arudi R.L; Reactivity of H_2O_2/O_2 radicals in aqueous solutions, *J. Phys. Chem. Ref. Data, Vol. 14*, 1041-1100, **1985**.
24. Bierbaum S., Öeller H.J.; Cost savings in the Ozone treatment of Paper Mill Effluents achieved by a closed-loop ozone control system, *Science & Engineering, Vol. 31*, 454-460, **2009.**
25. Bijan L., Mohseni M.; Integrated ozone and biotreatment of pulp mill effluent and changes in biodegradability and molecular weight distribution of organic compounds, *Water Research, Vol. 39*, 3763-3772, **2005**.
26. Biermann C.; Handbook of Pulping and Papermaking, Academic Press, San Diego, ISBN 9780080533681, **1997**.
27. Blomström M., Kokko, A.; From natural resources to high-tech production: The evolution of industrial competitiveness in Sweden

and Finland, *Stockholm school of economics*, Stockholm, Sweden, **2002**

28. Bossman S.H., Olivieros E., Göb S., Siegwart S., Dahlen E.P., Paywan L. Jr., Straub M., Wörner M, Braun A.M.; *J. Phys. Chem., Vol., 102*, 5542-5500, **1998.**
29. Boyden B. H. and Hijazin, O.; The use of ozone as a tertiary treatment for eucalypt bleachery effluent, *Proceedings of The First Australasian Conference of The International Ozone Association II-23–II-43*, Sydney, Australia, **1996**.
30. Boyles W.; The Science of chemical oxygen demand, Technical Information Series, Booklet No.9, *Hach Company*, **1997.**
31. Bowers A., Gaddipati P., Eckenfelder Jr W, Monsen R; Treatment of toxic or refractory wastewater with hydrogen peroxide, *Water Sci Technol Vol.21*,477–86, **1989.**
32. Brandhuber P., Clark S., Knocke W., Tobiason J.; Guidance for the treatment of manganese. Denver, *Water Research Foundation*, **2013**.
33. Bucheli-Witschel M, Egli T.; Environmental fate and microbial degradation of amino polycarboxylic acids, *FEMS Microbiol Rev.,* 25:69–106, **2016**.
34. Bühler R.F., Staehelin J., Hoigné J.; Ozone decomposition in water studied by pulse radiolysis. 1. HO_2/O_2^- and HO_3/O_3^- as intermediates, *J. Phys. Chem., Vol. 88*, 2560-2564**, 1984**.
35. Buxton G.V., Greenstock C.L.; Critical review of rate constants for reactions of hydrated electrons, *J. Phys. Chem. Ref. Data, Vol 17*, 513-886, **1988**.
36. Buzzini A.P, Sakamoto I.K., Varesche M.B., Pires E.C.; Evaluation of the microbial diversity in an UASB reactor treating wastewater from an unbleached pulp plant, *Process Biochemistry Vol. 41 (1)*, 168–176, **2006**.
37. Cabrera M.N.; Pulp Mill Wastewater: Characteristics and Treatment, *Intechopen*, DOI: 10.5772/67537, **2017.**
38. Cai M, Sun P., Zhang L., Huang C.; UV/peracetic acid for degradation of pharmaceuticals and reactive species evaluation, *Environ. Sci., Technol. Vol.51*, 14217-14224, **2017**.
39. Cleceri LS, Greenburg AE, Eaton AD (eds); Standard Methods for the Examination of Water and Wastewater, *21st edn. American Public Health Association*, Washington, D.C, **2005.**
40. Chun Y., Zaviska F., Kim S.-J., Mulcahy D., Yang E., Kim I.S., Zou L.; Fouling characteristics and their implications on cleaning of a FO-RO pilot process for treating brackish surface water, *Desalination Vol. 394*, 91-100, **2016.**

41. Civardi J., Tompeck M.; Iron and manganese removal handbook, *American Water Works Association*, **2015.**
42. Coburn L.A., Lockwood M.P., Englande A.J. Jr, Collins T.; Kraft bleach plant effluent treatment by ultraviolet/oxidation process, T*APPI 1984 Environmental Conference Proceedings*, 277-286, **1984**.
43. Cronström, E., Tanner, T.; Suomen Selluloosayhdistys 1918–1968 ja Suomen Selloloosateollisuus, *Suomen selluloosayhdistys-Finncell*, **1968**, Helsinki, Finland. (In Finnish)
44. Dahl O., Hynninen P., Watkins G.; Papermaking Science and Technology, Environmental Management and Control, *Environmental Management and Control, Vol. 19.* (Second Edition ed.). Helsinki, **2008**.
45. Dahlman O., Reimann A., Strömberg L. and Mörck R. On the nature of high molecular weight effluent materials from modern ECF- and TCF-bleaching, *Proc. Intl Pulp Bleaching Conf.*, Vancouver, BC, Canada, June 13-16, 123-132, **1994**.
46. Dahlman O, Reimann A, Stromberg L, Mörck R.; High molecular weight effluent materials from modern ECF and TCF bleaching. *Tappi J. Vol.78(12)*, 99–109. ISBN: 978-952-5216-30-1. **1995.**
47. Degussa Corporation; Environmental Uses of Hydrogen peroxide (H_2O_2), Allendale, NJ, **1997**.
48. Diyaúddeen B.H., Daud W.M., Aziz A.R.; Treatment technologies for petroleum refinery effluents: A review, *Process Safety and Environmental Protection, Vol. 89*, 95-105, **2011.**
49. Dogan E., Kilicoglu O., Narci A., Mert B., Druna E., Akback U., Aydiner C.; Fenton and photo-Fenton processes integrated with submerged ultrafiltration for the treatment of pulp and paper industry wastewater, *Journal of Environmental Chemical Engineering Vol. 9*, **2021.**
50. Dold P. L., Ekama G. A. & Marais G. v. R.; A general model for the activated sludge process. *Prog. Wat. Tech., Vol. 12(6)*, **1980.**
51. Duesterberg C.K., Mylon S.E., Waite T.D.; pH effects on iron-catalysed oxidation using Fenton's reagent, *Environ. Sci. Technol., Vol. 42*, 8522–8527, **2008**.
52. Ekama G. A., Dold P. L., Marais G.; Procedures for determining COD fractions and the maximum specific growth rate of heterotrophs in activated sludge systems. *Wat. Sci. Tech., Vol. 18(6),* 91-114, **1986.**
53. El-Ghenymy A., Oturan N., Oturan M.A., Garrido J.A., Cabot P.L., Centellas F., Rodríguez R.M., Brillas E.; Comparative electro-Fenton and UVA photoelectro-Fenton degradation of the antibiotic

sulfanilamide using a stirred BDD/air-diffusion tank reactor, *Chem. Eng. J. Vol. 234* 115–123, **2013.**

54. EPA 815-R-99-014; Alternative Disinfectants and Oxidants Guidance Manual, *http://www.epa.gov/ogwdw000/mdbp/mdbptg.html*, **1999.**
55. Erhardt C., Basegio T., Capela I., Adriane L., Machado E., Lopez D., Tarelho L., Bergmann C.; AOX degradation of the pulp and paper industry bleaching wastewater using nZVI in two different agitation processes, *Environmental Technology & Innovation, Vol. 22*, **2021**.
56. Eskelinen K., Särkkä H., Kurniawan T., Sillanpää M.; Removal of recalcitrant contaminants from bleaching effluents in pulp and paper mills using ultrasonic irradiation and Fenton-like oxidation, electrochemical treatment, and/or chemical precipitation: a comparative study. *Desalination, Vol. 255*,179–87, **2010**.
57. European Union; Directive 98/8/EC of the European Parliament and the Council of 16 February 1998 concerning the placing of biocidal products on the market, *Official Journal of the European Communities,* **1998.**
58. European Union; Directive 2012/27/EU of the European Parliament and of the Council of 25 October 2012 on energy efficiency, amending Directives 2009/125/EC and 2010/30/EU and repealing Directives 2004/8/EC and 2006/32/EC. *Official Journal of the European Union*, 1-56, (accessed 14.11.**2012**)
59. European Communities; Council Directive 1999/31/EC on the landfill of waste, *Official Journal of the European Communities* 16.7.**1999.**
60. European Communities; Council Directive (91/676/EEC) 12, December 1991, *https://www.eea.europa.eu/policy-documents/council-directive-91-676-eec* (accessed 5.8.**2012**)
61. European Commission; Integrated Pollution and Prevention Control (IPPC): Reference Document on Best Available Technologies in the pulp and paper industry, *http://eippcb.jrc.ec.europa.eu/reference/BREF/ppm_bref_1201.pdf* (accessed 5. 8. **2012**).
62. European Commission; Industrial Emission directive 2010/75/EU, *https://ec.europa.eu/environment/industry/stationary/ied/legislation.htm* (accessed 10.9.**2015***).*
63. European Parliament and Council; Directive (EU) 2020/2184, quality of water intended for human consumption, *Official Journal of the European Union, L 435/*1, 23.12.**2020**

