

Advanced Oxidation Processes for Removal of COD from Pulp and Paper Mill Effluents

A Technical, Economical and
Environmental Evaluation

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**ROYAL INSTITUTE
OF TECHNOLOGY**

Master of Science Thesis
Stockholm 2013



**KTH Industrial Engineering
and Management**

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A Technical, Economical and Environmental Evaluation

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Master of Science Thesis

STOCKHOLM 2013

PRESENTED AT

INDUSTRIAL ECOLOGY
ROYAL INSTITUTE OF TECHNOLOGY

TRITA-IM 2013:06

Industrial Ecology,
Royal Institute of Technology
www.ima.kth.se

SAMMANFATTNING

I Sverige, är massa- och pappersindustrin den dominerande utsläppskällan av nedbrytbart organiskt material till vatten. När det organiska materialet når recipienten ökar syreförbrukningen eftersom stora mängder syre erfordras för nedbrytningen av materialet. Detta leder i sin tur till att de vattenlevande organismerna hotas och utsätts för syrebrist. Förbättrad processteknik, ökad processlutning och utbyggnad av extern avloppsvattenrening har under de senaste åren drastiskt sänkt den biokemiska syreförbrukningen (BOD). Däremot har den kemiska syreförbrukningen (COD) inte reducerats i samma utsträckning då delar av det organiska materialet är mer persistent och måste behandlas med mer avancerad teknik.

Kemisk fällning kan idag binda stora delar av det kvarvarande COD till fast material som sedan kan avlägsnas via olika separationsmetoder. En stor nackdel med den här typen av rening är att stora mängder kemikalier används som i sin tur genererar stora mängder slam som måste tas om hand, vilket introducerar höga driftkostnader.

Inom en snar framtid kommer massa- och pappersbruk inom EU att möta nya regulatoriska krav för COD utsläpp, och bruk i Asien, Sydamerika och Oceanien kommer även de att möta väldigt hårda utsläppskrav. Det är därför av intresse att granska alternativa reningsmetoder och utvärdera dess tekniska, miljömässiga och ekonomiska genomförbarhet vid behandling av avloppsvatten från massa- och pappersbruk. Mycket intresse har visats för Avancerade Oxidationsprocesser (AOP), varför dessa tekniker valts att utvärderas i detta examensarbete. Första delen av rapporten innefattar en litteraturstudie där processer med följande oxidanter studerats:

1. Ozon (O_3)
2. Ozon + Väteperoxid (O_3/H_2O_2)
3. Fenton's reagens (Fe^{2+}/H_2O_2)
4. Ozon + Ultraviolett ljus (O_3/UV)
5. Väteperoxid + Ultraviolett ljus (H_2O_2/UV)
6. Foto-Fenton's reagens ($Fe^{2+}/H_2O_2/UV$)
7. Titaniumdioxid + Ultraviolett ljus (TiO_2/UV)

Utav dessa valdes ozon behandling (1) och ozon i kombination med väteperoxid (2) för vidare experimentella studier. Behandlingarna har utförts vid Wedecos (Xylem Water Solutions) laboratorium i Tyskland och undersökts på avloppsvatten från tre olika svenska bruk; A, B och C.

Experimentella resultat tyder på att ozonering är effektiv behandlingsmetod för reduktion av COD i avloppsvatten från massa- och pappersbruk. En relativt hög COD reduktion (41% för bruk A, 31% för bruk B, och 53% för bruk C) uppnåddes för samtliga avloppsvatten med en tillämpad ozondosering på 0.2 g O_3/L , utan någon märkbar inverkan på andra parametrar så som pH, N-tot, NO_2^- , NO_3^- , NH_4^+ , P-tot och PO_4^{3-} . Det förekommer indikationer om att typ av avloppsvatten har en inverkan på COD reduktionen och att TMP avloppsvatten är lättare att oxidera i jämförelse mot avloppsvatten från sulfatmassabruk. Kombinationen av ozon och väteperoxid uppnådde ingen ytterligare COD reduktion i jämförelse mot ozon som enda oxidant, och bekräftade därmed de resultat Ko et al. uppnådde i sin studie 2009.

Ozonering ses som ett miljövänligare alternativ till kemisk rening (fällning/flockning) eftersom föroreningarna i vattnet destrueras istället för att koncentreras, vilket innebär att COD, färg och toxicitet kan minskas utan att stora mängder slam genereras. Dock kan en efterföljande biologisk behandling vara nödvändig för avskiljning av BOD då en BOD ökning uppvisats för samtliga avloppsvatten i denna studie i takt med att COD brutits ned till lättnedbrytbart biologisk material.

Kostnaderna är däremot höga i jämförelse mot kemisk fällning även om det förekommer indikationer på fall när behandlingen kan vara lönsam (t ex om slamhanteringskostnaderna blir högre i framtiden, inköpspriset för kemikalier ökar och elpriset sjunker). Det råder vissa tveksamheter gällande systemet och det finns inga konkreta bevis på att toxiska biprodukter inte bildas. Mer forskning måste utföras och fler fullskaliga installationer måste rapporteras och innan massa- och pappersindustrin är villig att investera i oxidationstekniken.

SUMMARY

In Sweden, the dominating source for emissions of degradable organic substances to water is the pulp and paper industry. The organic substances increase oxygen consumption in the recipient which subsequently threatens aquatic species. Improved process engineering, process closures and use of external treatments have in recent years drastically lowered the Biological Oxygen Demand (BOD). However, the Chemical Oxygen Demand (COD) has not been reduced to the same extent, as some organic substances are more persistent and must be treated with more advanced techniques.

Chemical precipitation, which can bind large parts of the remaining COD into solid matter, making it possible to be removed from the effluent by various separation technologies, contributes to an efficient COD removal. However, the direct operating cost for the treatment is high as large amount of chemicals are used in the process, and large quantities of sludge generated.

In the near future EU pulp and paper industry will have to meet new regulatory demands on COD discharges, and pulp mills in Asia, South-America and Oceania will meet stringent discharge demands. It is therefore of interest to review alternative treatments in regards to technical, environmental and economical feasibility in the treatment of pulp and paper mill wastewaters. Much interest has been shown for Advanced Oxidation Processes (AOP), which is why these techniques have been evaluated in this thesis. The first part of the report consists of a literature review where processes with the following oxidants have been reviewed:

1. Ozone (O_3)
2. Ozone + Hydrogen peroxide (O_3/H_2O_2)
3. Fenton's reagent (Fe^{2+}/H_2O_2)
4. Ozone + Ultraviolet light (O_3/UV)
5. Hydrogen peroxide + Ultraviolet light (H_2O_2/UV)
6. Photo-Fenton's reagent ($Fe^{2+}/H_2O_2/UV$)
7. Titanium dioxide + Ultraviolet light (TiO_2/UV)

Ozone treatment (1) and ozone in combination with hydrogen peroxide (2) were chosen for further experimental studies. The experiments were conducted at Wedecos (Xylem Water Solutions) laboratory in Germany and tested on wastewater from three different Swedish mills: A, B and C.

The experimental results indicate that treatment with ozone is an efficient method for elimination of COD from pulp and paper mill wastewaters. A relatively high COD reduction (41 % for Mill A, 31% for Mill B and 53% for Mill C) was achieved for all wastewaters with an applied ozone dosage of 0.2g O_3/L , without an appreciable impact on other parameters such as pH, N-tot, NO_2^- , NO_3^- , NH_4^+ , P-tot and PO_4^{3-} . There are indications that the nature of the wastewater has an impact on the COD removal efficiency and that TMP wastewater is easier to oxidize in comparison to wastewater from sulphate mills. The combination with hydrogen peroxide did not show any further COD reduction compared to ozone treatment alone, thus confirming the results Ko et al. showed in their study in 2009.

Oxidation with ozone is seen as more environmental alternative in comparison to chemical treatment (precipitation/flocculation) because contaminants in the wastewater are destructed rather than concentrated or transferred into a different phase, which leads to the decrease of COD, colour and toxicity without the need to handle large amounts of sludge. However, a subsequent biological treatment may be necessary for removal of BOD as a BOD increase is registered for all wastewater treated in this study.

The costs are on the other hand higher in comparison to chemical treatment even though there are indications of cases when treatment with ozone can be profitable (e.g. if the cost for sludge handling increases in the future, price for chemicals increases and electricity price decreases). There are some uncertainties regarding the system and there is no clear evidence that toxic by-products are not formed. More research must be done and more full-scale installations must be reported before the pulp and paper industry is willing to invest in oxidation technology.

Keywords: Advanced Oxidation Processes, Ozone, Wastewater Treatment, COD, Pulp and Paper Industry

AKNOWLEDGEMENT

This master thesis is written as a part of the civil engineering program “Chemical Engineering for Energy and Environment” at the Royal Institute of Technology in Stockholm. It has been carried out during October 2012 – April 2013, at the Swedish consulting company ÅF AB within the market area Forest Industry and includes 30 credits. The thesis has been developed in collaboration with Wedeco (a part of the Xylem Water Solutions), which accounted for the costs of all analysis and test equipment. Sara Stemme from ÅF Industry is the supervisor of the thesis and the examiner is Per Olof Persson from the department of Industrial Ecology at the Royal Institute of Technology.

First of all, I would like to thank Sara Stemme for her time, support and mentorship throughout the thesis. I also want to give thanks to Per Olof Persson and Mårten Krogerus for supporting me in the process of planning, proceeding and writing the thesis. Special thanks to Mill A, B and C for providing wastewater for the case study and thanks to the Käppala Association for providing sludge. Many thanks to the staff at Wedeco for all help with the equipment and analysis and all my colleagues at ÅF. Finally, I would like to thank my beloved family and friends for always being there for me.

Without you all, I wouldn't have made it!

Irma Karat

TABLE OF CONTENTS

SAMMANFATTNING	III
SUMMARY	V
ACKNOWLEDGEMENT	VII
ABBREVIATIONS	2
1 INTRODUCTION	4
1.1 AIM AND OBJECTIVES.....	4
1.2 METHODOLOGY	5
1.3 LIMITATIONS	5
2 THE PULP AND PAPER INDUSTRY	6
2.1 PULP AND PAPER MANUFACTURING PROCESS.....	7
2.1.1 <i>Wood Handling and Debarking</i>	7
2.1.2 <i>Pulping</i>	7
2.1.3 <i>Bleaching</i>	8
2.1.4 <i>Papermaking</i>	9
3 BEST AVAILABLE TECHNIQUES (BAT)	10
4 WATER IN PULP AND PAPER PROCESSES	12
4.1 EFFLUENT CONSTITUENTS AND PARAMETERS	12
4.1.1 <i>Wastewater Characteristics</i>	13
4.1.2 <i>Total Suspended Solids (TSS)</i>	14
4.1.3 <i>Biological Oxygen Demand (BOD)</i>	14
4.1.4 <i>Chemical Oxygen Demand (COD)</i>	14
4.1.5 <i>Total Organic Carbon (TOC)</i>	14
4.1.6 <i>Adsorbable Organic Halides (AOX)</i>	14
4.1.7 <i>Total- Phosphorus and Nitrogen</i>	15
5 CURRENT EXTERNAL WASTEWATER TREATMENT	16
5.1 PRIMARY TREATMENT	16
5.2 SECONDARY TREATMENT	17
5.2.1 <i>Aerobic Treatment</i>	17
5.2.2 <i>Anaerobic Treatment</i>	18
5.3 TERTIARY TREATMENT.....	19
5.3.1 <i>Chemical Treatment (Precipitation/Flocculation)</i>	19
5.4 TREATMENT EFFICIENCIES	20
6 OXIDATION PROCESSES	22
6.1 REACTION MECHANISMS	22
6.2 PREVIOUS RESEARCH	24
6.3 OZONE (O ₃)	28
6.4 PEROXONE (H ₂ O ₂ /O ₃).....	29
6.5 FENTON'S REAGENT (Fe ²⁺ /H ₂ O ₂)	30

6.6	PHOTO-CHEMICAL PROCESSES.....	32
6.6.1	<i>Ozone + Ultraviolet Light (O₃/UV)</i>	32
6.6.2	<i>Hydrogen Peroxide + Ultraviolet Light (H₂O₂/UV)</i>	33
6.6.3	<i>Photo-Fenton's Process (Fe²⁺/H₂O₂/UV)</i>	33
6.7	PHOTO-CATALYTIC PROCESS WITH TITANIUM DIOXIDE (TiO ₂ /UV).....	33
6.8	EQUIPMENT AND REACTOR DESIGNS.....	34
6.8.1	<i>Ozone Systems</i>	34
6.8.2	<i>Peroxone Systems</i>	35
6.8.3	<i>Fenton's Systems</i>	36
6.8.4	<i>Photo-chemical Systems</i>	36
6.8.5	<i>Photo-catalytic Systems</i>	37
6.9	INTERFERING COMPOUNDS.....	38
6.10	ADVANTAGES AND DISADVANTAGES OF DIFFERENT AOPs.....	39
6.11	DEGRADATION PRINCIPLES AND BY-PRODUCTS.....	42
6.12	EXAMPLE OF FULL-SCALE INSTALLATIONS.....	43
6.12.1	<i>Gebr Lang Papier GmbH Ettringen</i>	43
6.12.2	<i>SCA Graphic Laakirchen AG</i>	44
7	TECHNOLOGIES ASSESSMENT AND COMPARISON	46
7.1	MECHANICAL RELIABILITY.....	46
7.2	FLEXIBILITY.....	46
7.3	STABILITY.....	47
7.4	ENERGY EFFICIENCY.....	47
7.5	OVERVIEW OF RATING.....	48
7.6	PLACEMENT OF AOP IN THE TREATMENT PLANT.....	48
8	CASE STUDY.....	50
8.1	CHOICE OF WASTEWATER.....	50
8.1.1	<i>Mill A</i>	51
8.1.2	<i>Mill B</i>	52
8.1.3	<i>Mill C</i>	53
8.2	MATERIALS AND METHODS.....	54
8.2.1	<i>Sampling</i>	54
8.2.2	<i>Characterization</i>	54
8.2.3	<i>Ozone Generation & Reactor Configuration</i>	55
8.2.4	<i>Experimental Procedure</i>	56
8.2.5	<i>Analytical Methods</i>	57
8.3	RESULTS.....	58
8.3.1	<i>Ozonation</i>	58
8.3.2	<i>AOP</i>	64
9	TECHNICAL EVALUATION	66
9.1	OZONATION.....	66
9.2	AOP.....	68
10	ECONOMICAL EVALUATION	70
10.1	OXIDATION WITH OZONE.....	71

10.2	CHEMICAL PRECIPITATION WITH FLOTATION	75
10.3	COMPARISON	76
10.3.1	<i>Investment</i>	76
10.3.2	<i>Direct operating cost</i>	77
10.3.3	<i>Specific operating cost (fixed + direct)</i>	77
10.4	SENSITIVITY ANALYSIS	79
10.4.1	<i>Change in Sludge Handling Cost</i>	79
10.4.2	<i>Change in Electricity Price</i>	80
10.4.3	<i>Change in Chemical Price</i>	81
10.4.4	<i>Change in fixed operating cost</i>	82
11	SOURCES OF ERRORS	84
12	DISCUSSION.....	86
13	CONCLUSION	88
14	RECOMMENDATIONS	90
15	REFERENCES	92
	APPENDIX 1 – DRAFT BAT 2012	96
	APPENDIX 2 – NEW EFFLUENT DISCHARGE STANDARDS OF CHINA 2008.....	98
	APPENDIX 3 – AOP RESULTS	100
	APPENDIX 4 – TECHNICAL DATA FOR VALIDATION OF LCK CUVETTE TESTS	102
	APPENDIX 5 – RAW DATA.....	104

ABBREVIATIONS

TERMS

Adt	Air dry ton
AS	Activated Sludge
AOP	Advanced Oxidation Process
AOX	Adsorbable Organic Halides
BAT	Best Available Techniques
BOD	Biological Oxygen Demand
CEPCI	Chemical Engineering Plant Cost Index
COD	Chemical Oxygen Demand
CTMP	Chemo-Thermo-Mechanical Pulp
ECF	Elemental Chlorine Free
EE/O	Electrical Energy Input per Order of Removal
EOP	Electrochemical Oxidation Potential
He	Henry's constant
HMW	High Molecular Weight
IPPC	Pollution Prevention and Control
LAS	Long-term Aerated Active Sludge
LMW	Low Molecular Weight
LP-UV	Low pressure mercury vapor lamps
MBBR	Moving Bed Bioreactor
MP-UV	Medium pressure mercury vapor lamps
NO _x	Nitrogen oxides
NSSC	Semi-chemical pulp
PAC	Poly Aluminium Chloride
P-UV	Pulsed UV xenon arc lamps
RIT	Royal Institute of Technology
SCB	Statistics Sweden
SS	Suspended Solids
TSS	Total Suspended Solids
TCF	Total Chlorine Free
TMP	Thermo-Mechanical Pulp
TOC	Total Organic Carbon
TSS	Total Suspended Solids
UV	Ultraviolet light

CHEMICALS

Al ³⁺	Aluminium ion
C ₂ H ₄ O ₃	Peracetic acid
Ca ²⁺	Calcium ion
Cl ⁻	Chloride ion
Cl ₂	Chlorine
ClO ₂	Chlorine dioxide
ClO ₃ ⁻	Chlorate ion
Co ²⁺	Cobalt ion
CO ₂	Carbon dioxide
CO ₃ ²⁻	Carbonate ion
F ₂	Fluorine
Fe ²⁺	Ferrous iron
Fe ³⁺	Ferric ion
FeOOH	Goethite
FeSO ₄	Ferrous sulphate
H ₂ O	Water
H ₂ O ₂	Hydrogen peroxide
H ₂ SO ₄	Sulphuric acid
HCO ₃ ⁻	Bicarbonate ion
HO ₂ ⁻	Hydroxide anion
HSO ₃ ⁻	Bisulphate
Mg ²⁺	Magnesium ion
N	Nitrogen
Na ⁺	Sodium ion
NaOH	Sodium hydroxide
Na ₂ S	Sodium sulphide
NH ₄ ⁺	Ammonium ion
NO ₂ ⁻	Nitrite ion
NO ₃ ⁻	Nitrate ion
O ₂	Oxygen
O ₂ [*]	Superoxide radical
OH [*]	Hydroxide radical
P	Phosphorous
PO ₄ ³⁻	Phosphate ion
SO ₃ ²⁻	Sulphite ion
SO ₄ ²⁻	Sulphate ion
TiO ₂	Titanium dioxide
Zn ²⁺	Zinc ion

1 Introduction

In Sweden, the dominating source for emissions of degradable organic substances to water is the forest industry. The organic substances increase oxygen consumption in the recipient which subsequently threatens aquatic species. During recent decades, much effort has been put on lowering the Biological Oxygen Demand (BOD) in the effluents, using various biological treatments. However, some organic substances that are discharged from the pulp and paper mills are more persistent and must be treated with more advanced techniques. For that reason Chemical Oxygen Demand (COD) has become a more relevant effluent pollution parameter in the pulp and paper industry worldwide. COD is a measure of the chemical oxygen demand where an oxidizer is used to degrade the more persistent organic matter.

Improved process engineering, process closures and use of external treatments have in recent years drastically lowered the BOD. However, the COD emissions have not decreased to the same extent and must therefore be further reviewed. Chemical precipitation, which can bind large parts of the remaining COD into solid matter, making it possible to be removed from the effluent by various separation technologies, contributes to an efficient COD removal. However, a major drawback with this type of treatment is the generation of large quantities of sludge which is difficult to dewater (consumes a lot of energy) and generates large quantities of waste.

In the near future EU pulp and paper industry will have to meet new regulatory demands on COD discharges, and pulp mills in Asia, South-America and Oceania will also meet very stringent discharge demands. It is therefore of interest to review alternative treatments in regards to technical, environmental and economical feasibility in the treatment of pulp and paper mill wastewaters.

1.1 Aim and Objectives

This master thesis is written as a part of the civil engineering program “Chemical Engineering for Energy and Environment” at the Royal Institute of Technology in Stockholm. It has been carried out at the Swedish consulting company ÅF AB in collaboration with Wedeco (a part of the Xylem Water Solutions). The aim with this thesis is to find a potential oxidation process for COD removal from pulp and paper effluents that can be used in the near future to meet the new emission standards. The first objective will be to review and compare advanced oxidation technologies and methods, and based on literature information assess their technical, environmental and economical feasibility in the treatment of pulp- and paper mill effluents. Secondly, the objective is to confirm the assumptions and demonstrate the actual performance of a selected technology in laboratory on actual effluent.

1.2 Methodology

The method of work within this thesis has comprised three work phases:

1. *Literature survey and information gathering*

Information has been gathered from books, universities, research organizations, journals, publications, suppliers and companies applying the technologies.

2. *Case Study and execution of lab scale tests*

Based on the information acquired in the literature survey, two of the reviewed oxidation technologies have been selected for a case study and testing in lab scale, performed at cooperation partner Wedeco (Part of the Xylem Water Solutions), and tested on wastewater from three different Swedish mills: A, B and C.

3. *Technical, Environmental and Economical Evaluation*

Results and assumptions obtained from the demonstrative part of the thesis have formed the basis for a design and cost estimation of a full scale installation. The methodology for performing the technical and economical evaluations in the case study is explained in detail in Chapter 8. The environmental evaluation is only briefly discussed, no advanced analysis have been studied.

The conclusion of the thesis is based on the theoretical review, the practical test results achieved and the economical evaluation. Regular progress follow-up and information review meetings have been arranged throughout the project with examiner from the Royal Institute of Technology and supervisor from ÅF AB. The thesis has also been qualitatively controlled by Wedeco.

1.3 Limitations

The main area of focus for the thesis is oxidation processes for external removal of COD from pulp and paper mill effluents. Process internal wastewater treatments for COD removal within the pulp and paper industry are left outside the scope.

Often, EU has more advanced wastewater treatment plants compared to rest of the world; this report has therefore put more focus on pulp and paper effluents and legislation within that region. Only a short discussion in regards to rest of the world is carried out.

External expertise is used for consultation within the fields and all laboratory work is carried out at cooperation partner Wedeco, a part of Xylem Water Solutions. Key data and potential cost data is documented in the report in order to compare different technologies, but other than that no advanced economic assessments are included. Assumptions and simplifications are made in the scale-up estimates, due to the short time frame of the thesis (20 weeks).

2 The Pulp and Paper Industry

Wood is a very important raw material because it comes from a renewable resource and can replace the fossil-based materials to a certain extent. Forest can bind carbon dioxide (CO₂) and produce products that are recyclable and can continue to store carbon throughout their lifetimes.

Pulping methods have been developed to produce pulp from wood fibres, which in turn are used to manufacture fibre products for protection (packaging), absorption (hygiene, tissue) and information distribution (newspaper, printing paper) etc. Apart from fibre production, the industry generates electricity from bio-fuels and supplies district heating to municipal networks. Tremendous amounts of natural resources and energy are consumed in the pulp and paper processes, which is why the industry is a significant source of pollutant discharges to the environment. The production generates significant amounts of liquid and solid wastes, is a producer of greenhouse gas emissions, and a major consumer of fresh water. A recent study showed that COD can be as high as 11 000 mg/L for industrial wastewater, which seriously can harm habitats near mills if discharged to the recipient untreated (Thompson et al., 2001).

Environmentally, the pulp and paper industry in Sweden has seen a great change since the 1970s, when emissions into local rivers and pollution from landfills were severe (Carlsson, 2004). According to statistics developed by Swedish Forest Industries Federation, annual COD emissions from Swedish pulp and paper mill effluents have decrease with over 50 % since 1978, while pulp production has increased with a similar speed, see Figure 1.

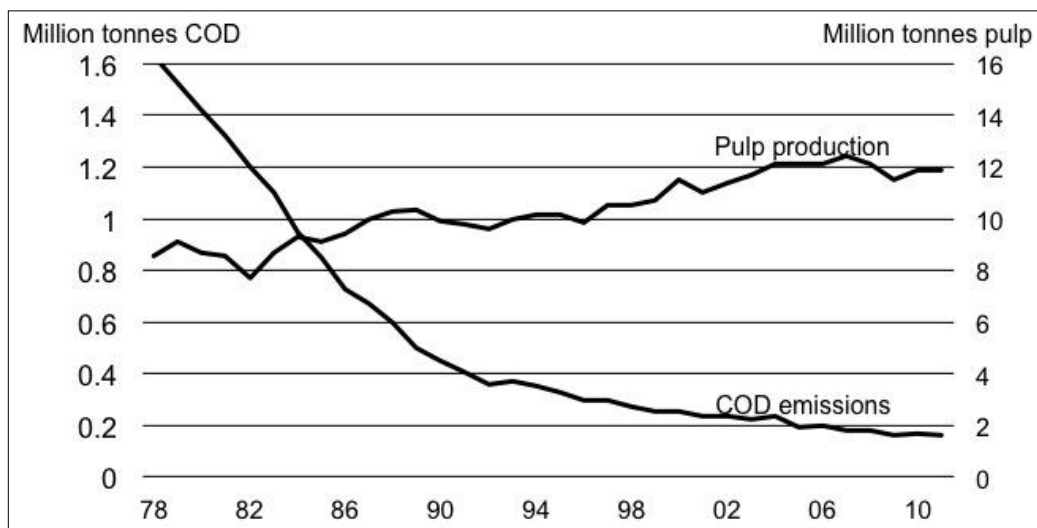


Figure 1: COD emissions from Swedish pulp and paper mills. (Swedish-Forest-Industries-Federation, 2012)

The emissions are considerably lowered but the rapid increase in population and demands for industrial products have put a huge stress on the environment. Urged by environmental and legislative force, the COD will probably have to be lowered even more in the nearest future, which is why new wastewater treatment technologies have to be developed and implemented.

2.1 Pulp and Paper Manufacturing Process

Wood contains cellulose, lignin and hemicelluloses, where cellulose is desirable for production of for e.g. paper and textiles, and depending on the end-usage of the pulp the level of separation can be varied. The pulp and paper manufacturing process can be divided into four steps; wood handling and debarking, pulping, bleaching and papermaking, and are described in following section.

2.1.1 Wood Handling and Debarking

The wood arrives to the pulp mill in the form of logs, and is debarked with help of debarking drums and chipped in the wood chipper before storage in stacks. The chips are then discharged from the stack base with help of screws and conveyors and send to the pulping process. (Ljungberg and Brännvall, 2011)

2.1.2 Pulping

The objective with pulping is to release and soften the cellulose fibres from the wood matrix with use of chemical and/or mechanical forces. Pulp mills produce either chemical or mechanical pulp, and the processes may be a combination of both depending on desired fibre quality. (Pokhrel and Viraraghavan, 2004)

Chemical Pulping

In chemical pulping, fibres are released from the wood matrix with use of chemicals in the presence of heat and pressure. The reaction continues to a certain predefined degree of delignification and the products receive a good strength. The fibre yield for chemical pulping is often around 40-50%, and the rest is burned in the recovery boiler or considered as by-product. (Hultman, 1997)

The kraft process, also known as the sulphate process, is the dominating chemical pulping technology worldwide with over 22 million tonnes produced in Europe as of 2011 (FAOSTAT, 2012). The process is based on an alkaline solution of sodium hydroxide (NaOH) and sodium sulphide (Na_2S), which degrades the carbohydrates by alkaline and peeling hydrolysis. Another common method is the sulphite process, which was a very popular way of producing textiles and other bio materials before the oil-based products had its breakthrough in the late seventeenth century. The process is based on an acidic or neutral cooking with salts of sulphites (SO_3^{2-}) or bisulphates (HSO_4^-) and bases like calcium (Ca^{2+}), magnesium (Mg^{2+}), ammonium (NH_4^+) or sodium (Na^+) etc. (Hultman, 1997)

Mechanical Pulping

In mechanical pulping, wood is processed mechanically with use of electrical energy. By utilizing a mechanical approach for fibre disintegration the original composition of the wood is retained within the derived fibres, resulting in a high yield of the process (up to 95%) (Pokhrel and Viraraghavan, 2004). The manufacturing process is simpler than for chemical pulping, partly because there is no need for chemical recovery systems. However, the quality of the pulp is low grade and contains a lot of lignin which can cause post yellowing if applied to papers. (Hultman, 1997)

There are two main types of mechanical pulp; ground wood pulp and refined pulp. In the manufacturing of ground wood pulp, debarked logs are pressed against a rotating cylinder constructed of sheets with ceramic sandstone. The refined pulp is produced by grinding the wood chips between disc refiners, and fibres are released as chips are heated and beaten between the disc(s). There are several types of refined pulp, but Thermo-Mechanical pulp (TMP) and Chemo-Thermo-Mechanical pulp (CTMP) are the most common once. If the chips are partially softened with steam before entering the disc refiners, the produced pulp is referred to as TMP. If chemicals are added in addition to the heat, CTMP is produced. (Hultman, 1997)

2.1.2.1 Recycled Fibre Processing

Recycled pulp is sometimes used instead of fresh pulp for board and newspaper manufacturing. This type of pulp has a lower strength and stiffness due to the many different origins of the paper. It is here important to remove detrimental substances such as ink, and prepare a component of a stock with uniform quality. (Hultman, 1997)

2.1.3 Bleaching

The importance of bleaching is to give the paper a specific brightness in order to obtain a certain printing quality and to purify the pulp from undesirable impurities that may be present in the final paper quality. (Ljungberg and Brännvall, 2011)

The process often starts with oxygen delignification where residual lignin is removed. The brightness can however only be increased marginally, which is why further bleaching steps are required. In the past, chlorine bleaching with elemental chlorine was the most common bleaching technology, but was associated with very high concentrations of Adsorbable Organic Halides (AOX) in the emissions and therefore replaced with other technologies. Today, Elemental Chlorine Free (ECF) bleaching with low AOX or Totally Chlorine Free (TCF) bleaching is used. The ECF bleaching is based on chlorine dioxide (ClO_2), consequently only small portions of AOX are formed. In TCF bleaching, neither elemental chlorine nor chlorine containing agents are used. Instead, hydrogen peroxide (H_2O_2), oxygen (O_2) and peracetic acid ($\text{C}_2\text{H}_4\text{O}_3$) are used, resulting in no AOX formation. Recently, ozone (O_3) has come into use as bleaching chemical. (sdguide.org, 2008)

2.1.4 Papermaking

A paper mill can either be integrated with the pulp mill or non-integrated. In the latter case pulp is bought and transported to the paper mill in form of bales. The main steps of papermaking are stock preparation, forming, pressing, drying and are performed with help of a paper machine, see Figure 2. In the stock preparation, pulp is diluted and mixed together with additives (pigment, binder etc.). The fibre suspension is distributed on a permeable wire with help of a head box, and the formed sheets are mechanically dewatered before entering the drying section with steam-heated cylinders. This is followed by a fifth step, which may include calendaring, coating, cutting, sheeting etc. (Ljungberg and Brännvall, 2011)

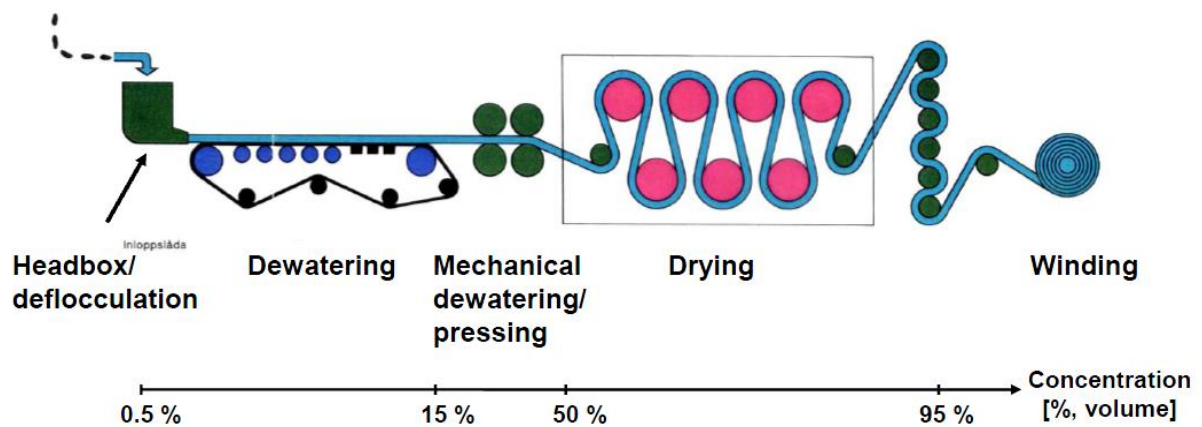


Figure 2: Principal layout of a paper machine. (Innventia, 2012)

3 Best Available Techniques (BAT)

The European Commission has developed the Integrated Pollution Prevention and Control (IPPC) directive with the reference document BREF on Best Available Techniques (BAT) for pulp and paper industries. The BREF document is covering pertinent environmental data connected to pulp and paper manufacturing processes, with conclusions based on experiences from real world examples and professionals. The basic requirement of the IPPC directive is that all appropriate preventive measures are taken against pollution, in particularly by using the BAT. For a technology to be considered as BAT, it should be developed on a scale which allows implementation under economical and technical viable conditions, in the relevant industrial sector. (Asplind, 2011)

Some of the BAT that are recommended for pulp mills in order to reduce water consumption and environmental impact are dry debarking of wood, efficient washing, ECF or TCF bleaching, recycling and reuse of chemicals and water. Primary and secondary wastewater treatment is suggested and sometimes chemical precipitation and flocculation for mechanical pulping and recycled fibre processing. BAT that is recommended for paper making are similar to those for pulp production; minimize the use of water and chemicals, construction of balanced white water system, separate pre-treatment of coating wastewaters, primary and secondary wastewater treatments, and in some cases chemical precipitation or flocculation. (IPPC, 2001)

BAT emission levels to water from various pulp and paper processes are presented in Table 1, and are based on annual averages and expressed in terms of air dry tone (cooling water and other clean water are not included). The IPPC directive is a minimum directive, which means that more stringent requirements can be incorporated into national legislation. The data is therefore not always comparable with all member states of EU. (IPPC, 2001)

Table 1: Best Available Techniques (BAT) emission levels for different pulp and paper processes. Based on annual averages and expressed in terms of air dry tonne (Adt). (IPPC, 2001)

Process	Flow rate [m ³ /Adt]	COD [kg/Adt]	BOD [kg/Adt]	TSS [kg/Adt]	AOX [kg/Adt]
<i>Bleached Kraft</i>	30-50	8-23	0.3-1.5	0.6-1.5	<0.25
<i>Unbleached Kraft</i>	15-25	5-10	0.2-0.7	0.3-1	-
<i>Bleached Sulphite</i>	40-55	20-30	1-2	1-2	-
<i>Non-integrated CMP</i>	15-20	10-20	0.5-1	0.5-1	-
<i>Integrated Mechanical</i>	12-20	2-5	0.2-0.5	0.2-0.5	<0.01
<i>Integrated RCF (without de-inking)</i>	<7	0.5-1.5	0.05-0.15	0.05-0.15	<0.005
<i>Integrated RCF (with de-inking)</i>	8-15	2-4	0.05-0.2	0.1-0.3	<0.005

There are several indications that EU pulp and paper industry will have to meet new regulatory demands on pollutant emissions in the nearest future, and also pulp and paper mills in China shall meet very stringent demands on COD discharges. In Appendix 1, information is extracted from IPPC:s draft reference document on BAT 2012 regarding COD emission levels, and in Appendix 2 new effluent discharge standards of China are presented.

