Combined biological and advance oxidation processes for paper and pulp effluent treatment

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Declaration:

I declare that this dissertation is my own unaided work. It is being submitted for the degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

………………………………………..
Antonie Brink

…………. day of ………………year……………….

Executive summary

Recently, the South African paper and pulp industry has become increasingly interested in the development of suitable wastewater treatment technologies able to assist in the closure of the water network and also to minimize their environmental footprint at their sites. Factors such as the rising cost of fresh water, stricter environmental legislation and socio-political pressure have forced water intensive users to become less dependent on the municipalities.

The research described here addresses wastewater problems from two separate mills. Mill X (Case A) is relying on the municipality for fresh water and the treatment of their effluent. The mill wants to become less dependent on the municipality by closing the water network (zero effluent discharge). A wastewater treatment plant (WWTP) would be required to reduce the chemical oxygen demand (COD), total suspended solids (TSS) and colour before any processes water could be reused. Mill Y (Case B) is currently using their effluent for the irrigation of the local plantation. The mill would like a wastewater treatment plant able to reduce the biodegradable material prior to irrigation. Excessive amounts of biodegradable organics in the effluents can cause bacterial and fungal growth in the irrigations systems and consequently clogging problems. More advanced treatment steps would also be required to lower the bio-recalcitrant COD to environmental discharge limits (<400 mg/L). As a result, this study investigated the potential of combining biological and advanced oxidation processes (AOP) for effluent treatment at both mill effluents.

An extensive literature study on the treatment of paper and pulp mill effluents was conducted to get a comprehensive understanding of the treatment technologies/combinations. The treatment of paper and pulp mill effluents can be divided into three distinct treatment stages namely:

- Primary treatment: For the removal of the total suspended solids (TSS)
- Secondary treatment: For the removal of the biochemical oxygen demand (BOD)
- Tertiary treatment: Mainly for the removal of bio-recalcitrant chemical oxygen demand (COD) and colour

Mill X and Mill Y already contained primary clarifiers to remove the majority of the total suspended solids (TSS). Consequently, the secondary and tertiary treatment steps were evaluated.

A detailed technology selection assessment was done to select the best suited secondary and tertiary treatment technologies for the purpose of this project. The work demonstrated that an aerobic MBBR could be used in combination with Fenton related treatment technologies in order to comply with the individual mill specifications. The applicability of both these biological and AOP treatment solutions was therefore extensively investigated.

The results indicated that the aerobic moving bed biofilm reactor (MBBR) was able to remove the majority of the biodegradable organics from the recycle and neutral semi-sulfite chemical pulping mill effluents. The optimal COD removal efficiency ranged between 46% and 57% for the various effluents. The effluent from Mill X was generally found to be more readily biodegraded than the effluents from Mill Y. Experimental results indicated that certain effluents contain organics that display antimicrobial properties. The maximum substrate removal rate decreased linearly with an increase in phenols. As a result, it was therefore assumed that lignin derived alkyl phenols might have inhibited aerobic and anaerobic microbial digestion processes. The results indicate that the MBBR system was not fully acclimatized for high phenolic wastewaters. It is therefore recommended that future experimental studies consider the effects of phenolic content and employ longer acclimatization periods. A significant fraction of the paper and pulp mill effluents were considered to be bio-recalcitrant and required tertiary treatment to be removed.

It was found that both the Fenton (Fe^{3+}/H_2O_2) and Fenton-like (Fe^{3+}/H_2O_2) oxidation processes can remove bio-recalcitrant organics from biologically treated mill effluents (BTME). However, preliminary experimental results indicated that the Fenton process had a faster oxidation rates. For the Fenton process, the optimal COD removal efficiencies ranged between 40% and 67% for the BTMEs. The experimental results also demonstrated that a combination of Fenton oxidation and slaked lime treatment can effectively remove the colour of BTMEs (97%). The COD removal rates for the neutral sulfite semi-chemical (NSSC) effluents were found to be higher than that of the recycle mill effluent (RME). The aromatic and volatile organic acid (VOA) content of the BTMEs had an important role in the oxidizing processes. The BTMEs with a higher volatile organic acid (VOA) content generally had slower oxidizing rates. The experimental results indicated that the combination of an aerobic MBBR and Fenton process can be implemented at both paper and pulp mills to assist with their individual treatment requirements.

An economic study for Case A (Mill X) was also conducted. The data obtained throughout this study was linked to previous water optimization work done at the mill. The economic analysis demonstrated that the aerobic moving bed biofilm reactor (MBBR) and Fenton treatment combination could treat the recycle mill effluent for reuse in a cost-effective manner. The total capital investment cost of the treatment plant was estimated to be R

28.5 million and the operational cost was found to be R12.21/m^3 of wastewater. The implementation of this treatment solution on the water network could save the mill approximately R 1.25 million/year. The rising cost of fresh water and discharge might increase the economic feasibility of such a WWTP in the near future.

Dedication

In loving memory of my sister, Marquerite

Acknowledgements

‘*The most exciting phrase to hear in science, the one that heralds the most discoveries, is not “Eureka!” (I found it!) but “ That’s funny….” Issac Asimov.*

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Nomenclature

C_o	Initial chemical oxygen demand concentration, mg/L
C_F	Effluent chemical oxygen demand concentration, mg/L
f_b	Biodegradable COD fraction
X	Biomass concentration, mg VSS/L
V	Reactor volume, m^3
Q	Volumetric flowrate, m^3/hr
k_x	First order kinetic rate constant, L/mg VSS.day
k_{x1}	Lumped first order rate constant, 1/hr
K_B	Saturation constant, g COD/L.d
U_{max}	Maximum substrate removal rate, g COD/L.d
a	Grau second order kinetic constants, hr
b	Grau second order kinetic constants (dimensionless units)
t	Reaction time, min
C_{CODo}	Initial chemical oxygen demand concentration, mg/L
C_{COD}	Chemical oxygen demand concentration, mg/L
COD_{rd}	Readily degradable chemical oxygen demand, mg/L
COD_{sd}	Slowly degradable chemical oxygen demand, mg/L
C_A	Concentration of readily degradable constituents, mg/L
C_B	Concentration of slowly degradable constituents, mg/L
A_i, B_i, C_i, D_i	2^k factorial design constants
k_i	First/second order reaction rate constants for individual reactions , min^{-1} (first order); $L.mg^{-1}.min^{-1}$(second order)
$k_{app,i}$	Apparent rate constants for first and second order models, min^{-1} (first order); $L.mg^{-1}.min^{-1}$(second order)
m	BMG kinetic parameter
b	BMG kinetic parameter
t	Reaction time (min)
x_i, y_i	Chemical oxygen demand conversion constants

Abbreviations

AOX	Adsordable organic halides
AOP	Advanced oxidation processes
BOD	Biochemical oxygen demand
$BTME$	Biologically treated mill effluent
COD	Chemical oxygen demand
DO	Dissolved oxygen concentration
HRT	Hydraulic residence time
LC_{50}	Lethal concentration 50%
$MBBR$	Moving bed biofilm reactor
$NSSC$	Neutral sulfite semi-chemical
OLR	Organic loading rates
$PPME$	Paper and pulp mill effluent
RME	Recycle mill effluent
$sCOD$	Soluble chemical oxygen demand
TSS	Total suspended solids
TDS	Total dissolved solids
VSS	Volatile suspended solids
VOA	Volatile organic acids
$WWTP$	Wastewater treatment plant
ZLD	Zero liquid discharge

Chapter 1. Background

The global dependence on limited usable water resources is a growing issue that greatly influences domestic needs and economic growth. The imbalance between supply and demand in South Africa is primarily caused by poor wastewater management, low rainfall and the increase in pollution load (DWAF 2010). The South African paper and pulp industry is highly water intensive and produces large volumes of organic rich wastewaters. The fresh water consumption and wastewater production is estimated to be around 130 million m^3/annum and 60 m^3/ ton of paper, respectively (WRC 1990; Reddy et al. 2005).