64. Fawell P; Solid–Liquid Separation of Clay Tailings, *Clays in the Minerals Processing Value Chain*, 327-380, Cambridge, Cambridge University Press. doi:10.1017/9781316661888.010, **2017.**
65. Fenton H.; Oxidation of tartaric acid in the presence of iron*. J. Chem. Soc. trans. Vol.65*, 899-910, **1894.**
66. Filippi A.; Ozone is the most effective disinfectant for dental treatment units: results after 8 years of comparison, *Ozone Sci. Engng*, 19, 527-532, **1997.**
67. Finska Cellulosaföreningen; Berättelse över Finska Cellulosaföreningens verksamhet 1927 9:e verksamhetsåret, *Mercators tryckeri*, Helsingfors, Finland, **1928.** (in Swedish)
68. Finska Cellulosaföreningen; Berättelse över Finska Cellulosaföreningens verksamhet 1938 21:e verksamhetsåret, *Mercators tryckeri*, Helsingfors, Finland, **1939.** (in Swedish)
69. Finska Cellulosaföreningen; Berättelse över Finska Cellulosaföreningens verksamhet 1939 22:e verksamhetsåret, *Mercators tryckeri*, Helsingfors, Finland, **1940.** (in Swedish)
70. Finska Cellulosaföreningen; Berättelse över Finska Cellulosaföreningens verksamhet 1940 23:e verksamhetsåret, *Mercators tryckeri*, Helsingfors, Finland, **1941.** (in Swedish)
71. Finska Cellulosaföreningen; Berättelse över Finska Cellulosaföreningens verksamhet 1942 25:e verksamhetsåret, *Mercators tryckeri*, Helsingfors, Finland, **1943.** (in Swedish)
72. Flemming H-C.; Biofouling in water systems – cases, causes, countermeasures*, Appl Environ Biotechnol.* Vol. 59, 629–640, **2002.**
73. Flemming H-C.; Biofilm highlights. *Heidelberg: Springer International. Chapter 8, Microbial biofouling – unsolved problems, insufficient approaches and possible solutions,* p. 81–109, **2011.**
74. Francoisse P., Gregor K.H.; Application of a New Fenton Process (FSR PROCESS) without Sludge Production for the Treatment of Non-Biodegradable Wastewater*, Chem.Oxid., Technol. for the Nineties, Vol.6*, 208-220, **1996.**
75. Franta J., Helmreich B., Pribyl M., Adamietz E., Wilderer P. A.; Advanced biological treatment of papermill wastewaters; effects of operating conditions on COD removal and production of soluble organic compounds in activated sludge systems, *Water Sci. Technol., Vol. 30(3)*, 199-207, **1994.**
76. Freire C, Silvestre A., Neto C, Silva A, Evtuguin D, Cavaleiro J.; Easily degradable chlorinated compounds derived from glucuronoxylan in filtrates from chlorine dioxide bleaching of eucalyptus globulus

kraft pulp, *Holzforschung Vol. 57(1),* 81– 7. doi:10.1515/HF.2003.013, **2003.**

77. Gao W., Leung K., Qin W., Liao B.; Effects of temperature and temperature shock on the performance and microbial community structure of a submerged anaerobic membrane bioreactor, *Bioresource Technology, Vol. 102*, 8733-8740, **2011.**
78. Gao W., Liang H., Ma J., Han M., Chen Z.L., Han Z.S., Li G.B.; Membrane fouling control in ultrafiltration technology for drinking water production: a review. *Desalination Vol. 272 (1),* 1-8, **2011.**
79. Gao W., Han M., Xu C., Liao B., Hong Y., Cumin J.; Performance of submerged anaerobic membrane bioreactor for thermomechanical pulping wastewater treatment, *Journal of Water Process Engineering 13*, 70-78, **2016.**
80. Gaya U.I., Abdullah A.H.; Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems. *J. Photochem. Photobiol. C Photochem. Rev. 9 (1),* 1-12, **2008.**
81. García-Montaño J., Ruiz N., Muñoz I., Doménech X., García-Hortal J., Torrades F.; Environmental assessment of different photo-Fenton approaches for commercial reactive dye removal, *J Hazard Mater Vol.A138*, **2006a.**
82. Gedam N., Rao Neti N., Kashyap S.M.; Treatment of recalcitrant caprolactam wastewater using electrooxidation and ozonation, *Clean: Soil, Air, Water Vol 42,* 932-938, **2014.**
83. Gilbert E.; Biodegradability of ozonation products as a function of COD and DOC elimination by example of substituted aromatic substances, *Water Research Volume 21 (10)*, 1273-1278, **1987.**
84. Ginni, G., Adishkumar, S., Rajesh Banu, J., Yogalakshmi, N.; Treatment of pulp and paper mill wastewater by solar photo-Fenton process. *Desalin. Water Treat. Vol.52*, 2457–2464, **2014.**
85. Glaze W.H., Kang J.W., Chapin D.H.; The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation, *Ozone Sci. Eng., Vol. 9(4),* 335-352, **1987.**
86. Gonze E., Commenges N., Gonthier Y., Bernis A.; High frequency ultrasound as a pre- or post-oxidation for paper mill wastewaters and landfill leachate treatment, *J Chem Eng. Vol.92,* **2003**.
87. Gorito A., Pesqueira J., Moreira N., Ribeiro A., Pereira F., Nunes O., Almeida C., Silva M.; Ozone-based water treatment (O_3, O_3/UV, O_3/H_2O_2) for removal of organic micropollutants, bacteria inactivation and regrowth prevention, *Journal of Environmental Chemical Engineering*

88. *Vol. 9*, Issue 4, **2021.**
89. Gray N.F.; Biology of wastewater treatment, *Imperial College Press*, **2004.**
90. Gray N.F.; Ozone disinfection; Microbiology of waterborne diseases (second edition), *Microbiological aspects and risks,* 599-615, **2014.**
91. Grötzner M., Melchiors E., Schroeder L.; Pulp and Paper Mill Effluent Treated by Combining Coagulation-Flocculation-Sedimentation and Fenton Processes*, Water Air and Soil Pollution Vol.229(11)*, **2018.**
92. Guo H., Wyart Y., Perot J., Nauleau F., Moulin, P. Low-pressure membrane integrity tests for drinking water treatment: a review. *Water Res. Vol.44 (1),* 41-57, **2010.**
93. Gytel U., Engström T.; Different treatment methods for effluents from pulp mill and their effluents on fish health and propagation, *Gothenburg Symposium,* Istanbul, Turkey, **2000.**
94. Haber F., Willsätter R.; Unpaarigkeit und Radiakalketten im reactionsmechanismus organischer und enzymaticher Vorgänge, Ber. *Deutsch. Chem. Ges., Vol. 64*, 2844-2856, **1931.**
95. Haber F., Weiss J.; Über die katalyse des Hydroperoxydes, *Naturwissenschaften, Vol. 20*, 948-950, **1932.**
96. Haber F., Weiss J.; The catalytic decomposition of hydrogen peroxide by iron salts. *Proc. R. Soe. London A145*, 332-251, **1934.**
97. Haberl R., Urban W., Gehringer P., Szinovatz W.; Treatment of pulp-bleaching effluents by activated sludge, precipitation, ozonation and irradiation, *Water Sci Technol Vol. 24*, 229-239, **1991**.
98. Hahn S., Melcching-Kollmuβ S., Bitsch A., Schneider K., Oltmanns J., Haussauer M., Schuhmacher-Wolz U., Voss J., Gartiser S., Jäger I., Mangelsdorf I.; *Health risks from biocide containing products and articles of daily use, final report research Project 204 61 218/05,* German Federal Environmental Agency, **2005.**
99. Hallberg, P.; Vesioikeuslaki 100v. *Vesitalous 5,* 7-8, ***2002.*** (In Finnish)
100. Hassler T., Lindberg M., Schenker A.; Slime and again. New knowledge and regulations spark the need for new ways to inhibit microbial growth. *Paper 360° Vol.8,* 28–32. **2007.**
101. He H., Wu D.; Advanced Oxidation Treatment of Papermaking Wastewater by Homogeneous Fenton Reaction, *Advanced Materials Research Vol. 726-731*, 2510-2514, August **2013**.
102. Hem J.D., Cropper W. H.; Survey of Ferrous-Ferric Chemical Equilibria and Redox Potentials, Chemistry of iron in natural water, *Geological survey water-supply paper 1459*, United States Government Printing Office, Washington, **1962.**