As seen in Appendix 1, bleached Kraft pulp mills in EU should reduce their COD emissions with approximately 26% compared to the discharge limits of 2001, and integrated RCF mills (with de-inking) up to 70%. These COD limits should partly be achieved with internal process measures and partly with extended external wastewater treatment plants.

In China, COD limits for existing pulp mills, paper mills and integrated pulp and paper mills are 100, 80 and 90 mg/L respectively. And the COD limit for new mills can be as low as 50 mg/L, see Appendix 2. To achieve the mandatory COD targets, upgrading of current wastewater treatment plants are necessary and advanced wastewater treatments have to be adopted.

4 Water in Pulp and Paper Processes

The pulp and paper industry is ranked as the third world's largest consumer of water and is consequently producing high amounts of wastewaters (Sevimli, 2005). High water consumption often goes hand in hand with high energy consumption, since more pumping and treating is needed. (sdguide.org, 2008)

Process water is needed for several process stages; wood preparation, cooking, pulp washing, bleaching, transportation, dilution and formation. Approximately 200 m³ of water is utilized per ton produced cellulose, and the amount is highly dependent on which type of process and chemicals that are used in the process, see Table 2 (Ince et al., 2011, Fontanier et al., 2006). The discharged water effluents can contain significant amounts of toxic substances, which can cause death to the living organisms in receiving waters, and affect the terrestrial ecosystems negatively. The effluents can also cause thermal impact, slime growth, scum formation, and loss of aesthetic beauty in the environment. (Pokhrel and Viraraghavan, 2004)

Table 2: Typical wastewater composition from various pulping processes, expressed in terms of air dry tonne (Adt). (Rintala and Puhakka, 1994, as cited in Pokhrel and Viraraghavan, 2004))

Process	Wastewater [m ³ /Adt]	COD [kg/Adt]	SS [kg/Adt]
<i>Wet debarking</i>	5-25	5-20	N/A
<i>Kraft-unbleached</i>	40-60	40-60	10-20
<i>Kraft-bleached</i>	60-90	100-140	10-40
<i>Mg-sulphite unbleached</i>	40-60	60-120	10-40
<i>Ground wood pulp</i>	10-15	5-20	N/A
<i>CTMP-unbleached</i>	10-15	70-120	20-50
<i>CTMP-bleached</i>	10-15	100-180	20-50
<i>TMP-unbleached</i>	10-30	40-60	10-40
<i>TMP-bleached</i>	10-30	50-120	10-40

Considerable volumes of cooling water are also used because of the high energy-intensity of the processes. This water is normally not contaminated and does not affect the environment negatively, if not reused as process water or discharged to small recipients where temperature-increase is a limiting factor. (sdguide.org, 2008)

4.1 Effluent Constituents and Parameters

Knowledge of the nature of the wastewater is crucial in the design and operation of a treatment, and in the engineering management of environmental quality. To promote this understanding, the physical, biological and chemical constituents of concern found in wastewater, and parameters used for analysis are discussed briefly in following chapter.

4.1.1 Wastewater Characteristics

The water effluents from pulp and paper industries are often very complex, and it is almost impossible to characterize all types of constituents. Chemical and mechanical pulping processes will generate different wastewaters because different quantities of water and/or additives are used. The wastewater will generally contain carbohydrates (glucose, xylose, galactose, manose, arabinose etc.), extractives (fatty acids, resin acids, triglycerides) and low molecular weight compounds (formic acid, acetic acid, oxalic acid). (Catalkaya and Kargi, 2007)

As seen in Figure 3, wastewater generated from wood preparation stage include mostly solid (bark, branches, dirt, sand etc.) and dissolved organic matter as wood is chipped and washed. The wastewater often has a brown colour, and contains mostly wood debris, soluble material and chemicals. The brown colour consists of mainly phenolic lignin derivatives, arising from lignin depolymerisation. These types of molecules are very hard to degrade, because of the strong bonds in their molecular structure and will contribute to a high COD. (Kreetachat et al., 2007)

Wastewater that is generated from the bleaching process is generally not higher strength than wastewater discharged from the pulping process; the toxicity is however more of an issue. If molecular chlorine or chlorine dioxide is used in the bleaching step, chlorinated organic substances such as chloro-phenols, dioxins, resin and fatty acids and furans can be generated. Many of these are very toxic, bio-accumulative, and mutagenic. Inorganic compounds containing chlorate (chlorates) are also formed when chlorine is used in any of its forms in the bleaching process. These are salts of chloric acid and contain the chlorate ion (ClO_3^-). Chlorates are powerful oxidizers and will often react easily with organic materials present in the wastewaters. Wastewaters from paper machines will contain high concentrations of suspended solids (SS), BOD, COD, and inorganic dyes as pigment, binder and fibres are lost in to the effluents. (Pokhrel and Viraraghavan, 2004, Fontanier et al., 2006)

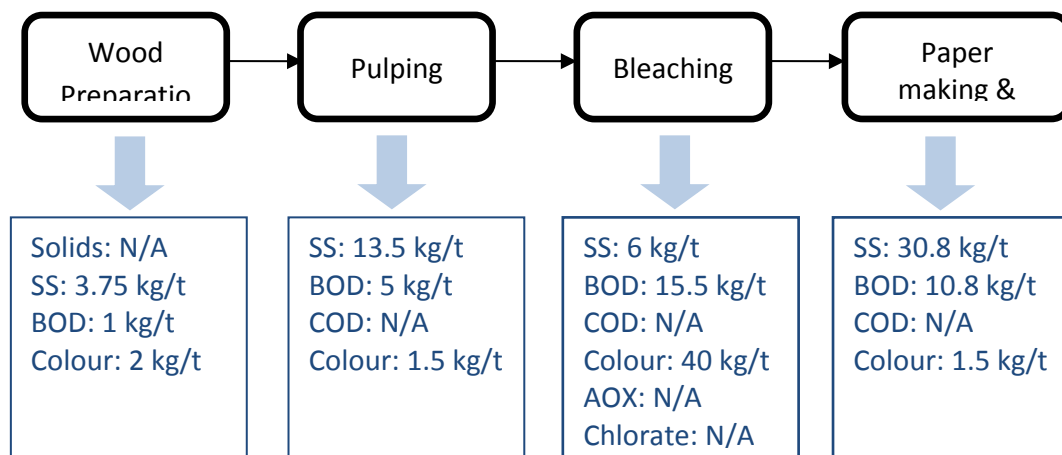


Figure 3: Typical constituents in process water streams per tonne of production. (Springer, 2000, as cited in Pokhrel and Viraraghavan, 2004)

4.1.2 Total Suspended Solids (TSS)

Total Suspended Solids, TSS, is a parameter that describes the amount of emitted suspended solids (fibres, inorganic fillers, pigments etc.) within the wastewater. As long as concentration of TSS is kept low, there is no specific environmental problem connected to the emissions. It is however important to separate as much TSS as possible since it affects the biological treatment negatively and the solids can cause clogging problems in pipes and pumps. (sdguide.org, 2008)

4.1.3 Biological Oxygen Demand (BOD)

BOD is a measure that relates to the biodegradability of the organic matter in the wastewater. It is often represented by the amount of oxygen consumed by microorganism in biological treatment to oxidize organic substances in a certain time. For example, if the oxygen consumption by microorganisms is measured over a period of 7 days, the parameter is called BOD₇. A high BOD level can be translated into a large amount of easily degradable organic substance present in the wastewater. Easily degradable organic substances that are released into the environment contribute to oxygen consumption in the recipient, and might cause oxygen depletion which threatens aquatic species. (sdguide.org, 2008)

4.1.4 Chemical Oxygen Demand (COD)

COD is a parameter that represents the amount of oxygen needed for complete decomposition of organic matter. In terms of pulp and paper production, COD originates from dissolved raw materials, process aids and all substances formed during pulp cooking that are not removed with the black liquor. These types of substances are often very persistent and cannot be removed efficiently, causing negative effects on environment. (sdguide.org, 2008)

The BOD/COD ratio is a parameter of great importance for quantification of biodegradability of a contaminated effluent. A high ratio (>0.5) indicates good biodegradability as reported by Ghaly et al. (2009) as cited in Jamil et al. (2011). A ratio less than 0.3 is considered low, and corresponds to low biodegradability of the organic material present in the wastewater.

4.1.5 Total Organic Carbon (TOC)

Total Organic Carbon (TOC) is the gross amount of carbon bound in the organic compounds in the wastewater. Suspended particulate, colloidal particles, BOD and COD are all part of the TOC, and it has in some cases been possible to relate TOC to BOD and COD values to measure pollution characteristics. (Eddy and Metcalf, 2003)

4.1.6 Adsorbable Organic Halides (AOX)

Effluents discharged from bleach plants, where chlorine-based chemicals are used, contain organically bound chlorine compounds such as dioxins and furans, measured as AOX (Jamil et al., 2011). These compounds should be minimized since they are showing toxic effects on aquatic organisms and causing severe ecological problematic. According to BAT, AOX can be fully

avoided with implementation of TCF bleaching processes and reduced to acceptable levels with ECF bleaching processes. (sdguide.org, 2008)

4.1.7 Total- Phosphorus and Nitrogen

Both phosphorus (P) and nitrogen (N) are essential nutrients for microbial growth, and can disturb the ecological balance negatively when discharged to a large extent. Eutrophication can occur in the recipient and pollution of groundwater can arise if discharged in excessive amounts on land. The emissions of N and P from the pulp and paper industry are not very specific since wood contain limited amounts of nutrients bound in the matrix. The nutrients are crucial for the growth of microorganism and thus for the BOD reduction, many mills must add external nitrogen and phosphorus to the effluents in order to keep the level in an appropriate range. (sdguide.org, 2008)

5 Current External Wastewater Treatment

There is a large variety in external treatment technologies used for pulp and paper mill effluents and the preferred technology depends on many factors; characteristics of the matter to be removed, requirements on the purity of the effluent water, economical factors etc.

The treatment is often divided into several process steps; primary, secondary and tertiary treatment as seen in Figure 4. Primary treatment is mainly based on a physical removal of solids, secondary treatment on removal of dissolved organic compounds, and tertiary treatment used for effluent polishing and elimination of more advanced constituents. Tertiary treatments are rare at present, but can be an obligation in future due to possible new legislation. (Thompson et al., 2001)

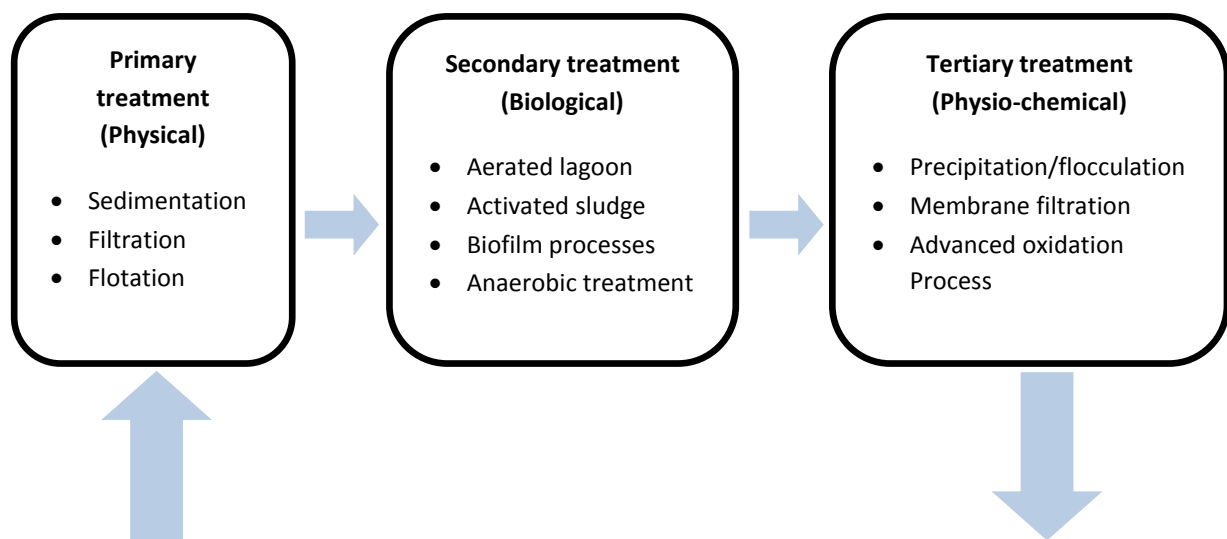


Figure 4: External wastewater treatment for pulp and paper mill effluents, divided into three sequences: primary, secondary and tertiary treatment.

5.1 Primary Treatment

The aim with primary treatment is to reduce suspended solids such as fibres, fibre debris, bark particles, filler and coating materials mechanically, and is accomplished by use of screens, and settling tanks. The function of the screens is to remove larger particles and operate according to sieving/filtration process (Ochre-Media, 2001). Sedimentation is generally the most common method used for mechanical purification where solids are separated by settlement in a settling basin. The particles sink to the bottom, forming a primary sludge that is continuously scraped, pumped or sucked from the basin. Dissolved air flotation, or dispersed air flotation, is another primary treatment seen in pulp and paper mills. Air is bubbled through the wastewater and small bubbles are formed which will attach to the suspended particles and rise them to the surface. Sludge is formed at the surface and removed with help of top scrapers and heavier fractions taken out in the bottom with sedimentation. (Hultman, 1997)

5.2 Secondary Treatment

Primary treatments remove suspended solids to a large extent. Dissolved organic compounds and colloidal particles on the other hand are still remained in the wastewater and must be removed with a secondary biological treatment (Thompson et al., 2001). Allowing microorganisms to utilize the pollutants as nutrients dissolved organic compounds and colloidal particles can be lowered and oxidized into low molecular fractions. The microorganisms grow and multiply in an aerobic or anaerobic environment, forming a sludge which later is separated. (Persson, 2011)

5.2.1 Aerobic Treatment

Aerobic microorganisms require oxygen to support their metabolic activity. Oxygen is supplied in the form of air by aeration equipment. There are numerous of aerobic systems available for degradation of oxygen-demanding organic compounds in industrial wastewater; aerated lagoons, activated sludge systems, biofilm processes etc. (Persson, 2011)

5.2.1.1 Aerated Lagoon

One type of biological treatment often used for pulp and paper effluents is the aerated lagoon, which is a large, shallow ($\approx 4\text{m}$) pond where wastewater is treated biologically with active microorganisms and mechanical aeration. The aerated lagoon is very space consuming because it is dimensioned for a residence time of 5-7 days and consumes a lot of energy for aeration. However, it is very easy to operate and maintain, and the shock load capacity is high. In recent years some aerated lagoons have been converted into LAS-facilities which are long-term aerated activated sludge treatment plants with a residence time of around one day. Parts of the old aerated lagoon have then been utilized for the aeration and other parts used for temperature stabilization and cooling of hot wastewater effluents. The aerated lagoon will primarily remove BOD but can also reduce emissions of AOX to some extent. The removal efficiency is dependent on residence time, pH, temperature, amount of sludge and degree of aeration. (Hultman, 1997, Persson, 2011)

5.2.1.2 Activated Sludge Process

Pulp and paper mills that have limited space and sensitive recipients are using the activated sludge (AS) process for biological treatment. The wastewater is treated in two steps; aeration and sedimentation. In the first step, wastewater is treated with a high concentration of microorganism and a powerful aeration, and the retention time can vary between a couple of hours and up to a day. In the second step water and sludge is separated in a sedimentation basin and parts of the sludge is pumped back to the aeration basin. The recirculation of sludge enables a high concentration of microorganisms which is of importance for extensive reduction in organic material. The activated sludge systems are more sensitive than aerated lagoons and cannot stand fast load changes. However, the degree of efficiency can be controlled, and very high BOD-reductions are seen. (Thompson et al., 2001, Persson, 2011)

5.2.1.3 Moving Bed Bioreactor

Several plants have invested in the Moving Bed Bioreactor (MBBR) due to stricter environmental regulations and increase in production. The basin is filled with thousands of suspended plastic carriers that are floating free in a reactor, which have microorganism attached on a film on the carriers. Air is supplied from the bottom of the reactor, which keeps the carriers moving and permits a higher load, a better mixing, and a higher flush. The biggest advantage with a suspended biofilm process is that it does not require return of activated sludge, has very small space requirements, has good shock resistance and can operate at very high concentrations of biomass. (Persson, 2011)

5.2.1.4 Biofiltration

Another type of biofilm reactor that is used for pulp and paper mill wastewater is the biofilter reactor. Here, the reactor is equipped with a biological filter of a fixed biomass carrier that serves as a filter as well as a biological contactor. Wastewater and air is fed from the bottom of the reactor and led in an upward direction through the dense granular bed. No subsequent clarifier is needed, because all material is retained within the filter, which with time must be cleaned (backwashed). The filter is operated with a hydraulic retention time of around 0.5 h, and very high BOD reductions are seen. The reactor is however only suitable for wastewaters containing low BOD concentrations due to clogging problems at higher concentrations. This treatment is also often used for tertiary treatment, where it functions as a polishing step. (Möbius, 2006)

5.2.2 Anaerobic Treatment

Anaerobic treatment is a treatment without presence of oxygen and is more appropriate for treatment of high strength wastewaters. Effluents originated from recycled fibres are often treated anaerobic; apart from that, this technology is not used as widely as the aerobic treatments in the pulp and paper industry (Ochre-Media, 2001). However, the investment in this technology is increasing due to its many advantages in comparison to aerobic treatment; lower sludge production, lower chemical consumption, smaller space requirements and energy production in the form of bio gas. (Persson, 2011)

The major problem with implementation of anaerobic treatment for pulp and paper effluents is the potential for hydrogen sulphide formation; since sulphate is widely used as active cooking chemical in many pulp mills. Another important issue with an anaerobic process is its sensitivity to toxic compounds present in the wastewater. (Thompson et al., 2001)

5.3 Tertiary Treatment

Some substances that are discharged from pulp and paper mills are very persistent and cannot be removed with secondary treatment alone. As a consequence, a tertiary treatment must be adopted to reduce concentrations of COD, AOX and colour, to meet the increasingly stringent discharge regulations (Jamil et al., 2011, Catalkaya and Kargi, 2007). These substances are then treated with more advanced techniques, for example tertiary biofilters, membrane processes, evaporation, chemical precipitation and flocculation and oxidation processes. Some of these techniques are well known and implemented in real life and others are still elaborated at research level (Ried et al., 2012). In this report, chemical precipitation and flocculation and later oxidation processes will be brought up for discussion as potential tertiary treatments.

5.3.1 Chemical Treatment (Precipitation/Flocculation)

Chemical treatment is today used increasingly by the pulp and paper industry since biological treatment does not give satisfactory results in regards of COD removal. It is necessary here to distinguish between two different types of chemical treatments; flocculation and precipitation, as they involve different types of purification mechanisms.

Flocculation, is based on an addition of ferric ions (Fe^{3+}), aluminium ions (Al^{3+}) or/and long-chained polymers to the effluents. Very small colloidal particles cannot be removed with sedimentation due to a negatively charged surface in water, causing a repellent force. The added metal ions will react with the water to form hydroxides, which in turn adsorb the colloidal particles by sweep coagulation and form larger flocks that easily can settle. The coagulants can also stick to the surface of the colloidal particles and neutralize the local negative surface charge, resulting in colloid destabilization and promote a formation of larger particles that can be separated with sedimentation. In a similar way, the addition of long-chained polymers as flocculating agent is based on bridging between the colloids and the polymer. The pH of the water must be controlled and the mixing in the beginning must be fast to prevent overdosing of chemicals. This type of process is very efficient for removal of fibre residues and colour. (Persson, 2011)

Chemical precipitation is a very common and well-known technology, especially for phosphorous removal in municipal wastewater treatment. It involves the addition of metal salts of aluminium, iron or calcium to alter the physical state of dissolved solids and facilitate their removal by sedimentation. The pulp and paper mill effluents do not contain especially high phosphorous concentrations, it is here more of relevance to remove residual phosphorus that might have been added in the biological treatment as nutrient. The positively charged metal ions will react with the residual phosphorus and resin acids in the wastewater, and form insoluble precipitates, which can be separated from the aqueous phase with sedimentation or flotation. (Persson, 2011)

Chemical treatment has been studied extensively. Thoren et al., (1997) reported that COD concentrations of <100 mg/L were obtained in final effluents of the Braviken paper mill in Sweden, as tertiary wastewater treatment in form of flocculation with Al³⁺ and organic polymer was applied. Kumar et al., (2011b) investigated the batch flocculation process on diluted black liquor effluent with initial COD and BOD of 7000 mg/L and 1400 mg/L respectively, and found that Poly Aluminium Chloride (PAC) as flocculation agent reduced COD to 84%. In addition, 92% of colour was removed when a coagulant dose of 8 ml/L was used at pH 4.

Although chemical treatment show good results, the treatment has associated drawbacks like dewatering and disposal of the generated sludge. Disposal strategy of solid wastes depends on the country and regulations obeyed. General applications such as land filling and incineration are the most common types. The landfill deposition is often not an alternative, especially not in EU, where deposition of organic material is not allowed. In Europe, the combination of incineration with steam and power generation is the most applied, but the water and ash content of the chemical sludge causes problems in energy efficiency and off-gases must sometimes be purified from NO_x. (Ince et al., 2011)

5.4 Treatment Efficiencies

To get a better insight and understanding about discussed treatments, the removal efficiencies for some mentioned processes are summarized in Table 3. As seen from the table, chemical treatment is the most efficient purification method for removal of COD from pulp and paper mill effluents.

Table 3: Example of removal efficiencies for different wastewater treatments, *= Adapted for mills using ECF-bleaching.

Treatment	Process	SS [%]	BOD [%]	COD [%]	AOX* [%]	Reference
Primary	<i>Sedimentation</i>	80-90	N/A	N/A	N/A	(Pokhrel and Viraraghavan, 2004)
Secondary	<i>Aerated Lagoon</i>	N/A	<95	60-70	50-65	(Pokhrel and Viraraghavan, 2004)
	<i>MBBR</i>	N/A	85-95	65-75	N/A	(Broch-Due et al., 1997)
	<i>Anaerobic</i>	N/A	60-90	40-80	N/A	(Hultman, 1997)
Tertiary	<i>Flocculation (Al³⁺)</i>	N/A	N/A	<96	N/A	(Pokhrel and Viraraghavan, 2004)

6 Oxidation Processes

The term oxidation refers to the transfer of one or more electrons from a reductant (electron donor) to an oxidant (electron acceptor), which leads to a change in the chemical composition of both the reductant and oxidant (Kommineni et al., 2008). In the past, chemical oxidation have been used to reduce concentrations of residual organics, remove ammonia, control odors, and for disinfection purposes. Today, chemical oxidation processes are recommended for improving the treatability of refractory organic compounds, to reduce the inhibitory effects of certain compounds to microbial growth and to eliminate the toxic compounds that might affect the microbial growth and aquatic flora in the recipient. (Eddy and Metcalf, 2003)

Recently, a series of new oxidation methods for wastewater purification called Advanced Oxidation Processes (AOP), have received an increased attention as tertiary treatments for pulp and paper mill effluents. These types of processes are utilizing combinations of several different oxidizers, and are based on formation of hydroxide radicals (OH^*). The radicals are then used to reduce/destroy dissolved organic compounds, aromatic compounds, toxic compounds, detergents, pesticides and many more. (Munter, 2001)

The AOP concept was first introduced by Glaze et al. (1987), and defined as:

“Near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radicals (OH^) in sufficient quantity to affect water purification”.*

These type of water treatments are sometimes called the *“water treatment processes of the 21st century”*, because if applied in a right place, contaminants concentrations can be significantly lowered (Munter, 2001). Many systems are qualified under the broad definition of AOP, and there are many technologies available to produce OH^* radicals in the aqueous phase. In this report, processes involving combinations of ozone (O_3), hydrogen peroxide (H_2O_2), Fenton’s reagent, ultraviolet light (UV) and titanium dioxide (TiO_2) are reviewed.

6.1 Reaction Mechanisms

During oxidation, species with one unpaired electron, namely radicals, are formed. The radicals tend to be very reactive and are followed by further oxidation reactions between the radical and other organic or inorganic reactants, until thermodynamically stable products are formed. Ideally, the end-products of complete oxidation are carbon dioxide (CO_2) and water (H_2O), see Reaction [1]. However, this might not always be feasible, because very large amounts of chemicals and energy are required. (Kommineni et al., 2008, Bijan and Mohseni, 2005)



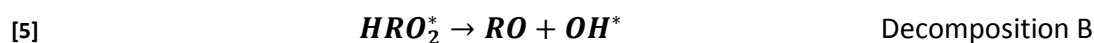
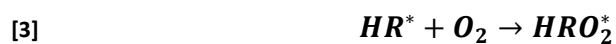
AOPs can generally be divided under two different categories; photo-chemical and non-photochemical processes. In the latter one OH^* radical formation is initiated when oxidizing agents such as O_3 , H_2O_2 are applied to the wastewater. Photo-chemical processes are based on same type of oxidizers, but in a combination with UV irradiation. Some systems are also used in a

combination with catalysts and pH adjustments to proceed or increase the rate of reaction. (Goi, 2005)

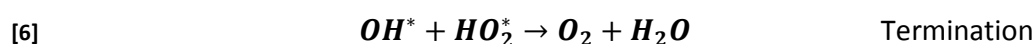
Once generated, the OH^* radical can in principle attack all organic and inorganic compounds, and depending on the nature of the substrate, three types of attacks are possible (Munter, 2001, Siitonen, 2007):

1. The OH^* radical can steal a hydrogen atom from the pollutant (alkenes, alcohols etc.).
2. The OH^* radical can add itself to the pollutant (aromatics, olefins, etc.)
3. The OH^* radical can transfer its unpaired electron to other substrates (carbonates, bicarbonates etc.).

Alkenes are treated most efficiently since the double bond is very susceptible to OH^* radical attack. Saturated molecules are harder to oxidize, and will thus react at much slower rates, because there is no simple chemical pathway for the mineralization to occur (Gogate and Pandit, 2004a). One of many possible reaction pathways is presented in Reaction [2-5], where R represents the carbon chain in the pollutant molecule. (Seneviratne, 2007)



The OH^* radical is very unstable and will self-terminate in a short time period, see Reaction [6].



Of the many properties that can be used to characterize redox reactions, the Electrochemical Oxidation Potential (EOP) is most commonly used, and is presented for some common oxidizing agents in Table 4. The higher EOP, the better oxidizing characteristics and apart from fluorine, the OH^* radical is one of the most active oxidants known, with an EOP of 2.80. (Eddy and Metcalf, 2003)

Table 4: Electrochemical Oxidation Potential (EOP) for some common oxidizing agents. (Eddy and Metcalf, 2003)

Oxidizer	EOP [eV]
Fluorine (F_2)	3.06
Hydroxyl radicals (OH^*)	2.80
Ozone (O_3)	2.08
Hydrogen peroxide (H_2O_2)	1.78
Chlorine (Cl_2)	1.36
Chlorine dioxide (ClO_2)	1.27
Oxygen (O_2)	1.23

6.2 Previous Research

A small number of oxidation processes have been investigated in detail, few field examinations have been carried out, and it is still uncertain what the exact reaction mechanisms are. Despite the unknown mechanisms, the scale of pilot and laboratory testing has begun to reach substantial properties. (Munter, 2001)

Previous studies in oxidation processes for the treatment of pulp and paper mill wastewaters have shown the merits of these systems; increasing the removal efficiencies of organic matter, decreasing the toxicity and enhancing the biodegradability of the effluents. Most of the studies have been made in laboratory scale with wastewaters collected from real pulp and paper mill effluents. As seen in Table 5, Biljan and Mohseni (2005), Bierbaum and Öeller (2009), Ko et al. (2009), Sevimli (2005), Perez et al. (2001), Kumar et al. (2011a), Yeber et al (1999), Boyd and Almquist (2004), Catalkaya and Kargi (2007), and Jamil et al. (2011), have all proved promising results in terms of effectiveness. They have also suggested some directions for experimental conditions to maximize the removal efficiencies.

Table 5: Previous research in oxidation technology in the treatment of pulp and paper mill wastewaters.