Wastewaters originating from the paper and pulp industry generally contain cellulosic material, lignin, phenols, mercaptans, chlorinated and sulfite complexes and volatile organic acids (Merayo et al. 2013; Carg 2012). As a result, this wastewater is generally high in chemical oxygen demand (COD), biochemical oxygen demand (BOD), suspended solids and colour (Pokhrel & Viraraghavan 2004). South African environmental legislation requires that paper and pulp mills treat their effluents prior to disposal. The direct discharge of untreated paper and pulp mill effluents can have a negative impact on both aquatic and terrestrial environments.

The excess biodegradable matter present in untreated effluents can cause oxygen depletion, slime growth and scum formation in surrounding waterbodies (Garg & Tripathi 2011). The toxic bio-recalcitrant organics are primarily lignin derived which include constituents such as phenols, resins, lignosulphonic acids and other hydrocarbons (Garg and Tripathi, 2011; Raj et al. 2007). Certain alkyl phenols originating from the paper and pulp industry can be considered detrimental to the aquatic environment at concentrations as low as 1- 20 mg/L (Staples et al. 2002). In addition, resin acids can accumulate in sediment and be responsible for chronic and acute toxicity in fish species (Liss et al. 1997). The dark colour of certain BTMEs lowers the aesthetic water quality and hinders natural photosynthesis in aquatic systems (Murugesan 2003; Kannan & Oblisami 1990). Chlorine bleaching effluents can contain harmful mutagenic constituents such as dioxins and furanones. Bleaching toxins can also alter the growth, mortality, maturation and metabolisms of various fish species (McMaster & Hewitt 2011). The disposal of mill effluents to the terrestrial environment by means of irrigation can have negative implications. Using diluted paper and pulp mill effluents for irrigation generally has positive effects on the physical and chemical properties of the soil as well as the growth of plants (Ullah 2012; Tripathi et al. 2014). However, non-diluted full strength paper and pulp mill effluents can have a negative impact on plant growth (Medhi et al. 2011). In South Africa, there have been cases reported where toxic bio-recalcitrant organic constituents present in the paper and pulp mill effluents percolated through irrigated lands and into surrounding waterbodies (Leske 1995). Consequently, the treatment of the biodegradable and bio-recalcitrant organics is considered to be a critical aspect for the future preservation of aquatic and terrestrial environments.

The market for wastewater treatment in the paper and pulp industry is expected to increase by 60% from 2012 to 2020 (Meyer & Edwards 2014). Wastewater treatment in the paper and pulp industry could be divided into primary, secondary and tertiary treatment technologies. Primary systems commonly include clarifiers and flotation units which remove the majority of the total suspended solids (TSS) (Biermann 1996). Secondary biological treatment is incorporated into wastewater treatment plants (WWTPs) to remove excess biodegradable material (Bishnoi et al. 2006). Secondary treatment systems incorporate a combination of aerobic and anaerobic biological processes to remove the majority of biodegradable compounds. These aerobic treatment systems could include activated sludge (AS) units, moving bed biofilm reactors (MBBR), aerated lagoons (AL), sequencing batch reactors (SBR) and membrane bioreactors. The anaerobic treatment systems includes upflow anaerobic sludge blanket (UASB) reactors, anaerobic baffled reactors (ABR), anaerobic fluidized bed reactors and anaerobic membrane reactors (AnMBR). Tertiary systems are incorporated in cases where the quality of biologically treated effluent is still insufficient for disposal or reuse. Advanced oxidation processes (AOP), membrane filtration and biological filters are usually implemented as a tertiary treatment system (Karat 2013).

The rising cost of fresh water, stricter environmental legislation and socio-political pressure are all factors that contributed to the paper and pulp industry adopting zero liquid discharge (ZLD) policies. The reuse of process water can ultimately decrease operational and discharge costs at the mill (Habets & Driessen 2007). The implementation of primary, secondary and tertiary treatment systems are required to close the water network at mills. Tertiary membrane filtration processes are generally required to achieve complete water network closure. The problem with employing membrane filtration processes directly are related to membrane fouling and highly concentrated bio-recalcitrant retentated streams. The coupling of membrane processes with advanced oxidation processes (AOP) have yielded promising results by reducing the initial membrane fouling (Oh et al. 2009) and cleaner retentate streams (Hermosilla et al. 2012).

The treatment of paper and pulp mill effluents with biological and advanced oxidation processes (AOP) will not only assist the paper and pulp industry to comply with environmental legislation but will also contribute in the closure of the water network. As a result, this technical and economic study investigates the potential of combining biological and AOP techniques for the treatment of PPMEs.

1.1 Problem statement

The research in this study aims to address the wastewater treatment problems at two separate mills. Mill X primarily uses recycled fibre as feedstock for the pulping process. The mill already contains a primary clarifier to remove the majority of the total suspended solids (TSS). However, the mill discharges the effluent and relies on the local municipality for freshwater and effluent treatment. The mill currently pays for fresh water (R15.60/m^3) and discharge (R4.60/m^3) of the effluent. Previous water network optimization research at the mill was aimed to minimize the fresh water demand and closing the water network (Vurdiah 2015). This research suggested that a wastewater treatment plant is required to reduce the COD, BOD, TSS and colour before more process water can be reused (Vurdiah 2015). The closure of the water network generally leads to the build-up of contaminants. By closing the water network, the organic and inorganic constituents can cause slaking, slime formation and clogging problems. To move one step closer to complete water network closure (zero liquid discharge) at the mill, it is necessary for both biological and advanced oxidation processes (AOP) be implemented at Mill X.

Mill Y uses both recycle and virgin fibre in a neutral sulfite semi-chemical (NSSC) pulping process. The wastewater is currently being treated by primary clarifiers, dissolved air floatation unit (DAF), cascading dams and filtration units prior to irrigation. Recent socio-political pressure has urged for the removal of the cascading dams. As a result, a wastewater treatment plant is required to reduce the biodegradable matter of the effluent prior to irrigation. Excessive amounts of biodegradable matter can initiate bacterial and fungal growth in the irrigation systems and evidently lead to clogging problems. Environmental legislation also requires that the chemical oxygen demand (COD) should be within irrigation limits (< 400 mg/L). The secondary biological treatment systems can reduce the biochemical oxygen demand (BOD). However, low BOD/COD ratios (0.22 - 0.35) indicate that biological systems alone will not be able to achieve the COD irrigations limits. Consequently, the implementation of both biological and AOP technologies are essential to reduce the BOD and COD concentrations prior to irrigation.

1.2 Aim and objective

The aim of this project was to investigate the technical and economic potential of combining biological and advanced oxidation processes (AOP) for the treatment of paper and pulp mill effluents. The main objectives of this dissertation are given as follows:

1. Identify and select suitable biological and AOP technologies for the treatment of paper and pulp mill effluents.

2. Determine the performance capabilities and kinetics of the biological treatment process selected in Objective 1.
3. Investigate the performance capabilities and kinetics of the AOP technology selected in Objective 1.
4. Evaluate the economic feasibility of the selected biological and AOP treatment technologies.

1.3 Dissertation description

Chapter 1 gives a brief description of the necessity of wastewater treatment in the paper and pulp industry. A comprehensive literature study was conducted for the purpose of identifying suitable treatment strategies and technologies in Chapter 2. The technology selection process for this project is given in Chapter 3. The potential of an aerobic moving bed biofilm reactor (MBBR) for the treatment of paper and pulp mill effluent was investigated in Chapter 4. Whereas, the potential of the Fenton and Fenton-like treatment processes are discussed in Chapter 5 and 6, respectively. Chapter 4 to Chapter 6 are written articles which were submitted to *Journal of Water Process Engineering*, *Process Safety and Environmental Protection* and *TAPPSA* for publication. The economic feasibility of aerobic MBBR, Fenton, Fenton-like treatment technologies are discussed in Chapter 7. The main conclusions and recommendations that could be devised from this research are presented in Chapter 8.

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Chapter 2. Literature review

2.1 Pulp and paper manufacturing process

Cellulosic fibres obtained from plant materials, agricultural residues and recycled paper are traditionally used in the pulp and paper manufacturing process (Bajpai 2011). The primary processes involved in the pulp and paper manufacturing are: wood handling and debarking, pulping and paper manufacturing. In this section; these primary processes are described.