103. Henze, M., Characterization of wastewater for modelling of activated sludge process, *Wat. Sci. Tech., Vol. 25(6)*, 1-15., **1992**.
104. Heinzle E., Geiger F., Fahmy M.,. Kut O.M; Integrated ozonation–biotreatment of pulp bleaching effluents containing chlorinated phenolic compounds, *Biotechnol Progr Vol*. 8, 67-77, **1992.**
105. Hofer T.; Method development for analysis of 8-oxide as biomarker for oxidative stress. *Karolinska Institutet, 141*, 57, Huddinge, Stockholm **2001.**
106. Hollo E.J.; Vesioikeuslaki 100 v - kehitystä ja mukautumista. *Vesitalous, Vol. 5*, 9-11, **2002**. (In Finnish).
107. Horn B., Richards G.; Use of degradable, non-oxidizing biocides and biodispersants for maintenance of capacity in nutrient injection wells, *The Ninth International In-situ and On-site Bioremediation Symposium,* Baltimore MD, May **2007**.
108. Hostachy J.L., Lachenal D., Coste C., Richard, Y.; Ozonation of bleaching effluents in order to reduce AOX, COD, BOD, acute toxicity and chlorophenolic derivates*, Proceedings of The Eleventh Ozone World Congress S-10-13 – S-10-23*, San Francisco, USA, 29.8.-3.9.**1993.**
109. Hu S.T., Yu Y.H.; Preozonation of chlorophenolic wastewater for subsequent biological treatment, *Ozone Sci Eng Vol.16*, 13-28, **1994.**
110. Huang C.P., Dong C., Tang Z.; Waste Manage, *Vol. 13*, 361-377, **1993**.
111. Huang, X., Leal, M., Li, Q; Degradation of natural organic matter by TiO_2 photocatalytic oxidation and its effect on fouling of low-pressure membranes. *Water Res. Vol.42*, 1142–1150, **2008.**
112. Huhtanen J.; The environmental problems of sulphate pulp industry in the beginning of 1900s, *Licentiate dissertation,* University of Helsinki, Finland **1996.**
113. Hunter F.; Fentons Treatment of 1,2,3-Trichloropropane: Chemical Reaction By-products, Pathway, and Kinetics*, Chem.Oxid., Technol. for the Nineties Vol.6,* 50-71, **1996**.
114. Hynninen P.; Papermaking Science and Technology: Environmental Control. *Fapet Oy,* Jyväskylä, **1998.**
115. Hynninen P.; Papermakerswiki. Ympäristönsuojelun innovaatioita, *https://www.papermakerswiki.com/innovations/ymp%C3%A4rist%C3%B6nsuojelu/ymp%C3%A4rist%C3%B6nsuojelun-innovaatioita*, **2009,** (accessed 10.1.2013). (in Finnish)
116. Hynninen P.; Sellu ja paperiteollisuuttemme jätevedenkäsittelystä. *Ympäristö ja Terveys-lehti 2,* 55–57, **2012** (In Finnish)

117. Islam A., Goodwill J., Bouchard R., Tobiason J., Knocke W.; Characterization of filter media MnOx (s) surfaces and Mn removal capability. *J Ame Water Works Assoc. Vol. 102(9), 71–83*, **2010.**

118. Jaafarzadeha N., Omidinasab M., Ghanbari F.; Combined electrocoagulation and UV-based sulfate radical oxidation processes for treatment of pulp and paper wastewater, *Process Safety and Environmental Protection Vol. 102*, 462–472, **2016**.

119. Ikehata K, Gamal El-Din M.; Aqueous pesticide degradation by hydrogen peroxide/ultraviolet irradiation and Fenton-type advanced oxidation processes: a review, *J Environ Eng Sci Vol.5*, 81-135, **2006**.

120. Islam A., Goodwill J., Bouchard R., Tobiason J., Knocke W.; Characterization of filter media MnOx (s) surfaces and Mn removal capability. *J Ame Water Works Assoc. Vol. 102(9), 71–83*, **2010**

121. Jalkanen, T-O. Tampere Tammerkosken tytär. *Promaint 8*, **2008**. (In Finnish)

122. Jansson K.; Reduktion av fosforutsläppen ur en vattenreningsanläggning för träförädlingsindustrin, *Master Thesis*, Åbo Akademi, Finland, **1992.**

123. Jansson K.; Kotimainen ratkaisu metsäteollisuuden vesistökuormitus ongelmiin. *Kemia-Kemi 5*, 357-359, **1996a.** (in Finnish)

124. Jansson K., Rampotas, C.; NetFloc a kidney in Pulp and Paper process waters. *TAPPI International pulping conference*. **1996b.**

125. Jansson K., Rampotas C., Terelius H.; Removal of extractives and heavy metals with the NetFloc system. 5th international conference on new available technologies. 696-708, *World Pulp and Paper weeks* Stockholm, Sweden, **1996c.**

126. Jansson K., Rampotas C., Terelius H.; The NetFloc system - the tool to remove extractives and non-process elements. Minimum Effluents Mills Symposium. Atlanta, USA.*Tappi Press*, 317-325, **1996d.**

127. Jansson K., Laine E., Korhonen S.; AOP treatment of an acidic pulp bleaching filtrate. *4th International conference on environmental impacts of the pulp and paper industry*, 133-136, Helsinki, Finland, 12-15, June **2000**.

128. Jansson K., Jäkärä J., Rampotas C.; Chemical kidney technology in mechanical pulp processes. *International mechanical pulp conference vol. 2*, 463-476, TAPPI Helsinki, Finland, 4-8, June **2001a.**

129. Jansson K., Jäkärä J.; Ousting the troublemakers. *Pulp and Paper Euro*pe, 12-15, December **2001b.**

130. Jansson K., Palonen H.; Effect of pH and oxidation on sludge dewatering. *Chemical water and wastewater treatment VII*, 309-316, IWA Publishing, London, UK, ISBN: 1 843 39 009 4, **2002.**
131. Jansson K., Palonen H.; Laine E.; Treatment of pulp bleaching filtrate with Fenton´s technologies. *Third International Conference on Oxidation Technologies for Water and Wastewater Treatment*. Goslar, Germany, **2003**.
132. Jeong K., Lee D.S., Kim D.G., Ko S.O.; Effects of ozonation and coagulation on effluent organic matter characteristics and ultrafiltration membrane fouling, *J. Environ. Sci. Vol. 26 (6),* 1325-1331, **2014.**
133. Jeworski M., Henzle E.; Combined chemical–biological treatment of wastewater containing refractory pollutants, *Biotechnol Annu RevVol.6*, 163–96, **2000.**
134. Jing H.Y., Wen T., Fan C.M., Gao G.Q., Zhon, S.L., Xu A.W.; Efficient adsorption/photodegradation of organic pollutants from aqueous systems using Cu 2 O nanocrystals as a novel integrated photocatalytic adsorbent. *J. Mater. Chem. Vol.A 2 (35),* 14563-14570, **2014.**
135. Jones P., Williams D.; Chemical speciation simulation used to assess the efficiency of environment friendly EDTA alternatives for use in the pulp and paper industry. *Inorg Chim Acta Vol. 33,*41–50, **2002.**
136. Jordano R., Medina L.; Petrifilm -an enhanced cultural technique, *Encyclopedia of food microbiology*, *Elsevier,* 1662-1671, ISBN 9780122270703, **1999.**
137. Jung K., Hwang M., Park D., Ahn K.; Performance evaluation and optimization of a fluidized three-dimensional electrode reactor combining pre-exposed granular activated carbon as a moving particle electrode for greywater treatment, *Separation and Purification Technology Vol.156, Part 2*, 414-423, **2015.**
138. Juuti P.S., Katko T.S.; From few to all, Long-term development of water and environmental services in Finland. *Kehrämedia,* Pieksämäki, Finland**, 2004**
139. Kamali M., Khodaparast Z.; Review on recent developments on pulp and paper mill wastewater treatment, *Ecotoxicol. Environ. Safety Vol. 114,* 326 - 342, DOI: 10.1016/j.ecoenv.2014.05.005, **2015.**
140. Karimi S.H, Abdulkhani A., Ghazali A. H. B., Ahmadun F., Karimi A.; Color remediation of chemimechanical pulping effluent using combination of enzymatic treatment and Fenton reaction, *Desalination Vol. 249*, 870–877, **2009.**

141. Karrasch B., Parra O., Cid H., Mehrens M., Pacheco P., Urrutia R., Valdovinos C., Zaro C.; Effects of pulp and paper mill effluents on the microplankton and microbial self-purification capabilities of the Biobío River, *Chile. Science of The Total Environment, Vol.359,* Issues 1–3, 194–208 (1-3), **2006.**
142. Kecskeméti I.; Paper Identification Database: Characterization and Documentation of the Papers of the First Finnish Paper Mill, Tomasböle 1667-1713. *The book and paper annual* 26, **2007**
143. Keeley J., Jarvis P., Smith A.D., Judd S.J.; Coagulant recovery and reuse for drinking water treatment, *Water Res. Vol.88*, 502-509, **2016.**
144. Kearney P.C., Muldoon M.T., Somich C. J., Ruth J.M., Voaden D.J.; Biodegradation of ozonated atrazine as a wastewater disposal system*, J. Agric. Food Chem. Vol. 36(6)*, 1301–1306, **1988.**
145. Khan S., Kim J., Sott, A., Van der Bruggen B.; Humic acid fouling in a submerged photocatalytic membrane reactor with binary TiO_2eZrO_2 particles, *J. Indust. Eng. Chem. Vol.21*, 779-786, **2015.**
146. Kim K., Ihm S.; Heterogeneous catalytic wet air oxidation of refractory organic pollutants in industrial wastewaters: *A review, Journal of Hazardous Materials. Vol. 186 (1*), 16–34, **2011.**
147. Kim J.K., Jang D.G., Campos L.C., Jung Y.W., Kim J.H., Joo J.C.; Synergistic removal of humic acid in water by coupling adsorption and photocatalytic degradation using TiO_2/coconut shell powder composite, *J. Nanomaterials,* https://doi.org/10.1155/2016/7109015, **2016.**
148. Kits M.; Disinfection of wastewaters with peracetic acid: a review, *Environ. Int. Vol.30*, 47–55, **2004**
149. Kiwi J., Pulgarín C., Péringer P.; Effect of Fenton and Photo-Fenton reactions on the degradation and biodegradability of 2 and 4-nitrophenols in water treatment, *Appl Catal B Environ Vol.3,* 335-350, **1994.**
150. Klahre J., Lustenberger M., Flemming H-C.; Mikrobielle Probleme in der Papierindustrie. Teil I: Schadensfälle, Ursachen, Kosten, Grundlagen, *Das Papier. Vol. 50*, 47–53, **1996.** (In German)
151. Knight D. Cooke M.; Regulatory control of biocides in Europe, *The Biocide Business, Vol. 379*, Wiley, Weinheim, **2002.**
152. Knocke W., Van Benschoten J., Kearney M., Soborski A., Reckhow D.; Kinetics of manganese and iron oxidation by potassium permanganate and chlorine dioxide, *J Am Water Works Assoc., Vol. 83(6), 80–7*, **1991.**