Oxidizer	Type of Wastewater	Initial Characteristics	Operating Conditions	Results	Reference
O_3	Kraft pulp mill with an annual capacity of 210 000 tonnes of bleached softwood pulp. Samples collected before biological treatment. Norske Skog pulp mill, Elk Falls, BC, Canada.	BOD ₅ : 282 mg/L COD: 1586 mg/L TOC: 701 mg/L	pH: 11 Temp: 20°C Dosage: 0.8 g O ₃ /L Reaction time: 2 h	Biological treatment combined with pre-ozonation enhanced the conversion of HMW to LMW compounds and resulted in 21% COD removal, 16% TOC removal and 13% BOD ₅ increase. Biodegradability of HMW compounds increased from 5% to about 50%.	(Bijan and Mohseni, 2005)
	Trials were conducted on pilot scale with effluents collected randomly from two different paper mills (A & B) which are processing paper from recycled fibres. Samples collected after biological treatment.	BOD _A : 20 mg/L BOD _B : 4 mg/L COD _A : 331 mg/L COD _B : 201 mg/L	pH: N/A Temp: N/A Dosage: A: 0.295g O ₃ /L, specific O ₃ dosage 0.9 g O ₃ /COD ₀ B: 0.174 g O ₃ /L, specific O ₃ dosage 0.9 g O ₃ /COD ₀ Reaction time: 15 min	The hard to biodegradable COD was reduced with ozonation. Mill A: 50% COD removal, BOD/COD ratio increased from 0.06 to 0.24. Mill B: 35% COD removal, BOD/COD ratio increased from 0.02 to 0.14.	(Bierbaum and Öeller, 2009)
O_3/H_2O_2	Simulated hardwood Kraft pulp mill effluent from mill in Taiwan. Samples were prepared by diluting black liquor (COD _{BL} : 165000 mg/L) with distilled water.	COD: 150 mg/L	pH: 7.5-7.9 Temp: N/A Dosage: 0.15 g O ₃ /L 0.09 g H ₂ O ₂ /L Reaction time: 30 min	High colour removal (≈90%) was observed when O ₃ was used in combination with H ₂ O ₂ . The COD removal efficiency (60%) was although not influenced by the addition of H ₂ O ₂ .	(Ko et al., 2009)

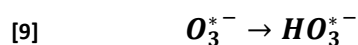
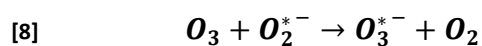
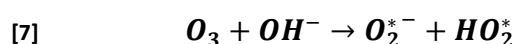
Fenton's Process	Corrugated board mill effluent, which produces 300 000 tonnes board/year from old paper and straw. Samples collected at outlets of biological treatment. Province of Tekirdag, Turkey.	COD: 470 mg/L Colour: 680 mg Pt-Co/L	pH: 4 Temp: 20°C Dosage: 0.2 g H ₂ O ₂ /L 0.1 g Fe ²⁺ /L Reaction time: 45 min	Fenton's process yielded higher removal efficiencies of refractory organics (83% COD, 95% colour) than O ₃ /H ₂ O ₂ process.	(Sevimli, 2005)
TiO₂/UV	Alkaline ECF effluent, obtained from Chilean pulp mill. Samples collected at end-of-pipe (end of pulping process, before wastewater treatment).	COD: 1400 mg/L TOC: 487 mg/L AOX: 58 mg/L	pH: 7.2 Temp: 22°C Dosage: 1 g TiO ₂ /L Reaction time: 450 min	Wastewater was illuminated with a 125 W HP-UV lamp ($\lambda > 254$ nm). Resulted in 95% AOX and 50% TOC removals using suspended TiO ₂ . GC/MS analysis showed that none of the initial LMW AOX was found after oxidation.	(Perez et al., 2001)
	Indian pulp and paper mill, which uses hardwood as raw material. Combined effluent from pulping, pulp bleaching and paper making. Samples collected at outlets of biological treatment.	BOD: 29 mg/L COD: 246 mg/L Colour: 680 mg Pt-Co/L	pH: 7 Temp: 20°C Dosage: 0.5 g TiO ₂ /L Reaction time: 4h	Wastewater was illuminated with an 18 W UV lamp ($\lambda \approx 365$ nm). Resulted in 64.6% COD, 36.7% BOD, and 75.3% colour removals.	(Kumar et al., 2011a)
O₃/UV	Alkaline ECF effluent, obtained from a Chilean pulp mill. Samples collected at end-of-pipe (end of bleaching process, before wastewater treatment).	BOD: 534 mg/L COD: 1550 mg/L TOC: \approx 1250 mg/L	pH: 7 Temp: 25°C Dosage: 2 g O ₃ /h (g O ₃ /L N/A) Reaction time: 1 min	Wastewater was illuminated with a high pressure 125 W UV lamp ($\lambda > 254$ nm). Resulted in 3.7% COD, 76% TOC removals after 1 min of reaction. BOD ₅ /COD ratio increased from 0.34 to 0.99.	(Yeber et al., 1999)

<i>H₂O₂/UV</i>	Pulp and paper mill effluent Samples collected at outlets of biological treatment, Dalaman, Turkey.	BOD: 240 mg/L COD: 400 mg/L TOC: 110 mg/L Colour: 0.78 (abs, m ⁻¹)	pH: 11 Temp: 20°C Dosage: 1.7 g H ₂ O ₂ /L Reaction time: 30 min	Wastewater irradiated with a 16W LP-UV lamp (λ = 254 nm). Color removal increased with increased pH, resulting in highest removal (41%) at pH 11. TOC removals were not affected by pH and the highest observed removal was 11%.	(Catalkaya and Kargi, 2007)
<i>Photo-Fenton's Process</i>	Egyptian board paper mill effluent, which produces 25 ton board/day from recycling wasted paper. Samples collected at end-of-pipe (end of paper process, before wastewater treatment).	BOD ₅ : 2200 mg/L COD: 10300 mg/L TSS: 5950 mg/L	pH: 3 Temp: 20°C Dosage: 1.5 g H ₂ O ₂ /L 0.5 g Fe ²⁺ /L Reaction time: 45 min	Wastewater irradiated with a MP-UV lamp (100<λ<280 nm). Yielded 79.6% COD and 96.6% TSS removals. BOD ₅ /COD ratio increased from 0.21 to 0.7.	(Jamil et al., 2011)

6.3 Ozone (O₃)

The use of O₃ as a chemical oxidant has been suggested in the latest literature as a potential technique for COD, AOX and colour removal from pulp and paper mill wastewaters (Sevimli, 2005, Fontanier et al., 2006). O₃ is a toxic gas with characteristic irritating and pungent odor. The molecule is relatively polar (dipole moment of 0.5337 D), has a specific weight of 2.1 kg/m³, and a boiling point of -111.5°C. (Siitonen, 2007)

When O₃ decomposes in water, a complex chain of reactions occur that result in formation of OH^{*} and superoxide (O₂^{*}) radicals according to Reaction [7-10] (Seneviratne, 2007). Hoigné et al. (1985) as cited in Hulse (2002), reported that for every decomposed O₃ molecule, 0.65 molecule of OH^{*} is formed.



As seen in Table 4 in Section 6.1, O₃ is a relatively strong oxidant in itself with an EOP of 2.08 V. However, direct reactions with dissolved O₃ and organic compounds take place very slowly with kinetic rate constants in the range of 0.01 to 10⁴ M⁻¹s⁻¹. By contrast, indirect oxidation with OH^{*} and O₂^{*} radicals is typically 10⁶-10⁹ orders of magnitude higher (Munter, 2001). To enhance the radical formation and thus the degradation of contaminants with higher strength, it is suggested in the literature that O₃ should be combined with other oxidants (i.e. H₂O₂ and/or UV irradiation) (Gogate and Pandit, 2004a).

The reactions of radicals are however unselective and instant, and there is a high risk that radicals are spent to undesirable reactions with surrounding substrates. Direct oxidation with O₃ on the other hand, is selective and restricted to unsaturated aromatic and aliphatic compounds and to particular functional groups with high electron density (N, P, O or S). All types of reactions may occur simultaneously, but depending on conditions and composition of the wastewater, one or another reaction pathway will dominate. (Goi, 2005)

Operating pH

Ozonation can be performed at different pH. Kreetachat et al. (2007) showed that pH changes of 5-10 in the system resulted in minimal impact on COD and TOC removal efficiencies. The OH^{*} radical formation was however dominant at high pH (≥10) and the oxidative reactions with O₃ are more selective at low pH (≤4), which is why a pH interval in between is preferred to obtain an oxidation that is relatively fast and selective at the same time. In addition, it is desirable to perform the reaction at neutral pH of effluents to minimize the need of pre and post pH adjustments.

Operating Temperature

Reactions with O₃ are traditionally carried out at ambient temperature (T≈25°C). Higher temperatures will generally increase the reaction rate, but will at the same time reduce the solubility of O₃ in water, consequently the amount of O₃ available for reaction. (Gogate and Pandit, 2004a)

Dosage of O₃

The dosage of O₃ that is used in the reaction is an important parameter affecting the extent of oxidation. O₃ is a gas that is very unstable in the liquid phase and will undergo decomposition upon absorption. It is therefore very difficult to obtain saturation in the regions where mass transfer is limiting, which results in a steady state concentration that often is much lower than the equilibrium (saturation) concentration. It is therefore important to carefully calculate the optimal O₃ dosage before operation in order to avoid overdosing. (Roth and Sullivan, 1981)

If ozonation is carried out at ambient pressure and a temperature, the concentration of O₃ in aqueous phase can be described according to Henry's Law seen in Equation 1. (Siitonen, 2007)

Equation 1: Henry's Law. (Siitonen, 2007)

$$c_{O_3} = H_{e_{O_3}} \cdot p_{O_3}$$

c_{O₃} = Concentration of O₃ in water

H_{e_{O₃}} = Henry's Constant

p_{O₃} = partial pressure of O₃

Henry's constant is a function of temperature. As seen in Equation 2, a higher temperature will thus result in a lower H_e, which in turn results in a lower concentration of O₃ in aqueous phase. (Siitonen, 2007)

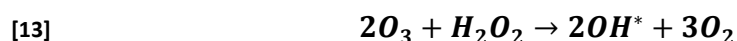
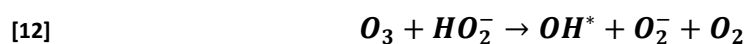
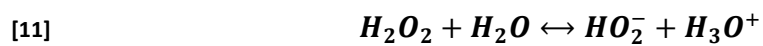
Equation 2: Henry's constant is a function of temperature for ozone. (Siitonen, 2007)

$$\ln(H_e) = 22.3 - 4030/T$$

6.4 Peroxone (H₂O₂/O₃)

O₃ can be combined with H₂O₂ to enhance the transformation of O₃ to OH* in aqueous phase and the treatment is then called peroxone. H₂O₂ has been used in industrial wastewater treatment for destruction of formaldehyde, phenols, detoxification of cyanide, hypochlorite and for removal of sulphides. (Gogate and Pandit, 2004a)

H₂O₂ is a weak acid that is fed from an aqueous solution, which in combination with water partially dissociates into hydroxide anions (HO₂⁻), see Reaction [11]. H₂O₂ is a powerful oxidizer with an EOP of 1.78, a boiling point of 150.2°C and is totally miscible with water (US Peroxide, 2008). H₂O₂ in itself does not react especially fast with O₃, HO₂⁻ ions on the other hand, react much faster and form OH* radicals, see Reaction [12-13] (Kommineneni et al., 2008).



It can be noticed that that two O₃ molecules produce two OH* radicals, which means that a larger quantity of radicals are produced for the same concentration of oxidant in the presence of H₂O₂ compared to O₃ used alone. Oxidation with H₂O₂ alone has not been recommended in literature since the efficiency is proved to be low. Here is a combination with O₃ and/or UV a significantly better alternative. (Gogate and Pandit, 2004a)

Operating pH

Ko et al. (2009) reported that the HO₂⁻ formation and thus the OH* radical formation, was accelerated with a more alkaline environment. It was explained with the high pK_a value of the equilibrium Reaction [11]. Beltrán et al. (1998) reported that the degradation efficiency of nitrobenzene increased as pH was increased from 2 to 7. However, a further increase to pH 12 resulted in decreased degradation efficiency, and was explained with the lower solubility of O₃ in water at high pH.

Operating Temperature

There is not much information available regarding the temperature dependence of the reaction, but very high temperatures are not recommended because the solubility of O₃ decreases with increasing temperature. (Gogate and Pandit, 2004b)

Dosages of H₂O₂ and O₃

Depending on the pollutant concentration and other wastewater quality parameters, different H₂O₂/O₃ ratios are used, often ranging from 0.3:1 to 3:1. O₃ has better disinfection characteristics than H₂O₂, and higher O₃ concentrations are therefore generally preferred for source waters requiring disinfection. For wastewaters requiring minimal disinfection, higher dosages of H₂O₂ can be applied. (Kommineni et al., 2008)

The radical formation will generally be improved with increased H₂O₂ concentration. However, it is also a risk for H₂O₂ to start acting as a radical scavenger at very high concentrations, causing a decrease in the OH* radical concentration, according to Reaction [14]. It is hence very important to carry fully evaluate the optimal H₂O₂ dosage to be able to reach maximum destruction of pollutants. (Catalkaya and Kargi, 2007)

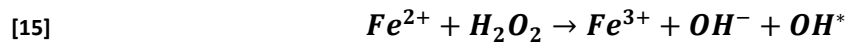


6.5 Fenton's reagent (Fe²⁺/H₂O₂)

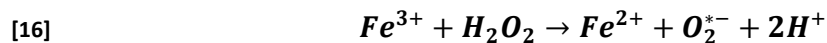
A rather old catalytic oxidative method (first recognized in the 1960s), is the Fenton's process, which utilizes H₂O₂ in a combination with ferrous iron (Fe²⁺) catalyst (Sevimli, 2005). This type of

treatment has been applied for detoxification, discoloration, odor removal and for destruction of non-biodegradable effluents from different sources (Gogate and Pandit, 2004a).

Iron salts such as ferrous sulphate (FeSO_4) or complexed iron such as Goethite (FeOOH) are used as source of Fe^{2+} (Sevimli, 2005). H_2O_2 reacts with Fe^{2+} to form the unstable iron-oxide-complex, also called the Fenton's reagent, which in turn reacts to form OH^* according to Reaction [15]. (Kommineni et al., 2008)



The produced ferric ion (Fe^{3+}) will partly act as a flocculant and react with the water to form hydroxides, which in turn adsorb the colloidal particles by sweep coagulation and form larger flocks that easily can settle. The ferric ion will partly also react with H_2O_2 and/or O_2^{*-} to regenerate Fe^{2+} as seen in Reaction [16-17]. Iron will thus be cycled between ferric and ferrous oxidation states until H_2O_2 is completely consumed. (Catalkaya and Kargi, 2007)



Operating pH

The oxidation is carried out in an acidic environment to keep the iron in solution. The effect of pH has been considered as a very significant operating factor by many researchers, because it is influencing the treatment efficiency. Trials have been performed at pH values ranging from 2 to 7, to determine the effect of pH, and the optimum pH has been seen at $\text{pH} \approx 3$ in most cases (Sevimli, 2005, Catalkaya and Kargi, 2007). At higher pH (≈ 6) iron hydroxide ($\text{Fe}(\text{OH})_2$) formation will start, and at lower pH (< 2.5) the formation of $(\text{Fe}(\text{H}_2\text{O}))^{2+}$ will occur. The degree of efficiency will thus be decreased because the free iron concentration will be lower. (Gogate and Pandit, 2004a)

Operating Temperature

Very little information is available depicting the temperature dependence on the degradation rates. For example, Lin and Lo (1997) reported that an optimum temperature of the process was 30°C , whereas Rivas et al. (2001) showed that a change of temperature in the interval of $10\text{-}40^\circ\text{C}$ left the degradation efficiency unaffected.

Dosages of Fe^{2+} and H_2O_2

The optimum Fe^{2+} dosage is still under discussion. Catalkaya and Kargi (2007) showed that the oxidation improved with increased Fe^{2+} concentration in regards to both extent and rate. However, at very high concentrations, the treatment efficiency started to decay (reason unknown). Also, at very high Fe^{2+} concentration there is a risk of an unutilized quantity of iron salts in the effluent, which is not allowed since it can threaten the recipient. An iron extraction system must then be introduced to remove residual iron from the treated wastewater.

As cited in Gogate and Pandit, (2004a), the concentration of H₂O₂ plays a more important role in deciding the overall efficiency of the process, and the optimum Fe²⁺ to H₂O₂ ratio is usually 1:5 wt/wt. A larger quantity of OH* radicals will be formed at higher concentration of H₂O₂. The dosage must however be balanced carefully to ensure that entire amount of oxidant is utilized because excess H₂O₂ in the effluents will contribute to COD, and might also be harmful for microorganisms in a potential subsequent biological treatment. Post-treatment of residual H₂O₂ may therefore be required.

6.6 Photo-chemical Processes

Photochemical processes are based on high-energy irradiation with wavelengths in the end of the visible light spectrum, i.e. 400nm. This irradiation will destroy contaminants through direct or indirect photolysis at relatively mild operating conditions. In direct photolysis, reactant molecule is placed in an electronically excited state when radiation is adsorbed, causing it to promote reactions. UV irradiation is often used in combination with O₃, H₂O₂, Fenton's reagent and TiO₂ catalyst to accelerate the radical formation, and thus cause an indirect photolysis. (Kommineni et al., 2008)

Turbidity

UV systems are affected by the turbidity of the wastewater. A high turbidity decreases the efficiency because it hinders the penetration of the UV irradiation into the wastewater. (Munter, 2001)

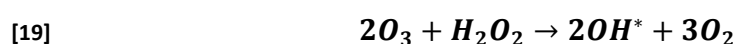
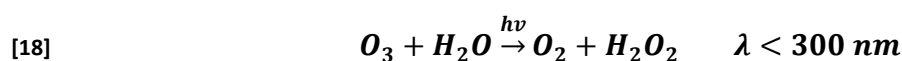
Operating pH and Temperature

Generally, the same pH and temperature dependence is observed when different oxidants are combined with UV; ambient temperature and neutral pH (apart from Fenton's process which is operated at acidic pH). It should however be born in mind that there is a potential risk that the temperature of the medium increases with time due to the presence of UV lamps. For small scale applications, it is therefore important to incorporate cooling systems to maintain a constant temperature as the reaction progresses. (Gogate and Pandit, 2004b)

6.6.1 Ozone + Ultraviolet Light (O₃/UV)

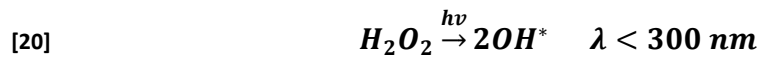
When UV irradiation is used in combination with O₃, a larger quantity of OH* radicals can be formed in comparison to UV or O₃ processes used alone. This AOP is considered as a very effective treatment for degradation of refractory and toxic organics, and is also used for decolourization of bleaching waters. (Legrini et al., 1993)

Destruction occurs by OH* radical reactions or direct photolysis with molecular O₃. As illustrated in Reaction [18-19], photolysis of O₃ in water generates H₂O₂ which then is further photolyzed into OH* radicals. (Kommineni et al., 2008)



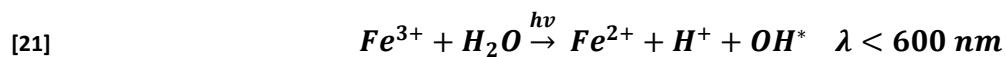
6.6.2 Hydrogen Peroxide + Ultraviolet Light (H₂O₂/UV)

UV irradiation can also be combined with H₂O₂. As in O₃/UV process, the oxidation occurs through either direct photolysis with H₂O₂ or indirect photolysis with OH* radicals. The radicals are produced when H₂O₂ is exposed for UV radiation in water according to Reaction [20].



6.6.3 Photo-Fenton's Process (Fe²⁺/H₂O₂/UV)

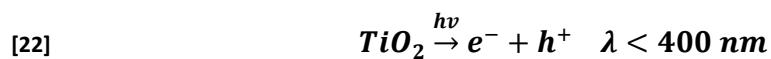
The Fenton's process which was discussed earlier in this report can also be combined with UV irradiation and is then referred to as the photo-Fenton's process. This treatment has shown a great potential for mineralization of recalcitrant organic compounds and is based on similar reaction mechanisms as explained in Section 0, but in presence of UV light. As a consequence, a higher and faster OH* production rate is accomplished in comparison to the conventional Fenton's process, see Reaction [21]. (Catalkaya and Kargi, 2007)



As mentioned earlier, H₂O₂ has a low extinction coefficient below 300 nm. In contrast, Fenton's reagent has a relatively large extinction coefficient, allowing mineralization even by visible light (up to 600 nm). (Munter, 2001)

6.7 Photo-catalytic Process with Titanium Dioxide (TiO₂/UV)

A wide range of organic contaminants can be oxidized by light with a band gap energy of $\lambda < 400$ nm in the presence of TiO₂ catalyst (Hulse, 2002). The reaction mechanism occurs in several steps, and is described in Reaction [22-24]. As light strikes the TiO₂ surface, valence band electrons (e⁻) are excited to the conduction band, creating holes behind (h⁺). The holes react with water molecules to produce OH* radicals. Aeration is often used to prevent electron-hole recombination, see Reaction [25]. The excited electron will then react with O₂ (electron acceptor) to form the O₂^{-*} ion which will act as an additional oxidant. (Kumar et al., 2011a)



The nature of the TiO₂ catalyst (surface area with active sites) plays an important role in the overall rates of degradation of pollutants. A larger surface area with increased number of active sites will result in a more rapid and extended reaction. (Gogate and Pandit, 2004a)

TiO₂ has band gap energy of 3.02 eV, which means that the optimal wavelength of irradiation is around 400 nm. This also means that sunlight in some cases can be used for electron excitation, which can result in considerable cost savings (Gogate and Pandit, 2004a). Moreover, an irradiation angle of 90° is recommended by Ray and Beenackers (1997) as cited in Gogate and Pandit (2004) to achieve maximum irradiation efficiency.

Operating pH

The negative effect of radical scavengers is minimized at neutral pH, because anions and cations that might be present in the wastewater will compete for the active sites on the TiO₂ surface. At low pH, the TiO₂ particles will be surrounded by positive charges, which cause an adsorption of anions to the surface. At high pH the opposite effect will occur; cations will be attracted to the surface. (Kommineni et al., 2008)

Operating Temperature

The photocatalytic process with TiO₂ has weak temperature dependence. Studies have been performed with temperatures in the range of 20-80°C, but have shown minimal impact on degradation rates. (Gogate and Pandit, 2004a)

Dosage of TiO₂

In relation to other AOPs, the TiO₂/UV process is much slower and must therefore incorporate large amount of TiO₂ catalyst in the reactor. It is hard to generalize the optimum TiO₂ dosage as it will be dependent on the quality of the wastewater to be treated and type of reactor configuration that is used. (Kommineni et al., 2008, Gogate and Pandit, 2004a)

6.8 Equipment and Reactor Designs

A number of devices can be used to transfer oxidants into aqueous solutions, and often relatively simple reactor designs are employed. It is however not always easy to determine which type of system that yields the most efficient oxidation for a given pollutant(s). Some general suggestions and considerations in process design are presented in following section.

6.8.1 Ozone Systems

Ozone is typically produced electrically on-site from either air or pure liquid oxygen due to its very short half-time (≈10min) (Kreetachat et al., 2007, Esplugas et al., 2002). The latter one is often preferred due to higher costs associated with dehumidification of air. In addition, higher quantities of O₃ can be produced from pure oxygen (14% O₂ by weight compared to 2% O₂ by weight), and less energy is needed relative to compressed air. (Kommineni et al., 2008)

Generated O₃ gas is fed from the base of the ozone contact reactor, with help of gas diffusers or injectors, see Figure 5 (Kreetachat et al., 2007). The gas is allowed to diffuse through the reactor,

which often is of a plug flow type or a continuously stirred one, until it reacts or escapes through the top (Kommineni et al., 2008). A major disadvantage of ozone diffusers is that they are easily clogged with suspended solids and precipitates, which is why O_3 often is injected with side stream injectors. Side injections facilitate higher mixing efficiency, but can at same time lower the contact times, resulting in poor gas diffusion. The transfer efficiency of O_3 in aqueous phase is generally increased with smaller bubble sizes (bigger interfacial area) and longer contact times between O_3 and the effluent. Continuous ozonation is needed due to the short half-life of O_3 , and static mixers are sometimes incorporated into the reactor to increase the transfer efficiencies of O_3 in the liquid (Gogate and Pandit, 2004a). An off-gas decomposer is placed above the contact reactor to collect and thermally destruct excess O_3 into O_2 with use of a catalyst. Automatic control and monitoring systems are installed to regulate feed rates, pH and other parameters. (Kommineni et al., 2008)

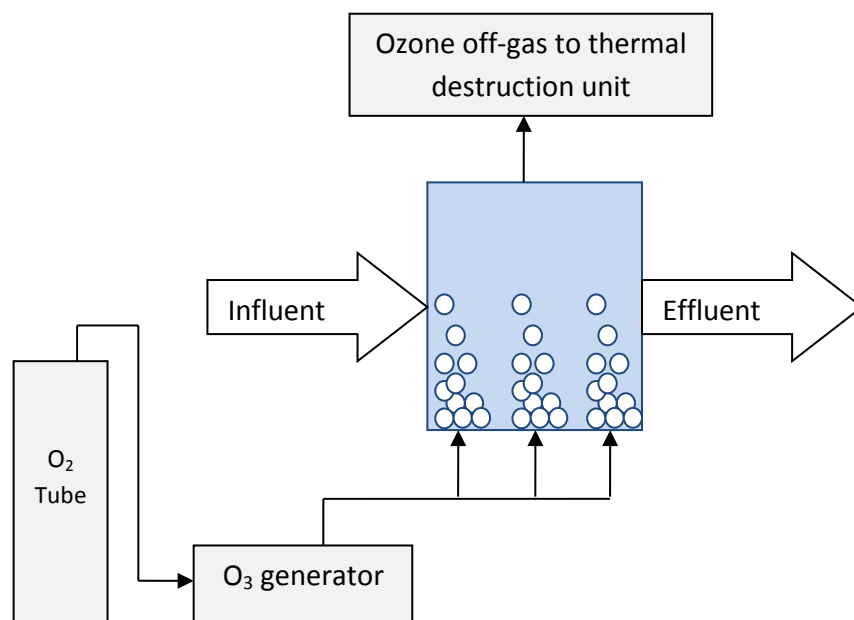


Figure 5: Ozone system with oxygen storage tank and thermal off-gas destructor.

6.8.2 Peroxone Systems

H_2O_2 is a relatively low-priced and readily available chemical, and produced by oxidation of alkyl hydroanthraquinones or by electrolysis of ammonium bisulphate, which typically consumes around 7.7 kWh per kg H_2O_2 produced (Munter, 2001). For wastewater treatment 30-50% H_2O_2 solutions are recommended, higher concentrations ($\approx 70\%$) will increase the reaction rates, but are not very safe because they can produce detonable mixtures during storage (Gogate and Pandit, 2004a). Similar process design and equipment is used in peroxone systems as for O_3 systems. It is much easier to dissolve and mix in H_2O_2 into the wastewater than O_3 . However, the stability of H_2O_2 in the aqueous phase is very low, and the introduction of H_2O_2 into the system must therefore be carefully evaluated. The most traditional way to inject the oxidants is with a single reactor module. H_2O_2 and O_3 are then injected in a single point through a diffuser and allowed to bubble through the contactor at atmospheric pressure. (Buratovich-Collins and Bowman, 2000)

6.8.3 Fenton's Systems

The Fenton process is typically carried out in four treatment steps; oxidation, neutralization, flocculation and solid-liquid separation. Non-pressurized stirred batch reactors are employed for the addition of reactants, pH adjustments and coagulants. The reactor vessels are often coated with an acid-resistant material, since Fenton's reagent is very corrosive. (Goi, 2005, Kommineni et al., 2008)

Wastewater and reactants are added to the first reactor vessel together with a dilute acid (often sulphuric acid). An acidic environment with low pH is required to keep the ferrous iron in solution, and it is important to have a proper control of the mixing. The discharged effluent from the oxidation vessel is led into a neutralization basin where an alkaline solution is added in order to neutralize the acidic environment. Residual iron is flocculated with use of a polymer coagulant in a flocculation unit, and followed by a solid-liquid separation tank before released to the recipient. The process is illustrated in Figure 6. (Goi, 2005)

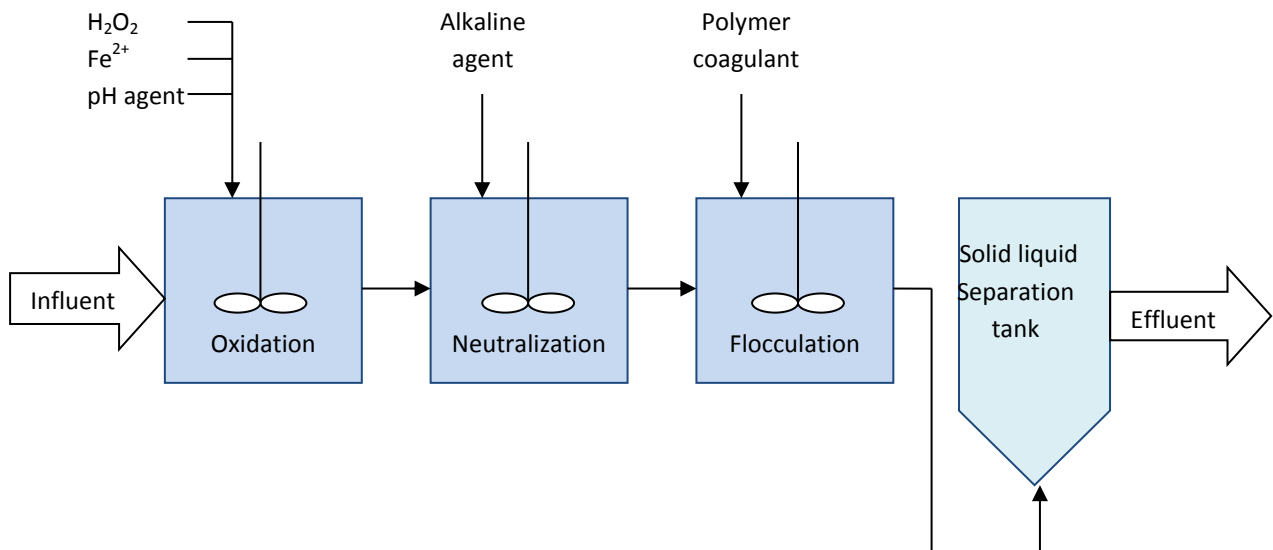


Figure 6: Schematic illustration of the Fenton's process with oxidation, neutralization, flocculation and solid liquid separation. (Goi, 2005)

6.8.4 Photo-chemical Systems

The reactor used for UV radiation is typically of a plug flow, and can either be an open channel or a closed vessel. Different light sources can be used to produce UV irradiation; Low pressure mercury vapour lamps (LP-UV), Medium pressure mercury vapor lamps (MP-UV) and Pulsed UV xenon arc lamps (P-UV). (Goi, 2005)

The difference among the different lamps lies in the output spectra. The LP-UV and MP-UV lamps produce a series of line outputs, while P-UV lamps produce continuous output spectra. The LP-UV lamps are the most electrically efficient, but MP-UV lamps have recently gained lots of attention because of their greater potential for direct photolysis and wider wavelength spectrum, see Table 6. The P-UV lamps have not been studied as extensively due to their short

life times. The lamps are often equipped with quartz sleeves and cleaning systems in case of high concentrations of fouling agents. (Kommineni et al., 2008)

Table 6: Characteristics of typical LP-UV, MP-UV and P-UV lamps. (Kommineni et al., 2008)

Characteristics	Unit	LP-UV	MP-UV	P-UV
<i>Emission</i>	-	Monochromatic	Polychromatic	Polychromatic
<i>Peak output wavelength</i>	[nm]	253.7	200-400	≈ 450
<i>Operating temperature</i>	[°C]	40-60	500-800	≈ 15 000
<i>Life time</i>	[h]	8-10·10 ³	2-5·10 ³	>100·10 ⁸ pulses
<i>Light intensity</i>	-	Low	High	High

The UV lamps are arranged in different ways in the reactor, depending on scale of water application. A system designed for large scale wastewater applications (water flows over 1000 m³/h), would typically consist of one single reactor vessel equipped with several UV lamps arranged perpendicularly to the wastewater flow, see Figure 7 (Xylem, 2013). The reaction vessel is filled with wastewater between the reactor walls and lamp system. The more wastewater to be treated, the more lamps are used. Generally, no cooling system is needed for systems handling large volumes of effluent, since heat transfers from the lamps are very low (<1°C). (Kommineni et al., 2008)

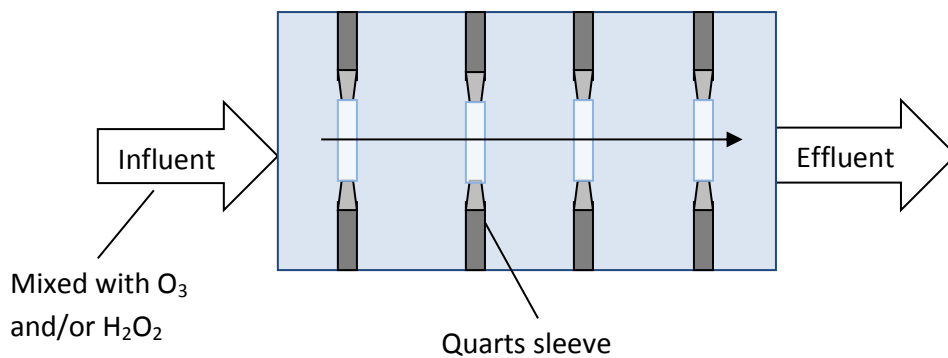


Figure 7: Schematic illustration of a possible UV reactor.