2.2 Wood handling and debarking

Bark accounts for 10-20% of the stem (Biermann 1996). The bark contained in the feed source is considered to be a contaminant in the paper and pulp manufacturing process. The tolerance for bark in the wood chips generally ranges between 0.2-0.5% (Bajpai 2011). After the initial debarking stages, the wood is cut into smaller pieces called chips, using mechanical chippers, and stored. Wood chips are then processed into pulp.

2.3 Pulp manufacturing

Most of the pollutants produced during the paper manufacturing process occur within the first pulping stage (Pokhrel & Viraraghavan 2004). In the paper industry, there are numerous methods of pulping, which directly affect the characteristics of the wastewater being produced. Mechanical, chemical, chemo-mechanical (CMP), thermo-mechanical (TMP) or chemi-thermomechanical (CTMP) pulping are used in the industry.

2.3.1 Mechanical pulping

Mechanical pulping is the process in which bonds between the fibres in the wood matrix are broken by means of mechanical energy. Consequently, single fibres and fragmented fibres are released into the surrounding solution (Smook 1992). The nature of the process ensures high pulp yields ranging from 90-95%, but the pulp produced is of a low grade (Pokhrel & Viraraghavan 2004). Paper produced using mechanical pulping techniques are more prone to discoloration due to the low resistance to aging.

Mechanical pulping can be divided into stone groundwood pulping (SGW), pressure groundwood pulping (PGW), chemi-mechanical pulping (CMP), thermo-mechanical pulping (TMP) and chemi-thermo-mechanical pulping (CTMP) (Bajpai 2011). The *stone groundwood (SGW) pulping* process involves the grinding of logs on the radial and tangential surfaces. During *pressure groundwood (PGW) pulping,* the grinder is pressurized with steam at 105-125°C (Biermann 1996).The addition of steam in the PGW pulping process softens the wood prior to the grinding process, ultimately leading to higher fibre separation. Both pressure (PGW) and stone groundwood (SGW) pulping could be seen as an economical method of pulping due to the effective utilization of all the wood. However, groundwood pulping in general has some drawbacks due to the occurrence of impurities. The c*hemi-mechanical pulping (CMP)* process involves mechanical abrasion in the presence of chemicals (Xu & Zhou 2007).

Thermo-mechanical pulping (TMP) uses mechanical energy with the addition of heat to produce the desired pulp. Before the refining process, high temperature steam is used to remove the outer layers of existing fibres which consequently assists in inter fibre bonding. Pulp derived from thermo-mechanical pulping is generally stronger than that of groundwood pulping, and is commonly used in printing papers, cardboard, and tissue paper applications. In the TMP process, softwood is generally preferred over hardwood due to high strength properties associated with softwood derived products (Karlsson 2010; Ahay et al. 2013).

Chemi-thermo-mechanical pulping (CTMP) is very similar to chemi-pulping, but less mechanical energy is needed. Chemicals such as sodium sulfate, carbonate and hydroxide are used to soften the pulp. The pulps produced from the CMTP process are usually high strength pulp, even if hardwood is used as virgin fibre.

2.3.2 Chemical pulping

Most commercially produced papers and boards use chemical pulping as a method of pulping. The yield of the pulp is about 40-50% from the initial wood (Pokhrel & Viraraghavan 2004). Chemical pulping uses either an alkaline or acidic medium for the pulping process. Chemical pulping could be divided into the Kraft and Sulfite process.

The *Kraft process (KP)* is the most widely used process in the paper industry today (Bajpai 2011). The wood chips are digested using a mixture of sodium hydroxide (NaOH) and sodium sulfite (Na_2S), which is called the white liquor (Biermann 1996). After digestion, non-cellulosic material is separated from the intact cellulosic fibres. The Kraft process produces high quality pulp, with high strength properties, which is then incorporated in high strength paper and board applications (Bajpai 2011).

The *Sulfite process (SP)* uses a mixture of sulfurous acid (H_2SO_3) and bisulfide (HSO_3^-), which removes the most of the lignin in the process (Pokhrel & Viraraghavan 2004). The SP can be conducted under acidic, neutral and alkaline conditions (Shahzad 2012; Antonides 2000; Kordsachia et al. 2004). The *neutral sulfite semi-chemical (NCCS)* is considered to be a traditional pulping technique which uses a combination of mechanical and chemical treatment (Pokhrel & Viraraghavan 2004). In the NSSC process a mixture of Na_2SO_3 and $NaHCO_3$ are used to soften the lignin (Ekstrand et al. 2013). The NSSC process is mainly used to produce coarser paper grades.

2.4 Recycled fibre processing

In the paper recycling industry, virgin fibres are occasionally used, along with secondary fibres, for the production of paperboard derived products. Solid paper waste is sorted and graded prior to the pulping process in terms of their properties, which affect the characteristics of the manufactured product (McKinney 1994). The recycling of secondary fibre begins in either a high or low consistency pulper, which disperses the pulp into slurry (Biermann 1996). A major aspect in recycling plants is the removal of contaminants which include inks, fillers and other solid particles. The slurry passes through a series of screening and cleaning processes, which remove the non-fibre contaminates based on differences in physical properties. Screens separate contaminants based on particle size. The problematic formation of fibrous mat is avoided by means of pressure pulses through the screens with the combination of fluidization of the mat on the screens surface. Centrifugal, vortex or cyclone cleaners separate particles based on density differences and further clean the pulp prior to entering the paper machine (McKinney 1994). De-inking can be implemented by the addition of chemicals or without chemicals. In chemical deinking, a variety of chemicals have been used in the industry, which includes sodium hydroxide, sodium carbonate, sodium silicate and sodium sulfates (Bajpai 2013). The efficiencies of the deinking process depend greatly on the pulp consistency and temperature of the process.

The reduction in the strength properties as a result of the reuse of fibres, poses challenges in recycling paper mills. Fibres can be recycled 10-12 times before the quality of the produced paper is significantly affected (Gulsoy et al. 2013).

2.5 Paper manufacturing process

Board or paper mills can either receive pulp from an onsite pulper, or pulp could be transported to the mill for further processing. The paper manufacturing process includes stock preparation, forming, draining, pressing and drying. Fourdrinier-type machines in Figure 2-1 are the most frequently used paper machines in the pulp and paper industry (Biermann 1996).