153. Knocke W., Hoehn R., Sinsabaugh R.; Using alternative oxidants to remove dissolved manganese from waters laden with organics, *J Am Water Works Assoc, Vol.* 79(3), 75–9, **1987.**
154. Komiteamietintö; Sulfatisellu Komitea, Helsinki, ***1908***. (In Finnish)
155. Komiteamietintö; Sulfiittisellu komiteamietintö Helsinki, *7*:***1978***. (In Finnish)
156. Komitébetänkande; Helsingfors, *6:**1875**.* (In Swedish)
157. Kommittébetänkade; Till Hans Kejserliga Majestät från fiskerikomiten, *N:o 66, 22/2***,** Helsingfors, ***1898*.** (In Swedish)
158. Komppa A., Neimo L.; Vähävetinen paperin valmistus CACTUS 1996-1999. *Teknologiaohjelmaraportti 1/2000.* TEKES, Helsinki, **2000**. (In Finnish)
159. Korhonen S., Tuhkanen T.; Ozone as a biocide in paper machine recycled white water, *Tappi Journal, Vol. 83(5)*:75, **2000.**
160. Korhonen S., Tuhkanen T.; Ozone-based Treatments of Process Waters and Effluents in the Pulp and Paper Industry. *Diss. Tampere University of Technology Publications 315*, **2000**.
161. Kovacs T.G, Martel P.H, Voss R.H.; Assessing the biological status of fish in a river receiving pulp and paper mill effluents, *Environmental Pollution, Vol. 118 (1)*, 123–140, **2002.**
162. Kremer M.L.; Phys. Chem., *Chem. Phys. Vol. 1*, 3595-3605, **1999.**
163. Kuisma, M.; Metsäteollisuuden maa. Suomi, metsä ja kansainvälinen järjestelmä 1620–1920, *SHS*, 421, **1993.** (In Finnish)
164. Kumar V., Punathil S., Ghosh P.; Optimization of COD Removal by Advanced Oxidation Process through Response Surface Methodology from Pulp & Paper Industry Wastewater, *Journal of Scientific and Industrial Research*, **2019.**
165. Laari A., Korhonen, S. Tuhkanen T., Kallas J.; The Effect of Hydrodynamic and Operational Parameters on the Deactivation Kinetics of Microbes in Paper Machine Circulation Water by Ozonation, *Proceedings of the 15th World Congress International Ozone Association*, *Vol. 1*, , 438 – 453, London, UK, 11.- 15.9. **2001.**
166. Lacrote S., Latorre A., Barcelo D., Rigol A., Malmqvist A., Welander T.; Organic compounds in paper-mill process waters and effluents, *TrAC. 22*, 525-737, **2003**.
167. Lahtinen T., Kosonen M., Tiirola M., Vuento M., Oker-Blom C.; Diversity of bacteria contaminating paper machines, *J Ind Microbiol Biotechnol. Vol. 33*, 734–740, **2006.**
168. Laine E., Jansson K., Korhonen S.; AOP treatment of an acidic pulp bleaching filtrate. *4th International conference on environmental impacts of the pulp and paper industry.* IWA Helsinki, Finland, **2000.**

169. Lal K., Garg A.; utilisation of dissolved iron as catalyst during Fenton-like oxidation of pre-treated pulping effluent, *Process Safety and Environmental Protection Vol. 111*, 766-774, **2017.**

170. Langlais B., Reckhow D. A., Brink D. (Ed.); Ozone in water treatment: application and engineering, Lewis *Publishers*, Chelsea, USA, **1991.**

171. Lapertot M., Pulgarín C., Fernández-Ibañez P., Maldonado M., Pérez-Estrada L., Oller I.; Enhancing biodegradability of priority substances (pesticides) by solar photoFenton. *Water Res, Vol.40,*1086–94, **2006.**

172. Lee J., Lee S., Rhew D.; Relationships between water quality parameters in rivers and lakes: BOD_5, COD, NBOPs, and TOC, *Environmental Monitoring and Assessment. Vol. 188*, Article number: 252, Springer, **2016.**

173. Larrea L., Forster C.F, Melé D; Changes in lignin during diffused air activated sludge treatment of kraft effluents, *Water Research, Vol. 3 (9)*, 1073–1080, **1989.**

174. Levlin J-E.; Den industriella papperstillverkningens historia- Ingen dag utan papper. Om papper och dess roll som kulturbärare, editor Häkli E. Söderströms, 61–97, Helsinki, **2008**, (in Swedish)

175. Li X., Wang C., Qjan Y., Wang Y., Zhang L.; Simultaneous removal of chemical oxygen demand, turbidity and hardness from biologically treated citric acid wastewater by electrochemical oxidation for reuse, *Sep. Purif. Technol. Vol.107*, 281-288, **2013.**

176. Liao X., Zou R., Chen C., Yuan B., Zhou Z., Zhang X.; Evaluating the biosafety of conventional and O_3-BAC process and its relationship with NOM characteristics, *Environ. Technol. https://doi.org/10.1080/09593330.2017.1297850*, **2017.**

177. Lim T.T., Yap P.S., Srinivasan M., Fane A.; $GTiO_2$/AC composites for synergistic adsorption-photocatalysis processes: present challenges and further developments for water treatment and reclamation. Crit. Rev., *Environ. Sci. Tech-nol. Vol.41 (13*), 1173-1230, **2011.**

178. Lin S.H., Lo C.C.; Fenton process for treatment of desizing wastewater, *Wat. Res., Vol. 31*, 2050-2056, **1997.**

179. Lindström K., Nordin J., Österberg F.; Chlorinated organics of low and high relative molecular mass in pulp mill bleachery effluents, In: Keith, L.H. (ed.), *Advances in the Identification & Analysis of Organic Pollutants in Water, Vol. 2*, Ann Arbor Science, Chelsea, MI, USA, 1039-1058, **1981.**

180. Liu S., Lim M., Amal R.; TiO_2-coated natural zeolite: rapid humic acid adsorption and effective photocatalytic regeneration, *Chem. Eng. Sci. Vol.105*, 46-52, **2014.**

181. Lucas M.S. Peres J., Amor C., Prieto-Rodríguez L., Maldonado M.I., Malato S.; Tertiary treatment of pulp mill wastewater by solar photo-Fenton, *Journal of Hazardous Materials Vol. 225–226*, 173-18, **2012.**

182. Luonsi A.; Massa- ja paperiteillisuuden jäteveden puhdistusteknologian kehitys Suomessa. *Kemia-Kemi, Vol. 2,* 83-91, **1987**. (In Finnish)

183. Luukkonen T., Pehkonen S.; Peracids in water treatment: a critical review, *Crit. Rev. Environ. Con. Vol. 47*, 1-39, **2017**.

184. Luukkonen T., Teeriniemi J., Prokkola H., Rämö J., Lassi U.; Chemical aspects of peracetic acid-based wastewater disinfection, *Water SA Vol.40*, 73, **2014.**

185. Länsi-Suomen Vesioikeus; Länsi-Suomen Vesioikeuden päätös, *Länsi-Suomen Vesioikeus,* Helsinki, ***1995***. (In Finnish)

186. Malmi, A.; Finska Cellulosaföreningen 1918–1928 återblick på cellulosaindustrins uppkomst och utveckling i Finland, *Frenckellska tryckeri Aktiebolaget*, Helsingfors, Finland,**1928**. (In Swedish)

187. Makkonen O., Leppo E.; Talous- ja likavesikysymys Suomen kaupungeissa ja kauppaloissa, *Kunnallistekniikka, Vol. 2*, No.4, 130–135, **1947**. (In Finnish)

188. Malaeb, L., Ayoub, G.M., Reverse osmosis technology for water treatment: State of the art review, Desalination *Vol. 267 (1*), 1-8, **2011.**

189. Mantzavinos D, Sahibzada M., Livingston A.G., Metcalfe I.S., Hellgardt K; Wastewater treatment: wet air oxidation as a precursor to biological treatment, *Catal Today Vol.53*, 96-106, **1999.**

190. Mantzavinos D, Psillakis E. Review. Enhancement of biodegradability of industrial wastewaters by chemical oxidation pre-treatment, *Chem Technol Biotechnol Vol. 79*, 431–54, **2004.**