6.8.5 Photo-catalytic Systems

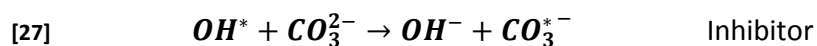
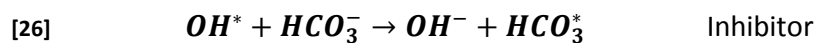
The photo catalytic process with TiO₂ can be carried out in a slurry reactor with suspended TiO₂ particles, or in a supported catalytic reactor. In the suspended form, very fine particles (<1µm) of solid TiO₂ are dispersed with stirrers into the liquid phase. The formed slurry is then directly or indirectly irradiated with UV light, and the reactor is often aerated with O₂ to hinder electron/hole recombination. The suspended form is not recommended for large-scale applications due to opacity problems and fouling of the equipment. In addition, catalyst particles have to be separated from the treated liquor after oxidation, which introduces high operating costs. (Gogate and Pandit, 2004a)

A more common design is the supported photo catalyst, where a carrier material is wash coated with TiO₂ catalyst particles. The biggest advantages with the supported catalyst system are the crystalline configuration and stability of the TiO₂ film in the reacting media, and that no advanced catalyst separation is needed after the treatment. However, this type of system requires a larger reactor volume, can be very sensitive to erosion, and mass transfer problems can sometimes limit the catalyst performance. (Gogate and Pandit, 2004a)

UV lamps are placed inside the reactor in various configurations, and the liquid to be purified is illuminated with light at wavelengths just below 400 nm. An efficient reactor should be able to attain a uniform irradiation of the entire active area, which for large scale designs can be a major problem because of high pollutant concentrations and occurrence of high turbidity. The TiO₂ catalyst can often be recovered and reutilized for many cycles after treatment. (Legrini et al., 1993, Gogate and Pandit, 2004a)

6.9 Interfering Compounds

It is in most cases very hard to obtain a complete mineralization of contaminants, i.e. an oxidation into CO₂ and H₂O. The main reason for this is that there are many interfering compounds present in the wastewater that act as radical scavengers, hence blocking the reaction pathways and lowering the reaction rates. Thus, very high amounts of chemical oxidants are needed to obtain concentrations at the treatment goals. Industrial wastewater will generally contain different types of salts which are present in ionized forms. The OH^{*} radical reactions are unselective and presence of organic or inorganic content other than pollutants of concern will affect the degradation processes negatively. Compounds like nitrates (NO₃⁻), nitrites (NO₂⁻) and chlorides (Cl⁻) will hinder the OH^{*} radical formation during UV oxidation because they adsorb light at similar wavelengths (200-300 nm). Presence of scaling agents such as ferrous (Fe²⁺) and magnesium (Mg²⁺) salts may result in fouling of UV lamps. Phosphates (PO₄⁻³), carbonates (CO₃²⁻), bicarbonates (HCO₃⁻) and sulphates (SO₄²⁻) in the source waters have the potential to act as scavengers, but the reactions with OH^{*} radicals are considered very slow and can therefore be neglected for most systems, see Reaction [26-27]. (Munter, 2001).



6.10 Advantages and Disadvantages of Different AOPs

Advantages and disadvantages of presented oxidation processes are summarized in Table 7.

Table 7: Advantages and disadvantages of different oxidation processes.

Oxidation Process	Advantages	Disadvantages
O_3	<ul style="list-style-type: none"> • Selective at $pH \leq 4$ towards unsaturated aromatic and aliphatic compounds, and functional groups with high electron density • Supplemental disinfectant 	<ul style="list-style-type: none"> • O_3 must be produced electrically on-site due to its very short half-time (≈ 10min) • Steady state concentration of O_3 in water is often much lower than the saturation concentration • O_3 solubility sensitive for temperature change • Off-gas treatment system for O_3 destruction needed • Energy and chemical intensive process
H_2O_2/O_3	<ul style="list-style-type: none"> • A more powerful system than H_2O_2 or O_3 used alone • Reduced operating costs as lower dosage of O_3 is needed (compared to O_3 used alone) • H_2O_2 is totally miscible with water • Supplemental disinfectant 	<ul style="list-style-type: none"> • O_3 must be produced electrically on-site due to its very short half-time (≈ 10min) • Steady state concentration of O_3 in water is often much lower than the saturation concentration • O_3 solubility sensitive for temperature change • H_2O_2 can produce detonable mixtures at very high concentrations • H_2O_2 itself can start act as a radical scavenger at very high concentrations • Post-treatment of residual H_2O_2 might be needed • Off-gas treatment system for O_3 destruction needed
Fenton's process	<ul style="list-style-type: none"> • Energy efficient since it does not require any electricity beyond the feed pumps and mixers • No off-gas treatment needed, since no gaseous emissions are formed 	<ul style="list-style-type: none"> • Large buffer tanks with H_2O_2, $FeSO_4$, and H_2SO_4 needed • An iron extraction system required to remove residual iron from the treated water • Pre- and post pH adjustments required because process is operated at low pH • Fenton's reagent is very corrosive and reactor must be coated with an acid-resistant material

<p><i>O₃/UV</i></p>	<ul style="list-style-type: none"> • More powerful system than O₃ and UV used alone • Supplemental disinfectant 	<ul style="list-style-type: none"> • O₃ must be produced electrically on-site due to its very short half-time (≈10min) • Steady state concentration of O₃ in water is often much lower than the saturation concentration • O₃ solubility sensitive for temperature change • Off-gas treatment system for O₃ destruction needed • UV light penetration negatively affected by turbidity • System sensitive to NO₃⁻, NO₂⁻ and Cl⁻ because they adsorb light in the same wavelength • Fe²⁺ and Mg²⁺ presence may result in fouling of UV equipment • Lamp failures can potentially contaminate treated water with Hg • Very energy and chemical intensive process
<p><i>H₂O₂/UV</i></p>	<ul style="list-style-type: none"> • More powerful system than H₂O₂ and UV used alone • H₂O₂ is totally miscible with water • No off-gas treatment needed since no gaseous emissions are formed • Supplemental disinfectant 	<ul style="list-style-type: none"> • H₂O₂ can produce detonable mixtures at very high concentrations • H₂O₂ itself can start act as a radical scavenger at very high concentrations • Post-treatment of residual H₂O₂ might be needed • UV light penetration negatively affected by turbidity • Sensitive to NO₃⁻, NO₂⁻ and Cl⁻ because they adsorb light in the same wavelength • Fe²⁺ and Mg²⁺ presence may result in fouling of UV equipment • Lamp failures can potentially contaminate treated water with Hg
<p><i>Photo-Fenton's process</i></p>	<ul style="list-style-type: none"> • A higher and faster OH[*] production rate accomplished in comparison to the conventional Fenton's process • Fenton's reagent has a relatively large extinction coefficient, allowing mineralization even by visible light (up to 600 nm) • No off-gas treatment needed since no gaseous emissions are formed 	<ul style="list-style-type: none"> • Large buffer tanks with H₂O₂, FeSO₄, and H₂SO₄ needed • An iron extraction system required to remove residual iron from the treated water • Pre- and post pH adjustments required because process is operated at low pH • Fenton's reagent is very corrosive and reactor must be coated with an acid-resistant material • UV light penetration negatively affected by turbidity • Sensitive to NO₃⁻, NO₂⁻ and Cl⁻ because they adsorb light in the same wavelength • Fe²⁺ and Mg²⁺ presence may result in fouling of UV equipment • Lamp failures can potentially contaminate treated water with Hg

<p><i>TiO₂/UV</i></p>	<ul style="list-style-type: none"> • More powerful system than UV used alone • Can be executed at higher wavelengths ($\approx 400\text{nm}$) compared to other UV processes, possibility to use sunlight or near UV light • No off-gas treatment needed since no gaseous emissions are formed • Catalyst can often be recovered and reutilized for many cycles after treatment 	<ul style="list-style-type: none"> • Catalyst sensitive for fouling • Slow reaction rate • If suspended TiO_2 particles are used, catalyst separation step is needed after treatment • If supported TiO_2 is used, system can be very sensitive to erosion • Potential for quick TiO_2 activity loss, requiring on-site storage of catalyst • Aeration is needed to prevent electron-hole recombination • Lamp failures can potentially contaminate treated water with Hg
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6.11 Degradation Principles and By-products

The degradation of contaminants can be divided into four categories depending on extent of oxidation:

1. *Primary degradation* - A structural change in parent compound
2. *Acceptable degradation* - Degradation into intermediates with low toxicity
3. *Complete degradation* - Degradation into CO₂ and H₂O
4. *Unacceptable degradation* - Degradation resulting in increased toxicity

(Eddy and Metcalf, 2003)

Bijan and Mohseni (2005) showed with help of the membrane process ultra-filtration that ozonation of an alkaline bleach plant effluent resulted in transformation of recalcitrant High Molecular Weight (HMW) compounds into more biodegradable Low Molecular Weight (LMW) compounds. Concentration of LMW compounds increased with 36%, suggesting that O₃ is an effective oxidizer for enhancing the biodegradability of wastewaters with high COD and TOC. See initial characteristics of the wastewater and reaction parameters in Table 5 Section 6.2.

Kreetachat et al. (2007) analyzed water effluent from a pulp and paper mill with GC/MC analysis, and observed two main groups of contaminants present; lignin derived compounds and aliphatic compounds (n-alkenes, fatty alcohols, fatty acids, esters). After 60 min of ozonation (0.02 g O₃/L) at pH 7.5 and 25°C, several compounds initially observed in the effluent were not detected or had decreased to low concentrations. The data indicated that BOD/COD ratio increased from 0.1 to 0.32 and lignin derived compounds were oxidized into aliphatic compounds and LMW products. Organic acids were on the other hand more efficiently removed with biological treatment involving microorganisms.

Jamil et al., (2011) performed several AOP studies (UV, H₂O₂/UV, Fenton's process, Photo-Fenton's process) on raw board paper mill effluent with high AOX concentration and confirmed that the free chloride ion concentration increased, which indicated that partial mineralization occurred. Chloride ions were released as AOX was oxidized into aliphatic chlorinated intermediates such as aldehydes and carboxylic acids. Maximum concentration of Cl⁻ was observed after 40 min of reaction and the concentration remained unchanged with further oxidation. See initial characteristics of the wastewater and reaction parameters in Table 5 in Section 6.2

Similar results were observed by Perez et al. (2001) with TiO₂-photocatalytic degradation of alkaline ECF effluent. The increase in free chloride ion concentration was explained with hydroxylation of aromatic groups. The finding suggested that Cl⁻ was released as aromatic ethers were broken down to HMW polyphenols, and after 3 h of irradiation polyphenols were further oxidized by ring opening mechanisms. See initial characteristics of the wastewater and reaction parameters in Table 5 in Section 6.2

6.12 Example of Full-Scale Installations

There are not many full-scale installations mentioned in literature regarding AOP technologies. However, two examples of ozonation in combination with subsequent biofiltration stage have been reported and are presented in following section. In both cases, tertiary biofilters are installed after the ozonation to ensure that all biodegradable molecules that are formed as by-products during oxidation are removed. Hence, the COD removal can be increased without simultaneously increasing the BOD.

6.12.1 Gebr Lang Papier GmbH Ettringen

The first realization of a wastewater treatment plant with an O_3 step followed by a biofiltration stage has been performed for the Gebr Lang GmbH paper mill in Ettringen (Germany) in 1999. The mill produces newspapers and magazines and aimed to increase its production capacity with 100% (to 560 000 tonnes/year). State of the art technology was implemented in the current existing two-tiered activated sludge facility, but the system was already working at maximum performance, which is why a subsequent tertiary treatment stage was installed according to process flow sheet in Figure 8. The treatment was first evaluated in laboratory, tested in pilot scale, and later WEDECO was entrusted with the construction of the full scale facility. (Schmidt and Lange, 2000)

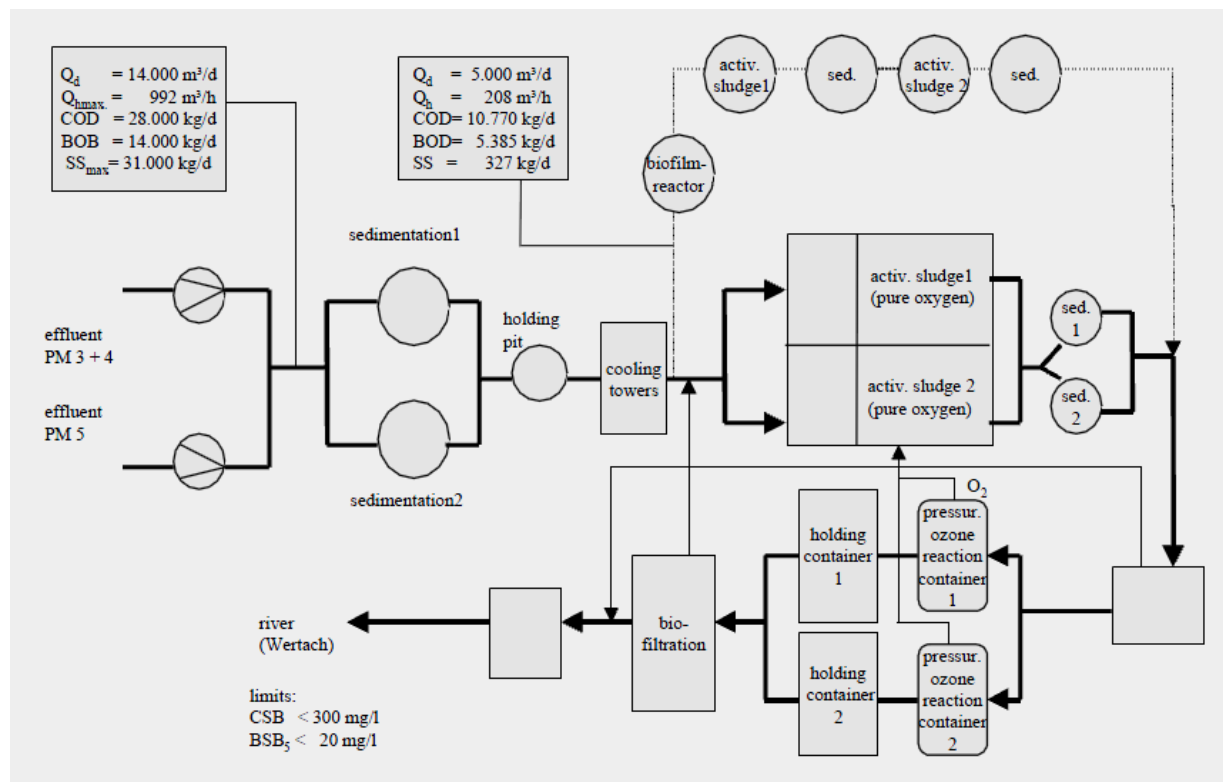


Figure 8: Process flow sheet of Gebr Lang GmbH paper mill. The raw wastewater is first clarified by sedimentation and then cooled down before entering the aerobic biological treatment equipped with selectors. After the activated sludge process, the wastewater is ozonated and then purified with biofilters. (Schmidt and Lange, 2000)

Two ozone generators were used in parallel with each a capacity of 50 kg O₃/h at 12 wt% O₃ and a specific energy consumption of 8.7 kWh/kg O₃. The results are described in Figure 9. At full utilization of the O₃ facility, COD at discharge point (outlet of biofiltration) could be lowered to around 100 mg/L at a specific O₃ dosage of 0.5 kg O₃/kg COD_{el}. The biofiltration ensured that BOD was maintained at 10 mg/L and the operating cost for O₃ production and introduction was 0.10-0.25 EUR/m³. (Schmidt and Lange, 2000)

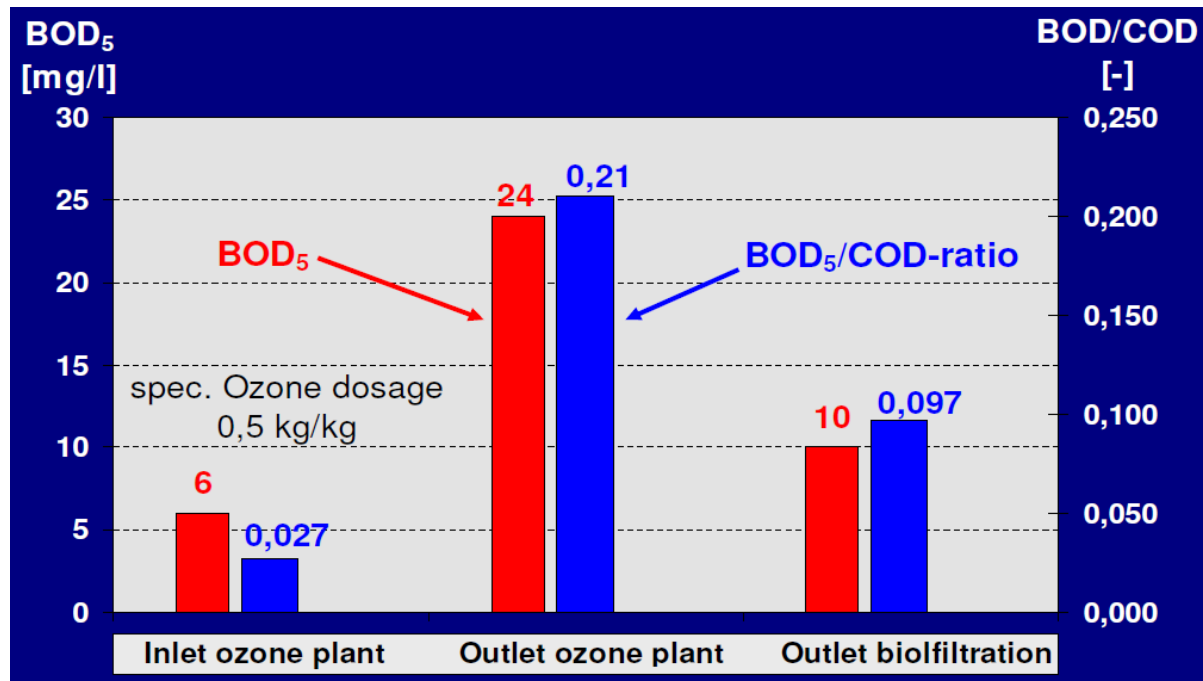


Figure 9: Wastewater composition before/after ozonation and biofiltration, during commissioning. (Schmidt and Lange, 2000)

6.12.2 SCA Graphic Laakirchen AG

Another example of a full scale installation of ozonation in combination with biofiltration is at the TMP paper mill SCA Graphic Laakirchen AG, located in Laakirchen (Austria). This mill has an annual production capacity of 485 000 tons of graphic paper (SC- and offset paper) and the wastewater treatment plant treats 7 240 000 m³ wastewater per year. The mill aimed in 2004 to increase the brightness of its paper products and at the same time increase the production capacity. Consequently, a more advanced wastewater treatment plant had to be built, see process scheme in Figure 10. The treatment was first evaluated in laboratory and tested in pilot scale in cooperation with CM Consult and consulting engineers Machowets & Partner. O₃ was supplied from three ozone generators, with a total capacity of 225 kg O₃/h. (Kaindl, 2010)

Kaindl presented the results in a relationship between applied O₃ dosage and the overall COD removal efficiency, which was based on measurements collected during several years of full scale operation, see Figure 11. The total investment cost for the installation of the O₃ step was 3.508 MEUR, and operational cost for ozonation plus biofiltration was 1.33 EUR per kg eliminated COD. (Kaindl, 2010)

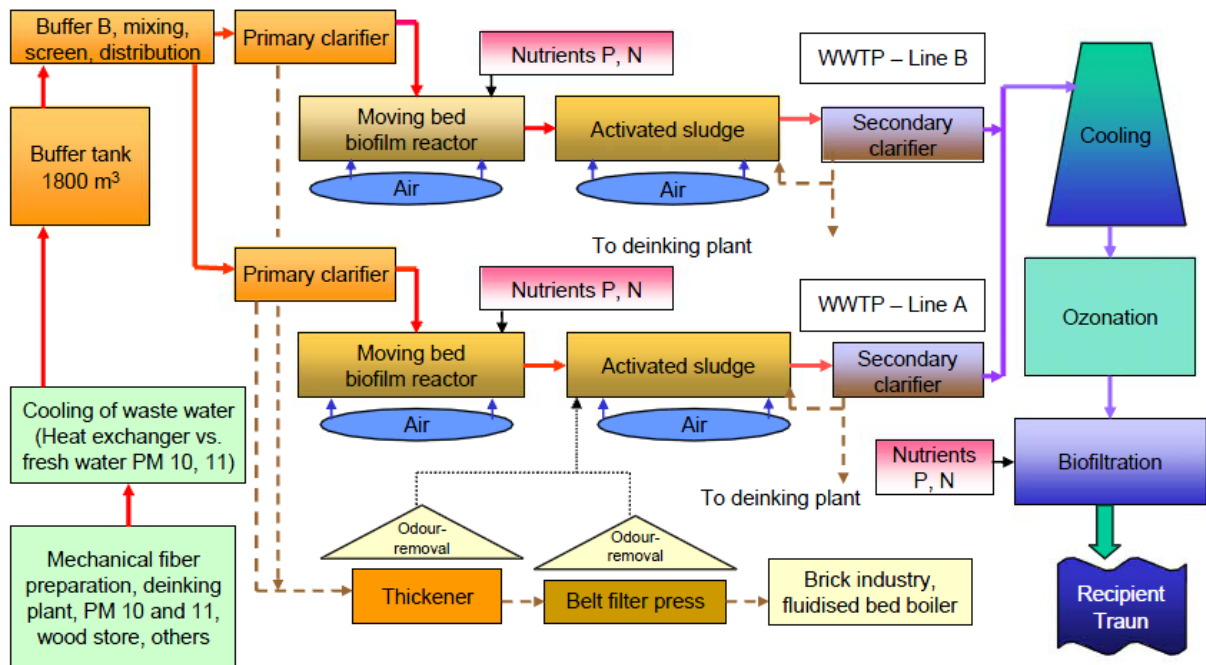


Figure 10: Process flow sheet of SCA Graphic Laakirchen AG. The raw wastewater is treated in two lines (A and B) and is first led to a primary clarifier (sedimentation), then led to a moving bed bioreactor (MBBR), followed by an additional biological treatment with activated sludge. After the biological purification, the wastewater is sent to an advanced treatment with ozonation followed by biofiltration. (Kaindl, 2010)

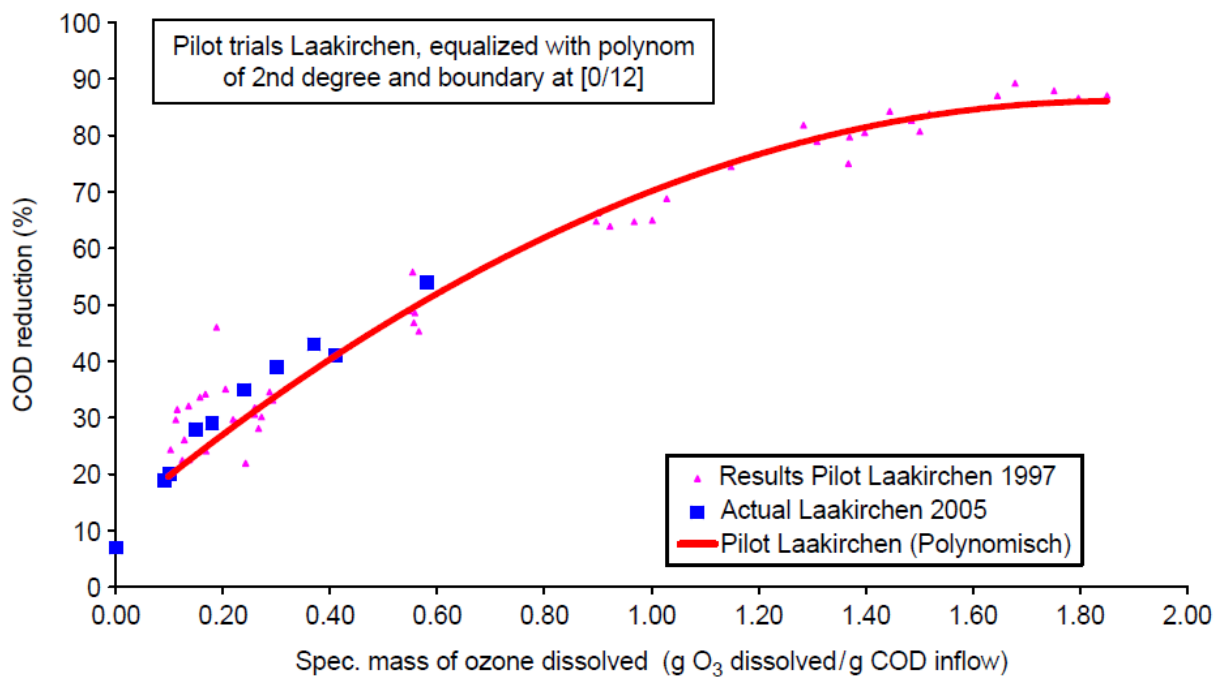


Figure 11: Results of ozonation plus biofiltration from pilot testing and commissioning at Laakirchen. (Kaindl, 2010)

7 Technologies Assessment and Comparison

In following chapter, each AOP is first evaluated in terms of reliability, flexibility, stability and energy efficiency, and then a discussion is brought up regarding the placement of the AOP technology in the wastewater treatment plant.

7.1 Mechanical Reliability

Processes that have a simple construction and contain a limited number of moving parts are considered more mechanically reliably because they probably will require less regular inspection and maintenance.

The O_3 and the H_2O_2/O_3 processes receive a high mechanical rating because of their relatively simple system configuration. However, inspection might still be required, especially for ozone generators and diffusers. Photo-chemical processes with O_3 and/or H_2O_2 receive a medium rating as they contain a number of specialty parts (UV lamps, quartz sleeves etc.) which require periodic inspection and replacement to prevent fouling and Hg leakage (UV lamp failure). The Fenton's process and the TiO_2/UV process get a low score in terms of mechanical reliability, since they need to be carried out under specifically controlled pH conditions and stirring. The Fenton's process must be carried out in four treatment steps, which means that several pumps and stirrers have to be incorporated. Close monitoring and control is especially important for the TiO_2/UV system due to potential for rapid activity loss.

7.2 Flexibility

Flexibility is referred to as the quality of a system to be adaptable to handle large fluctuations in influent wastewater flow rate and load. This is a very important property because the load will most likely change due to variations in production rate. A technology that is flexible should be able to handle fluctuations with no major impact on treatment efficiency.

Systems like O_3 , H_2O_2/O_3 , O_3/UV , H_2O_2/UV , will receive a high rating in terms of flexibility as the dosages of chemicals and/or UV light can easily be adapted and adjusted to respond to changing flow rate and load. The UV and/or chemical dosages can also be varied for the TiO_2/UV and the Fenton's processes and reactions are most likely carried out in semi-batch reactors that can handle large fluctuations. Yet a medium rating is suggested, because more advanced adjustments are needed. In the Fenton's process, all four process steps must be adapted to cope with changes in the flow rate. In the TiO_2/UV process, the amount of catalyst might be inadequate for a certain flow rate. This means that more catalyst might have to be incorporated into the reactor, which likely only can be done during process stop.

7.3 Stability

Some systems will require some kind of pre and/or post treatment for adjustment and control of temperature, alkalinity, interferences and by-products. A system that has a low stability and a high need for modifications in the process will receive a low rating and a system that has a good ability to alter such parameters itself will receive a high rating.

For example, the Fenton's process will most likely require pre- and post-adjustment of pH since the process is carried out at low pH. Moreover, a post-treatment for extraction of residual iron might be mandatory in order to prevent the release of iron to the recipient. Supported TiO_2 systems may require pre-treatment of effluents containing high concentrations of inorganic constituents to avoid fouling of active sites in catalyst. A catalyst separation unit must also often be included when TiO_2 is used in suspended form to remove TiO_2 particles from the treated wastewater. The TiO_2/UV and the Fenton's process will therefore receive a low rating.

Processes that are utilizing H_2O_2 will receive a medium rating, because presence of excess H_2O_2 in the treated wastewater might sometimes require post-treatment. O_3 based systems (O_3 , $\text{H}_2\text{O}_2/\text{O}_3$, O_3/UV) will receive a medium rating as they ordinarily will require an air permit for O_3 emissions and an off-gas treatment system to collect and destruct excess O_3 into O_2 . Automatic control and monitoring systems are also necessary to regulate temperature and thus the solubility of O_3 in aqueous phase.

7.4 Energy Efficiency

Energy efficiency is generally rated low for systems that are utilizing O_3 in combination with UV, because of the high amount of electricity needed in ozone generator(s) and lamps. In addition, the low solubility of O_3 in water will decrease the efficiency since more gas has to be produced on-site and bubbled through the reactor.

Systems that are using O_3 or UV in combination with other oxidants (TiO_2 or H_2O_2) do not require same amount of electricity and are therefore rated medium in terms of energy efficiency. For example, the $\text{H}_2\text{O}_2/\text{UV}$ system will require electricity for the UV lamps, but H_2O_2 is generally not limited by mass transfer limitations. The Fenton's process is the most energy efficient AOP since it does not require any electricity beyond the feed pumps.

7.5 Overview of Rating

In Table 8, the ratings for each oxidation process in terms of mechanical reliability, flexibility, stability and energy efficiency are summarized.

Table 8: Overview of rating for different oxidation processes in terms of mechanical reliability, flexibility, stability, and energy efficiency.

Oxidation Process	Mechanical Reliability	Flexibility	Stability	Energy Efficiency
O_3	High	High	Medium	Low
H_2O_2/O_3	High	High	Medium	Medium
O_3/UV	Medium	High	Medium	Low
H_2O_2/UV	Medium	High	Medium	Medium
TiO_2/UV	Low	Medium	Low	Medium
<i>Fenton's process</i>	Low	Medium	Low	High

7.6 Placement of AOP in the Treatment Plant

It can be discussed about where the optimal placement of the oxidation technology is in the wastewater treatment plant. Different positions in the plant will result in different degrees of effectiveness, costs and maintenance, because the chemistry and pollutant concentrations will vary throughout the treatment line. There are generally two potential locations mentioned in the literature; before (A) alternatively after a biological treatment (B), see Figure 12.

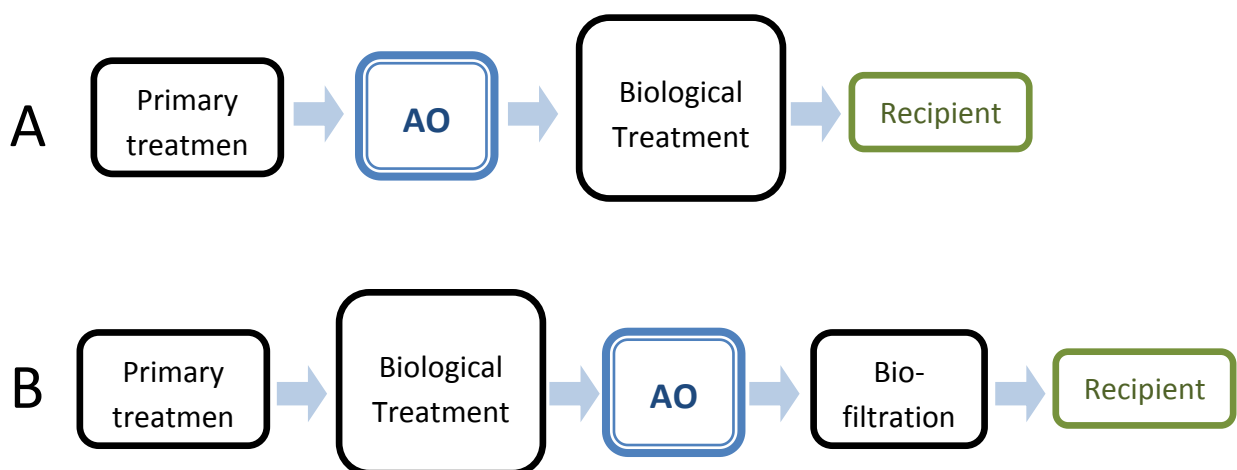


Figure 12: Potential positions of AOP in wastewater treatment plant. A = before biological treatment, B = after biological treatment.

Alternative A is an appropriate method to enhance biodegradability. Wastewater containing toxic and inhibitory compounds can be pre-treated to generate biodegradable intermediates, which then are treated biologically. However, due to the high volume of discharged effluent, very large reactors would be required, along with significant amount of expensive chemicals.

Alternative B seems like a more promising option because the treatment plant would be very flexible to variations in wastewater quality output, which can arise from production problems or change of raw material. Costs are minimized because the wastewater has already been biologically purified to the maximum possible extent, and much lower oxidant dosages would be needed. However, COD removal will simultaneously increase the BOD level in the discharged effluent, but the effect could potentially be minimized with recirculation of effluent to biological treatment or installation of a subsequent biofiltration stage. If O_3 is used in the AOP step, the O_2 gas that is produced when excess O_3 is thermally destructed in the off-gas decomposer could potentially directly be supplied to the oxygen requiring biological system.

8 CASE STUDY

This case study aims to use the information acquired in the literature study on advanced oxidation processes to evaluate and test the actual performance in laboratory in the treatment of pulp and paper mill effluents. All experiments are conducted in Wedecos laboratory in Herford (Germany) and the selection of oxidants is therefore based on the equipment available in that laboratory.