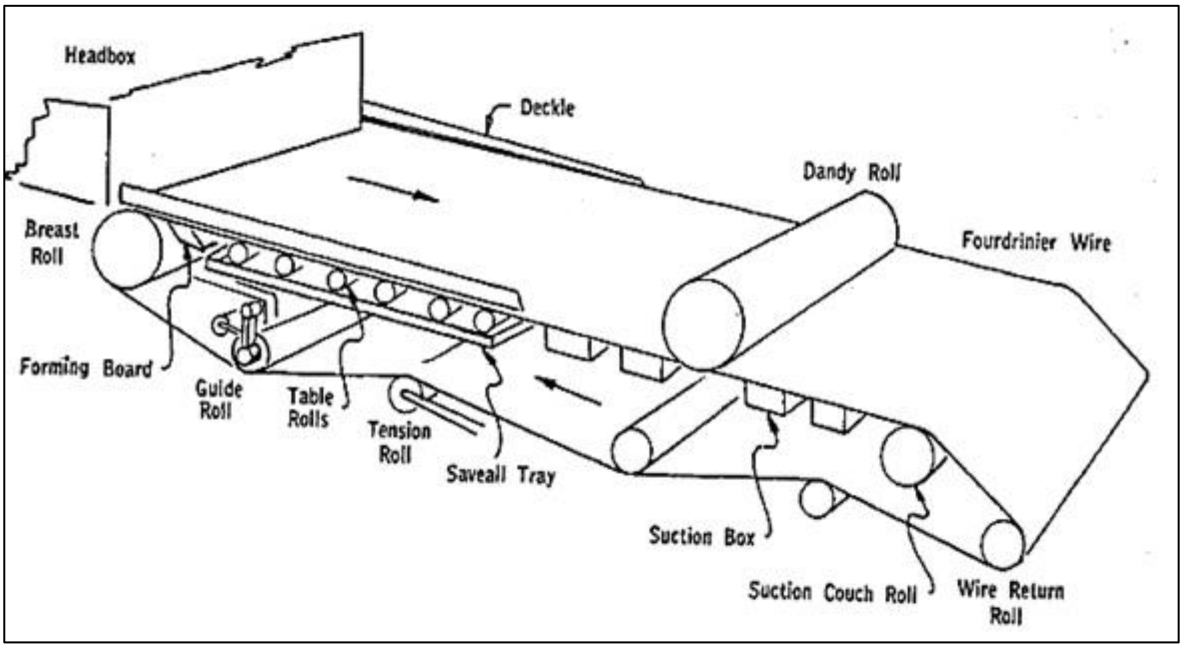
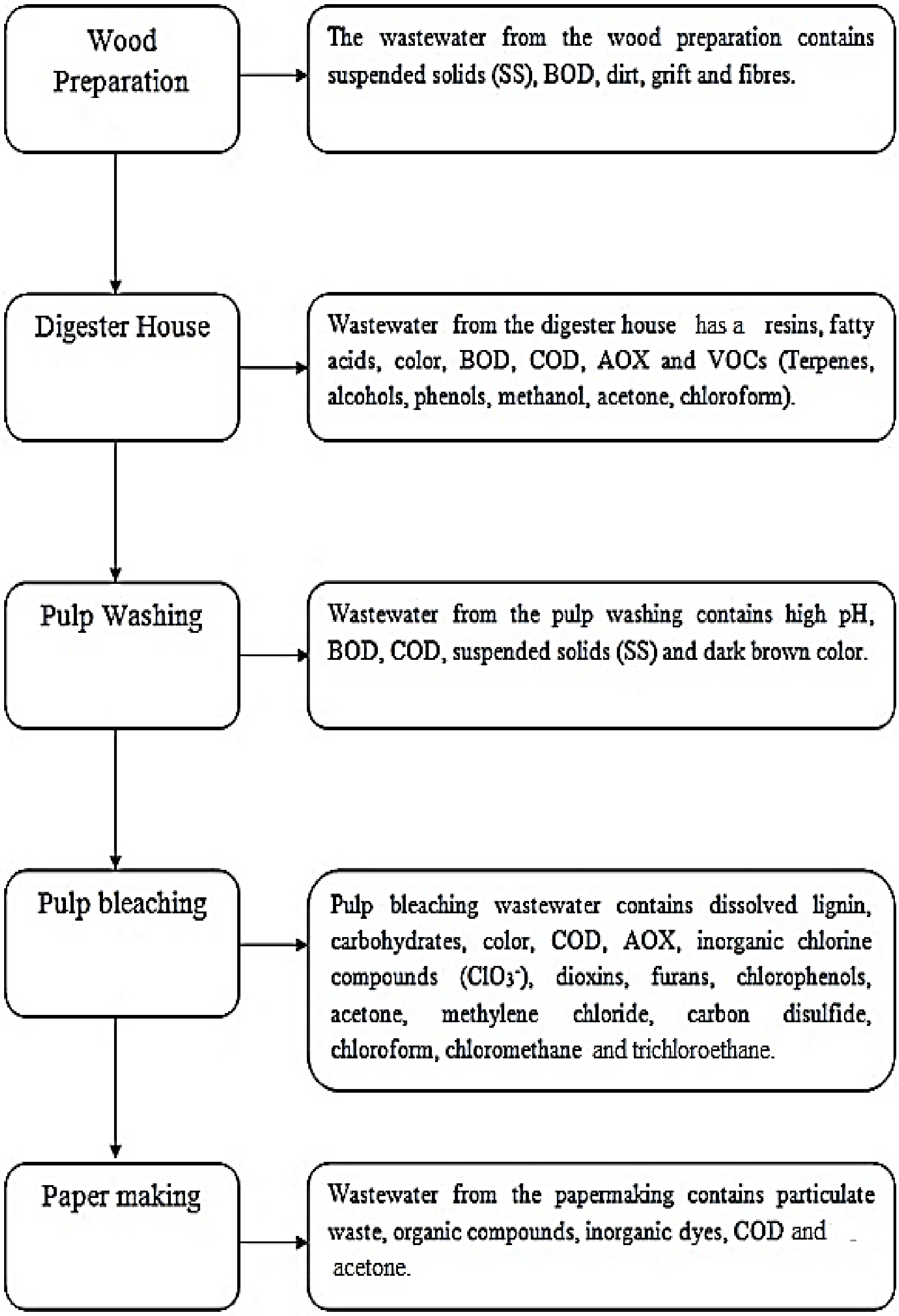


Figure 2-1: Schematic representation of the wet end of a fourdrinier-type paper machine (Biermann 1996).

A dilute solution which consists of fibres and additives are mechanically distributed over a thin wire screen or plastic fabric using a headbox. The formed sheets are then continuously dewatered by means of gravity and mechanical equipment which include table rolls, drill couch and suction equipment. The sheets are then dried using a steam heated cylinder. Post drying operations may include calendaring, cutting, coating and reeling (Vurdiah 2015).

2.6 Wastewater characteristics

Processes such as wood preparation, pulping, bleaching and paper manufacturing are the primary contributors of water pollution in the paper and pulp industry (Karat 2013). The various sources of water pollution in the paper and pulp industry are shown in Figure 2-2. The effluent normally consists out of a biodegradable and non-biodegradable fraction (Möbius 2006). The easily biodegradable compounds include starch (saccharides, carboxylic acid) and other carbohydrates (glucose, xylose, galactose, manose etc.) (Amat et al. 2005; Karat 2013). The toxic and non-biodegradable fraction includes chlorinated lignins, phenolics, unsaturated fatty acids and resin acids (Zhang & Chuang 1998).



The wastewater from the wood preparation contains suspended solids (SS), BOD, dirt, grift and fibres.

Wastewater from the digester house has a resins, fatty acids, color, BOD, COD, AOX and VOCs (Terpenes, alcohols, phenols, methanol, acetone, chloroform).

Wastewater from the pulp washing contains high pH, BOD, COD, suspended solids (SS) and dark brown color.

Pulp bleaching wastewater contains dissolved lignin, carbohydrates, color, COD, AOX, inorganic chlorine compounds (ClO_3^-), dioxins, furans, chlorophenols, acetone, methylene chloride, carbon disulfide, chloroform, chloromethane and trichloroethane.

Wastewater from the papermaking contains particulate waste, organic compounds, inorganic dyes, COD and acetone.

Figure 2-2: The sources of pollutants from the paper and pulp industry (Pokhrel & Viraraghavan 2004).

According to Pokhrel & Viraraghavan (2004), the characteristics of the wastewater produced from the paper and pulp industry is largely dependent on the process feed composition, technologies implemented, recirculation of effluent and the quantity of water utilised during the process. Table 2-1 shows the wastewater characteristics of paper mills using different pulping processes.

Table 2-1: Typical wastewater characteristics from the paper and pulp industry (Rintala & Puhakka 1994).

Process	Wastewater (m^3/Adt pulp)	Suspended solids (SS) (kg/Adt pulp)	Chemical oxygen demand (COD) (kg/Adt pulp)
Wet debarking	5-25	-	5-20
Groundwood pulping	10-15	-	15-32
TMP[a]-unbleached	10-30	10-40	40-60
TMP-bleached	10-30	20-50	70-120
CTMP[b]-unbleached	10-15	20-50	70-120
CTMP-bleached	10-15	20-50	100-180
NSSC[c]	20-80	3-10	30-120
Ca-sulfite (unbleached)	80-100	20-50	-
Ca-sulfite (bleached)	150-180	20-60	120-180
Mg-sulfite (unbleached)	40-60	10-40	60-120
Kraft-unbleached	40-60	10-20	40-60
Kraft-bleached	60-90	10-40	100-140
Paper making	10-50	-	-
Agrobased small paper mill	200-250	50-100	1000-1100

[a] Thermo-mechanical pulping (TMP) [b] Chemi-thermo-mechanical pulping (CTMP)

[c] Neutral sulfite semi chemical pulping (NSSC) Adt = Air Dried Ton

In Table 2-2 the wastewater characteristics of recycling paper mills is shown for a variety of produced products. The pH and suspended solids (SS) from recycling paper mills ranges from 6.9-8.7 and 412-1181 mg/l respectively (Rahman & Kabir 2010).