191. Mao H., Smith D. W.; Influence of ozone application methods on efficacy of ozone decolorization of pulp mill effluents, *Ozone Sci. Eng., Vol. 17*, 205-236, **1995a.**

192. Mao H., Smith, D.W.; Towards elucidating mechanism and kinetics of ozone decolorization and dechlorination of pulp mill effluents, *Ozone Sci. Eng., Vol.,* 17, 419-448, **1995b.**

193. Marco A., Esplugas S., Saum G.; How and why combine chemical and biological processes for wastewater treatment, *Water Sci. Technol, Vol. 35 (4),* 321–327, **1997.**

194. Martínez-Huitle C. A., Brillas E.; Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review, Applied Catalysis B: *Environmental, Vol. 87 (3-4),* 105–145, **2009.**

195. Masten S.J., Davies S.H.R.; The use of ozonation to degrade organic contaminants in wastewaters, *Environ. Sci. Technol., Vol. 28(4)*, 180A-185A, **1994.**

196. Matilainen A., Sillanpää M.; Removal of natural organic matter from drinking water by advanced oxidation processes, *Chemosphere Vol.80*, 351–365, **2010.**

197. McGrane W.; Advanced Oxidation Processes for Destruction and Enhanced Biodegradability of 1,4-Dioxane, *Chem.Oxid., Technol. for the Nineties, Vol.6*, 231- 245, **1996.**

198. McKague B., Carlberg G.; Effluent characterization and composition. In: Dence, C.; Reeve, D. (Eds.) *Pulp bleaching – principles and practice.* Atlanta: Tappi Press. 751-766, **1996.**

199. C V., Henríquez A., Radojkovic C, Schwederski B., Kaim W., Freer J., Contreras D.; Reduction reactivity of catecholamines and their ability to promote a Fenton reaction, *Inorganica Chim. Acta, 453*, **2016.**

200. Mensink B.; Refined aquatic environmental risk assessment of 28 priority biocides, *RIVM report 601506005*, **2000.**

201. Metsämuuronen S., Sillanpää M., Bhatnagar A., Mänttäri M.; Natural Organic Matter Removal from Drinking Water by Membrane Technology. *Separation and Purification Reviews - SEP PURIF REV. 43. 10.1080/15422119.2012.712080*, **2012.**

202. Meza P. R., Felissia F. E., Area M. C.; Reduction of the recalcitrant cod of high yield pulp mills effluents by AOP. Part 1. combination of ozone and activated sludge, *BioResources, Vol. 6 (2)*, 1053-1068, **2010.**

203. Mohammed A., Smith D.W.; Effects of ozone on kraft process pulp mill effluent, *Ozone Sci. Eng., Vol. 14,* 461-485, **1992.**

204. Molinari, R., Lavorato, C., Argurio, P. Recent progress of photocatalytic membrane reactors in water treatment and in synthesis of organic compounds. A review, *Catal. Today Vol.281*, 144-164, **2017.**

205. Moreira F., Boaventuraa R., Brillas E., Vilar V.; Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters, Applied Catalysis B, *Environmental Vol. 202*, 217–261, **2017.**

206. Mortazavi S.B., Asgari G., Hashemian S.J., Moussavi G.; Degradation of humic acids through heterogeneous catalytic ozonation with bone charcoal, *React. Kinet. Mech. Catal. Vol. 100 (2)*, 471-485, **2010.**

207. Mozia S., Darowna D., Wr□obel R., Morawski A.W.; A study on the stability of polyethersulfone ultrafiltration membranes in a photocatalytic membrane reactor, *J. Membr. Sci. Vol.495*, 176-186, **2015.**

208. Muna A., Sreekrishnan T.; Aquatic toxicity from pulp and paper mill effluents: a review, *Advances in Environmental Research*, *Vol. 5*, 175-196, **2011.**

209. Mustaranta A., Viikari L.; Dewatering of activated sludge by an oxidative treatment, *Wat. Sci. Technol., Vol. 28 (1), 213*–221, **1993.**

210. Murto, M.; Tampereen Vedenhankintakysymys. *Rakennustekniikka, Vol. 10*, 707-710, **1966**, (In Finnish)

211. Muñoz R., Guieysee B.; Algal–bacterial processes for the treatment of hazardous contaminants: a review. *Water Res, Vol. 40*,2799–815, **2006**.

212. Munter R., Kallas J., Pikkov L., Preis S., Kamanev S.; Ozonation and AOP for treatment of the wastewater from oil shale and pulp and paper industries, *Proceedings of The Eleventh Ozone World Congress, S-10-38 – S-10-53,* San Fransisco, USA, 29.8.-3.9. **1993.**

213. Murphy J.K., Hulsey, R.A., Long, B.W., Amarnath, R.K.; Use of ozone and advanced oxidation processes to remote color from pulp and paper mill effluents, Proceedings *of The Eleventh Ozone World Congress S-10-24- S-10-37,* San Fransisco, USA, 29.8.-3.9. **1993.**

214. Möbius C.H. and Cordes-Tolle M.; Enhanged biodegradability by oxidative and radiative wastewater treatment" *Proceedings of The Fifth International Forest Industry Wastewater Conference*, Vancouver, 259-265, Canada, 10.-13.6. **1996.**

215. Naghizadeh A., Nasseri S., Mahvi A.H., Rashidi A., Nabizadeh R., Kalantary R.R.; Fenton regeneration of humic acid-spent carbon nanotubes, *Desal. Water Treat. Vol. 54 (9),* 2490-2495, **2015.**

216. Naghizadeh A; Regeneration of carbon nanotubes exhausted with humic acid using electro-Fenton technology, *Arab. J. Sci. Eng. Vol. 41,* 155-161, **2016.**

217. Neoh, C.H., Noor, Z.Z., Mutamim, N.S.A., Lim, C.K.; Green technology in wastewater treatment technologies: integration of membrane bioreactor with various wastewater treatment systems, *Chem. Eng. J. Vol.283*, 582–594, **2016.**

218. Nerud F., Baldrian P., Gabriel J., Ogeifun D.; Decolorization of synthetic dyes by the Fenton reagent and the Cu/pyridine/H_2O_2 system, *Chemosphere, Vol. 44(5)*, 957-61, **2001.**
219. Neyens E., Baeyens J.; A review of classical Fenton´s peroxidation as an advanced oxidation technique, *Journal of Hazardous Materials. Vol. B98*, 33-50, **2003.**
220. Ni Y., Liu Z.; Pulp bleaching, In*: Kirk RE, Othmer DF (eds) Encyclopedia of chemical technology*. Wiley, New York, **2000.**
221. Nickull O.; Technology Director at Metsä-Serla Lielahti. BCTMP, *Interview by Jansson K.*, **2013.**
222. Nidheesh P., Scaria J., Babu D., Kumar M.; An overview on combined electrocoagulation-degredation processes for the effective treatment of water and wastewater, *Chemosphere Vol. 263,* **2021**.
223. Nikander, G., Sourander, I.; Lumppapersbruken i Finland, *Historik,* Åbo, **1955.** (in Swedish)
224. Noemi M., Hermosilla D., Blanco L., Cortijo L., Blanco A.; Assessing the application of advanced oxidation processes, and their combination with 52 biological treatment, to effluents from pulp and paper industry*. J Hazard Mater Vol.262*, 420-427, **2013.**
225. Nyer E., Vance D.; Hydrogen peroxide treatment: the good, the bad, the ugly. *Ground Water Monitoring and Remediation, Vol. 19(3),* 54-57. **1999.**
226. OECD; Ready biodegradability 301. *OECD guideline for testing of chemicals, Vol. 301*, **1992.**
227. Oeller H.J., Demel I., Weinberger, G.; Reduction of residual COD in biologically treated paper mill effluents by means of combined ozone and ozone/UV reactor stages, *Proceedings of The Fifth International Forest Industry Wastewater Conference*, 283-290, Vancouver, Canada, 10.-13.6. **1996.**
228. Oikeusministeriö; Hallituksen esitys Eduskunnalle vesilainsäädännön uudistamiseksi, *HE* 277/**2009**.(In Finnish)
229. Oikeusministeriö.; Laki vesilain 2 luvun 26 §:n muuttamisesta, 264/**1961**. (In Finnish)
230. Oikeusministeriö; Vesiasetus, *(*282/**1962**). (In Finnish)
231. Oikeusministeriö; Laki vesilain 21 luvun muuttamisesta*,* 467/**1987***.* (In Finnish)
232. Oikeusministeriö; Laki vesilain muuttamisesta, 308/**1990**. (In Finnish)
233. Oikeusministeriö; Laki vesilain muuttamisesta, 87/**1993**. (In Finnish)