1. In the first part of this study, the performance of ozone treatment is demonstrated. Parameters such as COD, BOD, pH, colour, P-tot, N-tot, NO_2^- , NO_3^- , NH_4^+ , and PO_4^{3-} are analyzed throughout the treatment as it is important to characterize the complete matrix of the wastewater.
2. Secondly, an AOP (ozone in combination with hydrogen peroxide) is tested and evaluated.
3. Results and assumptions obtained from the demonstrative part of this study are forming the basis for a design and cost estimation of a full scale installation.
4. Finally, the oxidative treatment is compared to a conventional chemical precipitation with flotation to assess the environmental and economic feasibility of oxidation processes in the treatment of pulp- and paper mill effluents. Also, a discussion regarding the need for further biofiltration, based on results from ozonation experiments is carried out.

8.1 Choice of Wastewater

Wastewater from three different mills (A, B & C), all situated in Sweden, are chosen for this case study. Each mill has a modern and developed biological treatment, with COD, BOD, TSS, P-tot and N-tot discharges that are considered to be representative of the Swedish forest industry and are all well within the allowed emission range. The effluent parameters are unique for each mill. This is due to differences in the production (type of product, proportion of bleached products, produced amounts of pulp, and differences in the external treatment processes) which result in different type of specific emissions. It is of interest to investigate different types of wastewater qualities in order to find out responds to oxidation and thus potential trends and differences.



8.1.1 Mill A

Mill A is an integrated pulp and paperboard mill with its own pulp supply. It produces bleached sulphate pulp which is used to manufacture solid bleached board used for high quality graphic products and packaging. Softwood and hardwood are used as raw materials and the cellulose factory has two separate pulp lines for each wood type. The mill has two board machines with an annual production capacity of about 330 000 tonnes of paperboard, the pulp consumption is 0.9 tonnes of pulp per tonne of board and the distribution between softwood and hardwood is 50/50. (ÅF, 2013)

Existing External Wastewater Treatment

Wastewater containing fibres from the pulp lines is pumped to three sedimentation basins (Inflow 1). The settled fibre-sludge is taken out from the sedimentation basins and led to a fibre recovery system, and the clarified wastewater is led to a pump station where it is mixed with Inflow 2 before entering the biological treatment. Inflow 2 contains wastewater from the coating machine, acidic wastewater from the bleaching, reject water from the chemical water treatment, leachate from the landfill, neutralized rest acid and wastewater from the recovery boiler and causticizing. The first part of the lagoon is anoxic in order to decompose chlorate in the wastewater. The second part of the lagoon is aerated with use of surface aerators to achieve an efficient BOD and COD reduction. One portion (30%) of the outgoing water from the aerated lagoon is directly discharged to the recipient and another portion (70%) is further purified by chemical treatment and flotation. Here, aluminium sulphate and polyacrylamide is added to form flocks together with colloidal particles and suspended solids present in the wastewater. The formed flocks rise to the surface of the flotation basin and the sludge is scraped off and pumped to the sludge treatment. The separated sludge is dewatered with two centrifuges and is used as a construction material for final cover of the mill landfill and the purified water is discharged to the recipient (a local bay). See Figure 13 for process flow scheme. (ÅF, 2013)

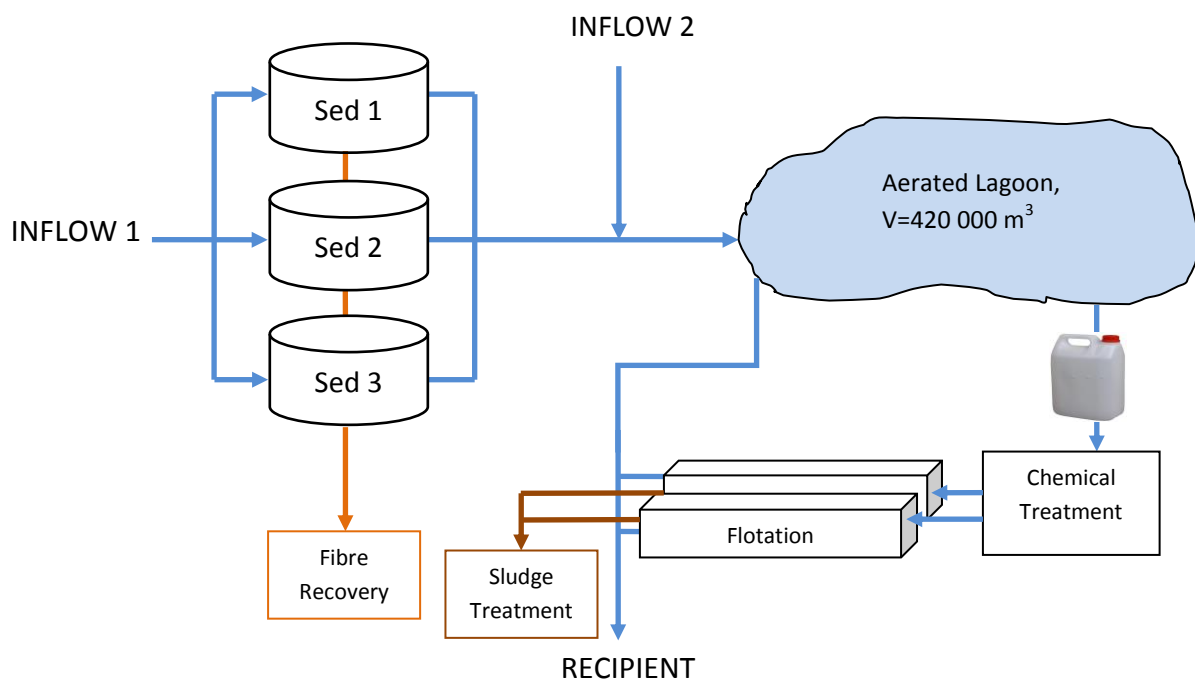


Figure 13: Process flow scheme of external wastewater treatment plant of Mill A.

8.1.2 Mill B

Mill B is an integrated pulp and paperboard mill with its own pulp supply. Bleached sulphate pulp and semi-chemical (NSSC) pulp is produced to manufacture kraft- and fluting paper with a total capacity of 685 000 tonnes per year. One part of the bleached sulphate pulp is sold as market pulp, but the major part is used on site. The factory uses only virgin soft- and hardwood fibres and has no elements of recycled fibres integrated in the production. The mill has five paper machines, one coater machine and three separate pulp lines for different fibres. (ÅF, 2013)

Existing External Wastewater Treatment

Wastewater from the pulp manufacturing process with a high COD load is first either sedimented or cooled down before it is led to the biological treatment (inflow 1 & 2). Paper mill wastewater (inflow 3) is clarified by sedimentation and then led directly to the recipient (a lake) and the industrial drain, which mainly consists of cooling and sealing water from the causticizing, is discharged directly to the recipient. A multi-biological treatment is used which is divided into three bio steps (Bio 1, 2 & 3) and two activated sludge steps (AS1, AS2). The wastewater is led through each step of the biological treatment, and air is supplied from the bottom of each reactor via blowers. The sludge that is separated in the post-sedimentation basin is aerated and pumped back to Bio 3. Nutrients are added to the incoming water to the biological treatment. Excess sludge is pumped to the sludge treatment and cleared water from the post-sedimentation basin is discharged to the recipient. The separated sludge is flocculated with help of a polymer, dewatered and hydrolyzed with 48% TS black liquor before it is further evaporated and burned in the recovery boiler. See Figure 14 for process flow scheme. (ÅF, 2013)

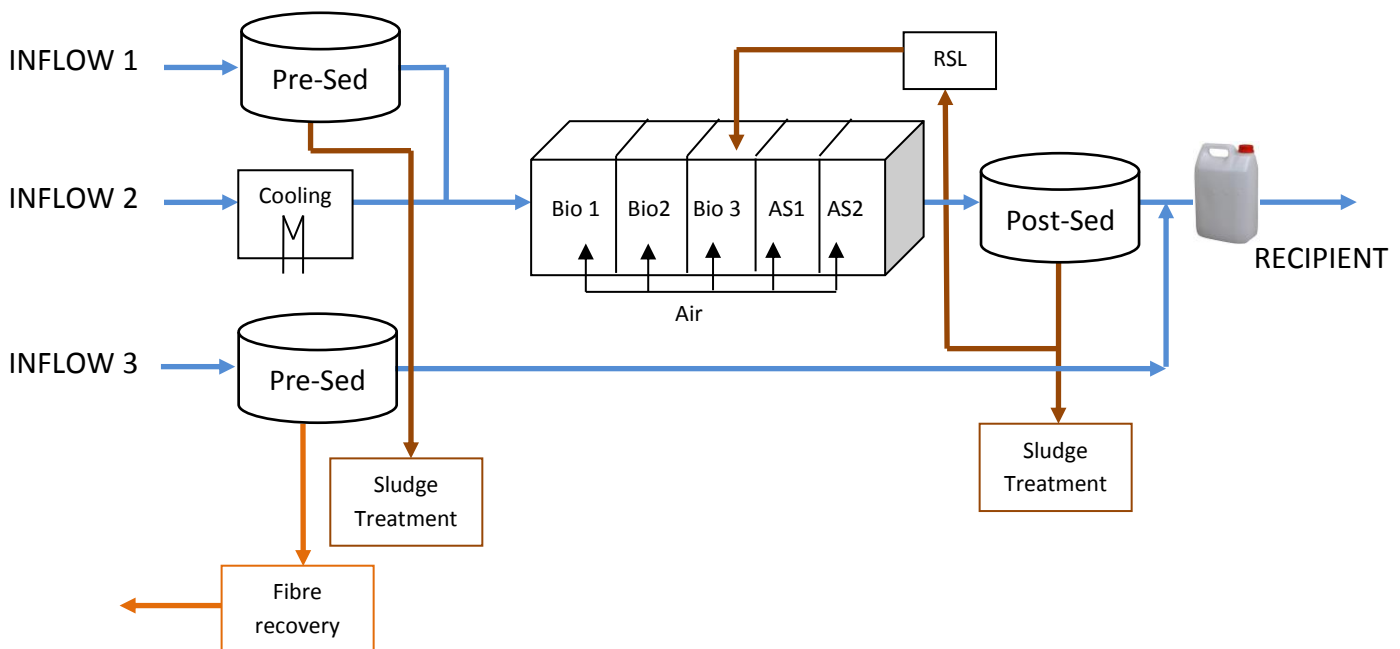


Figure 14: Process flow scheme of external wastewater treatment plant of Mill B.

8.1.3 Mill C

Mill C is a paper mill with its own pulp supply. Spruce is used as raw material to produce both bleached and unbleached TMP pulp which is used to manufacture newsprint and paper for uncoated magazines. Only virgin fibres are used and the mill has no elements of recycled fibres integrated in the production. The mill has four paper machines and has an annual production capacity of around 1 million tonnes of paper. (ÅF, 2013)

Existing External Wastewater Treatment

Wastewater from the pulp and paper manufacturing process is first clarified in two parallel pre-sedimentation basins. The settled fibre-sludge is taken out from the sedimentation basins and led to the sludge treatment, and the clarified wastewater is cooled down before entering two MBBR reactors with suspended carriers. After the MBBR, the wastewater is led to an activated sludge process consisting of three aerated basins. The biology is relatively poor in nutrient because softwood is used as raw material, thus nutrients are added in this part of the treatment. After the biological treatment, the wastewater is led to two parallel post-sedimentation basins and part of the formed sludge is recycled back to aeration and the excess sludge is collected in a sludge thickener. The plant is supplemented by a separation step with two parallel flotation units together with polymer is supplied to bring flocks of suspended particles to the surface where it is scraped off. The parts of particles which possibly settle to the bottom of the basins are removed with bottom scrapers. All excess sludge from the treatment is collected and dewatered with help of presses. One portion of the dewatered sludge is mixed with fly ash (from flue gas treatment) and used as a construction material for final cover of landfills and another portion of the dewatered sludge is burned in a recovery boiler. See Figure 15 for process flow scheme. (ÅF, 2013)

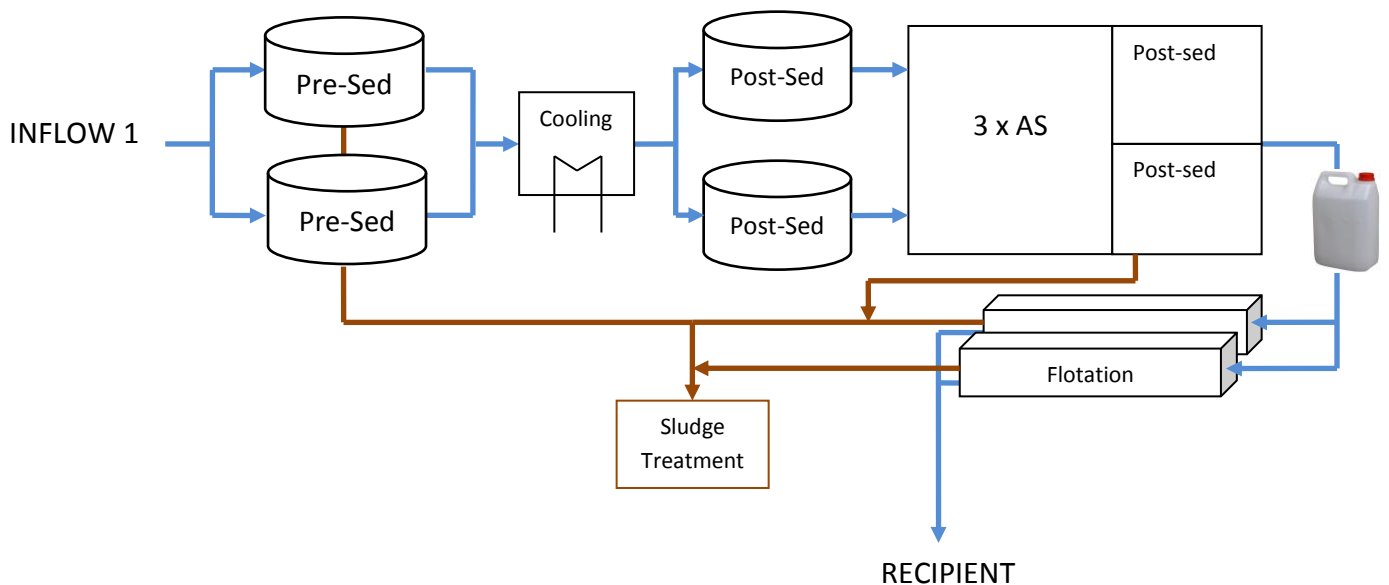


Figure 15: Process flow scheme of external wastewater treatment plant of Mill C.

8.2 Materials and Methods

8.2.1 Sampling

Wastewater is collected by staff at each mill and the sampling is made after respective biology (the sampling point is marked with a plastic can in each process scheme above):

Mill A – Wastewater sample collected after aerated lagoon

Mill B – Wastewater sample collected after activated sludge process

Mill C – Wastewater sample collected after activated sludge process

The wastewater is transported to Wedeco laboratory in Germany the same day as the sampling is made. At Wedeco, the raw wastewater is stored in a cold room at 11°C and mixed homogenous before any treatment or analysis. Due to logistical issues, ozonation and AOP cannot be commenced the same day as the samples are arriving to the laboratory. The wastewater is therefore one week old in average when experiments are started.

8.2.2 Characterization

Data on magnitude of flows and pollutant concentrations is provided by each mill and the wastewater quality is controlled by ÅF at arrival in Wedeco laboratory. The data has a degree of uncertainty because measurements originate from only one day measurements. Table 9 indicates that the wastewater quality did not change during transport. Slight differences are seen but are considered acceptable given the circumstances. It should be noted that the TSS concentration is slightly changing, but this is due to differences in analytical methods used by the mills and in Wedeco laboratory; filter papers of different pore sizes and different sample volumes are used.

Table 9: Wastewater characterization before and after transport, a = Measured with GF/A filter-paper (≈1.6 μm pore size), b = Measured with Macherey-Nagel MN 85/90 BF (0.5-1 μm pore size).

MILL	Position	Flow [m ³ /h]	COD [mg/L]	BOD [mg/L]	TSS [mg/L]	N-tot [mg/L]	P-tot [mg/L]	Temp [°C]	pH
A	Before transport	2446	314	20-30	44 ^a	4-5	0.5-0.55	30	7.1
	After transport	-	282	N/A	60 ^b	2.73	0.637	20	7.76
B	Before transport	1806	401	10	19 ^a	≈5	≈1	32	7.2
	After transport	-	495	N/A	13 ^b	2.94	0.952	20	7.55
C	Before transport	930	262	N/A	8 ^a	6.5	0.13	34	7.9
	After transport	-	250	N/A	6 ^b	5.89	0.14	20	8.7

8.2.3 Ozone Generation & Reactor Configuration

Ozone is generated from pure O₂ gas from AirLiquid and the principle is based on the dielectric barrier discharge phenomenon. O₂ gas is flowing through the electrodes inside the ozone generator and as a current (6-10 kV) is supplied to the system arcs are formed due to the electrical discharge. The arcs split O₂ into single oxygen atoms which eventually recombine and form O₃. The technical generation of O₃ from O₂ is limited due to physical limitations and O₃ is therefore never available in pure form. In this study, an O₃/O₂ ratio of around 7 wt% is achieved, which means that the largest portion of the utilized gas is still O₂.

The O₃ containing gas is supplied from the ozone generator through the top of the reaction column via venturi injectors at a flow rate of 0.01 m³/h. Part of the gas diffuses into the wastewater, dissolves and reacts with the pollutants and the part of the O₃ which is remained in the gas rises to the top of the column and gets destroyed in the catalytic ozone destructor. The concentration of O₃ is monitored and measured in the feed gas stream and in the off-gas stream with ozone analyzers. Figure 16 illustrates the complete test set-up of the experimental apparatus.

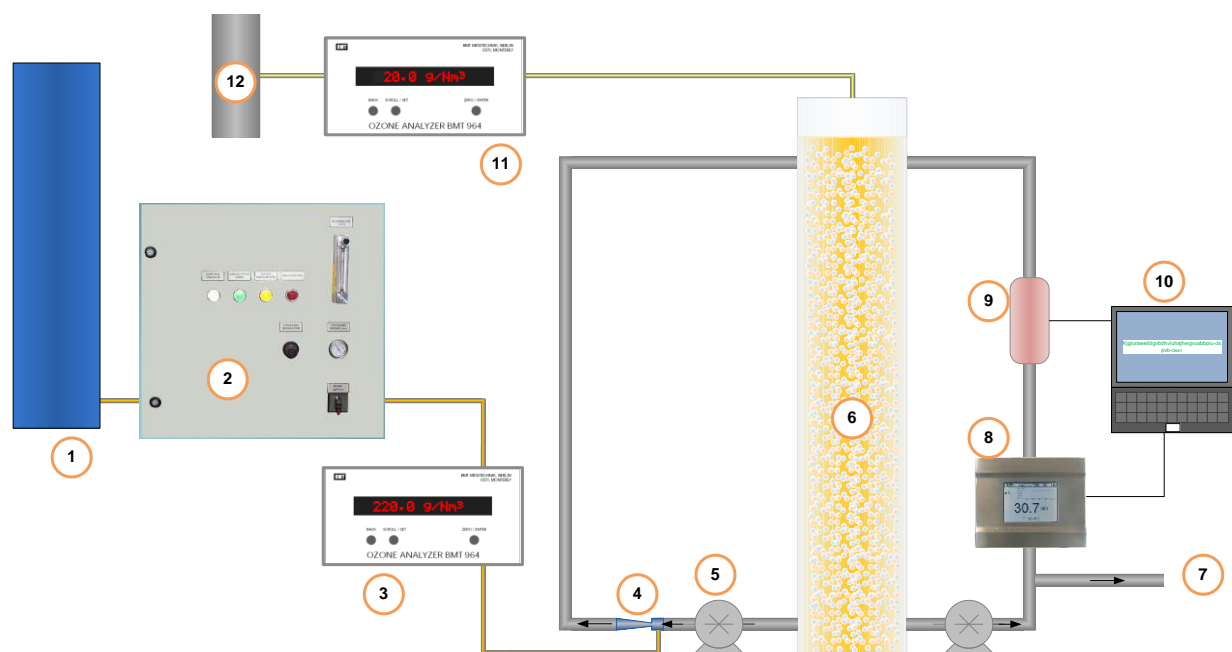


Figure 16: Test set-up used for ozonation and AOP. (Wedeco, 2013)

1. Oxygen supply (LOX, PSA or gas cylinder)
2. Ozone generator (WEDECO 8 HC, ozone capacity of 8 g/h)
3. Ozone analyzer for feed gas (BMT 964C)
4. Venturi injector
5. Circulation pump (peristaltic or membrane)
6. Reaction column (glass -reactor with a volume of 10L)
7. Sample point (ball valve)
8. Orbisphere measurement device (dissolved O₃)
9. Orbisphere sensor
10. Data logger (not installed)
11. Ozone analyzer for off-gas (BMT 964C)
12. Catalytic ozone destructor

8.2.4 Experimental Procedure

All the experiments are conducted at room temperature ($\approx 22^{\circ}\text{C}$) in a completely mixed batch mode. Raw wastewater from Mill A, B and C is poured into the reactor one by one and ozonated with O_3 gas of six different concentrations. The ozone dosage is adjusted (increased) as saturation arises which is monitored with help of the off-gas analyzer, and effluent is taken out from the reaction column at the pre-determined ozone dosages for analysis.

The AOP trials are only tested on wastewater from Mill A and B. The three highest ozone dosages (100, 150 & 200 $\text{g O}_3/\text{m}^3$) are combined with H_2O_2 (30% solution) from AppliChem in order to accelerate the OH^* radical formation. H_2O_2 is added to the reactor using a pipette and the wastewater is then ozonated according to description above. After each sampling, residual amount of H_2O_2 in the wastewater is checked with Quantofix Peroxide 25 test strips and removed from the AOP effluent with a solution of Peroxidase and Katalase to avoid interference with the COD measurement.

See Table 10 for a complete overview of used dosages of oxidants in ozonation and AOP. It is important to note that these concentrations of oxidants only are approximates, exact dosages are presented in respective result diagram later in the report.

Table 10: Dosages of oxidants used in the study, * = Mill A-25, Mill B-20

SAMPLE	MILL A, B, C Ozonation	MILL A, B AOP ($\text{O}_3 + \text{H}_2\text{O}_2$)	
	[$\text{g O}_3/\text{m}^3$ wastewater]	[$\text{g O}_3/\text{m}^3$ wastewater]	[$\text{g H}_2\text{O}_2/\text{m}^3$ wastewater]
Raw Wastewater	0	0	-
0	0	0	-
1	30	30	-
2	50	50	-
3	70	70	-
4	100	100	15
5	150	150	25/20*
6	200	200	45

8.2.5 Analytical Methods

Wastewater from each mill is characterized before and after treatment according to the standard methods presented in Table 11. A bench scale pH meter is used for the pH measurements and a spectrophotometer from Hach Lange (DR500) is used for the spectrometric Lange cuvette tests (COD, colour, N-tot, NO_2^- , NO_3^- , NH_4^+ , P-tot and PO_4^{3-}). The BOD content of the effluent is measured according to the “dilution method” (EN 1899-1) by an external laboratory. The analysis is conducted for five days and sludge from a municipal wastewater treatment plant is used as a source of bioactivity.

Table 11: Parameters analyzed in the experiments, and the method and equipment used.

Analysis	Method	Instruments	Note
COD	LCK614 (Mill A & C) LCK514 (Mill B)	DRLange HT200S Hach Lange DR500	15 min, 170°C
BOD ₅	“Dilution Method” EN 1899-1	-	Conducted for 5 days, 20°C, sludge from a municipal treatment plant
pH	-	Scott Instruments LAB 850 pH electrode Blue line 15pH	
Colour	-	Hach Lange DR500 1 cm Cuvette	$\lambda = 436 \text{ nm}$ (yellow)
TSS	Standard Method 2540D	Sartorius	Filter paper Macherey- Nagel MN 85/90 BF (0.5-1 μm pore size)
NO_2^-	LCK341	Hach Lange DR500	-
NO_3^-	LCK339	Hach Lange DR500	-
NH_4^+	LCK304 (Mill A & B) LCK305 (Mill C)	Hach Lange DR500	-
P-tot	LCK349	DRLange HT200S Hach Lange DR500	15 min, 170°C
P-tot (filtrated)	LCK349	DRLange HT200S Hach Lange DR500	15 min, 170°C Filtrated with membrane filter (0.45 μm pore size)
PO_4^{3-} (filtrated)	LCK349	Hach Lange DR500	Filtrated with membrane filter (0.45 μm pore size)

8.3 Results

Results presented in following section are based on batch studies conducted in Wedeco laboratory in Herford (Germany). Data should only be used for overview purposes as experiments are based on single measurements and in some cases on double measurements for Mill C. The result are interpreted in the following section and discussed in a broader perspective later in the report.

8.3.1 Ozonation

Chemical Oxygen Demand

Considerable COD removal is registered at increased ozone dosage according to the linear relationships seen in Figure 17. Inlet COD of 256, 422, 243 mg/L requires 0.2 g O₃/L to reduce the COD to 151, 290 and 112 mg/L respectively. All mills are showing the same trend with curves of similar slope; see Equation 3 for derived COD equation as a function of the ozone dosage.

Equation 3: COD as a function of the ozone dosage.

$$COD = k \cdot D_{O_3} + COD_{initial} \quad D_{O_3} = \text{Ozone dosage [g O}_3\text{/m}^3\text{]}$$

$$k_{MILL A} = -0.55 \quad k_{MILL B} = -0.65 \quad k_{MILL C} = -0.65 \Rightarrow k_{Average} = -0.62$$

$$\Rightarrow COD = -0.62 \cdot D_{O_3} + COD_{initial}$$

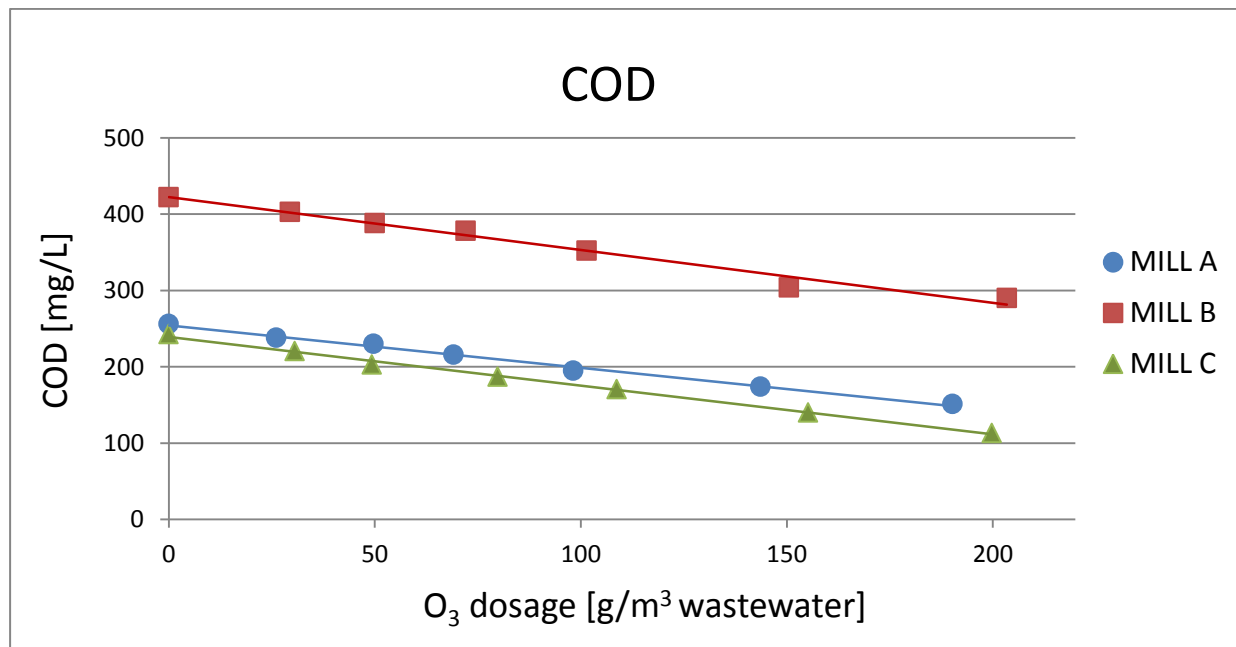


Figure 17: Registered COD elimination of wastewater from Mill A, B and C at increased ozone dosage. Results of Mill A and B are based on single measurements, whereas results of Mill C are averages of two measurements.

Biological Oxygen Demand

The BOD₅ is increasing with an increase in ozone dosage as seen in Figure 18, and a BOD_{max} of 39 mg/L is seen for Mill A at an ozone dosage of around 100 g O₃/m³. The last data point of Mill B is marked with a red cross because the BOD₅ analysis could not be completed. Instead, this point is based on the BOD₅ result from the AOP study where H₂O₂ is added to the treatment. H₂O₂ should not increase the BOD content of the effluent and the data is therefore considered as representative. It is however not completely obvious after which ozone dosage BOD_{max} is obtained for Mill B, hence difficult to determine when it is feasible to start a subsequent biofiltration stage. The graph is however indicating a fairly constant BOD₅ content towards the end, suggesting an expected BOD_{max} within this range.

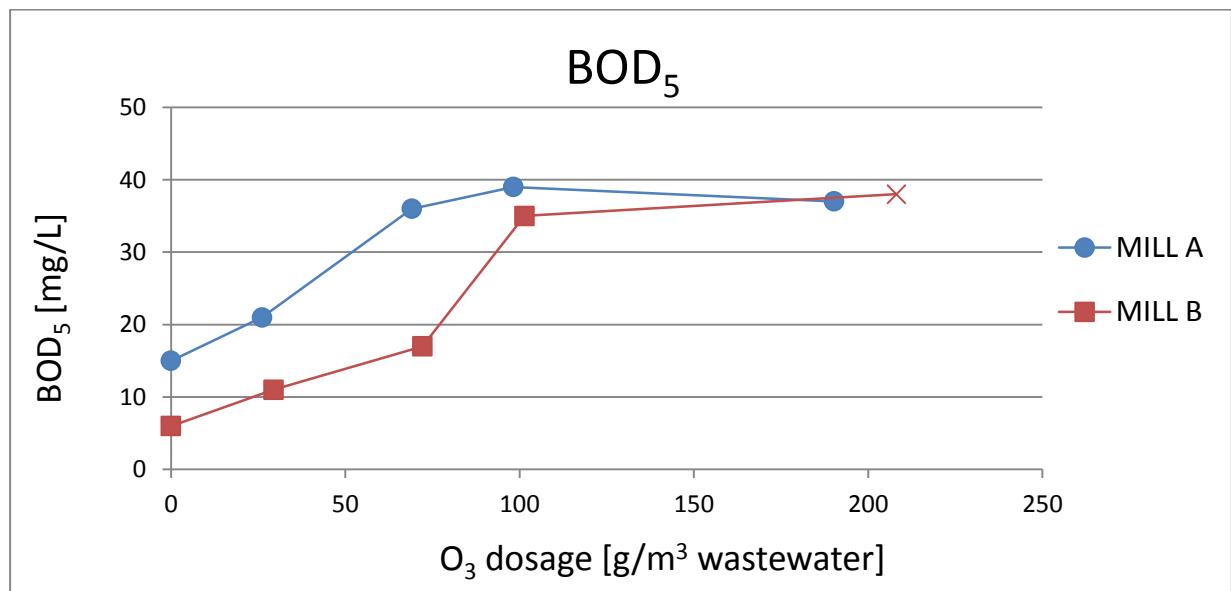


Figure 18: Graph showing the BOD₅ for Mill A and B at increased ozone dosage. Results of Mill A and B are based on single measurements.

The BOD₅ results of Mill C are presented separately in Figure 19 as analysis is made on a manipulated wastewater which is not part of this study. Here, a known concentration of activated sludge (45 mg/L) is added to the initial wastewater of Mill C, in order to increase the content of suspended solids in the wastewater. The graph is however still a part of this report because a similar trend is seen as for Mill A; showing a BOD_{max} of 34 at an ozone dosage of around 150 g O₃/m³.

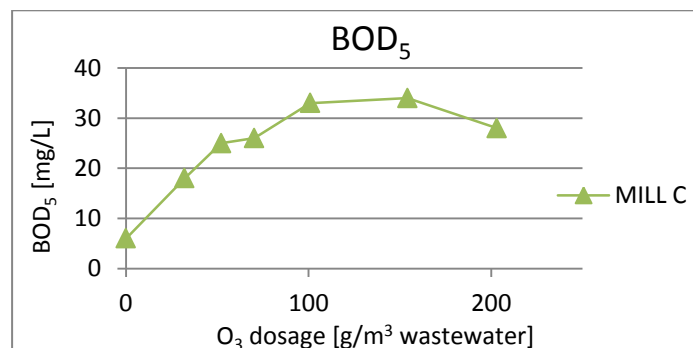


Figure 19: Graph showing the BOD₅ for Mill C at increased ozone dosage. Results are based on single measurements.

pH

pH is decreasing slightly throughout the treatment, but is kept in the range of 7-8, see Figure 20.