Table 2-2: Characteristics of wastewater originating from recycling paper mills in Germany (Möbius 2006).

Type of product	COD (mg/l)	BOD (mg/l)
Newsprint Paper	960-2400	460-1270
Corrugated Board	2190-5680	1280-2840
Carton Board	1140-5500	530-3000
Recycling Paper	540-790	250-400

The BOD/COD ratio represents the biodegradability of the specific wastewater sample. If this ratio is high, then the wastewater is relatively biodegradable, while low ratios indicate slow biodegradation rates (Vollertsen & Hvitved-Jacobensen, 2002). The average BOD/COD ratios of various paper mill effluents are illustrated in Figure 2-3.

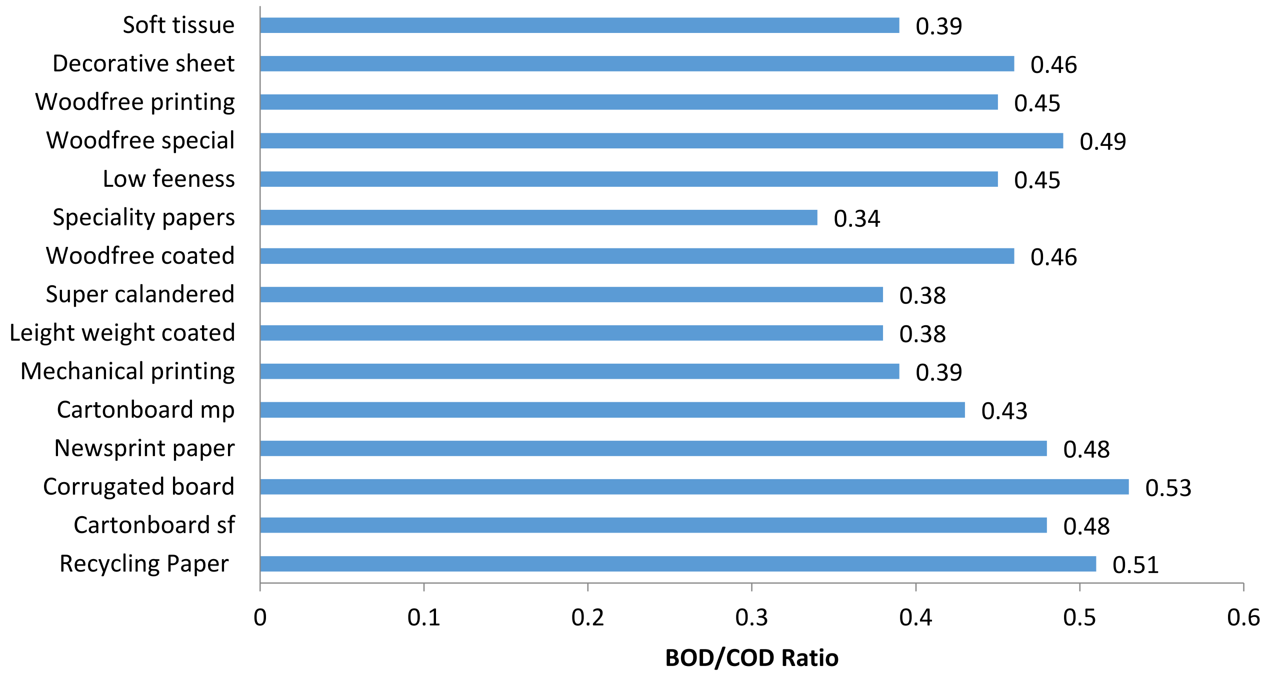


Figure 2-3: Average BOD/COD ratios of paper mill effluents (Möbius 2006).

2.7 Global water and environmental concern

The sustainable use of water has been identified as one of the major global issues, which is partly due to climate change (Bates et al. 2008). Only 0.77% of the global water is usable and accessible for economic growth. Contributing factors, such as urbanization and pollution, increases the pressure on these valuable water resources (Postel et al. 1996).

According to Molden (2010), water scarcity is a shared problem for 20% of the world's population.

The pollutants generated in the paper and pulp industry generally affect the terrestrial, air and aquatic environment. Global attention was captured in the late 1980s regarding the effect of paper mill effluent on the aquatic environment, after scientists in Sweden reported that the fish found near mill effluent discharges had altered growth, mortality, maturation and metabolisms (McMaster & Hewitt, 2010). The aquatic environment is polluted by a variety of heavy metals including cadmium, zinc, copper and chromium which are present in the majority of paper mill effluents (Zahrim et al. 2007). Mellanen et al. (1996) reported that trichloroguicol, chlorinated phenols, dichloroguicol and tetrachloroguicol generated in the paper and pulp industry are considered toxic to the majority of fish species. Untreated mill effluent can be considered severely toxic to fish species even at concentrations as low as 2% (Hutchins 1979). Paper mill effluent can lead to changes in the population of phytoplankton and macroinvertebrates in aquatic environments due to the changes in nutrient loadings (Ojunga et al. 2010). Globally, secondary wastewater treatment facilities have been implemented in an attempt to decrease the toxicity of the discharged effluent.

Numerous studies have been conducted on the impact of mill effluent on the physiochemical properties of soil (Sharma et al. 2014; Kannan & Oblisami 1990; Kumar et al. 2004). Kumar et al. (2011) reported that paper mill effluent in the agricultural industry had the potential to improve the physiochemical properties of soil. Therefore, this method of disposal could be seen as a safe and viable alternative. However, the build-up of contaminates, such as heavy metals, and alterations in soil salinity could occur as a result of direct disposal to the terrestrial environment (Sharma et al. 2014).

2.8 Effluent treatment in the pulp and paper industry

State of the art wastewater treatment facilities originating from the paper and pulp industry involve a primary mechanical/chemical treatment, followed by a secondary biological treatment facility (Helble & Mobius 2008). Depending on the water quality, post primary/secondary treatment, a tertiary treatment system could be implemented to further purify the water to the extent that up to 80% of the water can be recycled (Möbius 2006). The reuse of process water could add to substantial savings on operational and discharge cost (Habets & Driessen 2007). As a result, socio political pressure has increased to close water circuits in the paper industry (Simstich & Oeller 2010). The reuse of process water in the paper and pulp industry could only be optimized to a certain point without wastewater treatment; additional water recycling requires secondary and tertiary treatment to remove COD and BOD (Vurdiah 2015).

During the first primary clarification process, most of the suspended solids (SS) are removed with either a sedimentation or flotation process. Sedimentation is the preferred method of primary treatment in paper industry. More than 80% of the suspended solid (SS) are removed during primary sedimentation or flotation (Saunamäki 1997). Low amounts of COD and BOD are removed during the primary clarification process. A secondary treatment process is therefore required to remove the remaining dissolved/suspended organic material (Thompson et al. 2001). The primary treatment also serves the purpose to protect the secondary treatment systems (Möbius 2006).

The secondary treatment system conventionally consists of a combination of aerobic and anaerobic biological processes (Tezel et al. 2001; Habets & Driessen 2007). The anaerobic systems include upflow anaerobic sludge blanket (UASB), fluidized bed, anaerobic membrane filter or anaerobic baffled reactors (ABR). The formation of valuable biogas during anaerobic digestion makes anaerobic treatment methods an economically feasible alternative for the paper and pulp industry (Rintala & Puhakka 1994).

The implementation of aerobic treatment systems has also yielded promising results in the pulp and paper industry over the years (Thompson et al. 2001). Various aerobic treatment technologies suitable for the application of wastewater treatment in the paper and pulp industry, which includes an activated sludge tanks (AS), aerated lagoons (AL), moving bed biofilm reactors (MBBR), sequencing batch reactors (SBR) and aerobic membrane reactors exist.