234. Oikeusministeriö; Laki vesilain muuttamisesta, 653/**1993**. (In Finnish)
235. Oikeusministeriö; Laki vesilain muuttamisesta, 471/**1995**. (In Finnish)
236. Oikeusministeriö; Laki vesilain muuttamisesta, 1347/**1995**. (In Finnish)
237. Oikeusministeriö.; Laki vesilain muuttamisesta, 1105/**1996.** (In Finnish)
238. Oikeusministeriö.; Laki vesilain muuttamisesta, 689/**2000**. (In Finnish)
239. Oikeusministeriö.; Laki vesilain muuttamisesta, 121/**2001**. (In Finnish)
240. Oikeusministeriö.; Laki vesilain muuttamisesta, 1030/**2003**. In Finnish)
241. Oikeusministeriö.; Laki vesilain muuttamisesta, 1062/**2004**. (In Finnish)
242. Oikeusministeriö.; Laki vesilain muuttamisesta, 1301/**2004**. (In Finnish)
243. Oikeusministeriö.; Laki vesilain muuttamisesta, 732/**2005**. (In Finnish)
244. Oikeusministeriö.; Laki vesilain muuttamisesta, 386/**2009**. (In Finnish)
245. Oikeusministeriö; Laki vesilain muuttamisesta, 587/**2011**. (In Finnish)
246. Ojanperä K.; Uusi paperimassa voitti insinöörityöpalkinnon, *Tekniikka ja Talous* 19.5.**2005**. (In Finnish)
247. Ojanperä K.; Tulevaisuuden sellutehdas tuottaa kuitua, biodieseliä ja kemikaaleja, *Tekniikka ja Talous,* **9. 1, 2008***.* (In Finnish)
248. Olea N., Fernandez M., Araque P., Olea-Serrano F.; Perspectivas em Disrupcions Endocrina, Gac. Sanit., Vol. 16, No.3, 250-256, **2002.**
249. Oller I., S. Malato S., Sánchez-Pérez J.A., Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination—A review, *Science of the Total Environment, Vol. 409*, 4141–4166, **2011**.
250. Omorogie M.O., Babalola J.O., Unuabonah E.I.; Regeneration strategies for spent solid matrices used in adsorption of organic pollutants from surface water: a critical review. *Desal. Water Treat. Vol.57 (2),* 518-544, **2016.**
251. Opedal M. T., Stenius P., Johansson L., Hill, J., Sandberg C.; Removal of dissolved and colloidal substances in water from compressive

pre-treatment of chips using dissolved air flotation: Pilot Trial, *Nordic Pulp & Paper Research Journal,. Vol. 26*, p. 364-371, **2011.**

252. Orhon D., Artan N. & Ates E.; A description of three methods for the determination of the initial inert particulate, chemical oxygen demand of wastewater. *J. Chem.Tech. Biotech., Vol.,* 61 73-80, **1994.**
253. Orhon D. Ubay E., Çokgör; COD Fractionation in Wastewater Characterization—The State of the Art, *J. Chem. Tech. Biotechnol., Vol. 68,* 283-293, **1997.**
254. Oskoei V., Dehghani M.H., Nazmara S., Heibati B., Asif M., Tyagi I., Agarwal S., Gupta V.K.; Removal of humic acid from aqueous solution using UV/ZnO nano-photocatalysis and adsorption, *Journal of Molecular Liquids Vol.213*, 374-380, **2016.**
255. Paasonen, P.; Kymi Osakeyhtiö. *http://www.papermakerswiki.com/innovations/mets%C3%A4klusterin-tutkimuslaitokset-ja-aktiviteetit/kymin-osakeyhti%C3%B6.*, **2011.** (In Finnish)
256. Palo M.; Metsäteollisuus ympäristönsuojelijana ja luontopolulla, *Kansantaloudellinen aikakauskirja, Vol.* 88, 240–242, **1992.** (In Finnish)
257. Panizza M., Cerisola G.; Direct And Meditated Anodic Oxidation of Organic Pollutants, *Chem. Rev. 109*, 651-6569, **2009.**
258. Pankow J., Morgan J.; Kinetics for the aquatic environment*, Environ Sci Technol. Vol. 15(10),* 1155–64, **1981**.
259. Paraskeva P., Graham N.J.D.; Microbial reduction in a secondary effluent by ozonation, UV irradiation and microfiltration, *Proceedings of the 14th Ozone World Congress, Vol. 1*, 53-63, Dearborn, Michigan, USA, 22.-26.8. **1999**.
260. Park T.J.; Removal of Refractory Organics and Color in Pigment Wastewater with Fenton Oxidation, *Wat. Sci. Tech. Vol. 39 No 10-11,* 189-192, **1999.**
261. Parra S., Sarria V, Malato S., Péringer P., Pulgarín C.; Photochemical vs. coupled photochemical–biological flow system for the treatment of two biorecalcitrant herbicides: metobromuron and isoproturon, *Appl Catal B Environ Vol.27*, 153-168, **2000.**
262. Parsons S.A., Williams M.; Advanced Oxidation Processes for Water and Wastewater Treatment, *IWA Publishing*, 329-340, London (UK), **2004.**
263. Payne K.R. (Ed.); Critical Reports on Applied Chemistry, Vol. 23, Industrial Biocides, *Society of Chemical Industry*, USA, **1988**.

264. Pendergast M.M., Hoek E.M.; A review of water treatment membrane nanotechnologies. *Energy Environ. Sci. Vol. 4 (6)*, 1946-1971, **2011.**

265. Pekkala, M., Helander, A., Tanttu, A., Pyykkö, O., Walden, R.; Paperipuukysymys, *Silva Fennica, Vol.28*, 10–11, Helsinki, Finland, **1933**. (In Finnish)

266. Pérez M., Torrades F., Peral J., Lizama C., Bravo C., Casas S; Multivariate approach to photocatalytic degradation of a cellulose bleaching effluent, *Appl Catal B Environ, Vol.33*, 89–96, **2001.**

267. Pérez M., Torrades F., García-Hortal J., Doménech X., Peral J.; Removal of organic contaminants in paper pulp treatment effluents under Fenton and photo-Fenton conditions. *Appl Catal B Environ, Vol.36*,63–74, **2002**.

268. Pérez-Rey R., Chàves H., Baluja C.; Ozone inactivation of biologically-risky wastewaters, *Ozone Sci. Eng., Vol.* 17. 499-509, **1995**.

269. Pignatello J.J.; Dark and photoassisted iron (3+)-catalysed degradation of chlorophenoxy herbicides by hydrogen peroxide, *Environmental Science & Technology, Vol. 26 (5)*, 944-951, **1992.**

270. Pignatello J.J., Baehr K.; Ferric complexes as catalysts for "Fenton" degradation of 2, 4-D and metolachlor in soil, *Journal of environmental quality, Vol. 23 (2)*, 365-370, **1994.**

271. Pliego G., Zazo J.A., Garcia-Muñoz P., Munoz M., Casa, J.A., Rodriguez J.J.; Trends in the intensification of the Fenton process for wastewater treatment: an overview, *Crit. Rev. Env. Sci. Tec., Vol. 45*, 2611–2692, **2015.**

272. Pokhrel D., Viraraghavan T.; Treatment of pulp and paper mill wastewater—a review, *Science of the Total Environment, Vol. 333*, 37– 58, **2004.**

273. Polo-López M.I., L.S. Granados, P. Fernandez-Ibanez; Homogeneous Fenton and Photo-Fenton Disinfection of Surface and Groundwater, *Applications of Advanced Oxidation Processes (AOPs) in Drinking Water Treatment*, 155-177, Springer, **2018.**

274. Popp D., Hafne, T., Johnstone N.; Environmental policy vs public pressure: Innovation and diffucion of alternative bleaching technologies in the pulp industry. *Elsevier B.A.*, Netherlands. **2011.**

275. Pramanik B.K., Pramanik S.K., Sarker D.C., Suja F.; Impact of ozonation, anion exchange resin and UV/H_2O_2 pre-treatments to control fouling of ultrafiltration membrane for drinking water treatment, *Environ. Technol. Vol.38 (11*), 1383-1389, **2016.**

276. Prousek J.; Fenton Reaction After a Century, Chemicke *Listy, Vol. 89(1)*, 11-21, May **1995.**

277. Pulgarín C., Kiwi J.; Overview on photocatalytic and electrocatalytic pretreatment of industrial non-biodegradable pollutants and pesticides, *Chimia Vol. 50*, **1996**.