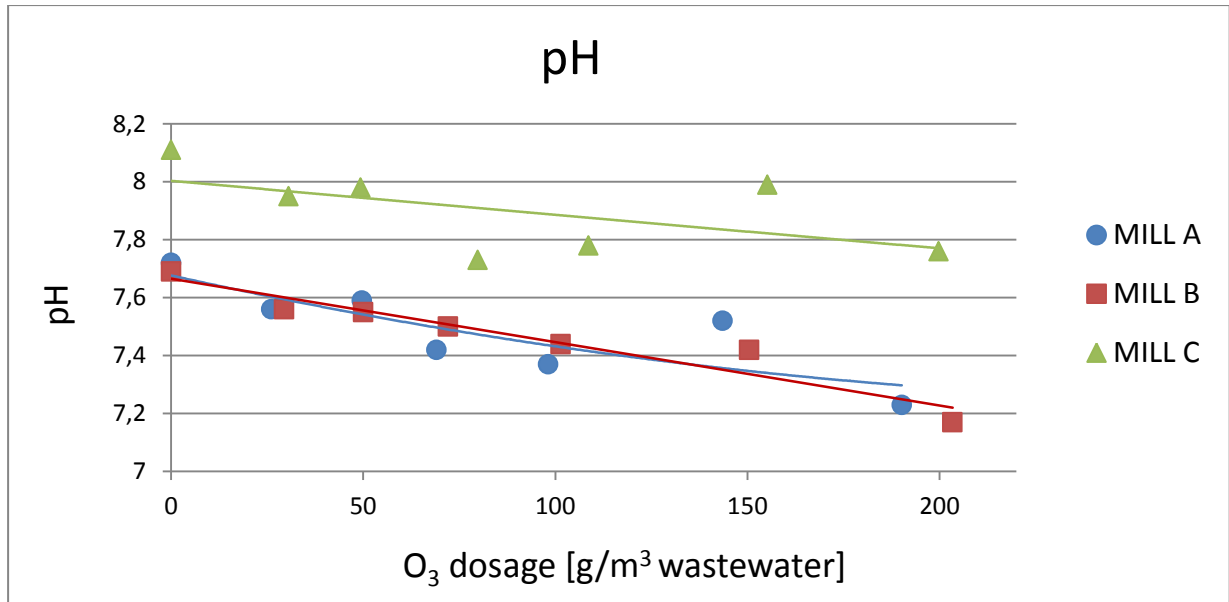


Figure 20: Graph showing the pH for Mill A, B and C at increased ozone dosage. All results are based on single measurements.

Colour

At a wavelength of $\lambda = 436$ nm (yellow), a decolourization of 83% (Mill A), 91% (Mill B) and 96% (Mill C) is achieved with an applied ozone dosage of 0.2 g O₃/L. Based on Figure 21, it can be seen that the colour removal process is divided into two established phases; one phase where a rather fast decolourization is occurring and one phase where the decolourization rate is lower.

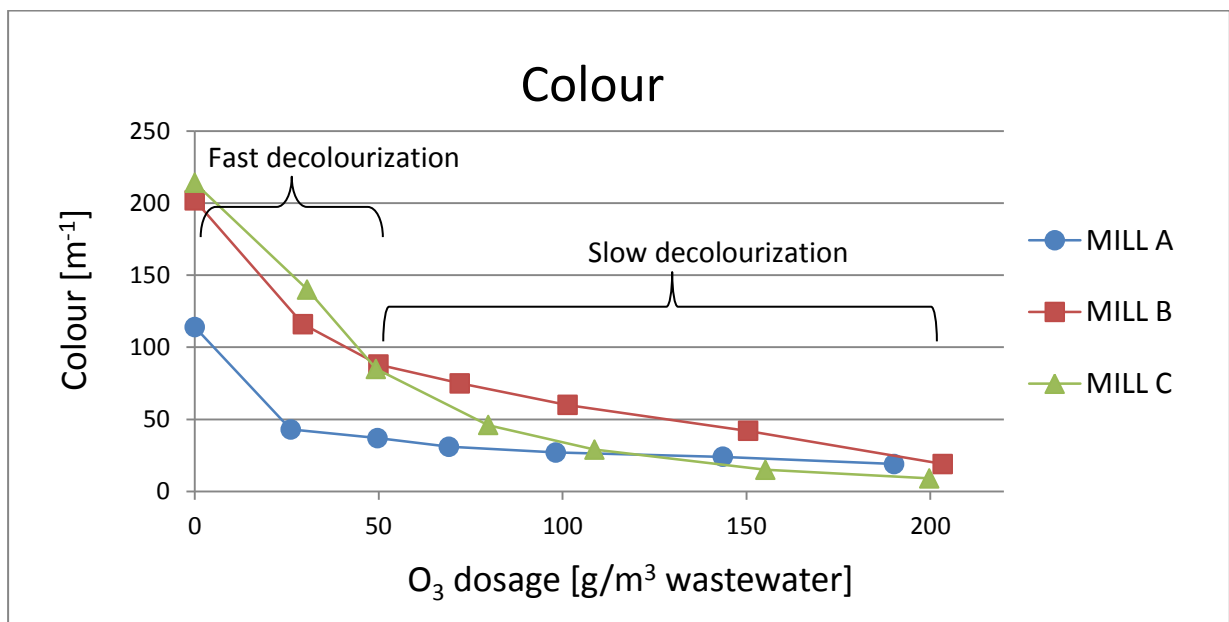


Figure 21: Graph showing the colour reduction for Mill A, B and C at increased ozone dosage, $\lambda = 436$ nm. All results are based on single measurements.

The decolourization effect is illustrated in Figure 22, where it is seen that the colour of the solution is changing accordingly from brown to almost colourless and transparent.

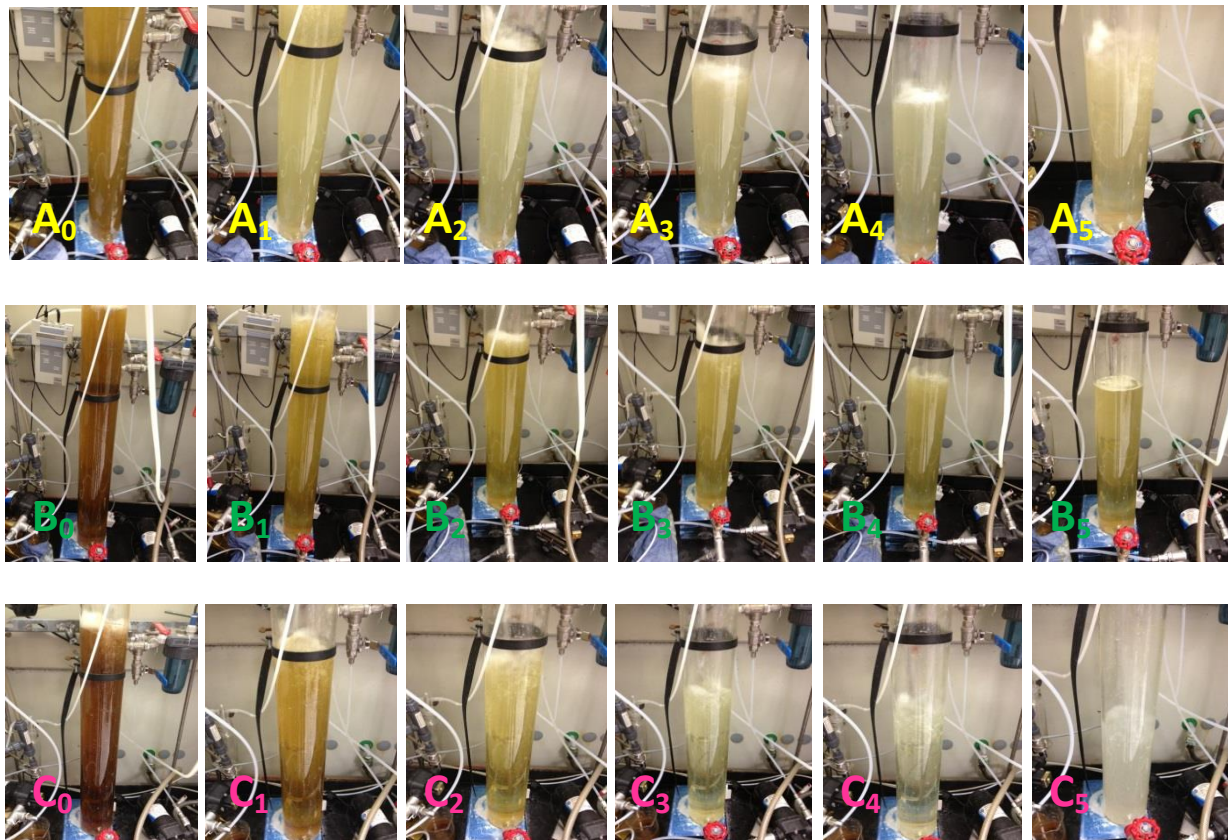


Figure 22: Observed colour reduction in the reaction column at increased ozone dosage. From the top to the bottom: Mill A, Mill B, Mill C. From the left to the right: increased ozone dosage.

Phosphorus

As seen in Figure 23, the P-tot concentration is relatively constant throughout the O_3 treatment for all mills. Only two measurement points are presented for Mill C because sample No. 2 ($50 \text{ g } O_3/\text{m}^3$) is contaminated and therefore removed out from the plot. Still, two points are considered as consistent and the relationship linear. Filtrated P-tot and PO_4^{3-} are also analyzed but the results are not presented as data cannot be interpreted and assured qualitatively. With the highest probability, sample handling has occurred in a wrong way, resulting in a vague outcome. There are however indications that filtrated P-tot and PO_4^{3-} are constant throughout the treatment.

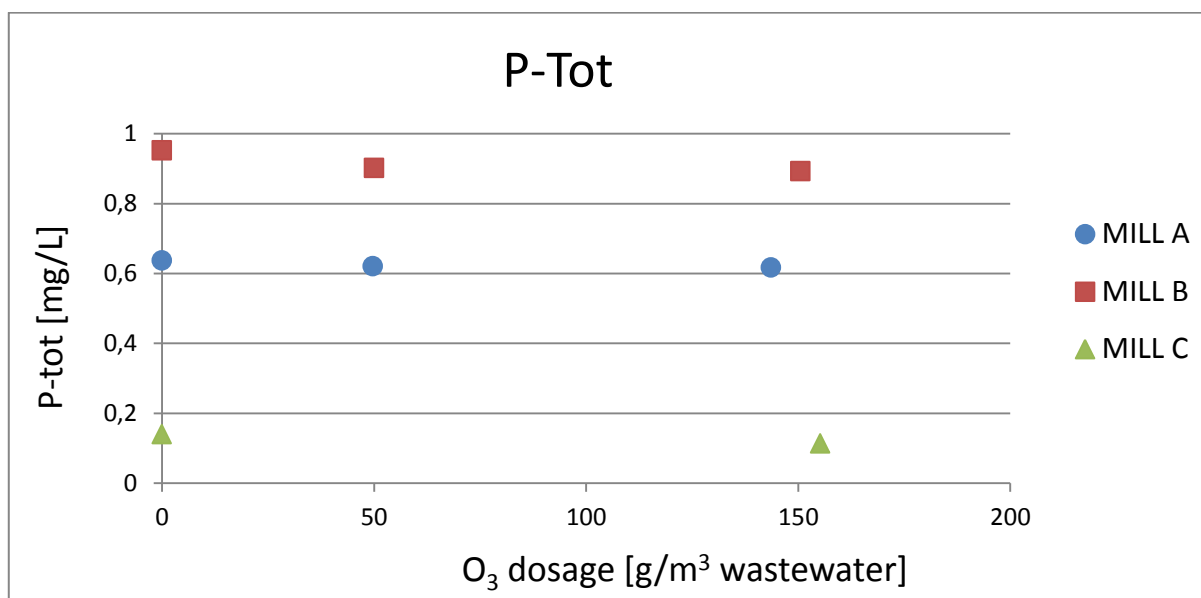


Figure 23: Graph showing the P-tot concentration for Mill A, B and C at increased ozone dosages. Sample No. 2 (50 g O₃/m³) for Mill C is contaminated and therefore removed out from the plot. Results of Mill A and B are based on single measurements, whereas results of Mill C are averages of two measurements.

Nitrogen

The N-tot concentration is not changed much during treatment, see Figure 24. A slight increase is seen for Mill A for the final ozone dosage (marked with a parenthesis), but can be caused by an improper sample handling.

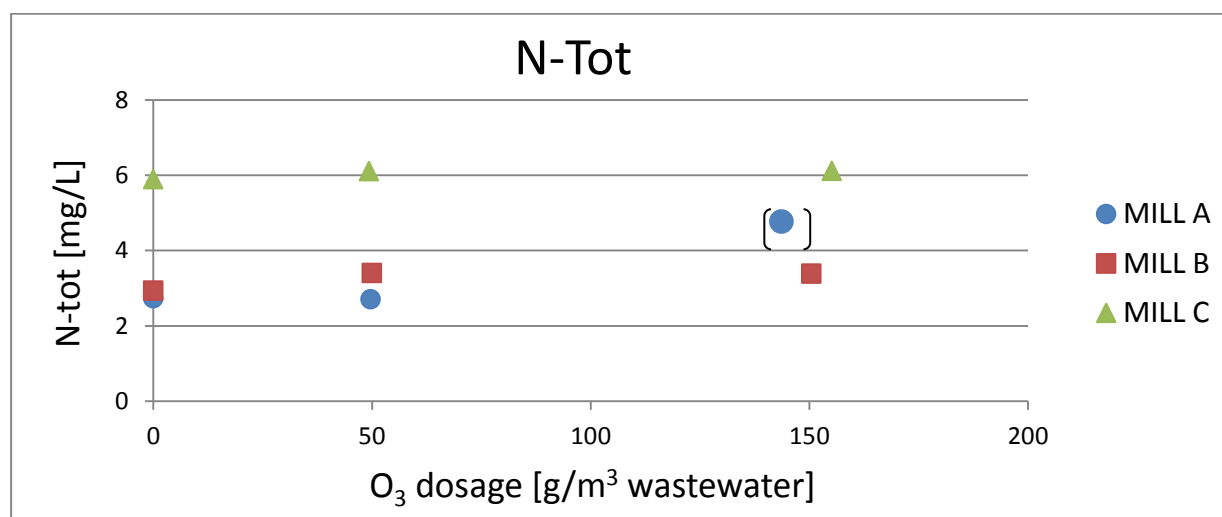


Figure 24: Graph showing the N-tot concentration for Mill A, B and C at increased ozone dosage. Results of Mill A and B are based on single measurements, whereas results of Mill C are averages of two measurements.

The ammonium concentration is relatively constant throughout the treatment for all mills, see Figure 25. The nitrite concentration is decreasing from 0.044 to 0.018 for Mill A, 0.045 to 0.017 for Mill B and 0.091 to almost zero for Mill C. This behavior is expected as nitrite likely is oxidized into nitrate. Because of the very low nitrite concentration in overall, results are not presented in any graph. A natural behavior would be to see an increase in nitrate as nitrite is oxidized by the ozone. However, this phenomenon is not the observed in Figure 26; nitrate is decreasing. According to the method description of LCK339 (nitrate analysis), the sample should be diluted for wastewater studies where the COD content is higher than 200 mg/L. This is because high

COD loads might discolour the reagents used in the analysis and thus yield higher results. This aspect was unfortunately missed during analysis, and could explain the decrease as the first two points (for all Mills) in the graph have a COD load which is higher than 200 mg/L (marked with parenthesis).

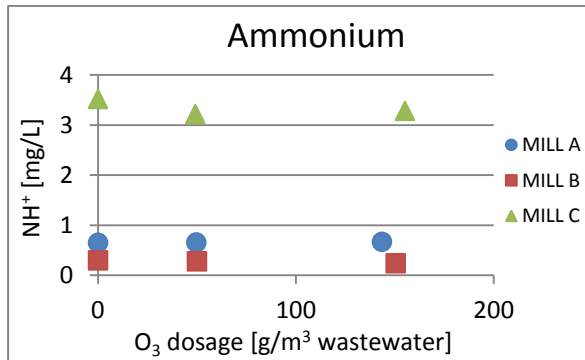


Figure 25: Graph showing the ammonium concentration for Mill A, B and C at increased ozone dosages. Results of Mill A and B are based on single measurements, whereas results of Mill C are averages of two measurements.

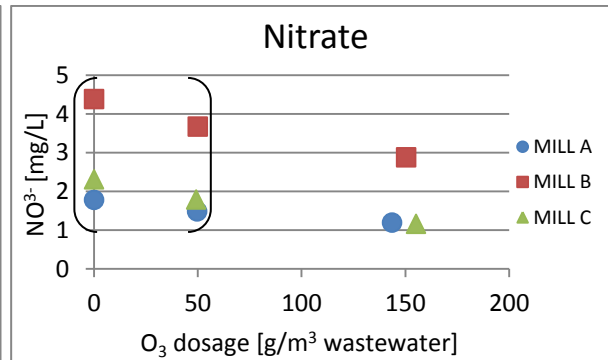


Figure 26: Graph showing the nitrate concentration for Mill A, B and C at increased ozone dosages. Results of Mill A and B are based on single measurements, whereas results of Mill C are averages of two measurements.

Suspended Solids

The TSS concentration is measured for the raw wastewater of each mill and for the final effluent (final ozone dosage) of Mill C. Unfortunately, no other TSS measurements are conducted. The result of Mill C shows an increase in TSS concentration from 6 to 45 mg/L. It is based on a double measurement and a sample volume of 500 ml. No obvious particles are seen in the final effluent; still the filter paper is clogged easily and fast. However, the water has a high turbidity and is almost sticky, which is why the filter paper is easily clogged. The increase in turbidity is seen for all mills and is illustrated in Figure 27.

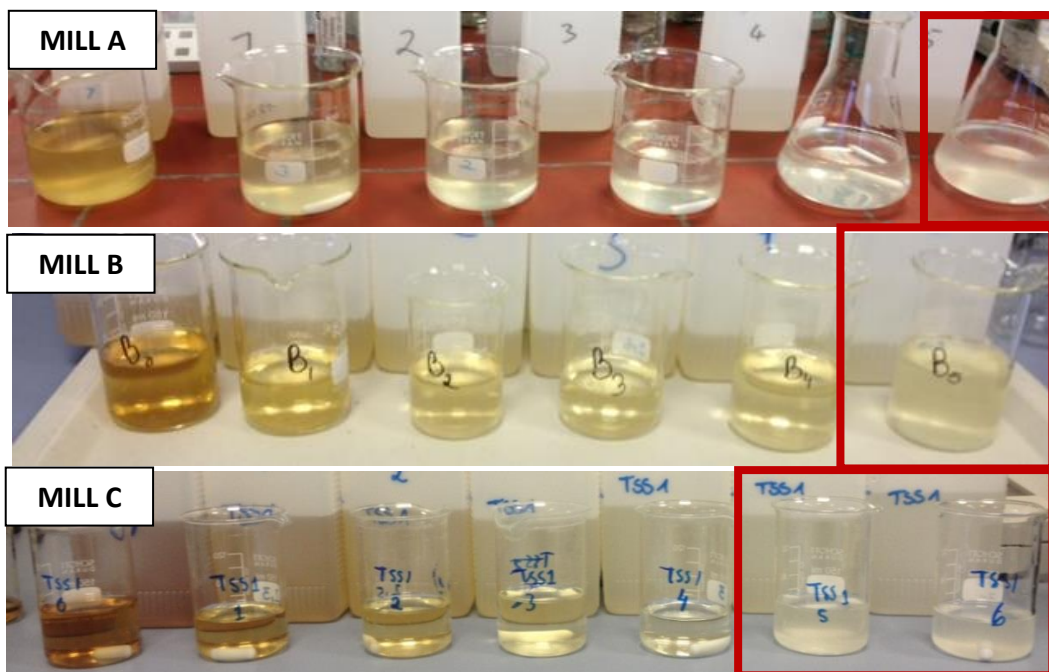


Figure 27: Wastewater samples for Mill A, B and C. From left to the right; increase in ozone dosage. Notice the increase in turbidity for the final samples (marked in red).

8.3.2 AOP

Effluent from the AOP treatment (O_3 in combination with H_2O_2) is analyzed with same type of analysis as effluent from the O_3 treatment. As seen in Figure 28-33, very small differences are seen in COD, pH and colour in comparison to O_3 treatment alone. The red dotted line in each graph represents the point where H_2O_2 is added to the system. Similar trends and results are seen in P-tot, P-tot (filtrated), PO_4^{3-} (filtrated), N-tot, NH_4 , NO_2^- and NO_3^- analysis as seen for the O_3 treatment. The results are therefore not presented in the report but can be found in Appendix 3.

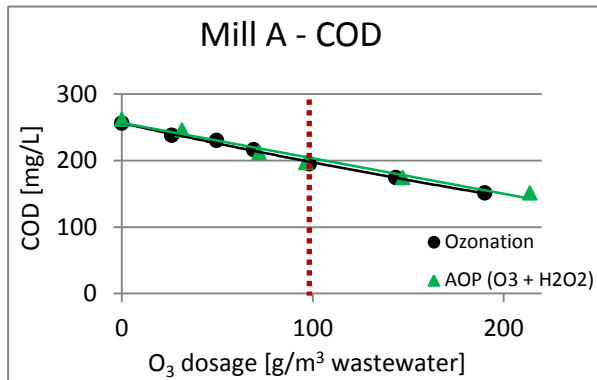


Figure 28: Comparison of COD results from ozonation and AOP for Mill A. Results are based on single measurements.

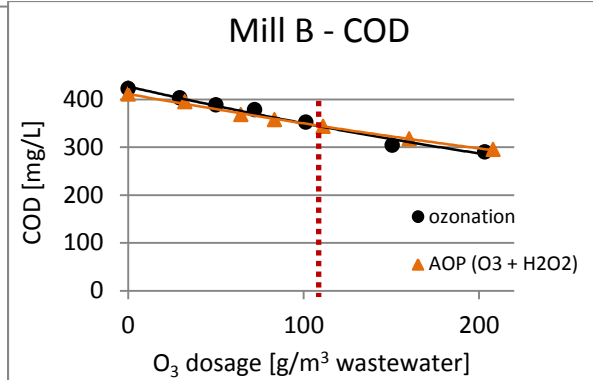


Figure 29: Comparison of COD results from ozonation and AOP for Mill B. Results are based on single measurements.

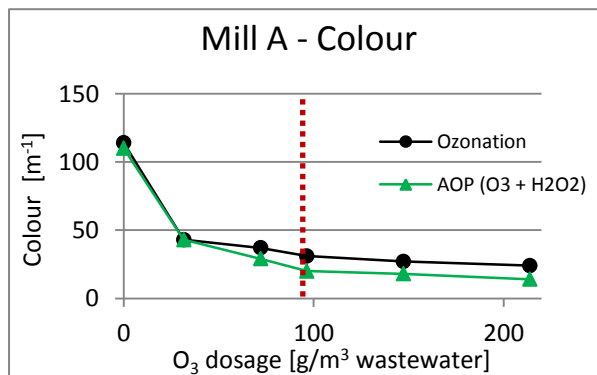


Figure 30: Comparison of decolourization effect from ozonation and AOP for Mill A. Results are based on single measurements.

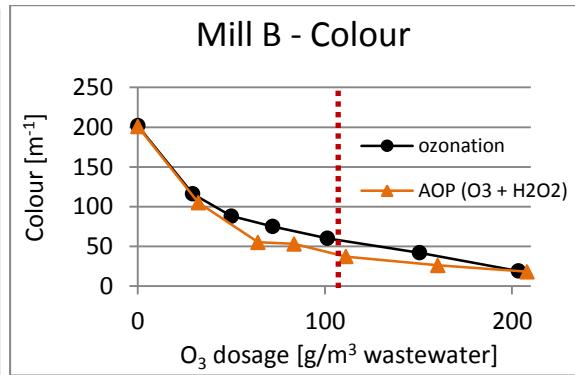


Figure 31: Comparison of decolourization effect from ozonation and AOP for Mill B. Results are based on single measurements.

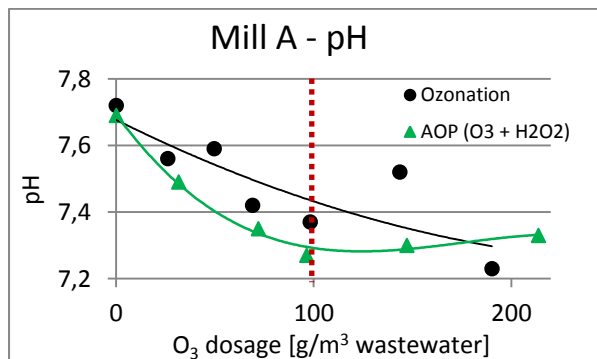


Figure 32: Comparison of pH from ozonation and AOP for Mill A. Results are based on single measurements.

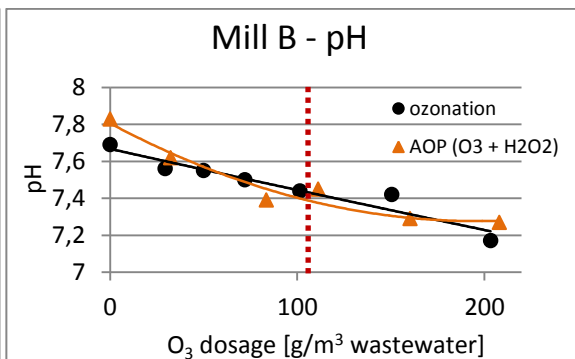


Figure 33: Comparison of pH from ozonation and AOP for Mill B. Results are based on single measurements.

9 Technical Evaluation

9.1 Ozonation

The results indicate that treatment with O_3 is an effective method to eliminate COD from pulp and paper mill wastewaters. High COD reductions are achieved without having an appreciable impact on other parameters such as N-tot, NO_2^- , NO_3^- , NH_4^+ , P-tot and PO_4^{3-} and no phase change is occurring from solid to dissolved phase. pH is decreasing slightly throughout the treatment but this is possibly due to formation of CO_2 , which has a relatively low pK_a value. Other acidic products could potentially also be formed as O_3 is cleaving long chained molecules into shorter chains (acetic acids, carboxylic acids etc.). However, the pH is kept in the range of 7-8 which is considered as neutral and no pre- or post-adjustment of pH is therefore needed.

The highest COD reduction is observed for Mill C (53.4%), followed by Mill A (41%) and B (31.3%) with an applied dosage of 0.2 g O_3 /L, see Figure 34.

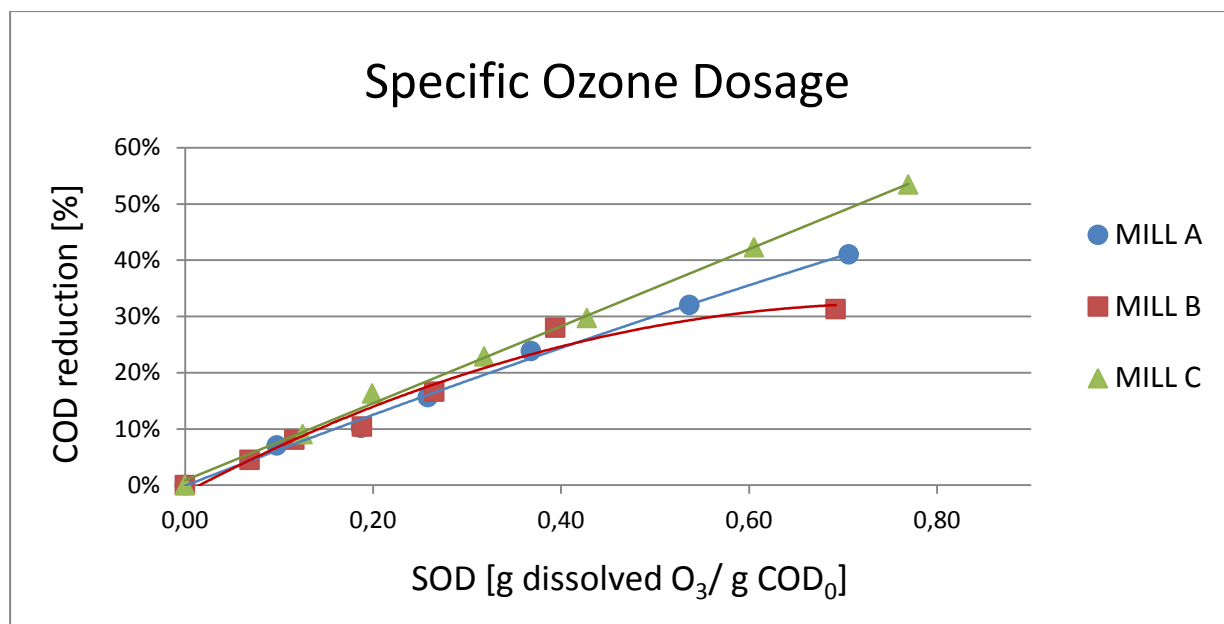


Figure 34: Graph showing the Specific Ozone Dosage (SOD) for Mill A, B and C.

Up to an Specific Ozone Dosage (SOD) of 0.4 same behaviour and percentual COD reduction is seen for all mills using the same specific ozone dosage. This could potentially mean that same type of reactions are occurring in the wastewater between the O_3 and pollutant molecules independently of water quality and initial COD.

The difference in the final COD reduction between the mills mainly depend on the difference in inlet COD concentration, but the nature of the wastewater seems to have an effect as well because different trends are observed when treated with higher ozone dosages; Mill A and C are showing a linear regression throughout the O_3 treatment whereas the slope of Mill B declines after a SOD of 0.4. Bierbaum and Öeller (2009) explained the differences in COD elimination and reactions with the difference in paper grades being produced by different mills. Mill A and B are

both producing sulphate pulp, whereas Mill C is producing TMP pulp, consequently having different COD loads in their effluents.

A COD reduction of 53% is observed at a SOD of 0.77 for Mill C. This result is consistent with the result of Kaindl in 2010 with the TMP wastewater from Laakirchen (see Figure 11). Kaindl reported a COD reduction of around 55% with the same SOD but with a biofiltration stage included. Even though Kaindl's result includes a biofiltration stage, the result is still comparable because the largest portion of COD is removed in the oxidation stage and not in the biological treatment. This can potentially mean that same type of COD elimination can be expected for the treatment of all types of TMP wastewaters. The slopes of Mill A and B will most likely also decline at higher SODs as only hard COD is left in the wastewater.

The results from the colour analysis are showing that O₃ treatment is a very efficient method to decolorize effluents as expected from literature. The highest colour reduction is observed for Mill C (96%), followed by Mill B (91%) and A (83%) with an applied dosage of 0.2 g O₃/L. A rather fast decolourization is seen even at very low ozone dosages and it is therefore considered more profitable to use ozone dosages under 0.05 g O₃/L. The slopes of the colour curves in Figure 21 are steeper compared to slopes in the COD curves in Figure 17, thus showing that ozone competing reactions between the residual organic and chromophoric molecules are different. This behavior may be explained by the greater selectivity of O₃ to oxidize readily degradable chromophoric structures compared with the ozone selectivity to oxidize remaining organic molecules.

The initial BOD₅/COD ratios of the effluents are low, i.e. 0.06 (Mill A), 0.01 (Mill B), 0.02 (Mill C), indicating that biorefractory organic molecules are present in the wastewater. As seen in Figure 35, the BOD₅/COD ratios of the treated effluents are increasing, showing an improved biodegradability. One part of the COD is converted into BOD which potentially can be removed efficiently with further reduction in subsequent biological treatment stage.