The combination of anaerobic and aerobic processes has produced high COD removal efficiencies (greater than 90%) (Tezel et al. 2001). Therefore, the consideration of anaerobic-aerobic technologies as a secondary treatment system is essential to ensure economic feasibility and high organic removal efficiencies.

In advanced systems, tertiary treatment systems are incorporated to further purify the process water. In some cases, the COD concentrations are still reasonably high after biological treatment, which require a different approach due to the COD: BOD ratios (Thompson et al. 2001). Literature suggests the incorporation of advanced oxidation processes (AOP), chemical precipitation and flocculation (Catalkaya & Kargi 2007; Möbius 2006; Stephenson & Duff 1996). Advance oxidation processes can increase the overall removal of colour and organics mill effluents that are difficult to treat. It can also enhance the biodegradability of the effluent (Karat 2013). Figure 2-4 illustrates the primary, secondary and tertiary treatment options used in the paper and pulp industry.

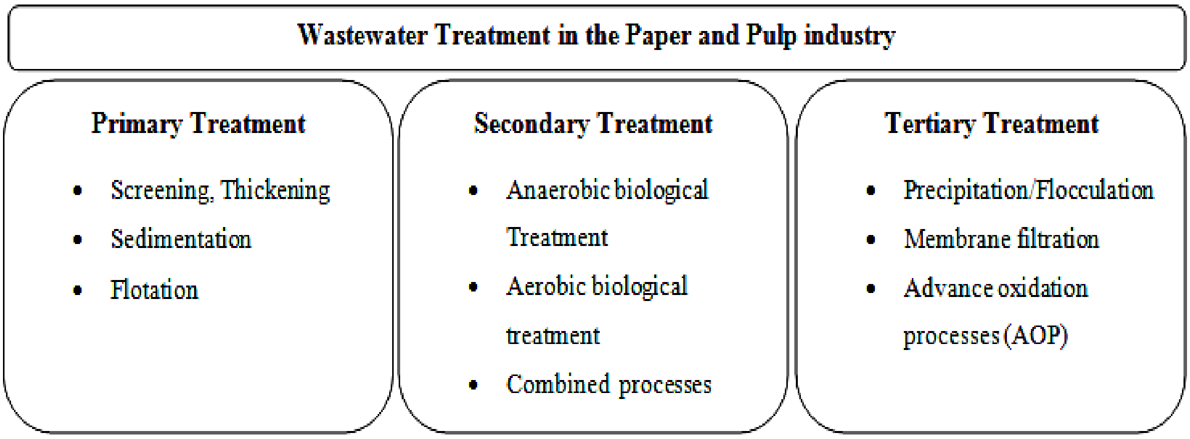


Figure 2-4: Wastewater treatment scheme in the paper and pulp industry divided into primary, secondary and tertiary treatment systems.

2.9 Primary treatment

Throughout primary treatment, the majority of suspended solids (SS) are removed from the effluent by means of screens, clarifiers or flotation units (Thompson et al. 2001; Pokhrel & Viraraghavan 2004). In some cases, coarse screens are used to remove the larger particles that would eventually clog equipment and pipes (Biermann 1996). Primary clarifiers in the paper and pulp industry became evident in the late 1950s as a primary wastewater treatment method. Mechanical clarifiers operate using the settling tendency of solids in wastewater, ultimately separating the solids from the clarified water. The primary sludge is formed from the settling of solid particles, with the sludge continuously raked to the central sump (Biermann 1996). Flotation is another technique used, which operates using the adsorption between fine bubbles and suspended solids. This attachment of suspended solids to the fine bubbles causes the suspended solids to float at the top of the floatation cell. The floating sludge layer is then skimmed (Thompson et al. 2001). Dissolved air floatation is a very effective process, although it is expensive (Biermann 1996). In cases where the toxicity of the effluent could affect the biological functions of the secondary treatment unit, dissolved air floatation units are preferred (Sanneskog & Reeves 1991).

2.10 Secondary treatment

More than 80% of the suspended solids (SS) are removed during primary treatment; however primary treatment does not remove the dissolved organics, nutrients and other constituents. As a result, a secondary biological treatment system need to be incorporated. In secondary biological treatment systems, microorganisms utilise the dissolved and suspended organics either under aerobic or anaerobic conditions (Hagelqvist 2013).

2.10.1 Anaerobic wastewater treatment technologies

In anaerobic digestion, microbial colonies utilise organics in the complete absence of oxygen. The anaerobic microbiological pathway in which organic substrates are utilized is shown in Figure 2-5. In the first phase (hydrolysations), complex organic matter (proteins, carbohydrates and lipids) are converted into soluble organic matter (sugars, fatty acids, glycerin amino acids). During the second phase (acidogenic stage), soluble organic matter is utilised to form mainly organic acids, such as volatile fatty acids (VFA) and ethanol. Hydrogen-producing acetogenic bacteria convert ethanol and volatile fatty acids (VFA) into acetic acid, H_2 and CO_2. In the acetogenesis phase, acetogenic bacteria partially oxidise organic acids into hydrogen and acetic acid. In the methanogenesis phase, methanogenic bacteria convert hydrogen and acetic acid into CH_4, CO_2 and H_2S (del Real Olvera & Lopez-Lopez 2012).

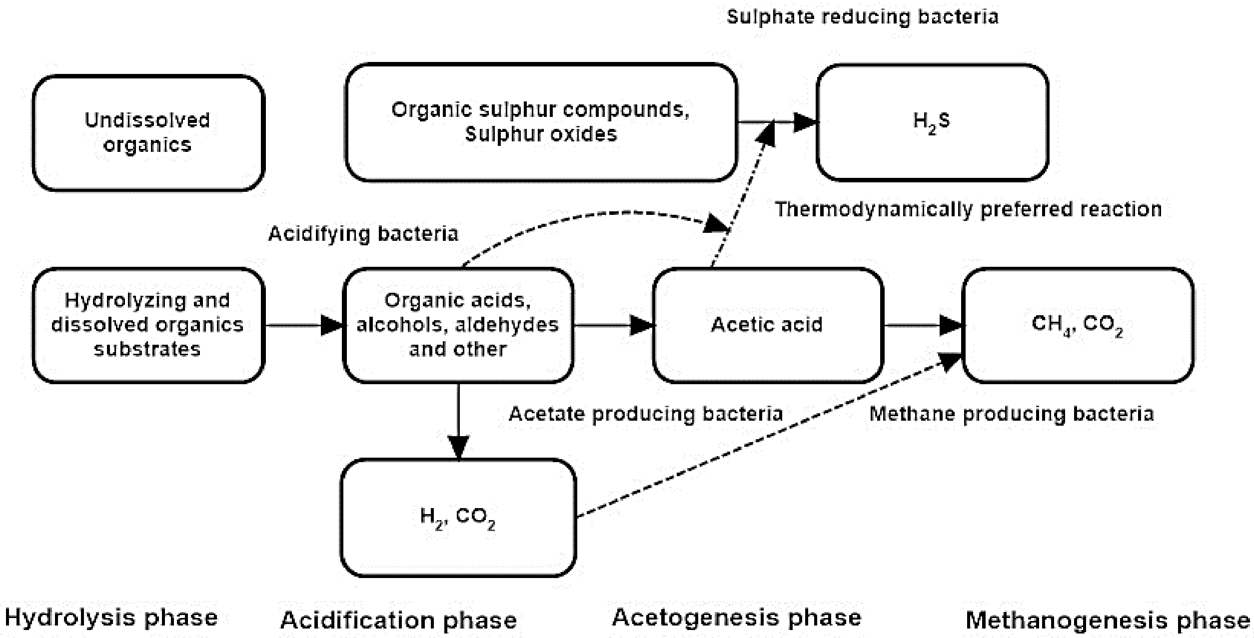


Figure 2-5: Anaerobic metabolic pathways in the biodegradation of organic matter (Möbius 2006).