278. Purkait M. K., Mondal P., Chang C.; Treatment of Industrial Effluents: Case Studies, *CRC Press, 11-12,* **2020.**

279. Rantakari, K.; Suomen Selluloosayhdistys 1918–1943. Lyhyt katsaus Suomen Selloloosateollisuuden syntyyn ja kehitykseen sekä Suomen Selluloosayhdistyksen neljännessatavuotiseen toimintaan, Frenckellin Kirjapaino Osakeyhtiö, Helsinki, Finland, **1944**. (In Finnish)

280. Reddy K.R., Hassan M., Gomes V.G.; Hybrid nanostructures based on titanium dioxide for enhanced photocatalysis, *Appl. Catal. A: General Vol.489*, 1-16, **2015.**

281. Reyes J., Dezotti M., Esposito E., Billasenor J., Mansilla H., Durnan N.; Biomass photochemistry—XXII: combined photochemical and biological process for treatment of Kraft El effluent, *Appl Catal B Environ Vol. 15*, 211-219, **1998.**

282. Ribeiro J.P., Marques C.C., Portugal I., Nunes M.I.; Fenton processes for AOX removal from a kraft pulp bleaching industrial wastewater: Optimisation of operating conditions and cost assessment, *Journal of Environmental Chemical Engineering Vol. 8 (4)*, **2020.**

283. Rice R., Wilkes F.; Fundamental aspects of ozone chemistry in recirculating cooling water systems – data evaluation need, *Ozone Sci. Eng., Vol.14*, 329-365, **1992.**

284. Riddick T., Lindsay N., Tomassi A; Iron and manganese in water supplies. *J Am Water Works Assoc. Vol.50(5),* 688–96, **1958.**

285. Rigg T., Taylor W., Weiss J.; The rate constant of the reactions between hydrogen peroxide and ferrous ions, *J. Chem. Phys., Vol. 22,* 575-577, **1954.**

286. Rincón, A.G., Pulgarin, C.; Comparative evaluation of Fe^{3+} and TiO_2 photoassisted processes in solar photocatalytic disinfection of water. *Appl. Catal. B 63*, 222–231, **2006.**

287. Robertson L.; TAPPI Microbiology and Microbial Technology Committee (2007): monograph on microbiology of papermaking systems. Norcross, GA: *TAPPI Press*. ISBN 1-59510-162-0, **2009.**

288. Rodríguez F.J., Marcos L.A., Núnez L.A., García M.; Effects of ozonation on molecular weight distribution of humic substances and coagulation processes - A case study: the Úzquiza reservoir water. *Ozone Sci. Eng. Vol.34 (5)*, 342-353, **2012.**

289. Rokhina E., Makarova K., Golovina E., Van As H., Virkutyte J.; Free radical reaction pathway, thermochemistry of peracetic

acidhomolysis, and its applications for phenol degradation: spectroscopic study and quatum chemistry calculations, *Environ Sci. Technol. 44,* 6815-6821, **2010.**

290. Rostam A., Taghizadeh M.; Advanced oxidation processes integrated by membrane reactors and bioreactors for various wastewater treatments: A critical review, *Journal of Environmental Chemical Engineering, Vol 8,* **2020.**
291. Roy-Arcand L., Archibald F.S.; Ozonation as a treatment for mechanical and chemical pulp mill effluents; *Ozone Sci. Eng., Vol. 18,* 363-384, **1996a.**
292. Roy-Arcand, L., Archibald, F.S.; Selective removal of resin and fatty acids from mechanical pulp mill effluents by ozone, *Water Research, Vol. 30(5)*, 1269–1279, **1996b**.
293. Ruonala S.; Sytyke-ohjelman projektien yhteenvedot, *Vesi- ja ympäristöhallitus*, Helsinki, **1993**. (In Finnish)
294. Rycroft R., Calnan C.; Dermatitis from slimicides in paper mill, *Contact Dermatitis*, 435-439, October **1980.**
295. Saarinen K., Lammi R., Silvo K., Hietamäki M.; Päästötietojen tuottamismenetelmät Metsäteollisuus, *Ympäristöhallinto – Metsäteollisuus, 8–9,* **2004.** (In Finnish)
296. Safade T.; Tackling the slime problem in a paper-mill, *Pap.Technol Ind., September*, 280-285, **1998.**
297. Salazar C, Sirés I, Salazar R, Mansilla H.D., Zaror C.A.; Treatment of cellulose bleaching effluents and their filtration permeates by anodic oxidation with H_2O_2 production, *J. Chem. Technol. Biotechnol.Vol.90*, 2017-2026, **2015.**
298. Salgado P., Melin V., Durán Y., Mansilla H., Contreras D.; The Reactivity and Reaction Pathway of Fenton Reactions Driven by Substituted 1,2-Dihydroxybenzenes, *Environ. Sci. Technol., Vol. 51,* **2017**.
299. Sallanko J., Väaisäanen T.; Effects of ozonation on AOC content of humic Finnish groundwater, *Ozone Sci. Eng. Vol.35 (2),* 86-89, **2013.**
300. Sarria V., Parra S., Adler N., Péringer P., Pulgarín C.; Recent developments in the coupling of photoassisted and aerobic biological processes for the treatment of biorecalcitrant compounds, *Catal. Today Vol-76*, 301–15, **2002**
301. Sarria V., Deront M., Péringer P., Pulgarín C.; Degradation of a biorecalcitrant dye precursor present in industrial wastewater by a new integrated iron (III) photoassisted-biological treatment, *Appl Catal B Environ Vol.40*, 231-246, **2003.**

302. Savolainen M., Saunamäki R., Järvinen R.; Oxidative Precipitation of Kraft Mill Effluents, Nordic environmental biotechnology programme 1990-1993, Final report, Helsinki, **1993**
303. Saunamäki R.; Teollisuuden jätevesiprojekti. *Suomen itsenäisyyden juhlavuoden 1967 rahasto*. Helsinki, **1980.** (In Finnish)
304. Saunamäki, R., Sorvari J.; Treatment of bleached raft mill wastewaters with ozone and electrochemical methods, *Nordic Pulp Paper Res. J., Vol.3,* 113-120, **1992**.
305. Sharman, P.; BCTMP Special Report, *Pulp and Paper International May* **1989.**
306. Schumb W.C., Satterfield C.N., Wentworth R.L.; Hydrogen peroxide, *American Chemical Society Monograph No. 128,* Reinhold, New York, **1955.**
307. Schumb W.C., Satterfield C.N., Wentworth R.L.; Hydrogen Peroxide; *Reinhold Publishing Corp.*, New York, **1955**.
308. Schrijver J., Wirth B.; Biocides for deposit control of corrugated base paper. Wochenbl *Papierfabr. Vol.22*, 37–43, **2006.**
309. Scott J.P., Ollis D.F.; Integration of chemical and biological oxidation processes for water treatment: review and recommendations, *Environ Prog Vol.14*:88-103. **1995**.
310. Scott J.P., Ollis D.F.; Integration of chemical and biological oxidation processes for water treatment: review and recommendations, *Environ. Prog., Vol. 14*, 88–103, **1995.**
311. Selcuk H., Rizzo L., Nikolaou A.N., Meric S., Belgiorno V., Bekbolet M.; DBPs formation and toxicity monitoring in different origin water treated by ozone and alum/PAC coagulation, *Desalination Vol.210 (1-3)*, 31-43, **2007.**
312. Shi X., Zhu L. Liu J., Hu H.; Application analysis of Fenton/flocculation process for advanced treatment of pulp and papermaking wastewater, *Chinese Journal of Environmental Engineering*, 15/09/**2103.**
313. Sillanpää M., Raimo K.B., Sihvonen M.L.; Determination of EDTA and DTPA as their Fe(III) complexes in pulp and paper-mill process and wastewaters by liquid-chromatography. *Anal Chim Acta, Vol.* 303, 187–192, **1995.**
314. Sillanpää M., Ncibi M.C., Matilainen A.; Advanced oxidation processes for the removal of natural organic matter from drinking water sources: A comprehensive review, *J Environ Manage., Vol.208,* 56-76, **2018.**

315. Simons B., Da Silva Santos C.; The hidden costs of oxidants in microbial deposit control in papermaking, *Pulp Pap. Vol. 87*, 166–169, **2005.**

316. Sinclair W.F.; Controlling pollution from Canadian pulp and paper manufactures: a federal perspective, *Canadian Government Publishing Centre*, Ottawa, **1990.**

317. SITRA; Teollisuuden Jätevesprojekti TESI, *Suomen Itsenäisyyden Juhlavuoden 1967 Rahasto,* ISBN 951-563-045-2, **1981**. (In Finnish)

318. Skoronski E., Ferrari A., Fernandes M., Fernandes M., Ely C., João J.J.; Desempenho de um reator Fenton em escala industrial aplicado à remoção de fenóis em uma planta de recuperação de resíduos da indústria de papel e celulose, *Revista Ambiente & Água, Vol. 10*, 863-874, **2015.**

319. Song W.J., Cheng M.M., Ma J.H., Ma W.H., Chen C.C., Zha, J.C.; Decomposition of hydrogen peroxide driven by photochemical cycling of iron species in clay. *Environ. Sci. Technol., Vol. 40 (15)*, 4782–4787, **2006.**

320. Sozanska Z., Sozansk, M.M.; Efficiency of ozonation as a unit process in the treatment of secondary effluents from the pulp and paper industry, *Ozone Sci. Engng, Vol. 13,* 521-534, **1991.**

321. Staehelin, J., Hoigné, J.; Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide, *Environ. Sci. Technol. Vol. 16,* 676-681, **1982.**

322. Snell F. D., Ettre L. S.; Encyclopedia of Industrial Chemical Analysis, *Vol. 13,* 100–117, John Wiley & Sons, New York, **1971.**

323. Steber J, Wierich P; Properties of hydroxyethano diphosphonate affecting environmental fate: degradability, sludge adsorption, mobility in soils, and bioconcentration, *Chemosphere, Vol.15;* 929–45, **1986.**

324. Stenlund B. and Ranua J.; Kemiallisten tuotteiden talteenotto; *Puumassan valmistus II, osa 2. Suomen Paperi-insinöörien yhdistyksen oppi- ja käsikirja*. Editor Virkola N-E., Second edition. **1983.** (In Finnish)

325. Sutzkover-Gutman I., Hasson D., Semiat R.; Humic substances fouling in ultrafiltration processes, *Desalination Vol.261 (3)*, 218-231, **2010**.