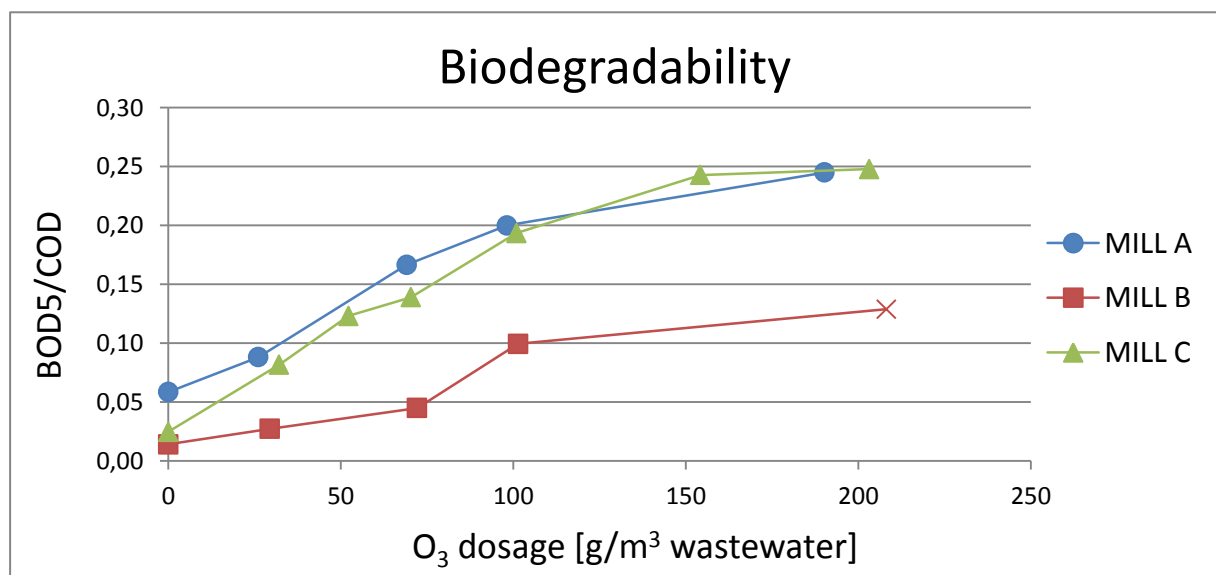


Figure 35: Graph showing the biodegradability (BOD₅/COD ratio) for wastewater of Mill A, B and C. The results of Mill C are based on analysis made on a manipulated wastewater which is not part of this study.

The final BOD₅/COD ratios of the effluents are lower than 0.3. According to Jamil et al. (2011), a ratio less than 0.3 is considered low, and corresponds to low biodegradability of the organic material present in the wastewater. A further increase in biodegradability could potentially be achieved with a higher ozone dosage but would introduce very high economical losses. Therefore, no further increase in ozone dosage is preferable and despite the low ratios, a great improvement in biodegradability is seen for the wastewaters. Similar trend and ratios are observed by Bierbaum and Öeller (2009).

9.2 AOP

The goal with adding H₂O₂ to the wastewater after a certain ozone dosage is to enhance the transformation of O₃ to OH^{*} in aqueous phase, and thus the amount of O₃ needed for oxidation. Even though H₂O₂ has a lower EOP compared to O₃ (1.78 Vs. 2.08), a larger quantity of radicals are produced for the same concentration of oxidant in the presence of H₂O₂ compared to O₃ used alone.

However, the effect of adding H₂O₂ to the wastewater after a certain ozone dosage in order to improve the COD reduction is insignificant. Very small differences are seen in comparison to O₃ treatment alone, and the differences may equally well have occurred by random variations. The addition of H₂O₂ after a certain O₃ dosage is therefore considered as an inefficient treatment for pulp and paper mill wastewaters as it only introduces higher operating costs. This observation is also confirmed by Ko et al. (2009).

10 Economical Evaluation

Investments, direct and fixed operating costs are estimated separately for implementation of oxidation with O_3 and chemical precipitation with flotation to make a comparison between the treatments. No estimation is made for an oxidation with the combination of O_3 and H_2O_2 because it does not show any further COD reduction.

It is important to emphasize that the data for the cost estimations is provided by two different parts; data and costs for the ozonation is provided by Wedeco and data for the chemical treatment is calculated with support from ÅF. Thus, there are room for different assumptions and interpretations and one should be careful to directly compare the results. Some examples of what is needed to be studied further to increase the accuracy of the calculations are:

- *Include costs for substations for transformation of electricity (ozonation will for example need high investments for electricity infrastructure).*
- *Cost for the sludge handling from the biofiltration stage (is not checked if it is included, might possibly need e.g. a flotation unit and a centrifuge for dewatering the biological sludge)*
- *There may be different instrumentation levels for the different calculations.*
- *There are only very rough estimate for buildings included.*

Still, results are of interest because they indicate trends and parameters of importance.

Costs for the O_3 treatment are estimated for two different principles of design; full oxidation and partial oxidation. In the full oxidation, costs are based on a rather high ozone dosage and a full mineralization to target COD. In the partial oxidation, a lower ozone dosage is used to first crack the long-chained organic molecules into smaller fractions (to improve the BOD/COD ratio), which then are eliminated in a subsequent biofiltration stage, see Figure 36.

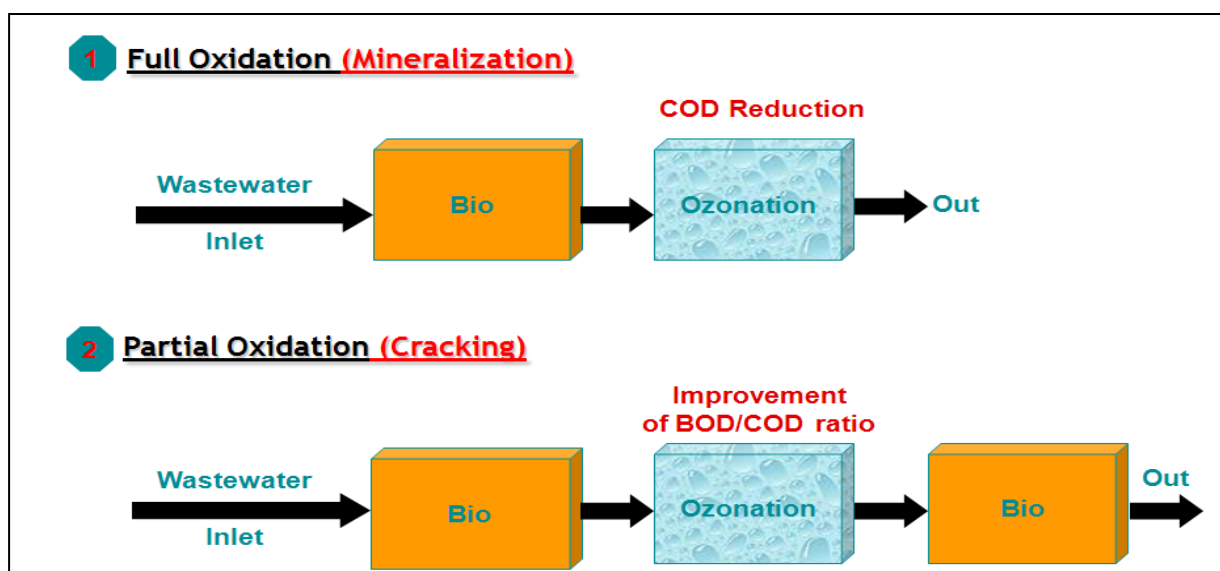


Figure 36: Costs for the ozone treatment are calculated for two different principles of design; full oxidation (1) and partial oxidation (2) with subsequent biofiltration stage.

Calculations are estimated for the treatment of a wastewater quality similar to that of Mill A, and are based on the results from the experimental part of this study. The design parameters are presented in Table 12 and should therefore not be used as absolute values. The goal is to reduce the COD from 260 mg/L to around 150 mg/L with the various treatments. The dosage of ozone in the full oxidation corresponds to the highest ozone concentration used in the experiments (0.2 g O₃/L), whereas the dosage of ozone in the partial oxidation is derived from the BOD₅ results of Mill A as seen in Figure 18. The point where BOD_{max} is observed is considered as the optimal dosage to use because the largest portion of biodegradable by-products are present there. The costs for the partial oxidation are therefore estimated for an ozone dosage of 0.07-1 g O₃/L.

Table 12: Design parameters for the dimensioning of the different treatments.

Design Parameters	Unit	Chemical precipitation	Complete oxidation	Partial oxidation
Wastewater Flow	m ³ /h	2500	2500	2500
BOD _{initial}	mg/L	20-30	20-30	20-30
COD _{initial}	mg/L	≈260	≈260	≈260
COD _{target}	mg/L	≈150	≈150	≈150
O ₃ dosage, 12 wt%	g/L	-	0.2	0.07-0.1
	kg/h	-	500	171
Cooling water demand, 15°C	m ³ /h	-	800	280

10.1 Oxidation with Ozone

Costs of building an ozone plant are based on the process design presented in Figure 37 and a reaction time of up to 30 min. The biofilters are marked in red and are only part of the total costs for the partial oxidation. The major investments are the ozone generators, injection system and the concrete reactor. Costs for pumps, pipes, residual ozone destructors, compressor, control systems, instruments, cooling system, installation and electricity are also included in the costs to get representative calculations for a full scale implementation. All costs are provided by Wedeco according to the Wedeco product catalogue of 2012/2013. Associated building and soil preparation costs are estimated according to standards methods of ÅF. The technical contingency is estimated to 20% of the total investment, 10% for auxiliary equipment and 10% for project and administration.

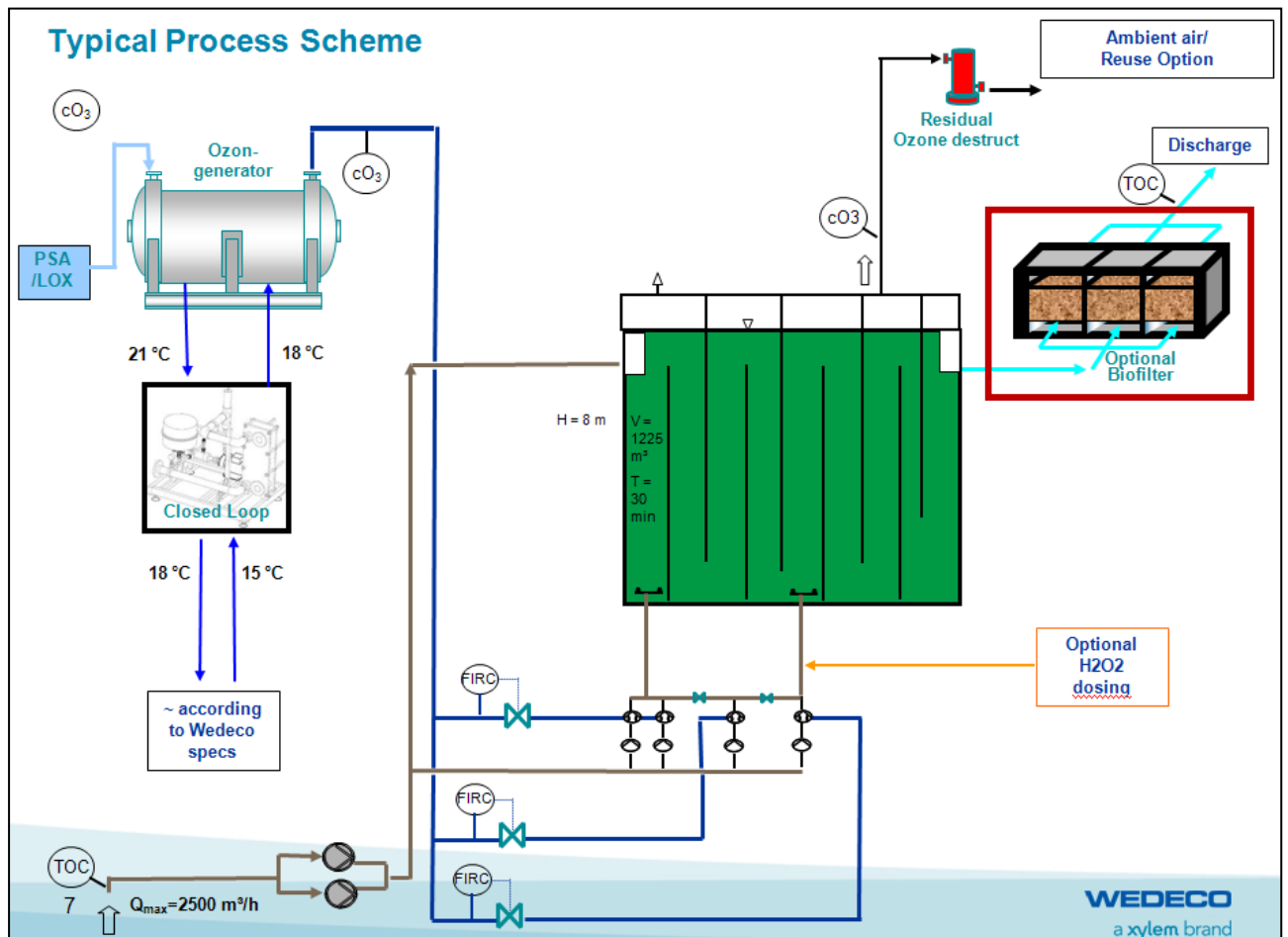


Figure 37: Typical process scheme for an ozone plant. The biofilters are marked in red.

The costs are estimated for 346 days of operation (95% availability per year) and the personnel costs are assumed to be the same in all three treatments, even though oxidative treatment might need less operating workers. The specific power consumption of the ozone generators is estimated to around 2 kWh/m³ for the full oxidation and to 0.71 kWh/m³ for the partial oxidation. The specific energy demand of the ozone plant is estimated to 11.2 kWh/kg O₃ for both the full and partial oxidation, and an electricity price of 0.05 EUR/kWh is assumed throughout. Oxygen is supplied “over the fence” by the industrial gas company AGA with a price of 50 EUR/tonne O₂ for the full oxidation and 85 EUR/tonne O₂ for the partial oxidation. The higher amount that is bought from the supplier delivering the oxygen the cheaper the price is.

A small portion of sludge is formed in the biofiltration stage but because no exact costs for sludge handling can be given by Wedeco, a standard cost of 59 EUR/tonne sludge dewatered to 20% solids is used based on experience from ÅF. The amount of sludge that is separated in the biofiltration stage is estimated to one tonne per day, assumed a 90% BOD reduction is achieved and that 0.3 g sludge is formed per g eliminated BOD.

Estimated investments for the full oxidation are shown in Table 13 and direct operating costs in Table 14. Investment for the partial oxidation with subsequent biofiltration stage is seen in Table 15 and direct operating costs in Table 16.

Table 13: Investment for the full oxidation.

INVESTMENT	[MEUR]	REFERENCE
3 Ozone generators (3 x 20 m ²)	3,60	(Wedeco, 2013)
2 Residual ozone destructors	0,40	(Wedeco, 2013)
Interconnecting pipes	0,60	(Wedeco, 2013)
Other pipes	0,15	
Pump station	0,20	(Wedeco, 2013)
Reactor (153m ² x 8m)	1,00	(Wedeco, 2013)
Injection system	1,90	(Wedeco, 2013)
Compressor for feed gas	0,04	(Wedeco, 2013)
Cooling system	0,40	(Wedeco, 2013)
Control system + measurement device	0,20	(Wedeco, 2013)
Installation	0,20	(Wedeco, 2013)
Electricity	0,60	(Wedeco, 2013)
Building	0,92	
Soil preparation	0,60	
Technical contingency, 20% of total investments	2,16	
Auxiliary equipment, 10% of total investments	1,08	
Project and administration, 10% of total investments	1,08	
TOTAL		15,13

Table 14: Direct operating cost for the full oxidation.

DIRECT OPERATING COST	[MEUR/year]	REFERENCE
Electricity (0,05 EUR/kWh)	2,33	(Wedeco, 2013)
Oxygen gas (0,07 EUR/Nm ³ = 50 EUR/tonne O ₂)	1,69	(Wedeco, 2013, AGA, 2013)
Personnel	0,06	
Maintenance, 2.5% of total investments	0,38	(Wedeco, 2013)
TOTAL		4,46

Table 15: Investment for the partial oxidation with subsequent biofiltration stage.

INVESTMENT	[MEUR]	REFERENCE
2 Ozone generators (2 x 20 m ²)	1,10	(Wedeco, 2013)
2 Residual ozone destructor	0,10	(Wedeco, 2013)
Interconnecting pipes	0,20	(Wedeco, 2013)
Other pipes	0,15	
Pump station	0,10	(Wedeco, 2013)
Reactor (153m ² x 8m)	1,00	(Wedeco, 2013)
Injection system	0,80	(Wedeco, 2013)
Compressor for feed gas	0,03	(Wedeco, 2013)
Cooling system	0,10	(Wedeco, 2013)
Control system + measurement device	0,10	(Wedeco, 2013)
Biofilters	2,80	(Wedeco, 2013)
Installation	0,10	(Wedeco, 2013)
Electricity	0,30	(Wedeco, 2013)
Building	1,40	
Soil preparation	1,05	
Technical contingency, 20% of total investments	1,88	
Auxiliary equipment, 10% of total investments	0,94	
Project and administration, 10% of total investments	0,94	
TOTAL		13,06

Table 16: Direct operating cost for the partial oxidation with subsequent biofiltration stage.

DIRECT OPERATING COST	[MEUR/year]	REFERENCE
Electricity (0,05 EUR/kWh)	1,01	(Wedeco, 2013)
Oxygen gas (0,11 EUR/Nm ³ = 85 EUR/ tonne O ₂)	0,91	(Wedeco, 2013, AGA, 2013)
Sludge handling	0,02	
Personnel	0,06	
Maintenance, 2.5% of total investments	0,33	(Wedeco, 2013)
TOTAL		2,34

10.2 Chemical Precipitation with Flotation

The cost for building a chemical treatment plant with precipitation and flotation is based on the process design of Mill A presented in Figure 13, thus a flotation unit with a total area of 560 m² (including dosing, tanks and control room) and a sludge dewatering system of 300 m². Cost for each process unit is estimated by ÅF from several years of experience. All process costs are adjusted to the market price of 2013 with help of the Chemical Engineering Plant Cost Index (CEPCI). In a similar way, all building costs are adjusted to 2013 with help of the construction index which is provided by Statistics Sweden (SCB). Installation cost for the machinery and equipment is estimated to 100% of the total machinery cost for pumps, 30% for mixers and 10% for other machines. The technical contingency is estimated to 20% of the total investment, 10% for auxiliary equipment and 10% for project and administration.

The cost is estimated for 346 days of operation (95% availability per year) and the personnel cost is assumed to be the same as in the oxidative treatments. An energy demand for the complete system is calculated according to supplier guidelines, and the specific energy demand of the plant is estimated to 0.12 kWh/m³. The costs for the chemicals are provided by Kemira (European manufacturer and supplier of industrial chemicals) and the amount estimated with help of data from Mill A. Because no exact costs for sludge handling and final disposal can be given, a standard cost of 59 EUR/tonne sludge dewatered to 20% solids is used based on experience from ÅF. The amount of sludge that is separated in the unit is estimated to 50 tonnes per day. Investment for the chemical treatment with precipitation and flotation are shown in Table 17 and direct operating costs are seen in Table 18.

Table 17: Investment for the chemical treatment with precipitation and flotation.

INVESTMENT	[MEUR]
Pump station	0,24
Flotation (560 m ²)	0,90
Sludge dewatering	0,41
Pipes	0,75
Electricity	0,27
Instruments	0,95
Control Systems	0,35
Installation	0,37
Building	1,52
Soil preparation	1,05
Technical contingency, 20% of total investments	1,36
Auxiliary equipment, 10% of total investments	0,82
Project and administration, 10% of total investments	0,90
TOTAL	9,88

Table 18: Direct operating cost for the chemical treatment with precipitation and flotation.

DIRECT OPERATING COST	[MEUR/year]
AVR	0,80
NaOH	0,16
Polymer, flotation	0,12
Polymer, sludge dewatering	0,09
Ferri sulphate, sludge dewatering	0,03
Electricity	0,12
Sludge handling	0,70
Personnel	0,06
Maintenance, 2.5% of total investments	0,25
TOTAL	2,32

10.3 Comparison

In following section the investment and direct operating costs are summarized and compared, and later the fixed and specific operating costs are derived for each treatment type for a design flow of 2500 m³/h.

10.3.1 Investment

As illustrated in Figure 38, full oxidation with ozone is the treatment with the highest investment (15.1 MEUR), followed by partial oxidation with subsequent biofiltration stage (13.1 MEUR) and chemical treatment (9.9 MEUR).

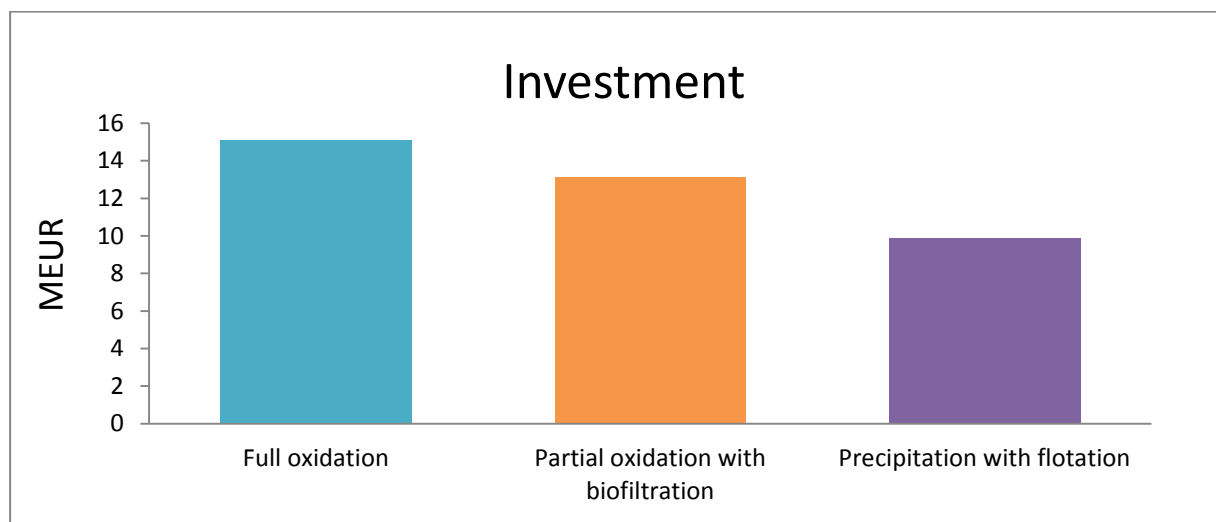


Figure 38: Investment for the chemical treatment with precipitation and flotation, full oxidation and partial oxidation with subsequent biofiltration stage.

10.3.2 Direct operating cost

Full oxidation is also the treatment with the highest direct operating cost (4.5 MEUR/year). However, the direct operating costs are almost equal for the partial oxidation and the chemical treatment (2.34 and 2.32 MEUR/year respectively), see Figure 39.

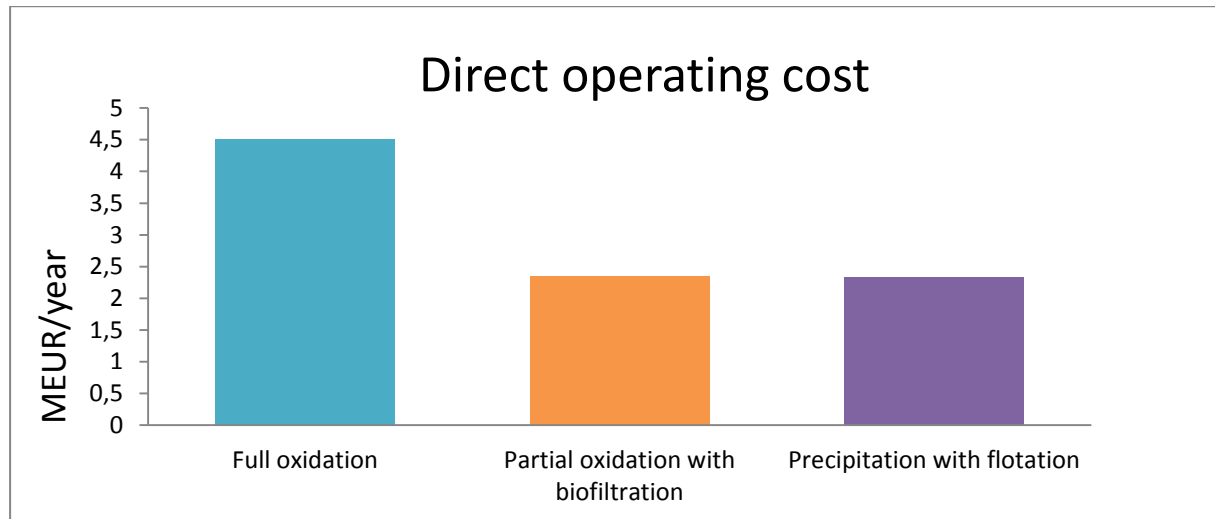


Figure 39: Direct operating cost for the chemical treatment with precipitation and flotation, full oxidation and partial oxidation with subsequent biofiltration stage.

10.3.3 Specific operating cost (fixed + direct)

In Table 19 and Figure 40, the annual fixed and direct operating costs are summarized and the specific operating cost (fixed + direct) presented for each treatment. The costs are based on a depreciation time of 10 years, an annual availability of 95%, an interest rate of 5.5%, and an annuity of 10.03%.

Table 19: Design parameters for estimating the specific operating cost (fixed + direct) for each treatment type.

DESIGN	UNIT	FULL OXIDATION	PARTIAL OXIDATION	CHEMICAL TREATMENT
Water flow rate, design, 95% availability	m ³ /year	20820000	20820000	20820000
Investments	MEUR	15,1	13,1	9,9
Depreciation time	year	10	10	10
Interest rate	%/year	5,50	5,50	5,5
Annuity	%	10,03	10,03	10,03
Annual fixed operating cost	MEUR/year	2,01	1,73	1,31
Annual direct operating cost	MEUR/year	4,46	2,33	2,32
Total annual operating cost (fixed+direct)	MEUR/year	6,47	4,07	3,64
Specific operating cost	EUR/ m³	0,31	0,20	0,17

Full oxidation is the treatment with the highest specific operating cost (fixed + direct); (0.31 MEUR/m³). However, the specific costs are almost equal for the partial oxidation and the chemical treatment (0.20 and 0.17 MEUR/m³ respectively), see Figure 40.

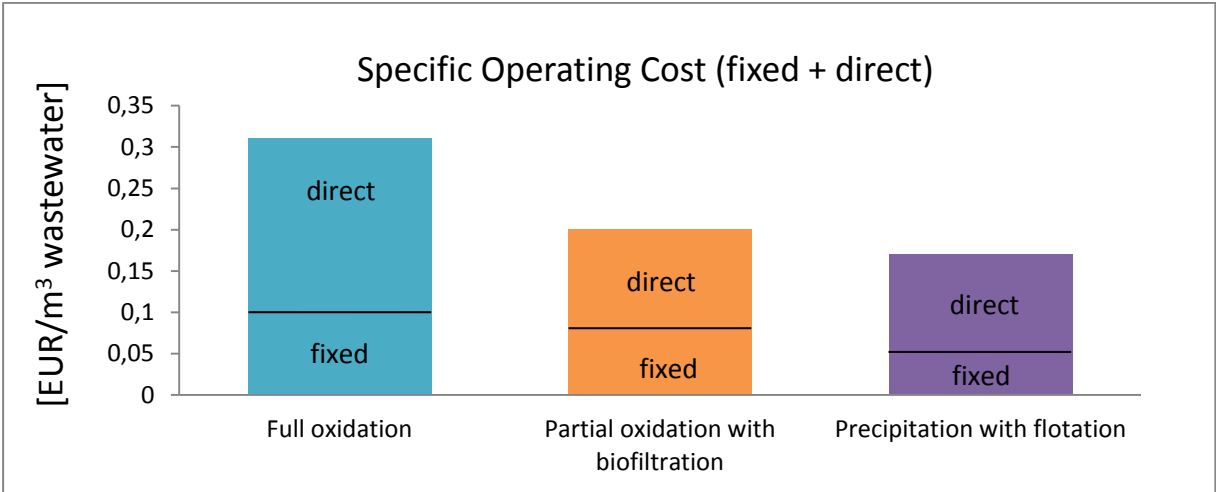


Figure 40: The specific operating cost (fixed + direct) per m³ treated water for the chemical treatment with precipitation and flotation, full oxidation and partial oxidation with subsequent biofiltration stage.

10.4 Sensitivity Analysis

10.4.1 Change in Sludge Handling Cost

The cost associated with the sludge handling procedure in the chemical treatment is of great importance as it will have a great impact on the total operating cost. Figure 41 is showing the specific operating cost (fixed + direct) per m^3 treated water for the treatments as a function of the sludge handling cost. The costs presented earlier are derived for a sludge handling cost of 59 EUR/tonne sludge, but if the sludge handling cost becomes higher than 100 EUR/tonne, partial oxidation will become a more economical alternative than chemical treatment, and if the sludge handling cost becomes higher than 285 EUR/tonne, full oxidation will also become a profitable alternative. No sludge is formed in the in the full oxidation process, and very small amounts of sludge is formed in the partial oxidation, which is why these graphs are linear.

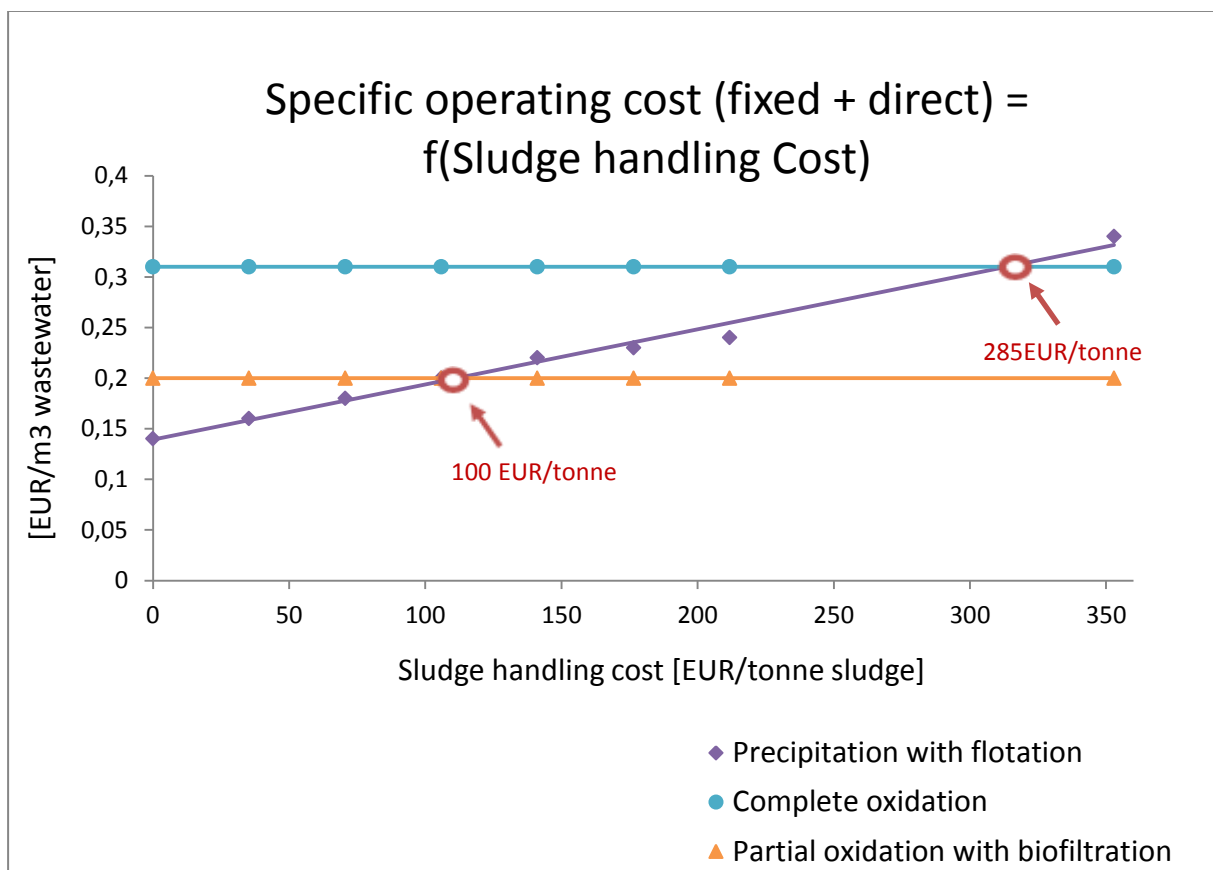


Figure 41: Specific operating cost (fixed + direct) per m^3 treated water as a function of the sludge handling cost for the chemical treatment with precipitation and flotation, full oxidation and partial oxidation with subsequent biofiltration stage.

10.4.2 Change in Electricity Price

In Figure 42 the specific operating cost (fixed + direct) is presented for a $\pm 25\%$ change in electricity price for each type of treatment. As seen from the figure, the specific operating cost for the chemical treatment is not affected by an increase/decrease in energy price, i.e. the curve is linear throughout (0.17 EUR/m^3). The electricity price will however have an impact on the final costs of the full and partial oxidation (the curves are leaning). A 25% increase in electricity price (0.0625 EUR/kWh) will yield a specific operating cost of 0.34 EUR/m^3 for the full oxidation and a cost of 0.21 EUR/m^3 for the partial oxidation. A 25% decrease in electricity price (0.0375 EUR/kWh) will yield a specific operating cost of 0.28 EUR/m^3 for the full oxidation and a cost of 0.18 EUR/m^3 for the partial oxidation. This means that the specific operating cost will almost be the same for the chemical treatment and the partial oxidation if the electricity price decreases by 25%. The full oxidation is the most expensive alternative, regardless if the electricity price drops.