Anaerobic handling of wastewater was implemented as early as 1881 in France, where Louis Mouras patented his concept of a septic tank (Mang & Li 2010). This type of treatment is widely used in the municipal and agricultural sectors. In recent years, the use of anaerobic systems as a method of wastewater treatment has generated significantly more interest in the paper and pulp industry. This increasing trend in anaerobic reactor installations is shown in Figure 2-6. This particular treatment method generated interest due to the simplicity and low capital/operational cost associated with the technology (Zwain et al. 2013).

Many studies have shown that anaerobic treatment is effective to treat both recycling paper and non-recycling effluents. Hall (1988) reported that remarkably 50% of the effluents tested from Canadian paper and pulp mills were suitable for anaerobic digestion.

Implementation of anaerobic treatment technologies at recycled paper mills (RPM) is preferred over non-recycling mills due to the high amount of easily degradable starch found in RPM effluent (Möbius 2006). Two thirds of anaerobic treatment systems were installed in recycling paper mills (RPM) and one third in conventional pulp mills (Habets & De Vegt 1991).

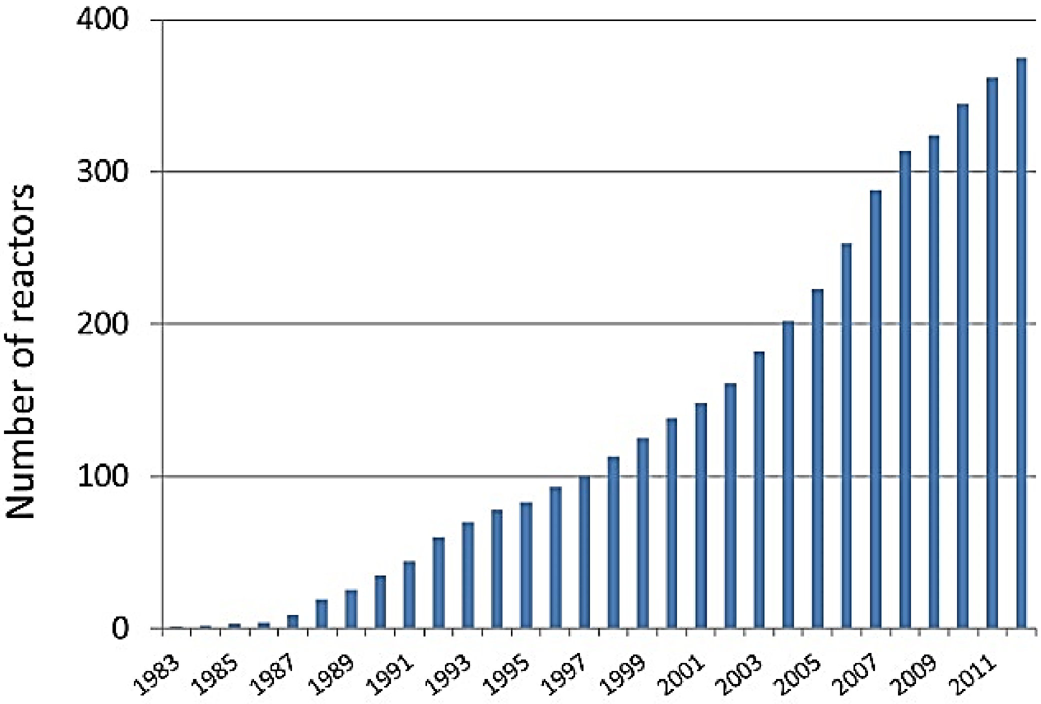


Figure 2-6: The global cumulative installations of anaerobic treatment facilities in the Paper and Pulp industry (Meyer & Edwards 2014).

2.10.2 Advantages of anaerobic wastewater treatment

Anaerobic reactor operational and capital costs

According to Zwain et al. (2013), anaerobic wastewater treatment is the preferred method compared to the aerobic and physic-chemical processes due to the low energy requirements and the low capital and operational cost. In a comparative study done by Helble & Mobius (2008), it was evident that the operational and capital cost of anaerobic treatment (expanded granular sludge blanket reactor) was considerably lower than aerobic treatment. Paasschens et al. (1991) found that the power usage for a full scale UASB reactor was 1.1 MWh per day. The biogas being produced from that specific anaerobic reactor was converted into 9.6 MWh of electricity; consequently the UASB reactor had a positive energy gain of 8.5 MWh. It was also reported in the same study that the equivalent aerobic treatment facility required 21.5 MWh/day. Although the usage of anaerobic reactors may seem most cost effective, a combination of aerobic and anaerobic treatments is usually required to improve the water quality to the extent that the water can be reused (Amat et al. 2005).

Space requirements

Compared to anaerobic treatment facilities, aerobic treatment facilities take up a large amount of space due to the large surface area required for sufficient oxygen transfer (Meyer & Edwards 2014). Studies done by Maat (1990) showed that a combination of aerobic-anaerobic treatment led to a space reduction of 50%, when compared to a single aerobic treatment unit.

2.10.3 Anaerobic reactor types and configurations

The most frequently implemented reactor configuration used to treat paper mill effluent is upflow sludge blanket (UASB), fluidized bed, anaerobic membrane filter and anaerobic baffled reactors (ABR) (Zwain et al. 2013).

Upflow anaerobic sludge blanket (UASB) reactors

The preferred reactor types for the treatment of wastewater from paper and pulp industry are upflow anaerobic sludge blanket (UASB) reactors (Meyer & Edwards 2014). This type of reactor configuration has been widely used for the treatment of wastewater with great success. Approximately 70% of all anaerobic reactors installed worldwide are UASB reactors (Bodkhe 2009). Typical examples of UASB reactors that are currently being used in the paper and pulp industry are internal circulation (IC) reactors and BIOBED reactors (Möbius 2006). In a UASB reactor, a blanket of sludge and granules is formed in the reactor where the largest extent of microbial activity happens. The sludge blanket is responsible for the removal of organic matter from wastewater.

Modified versions of the upflow anaerobic sludge blanket (UASB) reactor include the expanded granular sludge bed (EGSB) reactor. The main difference between UASB and EGSB is that the EGSB operates at higher superficial velocities (7-10 m/h) and operates at higher recycling rates (Jeison & Chamy 1999). In EGSB’s higher hydraulic mixing inherently increases the wastewater-sludge contact and decreases mass transfer limitations. The increase in velocities raises the height to diameter ratio of the reactor design (Jeison & Chamy 1999). Comparative studies done by Puyol et al. (2009) and Jeison & Chamy (1999), compared the performance of both UASB and EGSB reactors. The studies revealed that the EGSB could operate at higher loading rates than the UASB. The morphological structures of the granules in both EGSB and UASB reactors have not physically differed in shape or size.

One of the drawbacks of the UASB reactor is the start-up time. This is partially due to the long time it takes for the granulation process to take place inside the reactor. According to Liu et al. (2003) this granulation process inside UASB reactor from start-up could take 2-8 months. These sludge granules are seen as a microbial community which flourishes on complex organic waste. To reduce the start-up time, it’s necessary to look at the complex mechanisms of granulation to ensure the best start-up conditions.

Buzzini & Pires (2002) evaluated the potential of an upflow anaerobic sludge blanket reactor (UASB) to treat black liquor from a Kraft pulp plant. An average COD removal efficiency of 80% over a 635 day period was reported. Anaerobic/aerobic experiments conducted by Tezel et al. (2001) showed that 85% of the COD in the paper and pulp mill effluent were removed by means of an upflow anaerobic sludge blanket reactor (UASB).

Anaerobic baffled reactors (ABR)

The anaerobic baffled reactor (ABR) was developed by McCarty, which inherently did not need either a sludge blanket or granular biomass (Bodkhe 2009). The prospect of modified anaerobic baffled reactor (MABR) as an effective wastewater treatment system has been shown in recent publications (Zwain et al. 2013; Krishna et al. 2008). In some cases it’s reported that an anaerobic baffled reactor is preferred due to the simplicity of the design (Barber & Stuckey 1999). Another essential advantage of a baffled anaerobic reactor (ABR) is that the reactor behaves as a two phase system, essentially separating the acidogenesis and methanogenesis phases (Weiland & Rozzi 1991). A two phase system allows individual bacterial species to develop under more favourable conditions. Studies done on the hydrodynamics of anaerobic baffled reactor (ABR) show small dead spaces inside the reactor (<8 %) which is significantly larger in other anaerobic reactors (Grobicki & Stuckey 1989). As a result of dead space inside the reactor, inefficient utilization of the reactor volume would have cost related implications. The capital cost of an anaerobic baffled reactor (ABR) is 20% less than that of a UASB (Barber & Stuckey 1999).