326. Tabrizi G.B., Mehrvar M.; Integration of advanced oxidation technologies and biological processes: recent developments, trends and advances, *J Environ Sci Health Vol.39*, 3029–81, **2005.**

327. Thompson G., Swain J., Kay M., Forster C.F.; The treatment of pulp and paper mill effluent: a review, *Bioresource Technology, Vol. 77,* 275-286, **2001**.

328. Tekniska Föreningen i Finland; Tekniska Föreningens extra möte den 18 november 1909, *Tekniska föreningens i Finland förhandlingar no 12, **1909** årgång XXIX,* Helsingfors. (in Swedish)

329. Tekniska Föreningen i Finland; Sulfatsprit, *Tekniska föreningens i Finland förhandlingar no 10, **1910** årgång XXX,* Helsingfors. (in Swedish)

330. Timothy C., Ballantyne B.; Pesticide toxicology and international regulations, John Wiley & Sons. 592, **2004.**

331. Tobiason J., Bazilio A., Goodwill J., Mai X., Nguyen C.; Manganese Removal from Drinking Water Sources, *Water Pollution,* 168–177, DOI 10.1007/s40726-016-0036-2), **2016.**

332. Trang V.N., Dan N.P., Phuong L.D., Thanh B.X.; Pilot study on the removal of TOC, THMs, and HAAs in drinking water using ozone/UV-BAC, *Desal. Water Treat. Vol.52 (4-6),* 990-998, **2014.**

333. Torrades F., Pérez M., Mansilla H., Peral J; Experimental design of Fenton and photo-Fenton reactions for the treatment of cellulose bleaching effluents, *Chemosphere Vol.53,* 1211–20, **2003.**

334. Tuhkanen T.; Oxidation of Organic Compounds in Water and Wastewater with the Combination of Hydrogen Peroxide and UV Radiation. *Doctoral Dissertation, University of Kuopio, Department of Environmental Sciences,* Kuopio, Finland, **1994.**

335. Uğurlu M., Gürses A., Doğar Ç., Yalç M.; The removal of lignin and phenol from paper mill effluents by electrocoagulation, *J. Environ. Manag., Vol. 87(3)*, DOI: 10.1016/j.benvman.2007.01.007. **2007.**

336. Upadhyay R.K., Soin N., Roy S.S; Role of graphene/metal oxide composites as photocatalysts, adsorbents and disinfectants in water treatment: a review, *RSC Adv. Vol.4 (8),* 3823-3851, **2014.**

337. Uyguner C.S., Suphandag S.A., Kerc A., Bekbolet M.; Evaluation of adsorption and coagulation characteristics of humic acids preceded by alternative advanced oxidation techniques, *Desalination Vol.210 (1-3),* 183-193, **2007.**

338. Venkatadri R., Peters R.W., Chemical oxidation technologies: Ultraviolet light/hydrogen peroxide, Fenton's reagent and titanium dioxide-assisted photocatalysis, *Hazard. Mater., Vol. 10,* 107-149, **1993.**

339. Waclawek S., Lutze H., Grübel K., Padil V., Cernik M., Dionysiou D.; Chemistry of persulfates in water and wastewater treatment: a review, *Chem. Eng. J., Vol.330*, 44-62, **2017.**

340. Walling C., Goosen A.; Mechanism of the ferric ion catalysed decomposition of hydrogen peroxide; effect of the organic substrate, *J.Am. Chem. Soc., Vol. 95*, 2987-2991, **1978.**
341. Walling C., Kato S.; The oxidation of alcohols by Fenton's reagent: the effect of copper ion, *J. Am. Chem. Soc., Vol. 93,* 4275-4281, **1971.**
342. Wang Y., Yu J., Han P., Sha J., Li T., An W., Liu J., Yang M.; Advanced oxidation of bromide-containing drinking water: a balance between bromate and trihalomethane formation control, *J. Environ. Sci. Vol.25 (11*), 2169-2176, **2013a.**
343. Wang X., Wu Z., Wang Y., Wang W., Wang X., Bu Y., Zhao J.; Adsorption-photodegradation of humic acid in water by using ZnO coupled TiO_2/bamboo charcoal under visible light irradiation. *J. Hazard Mater. Vol.262*, 16-24, **2013b.**
344. Wardman P., Candeias L.P.; Fenton Chemistry; An Introduction, *Radiation Research Vol. 145, Vol. 5*, 523-531, May **1996**.
345. Watts R.J., Udell M.D., Rauch P.A., Leung S. W.; Treatment of Pentachlorophenol-Contaminated Soils Using Fenton's Reagent, *Hazardous Waste and Hazardous Materials,* 335-345, **1990.**
346. Watts R.J.; Hydrogen peroxide for physicochemically degrading petroleum-contaminated soils, *Remediation Vol.2 (4),* 413-425, **1992.**
347. Weiss J.; Elektronenübergangsprozesse im Mechanismus von Oxydations- und Reductionsreactions in Lösnungen, *Naturwissensschaften, Vol. 23,* 64-69, **1935**. (In German)
348. Winter J., Uhl W., B⍰erub⍰e P.R.; Integrated oxidation membrane filtration processes NOM rejection and membrane fouling. *Water Res. Vol.104*, 418-424. **2016.**
349. Wuorimaa A., Jokela R., Aksela R.; Recent developments in the stabilization of hydrogen peroxide bleaching of pulps: an overview, *Nord Pulp Pap Res J Vol. 2,* 435–443, **2006.**
350. Xiong Y., He C., Karlsson H.T., Zhu X.; Performance of three-phase three-dimensional electrode for reduction of COD in simulated wastewater containing phenol. *Chemosphere Vol.50*, 131-136, **2003.**
351. Xue G., Liu H., Che, Q., Hills C., Tyrer M., Innocent F.; Synergy between surface adsorption and photocatalysis during degradation of humic acid on TiO_2/activated carbon composites, *J. Hazard Mater. Vol.186 (1)*, 765-772, **2011.**
352. Yan M., Wang D., Ma X., Ni J., Zhang H.; THMs precursor removal by an integrated process of ozonation and biological granular activated carbon for typical Northern China water, *Separ. Purif. Technol. Vol.72 (3*), 263-268, **2010.**

353. Yoneyama H., Torimoto T.; Titanium dioxide/adsorbent hybrid photocatalysts for photo destruction of organic substances of dilute concentrations, *Catal. Today Vol.58 (2),* 133-140, **2000.**

354. Yu G., Peng H., Du C., Chen H., Zhang W.; Integrated Process Combined with Fenton Reaction for the Treatment of Papermaking Deinking Wastewater, *Journal of Chemical Engineering of Japan Vol. 53(10*), 653-659, **2020.**

355. Zhang C., Brown P., Hu Z.; Thermodynamic properties of an emerging chemical disinfectant, peracetic acid., *Sci. Total. Environ. Vol.621*, 948-959, **2018**.

356. Zepp R.G., Faust B.C., Hoigné J.; Hydroxyl radical formation in aqueous reactions pH (3-8) of iron (II) with hydrogen peroxide: The photo-Fenton reaction, *Environmental Science and Technology, Vol. 26 (2*), 313-319, **1992.**

357. Zhang K., Zhou X., Du P., Zhang T., Cai M., Sun P., Huang C.; oxidation of β-lactam antibiotics by peracetic acid: Reaction kinetics, products and pathways evaluation, *Water Res., Vol. 123*, 153-161, **2017.**

358. Zhao L.J., Zhang Y.F., Hong J.F. and Tu W.W.; papermaking wastewater treatment _ A brief review, *Adv. Mater. Res.* 926-930, 4276-4279. DOI: 10.4028/www.scientific.net/AMR.926-930.4276, **2014**.

359. Zhou H., Smith D.W.; Process parameter development for ozonation of Kraft pulp mill effluents, *Proceedings of The Fifth International Forest Industry Wastewater Conference,* Vancouver, Canada, 10.-13.6.1996, 267-274, **1996.**

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Development of advanced oxidation processes for the Finnish pulp and paper industry water treatment

Advanced oxidation processes (AOP) have been developed since the1990s for the Finnish pulp and paper industry as a pinnacle of chemical water treatment to face the tightening environmental limits. Whenever neither pure coagulation & flocculation nor biological technologies can reach the required environmental limits, AOP technologies can be utilised. This thesis presents four AOP methods to treat different types of water encountered in the pulp and paper industry. This thesis summarises the author’s research and experience on water treatment topics since 1986.

Avancerade oxidationsprocesser (AOP) representerar spetskunskapen inom den kemiska vattenreningsteknologin. AOP har utvecklats för den finska skogsindustrin sedan 1990-talet för att möta skärpta miljökrav. Då kemiska vattenreningstekniker så som koagulering och flockning eller biologisk vattenrening inte kan uppnå de ställda miljökraven, erbjuder AOP-teknikerna en lösning. I den här avhandlingen presenteras fyra AOP-tekniker för att behandla vatten inom massa- och pappersindustrin. Denna avhandling summerar författarens forskning och erfarenhet av vattenreningsfrågor inom massa- och pappersindustrin sedan 1986.

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