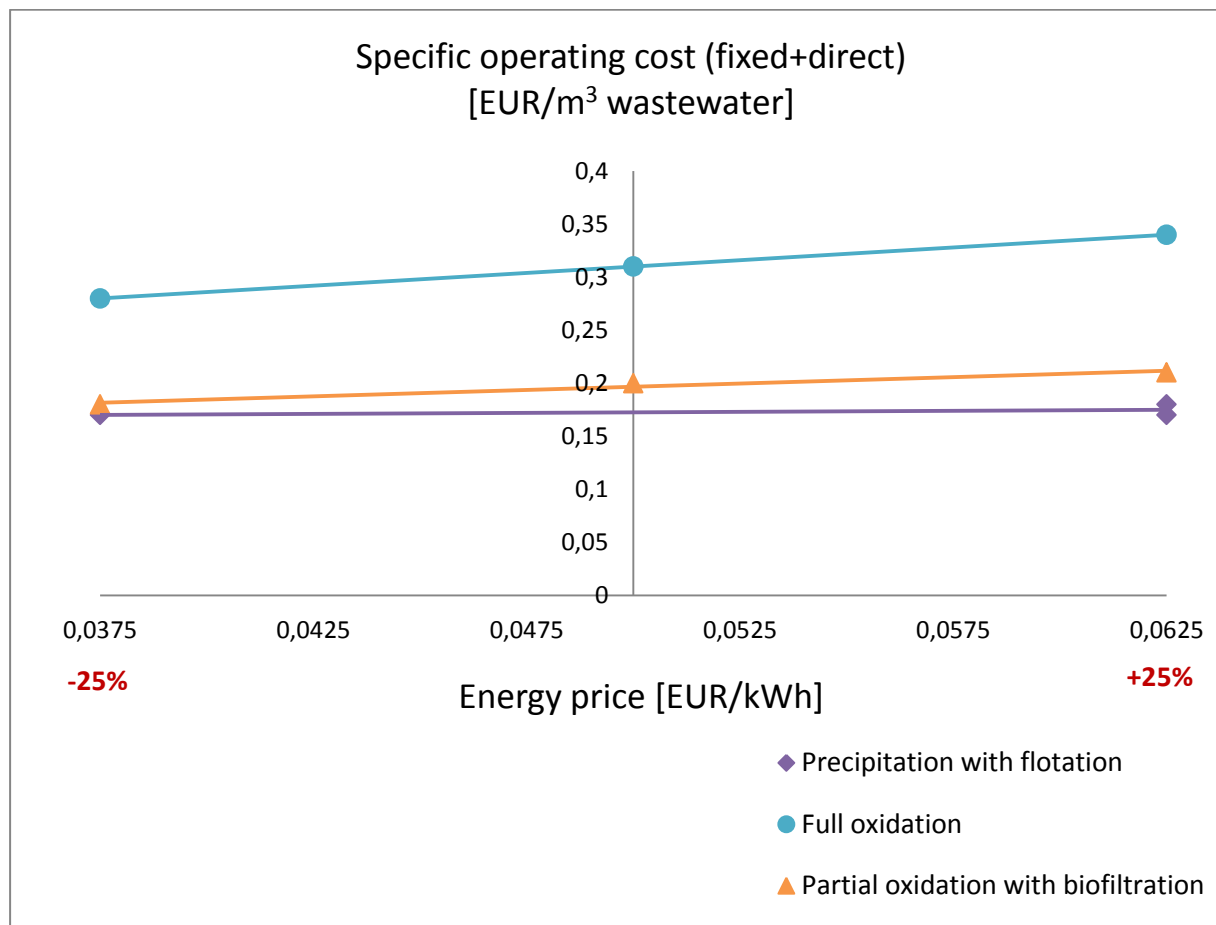


Figure 42: Specific operating cost (fixed + direct) per m^3 treated water as a function of the energy price for chemical treatment with precipitation and flotation, full oxidation and partial oxidation with subsequent biofiltration stage.

10.4.3 Change in Chemical Price

In Figure 42 the specific operating cost (fixed + direct) is presented for a $\pm 25\%$ change in chemical price for each type of treatment. As seen from the figure, the specific operating cost for the chemical treatment is affected by a change in the total chemical price as expected (the curve is leaning), i.e. an increase by 25% yields a specific operating cost of 0.19 EUR/m³ and a decrease with 25% yields a cost of 0.16 EUR/m³. The full and partial oxidations are not affected by a change in chemical price (the curves are linear) as no precipitation chemicals are used in the processes. This means that the specific operating cost will almost be the same for the chemical treatment and the partial oxidation if the chemical price increases by 25%. The full oxidation will be the most expensive alternative, regardless if the chemical price increases or not.

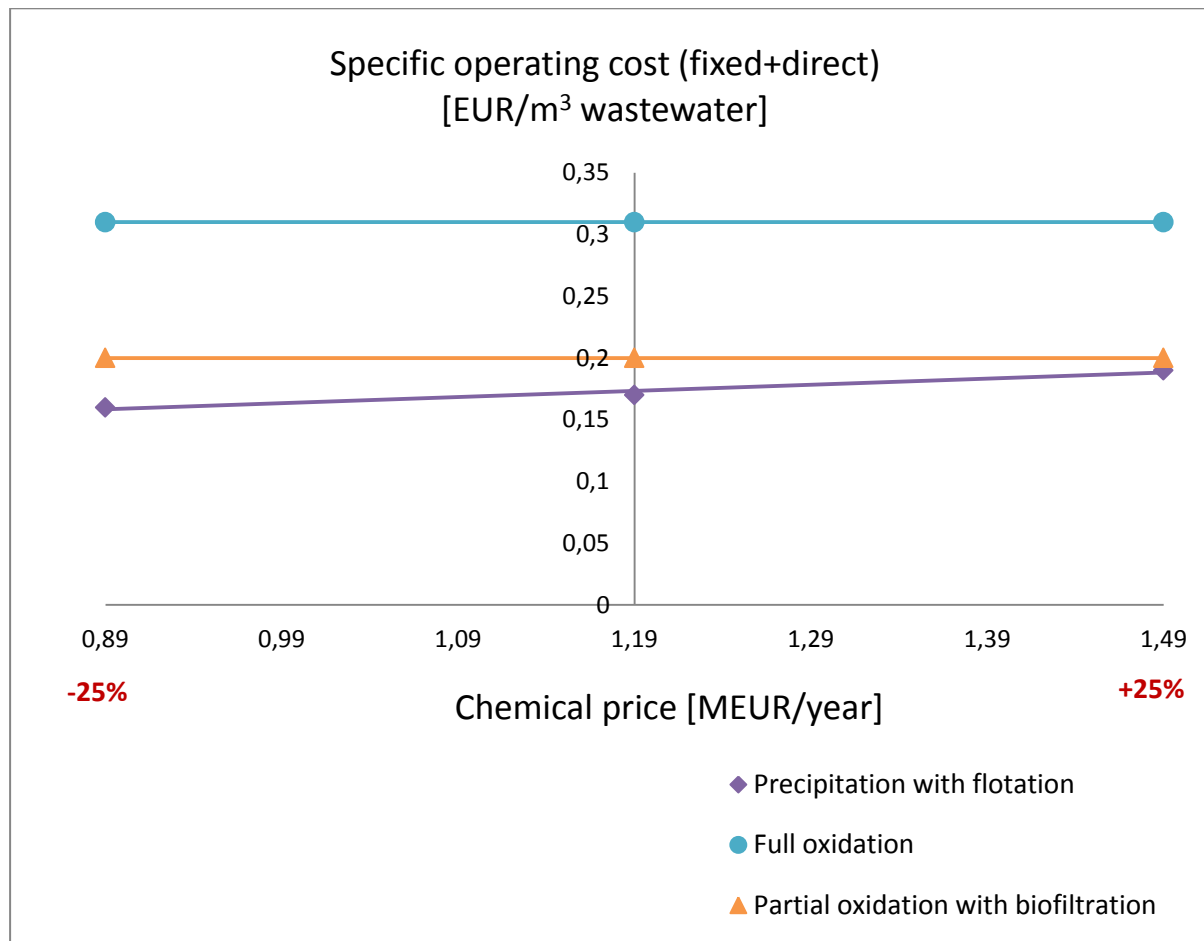


Figure 43: Specific operating cost (fixed + direct) per m³ treated water as a function of the chemical price for chemical treatment with precipitation and flotation, full oxidation and partial oxidation with subsequent biofiltration stage.

10.4.4 Change in fixed operating cost

In Figure 44, the fixed operating cost is varied with $\pm 25\%$ for each treatment type. This variation could potentially cover future change in interest rate, depreciation time and annuity as the market is changing. The shaded bars represent the specific operating costs (fixed + direct) which were presented earlier and the filled bars represent the $\pm 25\%$ change. As seen from the figure, a quite small change is observed in the overall specific cost for respective treatment when the fixed operating cost is varied. The full oxidation is still the most expensive treatment, and the partial oxidation and chemical treatment have similar costs. This means that the interest rate, depreciation time and annuity etc. can be varied with $\pm 25\%$ without having a significant impact on the outcome.

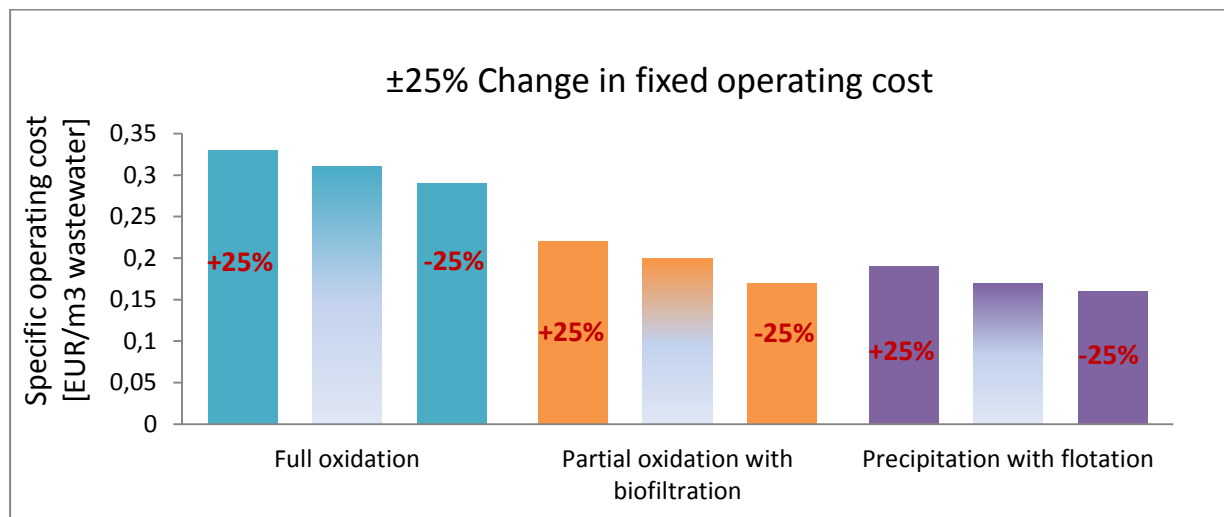


Figure 44: The specific operating cost (fixed + direct) for a $\pm 25\%$ variation in fixed operating cost.

11 Sources of Errors

The wastewater samples from Mill A, B and C all originate from cluster sampling. The wastewater flow rate and thus the pollutant concentrations are often fluctuating and are not constant in the pulp and paper industry. It is therefore preferable to collect wastewater during a longer time period to obtain representative averages from each mill. Wastewater samples are collected by staff that work at each mill who is not directly involved in the thesis, thus there may be room for improper sampling. Average flow rates are also preferable for the cost estimation as the dimensioning of a full scale plant is dependent on the wastewater flow rate.

Equipment and instruments do not always show the exact values, and it is therefore important to perform double measurements to identify the spread of the results. Because of the limited amount of time for this study, only a limited number of measurements are done. Results of Mill A and B are based on single measurements, whereas the COD, P-tot, PO_4^{3-} , N-tot, NH_4^+ , NO_3^- and NO_2^- results of Mill C are averages of two measurements. Lange cuvette tests used for the spectrophotometric analysis generally have a high precision and are well developed to deliver high-qualitative data. As shown in Appendix 4, the contingency for all Lange cuvettes is in general lower than 2%, which is considered low. However, results of Mill A and B are also qualitatively assured with help of the AOP plots in Figure 28-33. In the first three data points of the AOP graphs no H_2O_2 is added to the wastewater, which means that these point can be seen as double measurements and complement to the ozone treatment. From those graphs it is easy to see that there are very small variations occurring.

However, the main bias does not lay in the ozone detector, scale, Lange cuvettes, spectrophotometer or pipettes, but in the sample handling procedure. The samples are transported from Sweden to Germany and are kept cold and insulated. The transport is however not always smooth and samples are for sure mixed during transport. This will in turn affect the water matrix, but based on the circumstances this is accepted as the water is controlled at arrival in the laboratory.

Wastewater samples are carried in and out of the refrigerator and analysis are conducted during several days, which contribute to an aging of the wastewater. Suspended particles in the wastewater will with time dissolve and increase the concentrations of certain parameters in the water. Also, even though samples are shaken homogeneous before any treatment or analysis, there is a risk for sedimentation occurring in the sample bottles. This is an important consideration since most of the analysis are based on spectrophotometric measurements, and the amount of suspended particles will affect the outcome.

The assumption is made that all of the equipment used in the laboratory is clean. This is however very difficult to prove since it may be traces of detergents or dirt in containers that are not visible by eye, which in turn can contaminate the sample or interfere with the analysis. Finally it is important to remember that different laboratories have different routines, standards and people handling the equipment and instruments, and one should be careful to directly compare the data. All BOD analysis are conducted by an external laboratory in Germany, and it is

therefore necessary to freeze the effluent samples prior transport. The freezing will lower the bioactivity of the wastewater to a certain degree, but the impact is considered small enough to be neglected. Unfortunately no double measurements are conducted for the BOD tests.

12 Discussion

Chemical treatment (precipitation/flocculation) is applied at a number of sites, and today the most established purification method to remove COD from pulp and paper mill effluents. The technology has been used for several years and the costs are therefore well known. The treatment is relatively fast, reaction mechanisms are known and apart from COD, residual BOD and phosphorus are removed from the system, contributing to relatively pure water that is discharged to the recipient. However, the direct operating cost for the treatment is high as large amounts of chemicals are used in the process, and consequently a large quantity of sludge is generated that has to be disposed. The sludge contains a high concentration of microorganisms and residues of chemicals which put stress on surrounding land and water if disposed on landfills. Incineration is not an energy efficient alternative because of the high water and ash content of the sludge, and sometimes off-gases containing harmful components (NO_x etc.) are produced which have a negative impacts on the environment.

Oxidation technology has many advantages in comparison to chemical treatment. For example, pollutants are destructed rather than concentrated or transferred into a different phase, which means that COD, colour and toxicity is decreased without the need to handle large amounts of sludge. There is for example no production of excessive sludge in the full oxidation with ozone and only a small portion of sludge is produced in the subsequent biological stage of the partial oxidation with ozone. Oxidation technology is therefore seen as a more environmental alternative in regards to sludge handling compared to the chemical treatment.

Oxidation processes (as ozone treatment or combined oxidation processes) are often very flexible concerning water quality variations and the possibility to control the quality contents of the residual wastewater is high. High COD reductions are observed for wastewaters treated with ozone in the experimental part of this study without having an appreciable impact on other parameters such as N-tot, NO_2^- , NO_3^- , NH_4^+ , P-tot and PO_4^{3-} . In addition, an extensive decolourization is observed which enables a recycling of wastewater in the pulp and paper making process and perhaps for white water production.

The ozone treatment has a simple process design and operation. The system enables an automatic and independent operation with online control equipment that can measure COD and residual ozone in the off-gas. This means that the human factor is limited to occasional inspection tours and the major services, and thus few personnel is needed to supervise the process. As the system works automatically it immediately reacts on online parameters indicating the current COD load respectively variations in flow, which means that the effluent quality can be modified by the ozone dosage. The chemical treatment on the other hand is manually adapted and has to consider maximum condition in flow and load, which introduces a higher risk of overdosing.

Ozone is however a quite toxic gas which could cause health and safety problems for workers in the treatment plant if released to the surrounding air. This effect is on the other hand minimized by process closure and highly developed safety systems. In addition, the residual ozone is

transferred back into oxygen after passing the ozone destructor which then can be discharged directly to the atmosphere (respectively reused somewhere else in the process).

Ozone treatment is a more expensive alternative for COD elimination in pulp and paper mill effluents in comparison to the chemical treatment. This is mainly because of the large amount of oxidant needed for mineralization of the organic material and the high power demand of the process. The direct operating cost can be lowered if partial oxidation is applied where a lower amount of ozone is used to first crack the long-chained organic molecules into smaller fractions (to improve the BOD/COD ratio of the effluent), which then are eliminated in a subsequent biofiltration stage.

The biofiltration stage will remove excess BOD and perhaps parts of the remaining COD but will on the other hand introduce new concerns. There might be problems with the design of the system if for example floating sludge is formed in the filters. A chemical treatment plant with a flotation unit has a better design and capacity to handle such phenomena. It is also difficult to tell if the final effluent quality will differ for a partial oxidation with a biofiltration stage in comparison to a full oxidation with no biofiltration stage. The biodegradability and thus the BOD load of the final effluent will increase with an increase in ozone dosage according to the test results. Only at very high ozone dosages, excess BOD can be eliminated also for the full oxidation but would introduce very high costs. Recirculation of effluent to a secondary biology could potentially be an alternative to post treatment with biofilters, but would mean on the other hand an extension of the treatment plant because very large flows and loads would have to be taken care of.

There are very few AOPs that have been applied in large scales yet for the treatment of pulp and paper mill wastewaters, and thus the uncertainties regarding the system are high. Reactions with OH^* radicals are very unselective, mechanisms and kinetics are relatively unknown, and there is no clear evidence that toxic by-products are not formed during reaction. Ozonation is used extensively in the pulp bleaching but is a new concept on the market in terms of wastewater treatment. People are therefore cautious, and more full scale installations have to be reported before the pulp and paper industry is willing to invest in the AOP technology.

13 Conclusion

The oxidation technology, and especially treatment with ozone, offers several advantages in comparison to chemical treatment used today. For example, pollutants are destructed rather than concentrated or transferred into a different phase, which means that COD, colour and toxicity is decreased without the need to handle large amounts of sludge. The processes are often very flexible concerning water quality variations and the possibility to control the quality contents of the residual wastewater is high.

The experimental results indicate that treatment with ozone is an efficient method for elimination of COD from pulp and paper mill wastewaters. A relatively high COD reduction (41 % for Mill A, 31% for Mill B and 53% for Mill C) was achieved for all wastewaters with an applied ozone dosage of 0.2g O₃/L, without an appreciable impact on other parameters such as pH, N-tot, NO₂⁻, NO₃⁻, NH₄⁺, P-tot and PO₄³⁻. There are indications that the nature of the wastewater has an impact on the COD removal efficiency and that TMP wastewater is easier to oxidize in comparison to wastewater from sulphate mills. The combination with hydrogen peroxide did not show any further COD reduction compared to ozone treatment alone, thus confirming the results Ko et al. showed in their study in 2009.

However, the total cost is very high in comparison to chemical treatment (precipitation/flocculation) even though there are indications of cases when treatment with ozone can be profitable (e.g. if the cost for sludge handling increases in the future, price for chemicals increases and electricity price decreases). There are also some uncertainties regarding the system and there is no clear evidence that toxic by-products are not formed. More research must be done and more full-scale installations must be reported before the pulp and paper industry is willing to invest in oxidation technology. An interesting approach is the attempt to develop an even better designed treatment option as oxidation and subsequent biofiltration as nearly "one" tertiary treatment unit.

14 Recommendations

Much research has been done within the field of advanced oxidation processes and there is no doubt that these methods work and are efficient for COD elimination in pulp and paper mill wastewaters. It is more a question about how much people are willing to pay for the technique. However, there is still no one who has managed to characterize the water matrix completely in order to determine whether hazardous by-products are formed or not. This thesis provides a good overview of the different effluent parameters and how they are changing throughout the oxidative treatment, but a survey on molecular level would be required in the future for a complete characterization. Additional parameters such as TOC and AOX should also be specified in such study.

It would also be of interest to investigate how the TSS concentration of a wastewater is affecting the COD reduction for a specific ozone dosage, as suspended particles probably will influence on the treatment efficiency. This aspect is important to consider for a full scale implementation in order to make a complete dimensioning and to know if pre- or post-clarification is required in the treatment plant. However, in able to investigate that, the test equipment must be developed to manage high concentration of solids in pumps and injectors without clogging the system.

An increase in turbidity is seen for all wastewaters tested in this study at ozone dosages above 0.15 g O₃/L, and even if no obvious particles are seen in the final effluent; the filter paper is clogged easily and fast in the TSS analysis. This observation should be further examined because it may indicate that ozone can be used in the future to improve the flocculation ability of wastewaters.

The wastewater quality is unique for every mill in the world as there are variations in product lines, design and legislation. In this study only three types of wastewaters are tested. It would be preferable to test even more wastewaters in order to find out how ozone is reacting with different types of water. For example, a CTMP wastewater would be suitable for such a study.

One part of the economic study in this thesis is based on a subsequent biofiltration stage although no experimental trials are conducted. Here, it is desired to follow up with testing in order to find out how large portion of the BOD and COD actually is removed in such step. Finally, it is of interest to test the actual performance of other AOPs as well, and not only O₃ and O₃ in combination with H₂O₂ as in this study.

15 References

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Appendix 1 – Draft BAT 2012

Integrated Pollution Prevention and Control

Draft Reference Document on Best Available Techniques (BAT)

Reference Document for Production of Pulp, Paper and Board

Data compared to BAT 2001.

PROCESS	Flow rate [m ³ /Adt]	COD [kg/Adt]	BOD [kg/Adt]	TSS [kg/Adt]	AOX [kg/Adt]
<i>Bleached Kraft 2001</i>	30-50	8-23	0.3-1.5	0.6-1.5	<0.25
<i>Bleached Kraft 2012</i>	25-50	5-17	-	0.02-1.5	0-0.2
<i>Unbleached Kraft 2001</i>	15-25	5-10	0.2-0.7	0.3-1	-
<i>Unbleached Kraft 2012</i>	15-40	1.2-8	-	0.3-1	-
<i>Bleached Sulphite 2001</i>	40-55	20-30	1-2	1-2	-
<i>Bleached Sulphite 2012</i>	25-50	10-30	-	0.4-1.5	0.5-1.5*
<i>Non-integrated CMP 2001</i>	15-20	10-20	0.5-1	0.5-1	-
<i>Non-integrated CMP 2012</i>	9-15	12-15	-	0.5-0.9	-
<i>Integrated Mechanical 2001</i>	12-20	2-5	0.2-0.5	0.2-0.5	<0.01
<i>Integrated Mechanical 2012</i>	9-15	0.9-5	-	0.06-0.4	<0.004
<i>Integrated RCF (without de-inking) 2001</i>	<7	0.5-1.5	0.05-0.15	0.05-0.15	<0.005
<i>Integrated RCF (without de-inking) 2012</i>	1.5-5	0.4-1.2	-	0.02-0.2	<0.001
<i>Integrated RCF (with de-inking) 2001</i>	8-15	2-4	0.05-0.2	0.1-0.3	<0.005
<i>Integrated RCF (with de-inking) 2012</i>	8-15	0.6-3	-	0.08-0.3	<0.0004

* Not applicable to TCF bleaching, gentle ClO₂ bleaching

Example of calculation for comparison of COD discharge limits of BAT 2001 and 2012 (Bleached Kraft pulp mill)

COD limits of 2001 converted into mg/L:

$$\text{Lower limit: } \frac{8 \text{ kg/Adt}}{30 \text{ m}^3/\text{Adt}} * 1000 = 267 \text{ mg/L}$$

$$\text{Upper limit: } \frac{23 \text{ kg/Adt}}{50 \text{ m}^3/\text{Adt}} * 1000 = 460 \text{ mg/L}$$

$$\Rightarrow 267 - 460 \text{ mg COD/L}$$

COD limits of 2012 converted into mg/L.

$$\text{Lower limit: } \frac{5 \text{ kg/Adt}}{25 \text{ m}^3/\text{Adt}} * 1000 = 200 \text{ mg/L}$$

$$\text{Upper limit: } \frac{17 \text{ kg/Adt}}{50 \text{ m}^3/\text{Adt}} * 1000 = 340 \text{ mg/L}$$

$$\Rightarrow 200 - 340 \text{ mg COD/L}$$

Reduction in COD since 2001:

$$\text{Lower limit: } \left(1 - \frac{200}{267}\right) * 100 = 25\%$$

$$\text{Upper limit: } \left(1 - \frac{340}{460}\right) * 100 = 26\%$$

Appendix 2 – New Effluent Discharge Standards of China 2008

New paper industry effluent pollutant discharge standards - China 2008

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Table 2, Limits for Pulp and Paper Mills started after July 1st 2008

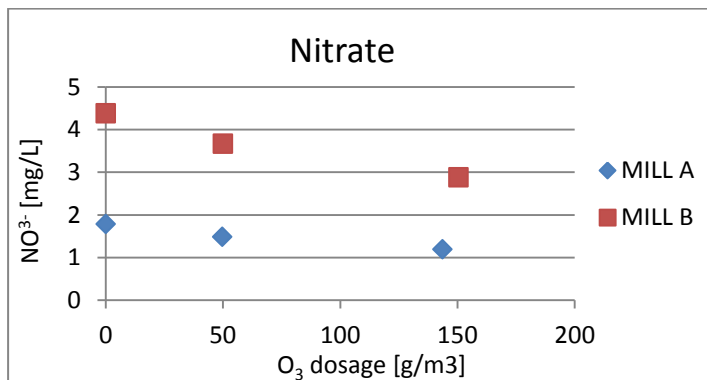
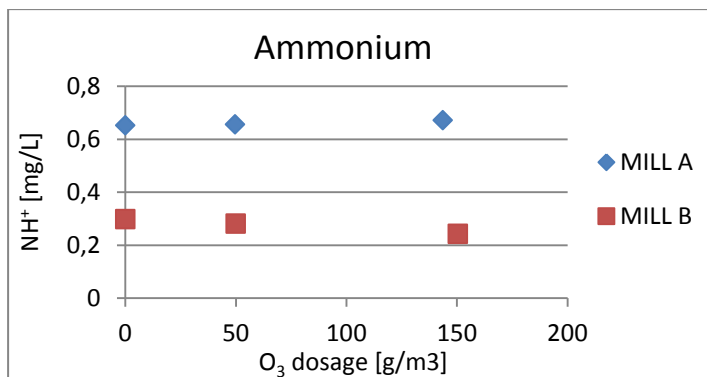
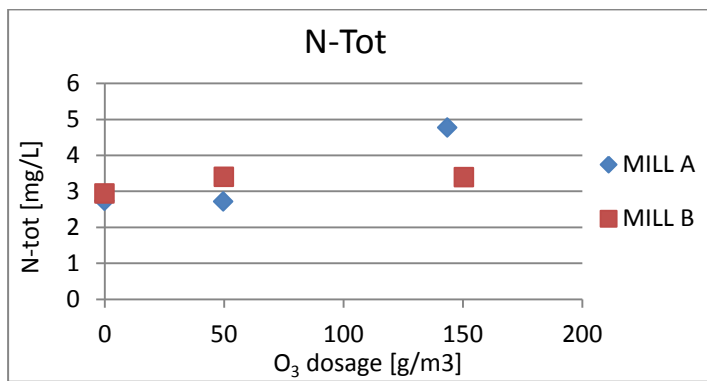
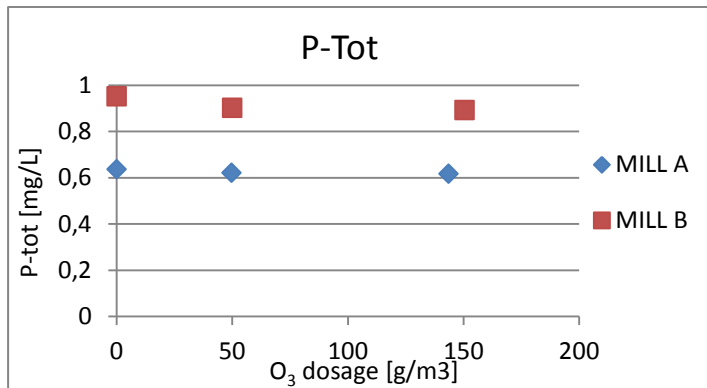
	type of mill		pulp mill	Pulp & Paper integrated mill	paper mill	monitoring point for pollutant discharge
	discharge concentration limit	1	CODCr, mg/L	100	90	80
2		total P (mg/L)	0,8	0,8	0,8	exit of effluent treatment plant
3		total N (mg/L)	15	12	12	exit of effluent treatment plant
4		NH3N (mg/L)	12	8	8	exit of effluent treatment plant
5		BOD5, mg/L	20	20	20	exit of effluent treatment plant
6		SS, mg/L	50	30	30	exit of effluent treatment plant
7		AOX, mg/L	12	12	12	discharge point of plant or manufacturing facility
8		pH	6□9	6□9	6□9	exit of effluent treatment plant
9		Color (dilutiontimes)	50	50	50	exit of effluent treatment plant
10		Dioxin (pgTEQ/L)	30	30	30	discharge point of plant or manufacturing facility
specific effluent discharge limit as per ton of product, t/t (pulp)			50	40	20	
note: 1 AOX and Dioxin are applicable for processes using elemental chlorine bleaching. 2. specific production of pulp and paper as bone dry ton 3. for integrated pulp and paper mills, the effluent discharge limits are based the total of own pulp production and market pulp 4. mills with own-generated RC pulp accounting for more than 80% of the fiber used, effluent discharged limit base on 20t/t(pulp) . 5. mill with non-wood bleached pulp accounting for more than 60% of fiber used , effluent discharged limit base on 60t/t(pulp)						

- existing pulp and/or paper mills should comply with limits set by table 2 by 1st Jan 2010;
- new pulp and paper mills should comply with the limits set by table 2 starting from 1st July 2008.

Table 3, Limits for both existing and new pulp and paper mills located in sites requiring for extra environmental care.

	type of mill		pulp mill	Pulp & Paper integrated mill	paper mill	monitoring point for pollutant discharge
		1	CODCr, mg/L	80	60	50
2		total P (mg/L)	0,5	0,5	0,5	exit of effluent treatment plant
3		total N (mg/L)	10	10	10	exit of effluent treatment plant
4		NH3N (mg/L)	5	5	5	exit of effluent treatment plant
5		BOD5, mg/L	10	10	10	exit of effluent treatment plant
6		SS, mg/L	20	10	10	exit of effluent treatment plant
7		AOX, mg/L	8	8	8	discharge point of plant or manufacturing facility
8		pH	6□9	6□9	6□9	exit of effluent treatment plant
9		Color (dilutiontimes)	50	50	50	exit of effluent treatment plant
10		Dioxin (pgTEQ/L)	30	30	30	discharge point of plant or manufacturing facility
specific effluent discharge limit as per ton of product, t/t (pulp, paper)			30	25	10	
note: 1 AOX and Dioxin are applicable for processes using elemental chlorine bleaching. 2. Specific production of pulp and paper as bone dry ton 3. for integrated pulp and paper mills, the effluent discharge limits are based the total of own pulp production and market pulp 4. mills with own-generated RC pulp accounting for more than 80% of the fiber used, effluent discharged limit base on 15t/t(pulp) .						

Appendix 3 - AOP results



Appendix 4 – Technical data for Validation of LCK Cuvette Tests

Data collected from Quality certificate of each LCK method.

Analysis	Method	Method variation coefficient	Method standard deviation	Confidence interval (95%)
COD	LCK614 (Mill A & C)	0.33%	3.5 mg/L	± 8.7 mg/L
	LCK514 (Mill B)	0.98%	1.6 mg/L	± 3.9 mg/L
NO ₂ ⁻	LCK341	1.32%	0.015 mg/L	± 0.035 mg/L
NO ₃ ⁻	LCK339	0.57%	0.19 mg/L	± 0.45 mg/L
NH ₄ ⁺	LCK304 (Mill A & B)	0.57%	0.19 mg/L	± 0.45 mg/L
	LCK305 (Mill C)	1.63%	0.13 mg/L	± 0.33 mg/L
P-tot/ PO ₄ ³⁻	LCK349	0.36%	0.005 mg/L	± 0.012 mg/L

Appendix 5 – Raw Data

All raw data belongs to ÅF and is considered as internal information. However, the raw data may be assigned upon request by Irma Karat or authorized person at ÅF Forest Industry.

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