Hassan et al. (2014) evaluated the start-up and steady state performances of a modified anaerobic baffled reactor (MABR) to effectively treat recycled paper mill effluent (RPME). It was reported that 85 % of the COD were removed at steady state in the MABR. Grover et al. (1999) tested the performance of an anaerobic baffled reactor on black liquors. The anaerobic baffled reactor (ABR) removed 60% of the COD with organic loading rates (OLR) of 5 kg m^{-3} d^{-1}.

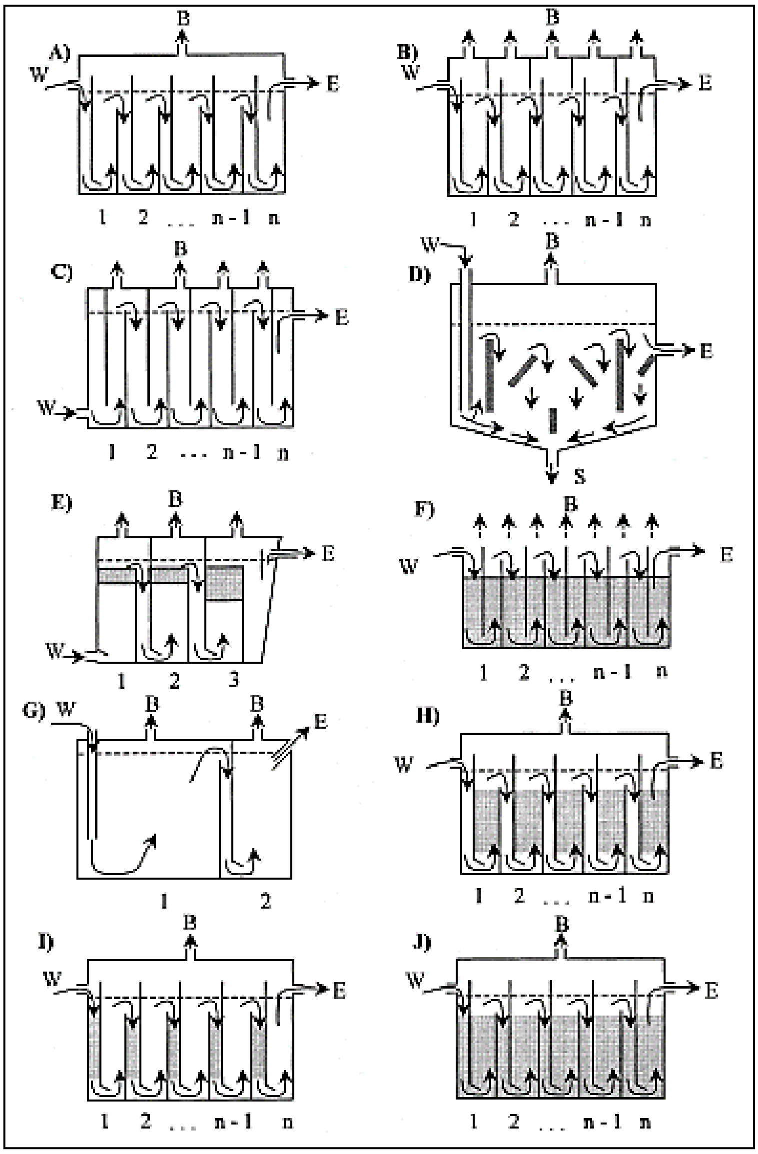


Figure 2-7: Different reactor modifications and configurations inside an anaerobic baffled reactor (ABR) (Barber & Stuckey 1999).

Anaerobic membrane bioreactor (AnMBR)

Anaerobic membrane bioreactor (AnMBR) is an effective treatment technology that has become an attractive alternative due to advantages over traditional anaerobic reactors (Lin et al. 2013). This type of technology has been implemented in various industries which uses bioreactors (UASB, CSTR or AF) fitted with membranes. This is a fairly new technology which has emerged in the paper and pulp industry in selected plants. Although this a fairly new technology, Germany has taken a keen interest in MBR's and have commissioned at least 10 membrane bioreactors on paper mill effluents (Simstich & Oeller 2010).

In anaerobic membrane bioreactors (AnMBR) there are two types of configurations, external/side-stream and submerged/immersed systems (Lin et al. 2013). Some advantages of the external configuration over the submerged configuration include controllable fouling, easier membrane replacement and high fluxes. The submerged surpasses the external configuration in aspects such as power consumption and the level of severe cleaning (Le-Clech et al. 2006). The schematic representation of an external membrane configuration is shown in Figure 2-8.

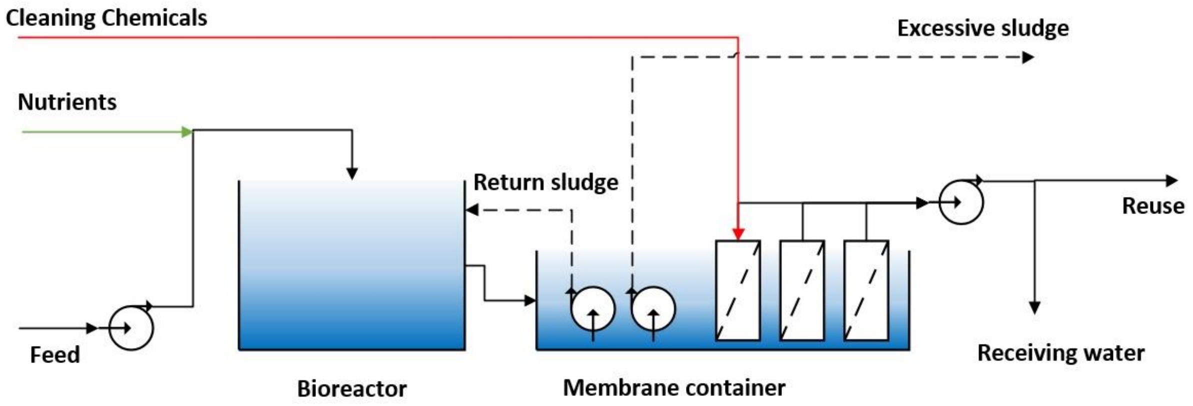


Figure 2-8: External membrane reactor configuration (Helble & Mobius 2008).

In anaerobic membrane reactor (AnMBR), the growth of mesophilic bacteria compared thermophillic bacteria leads to a more stable membrane operation and ultimately superior membrane filtration (Lin et al. 2009). Consequently, operation conditions for selective growth are important if anaerobic membrane bioreactors are considered.

It is reported that the reactor volumes from MBR are much smaller due to higher biomass concentrations found in these reactors (Helble & Mobius 2008). According to Helble & Mobius (2008) the use of a membrane bioreactor makes the reuse of water in the system a real possibility due to the high quality of the effluent. The effluent from a MBR is essentially free from all suspended solids (SS). The downside of an MBR compared to the traditional anaerobic reactors is the high capital and operational costs as well as fouling associated with this type of technology. According to Simstich & Oeller (2010), the capital investment is approximately 30% higher than that of the traditional systems. As a result, this would only be implemented in cases where the above-mentioned advantages justify the higher cost.

Lin et al. (2011) evaluated the performance of an anaerobic membrane bioreactor (AnMBR) on thermo mechanical pulping (TMP) whitewater. The study showed that 90% of the COD was removed from the TMP wastewater with hydraulic residence time (HRT) of 4.8-9.1 hr.

Anaerobic fluidized bed (AFB) reactor

In contrast to other anaerobic reactors, anaerobic fluidized bed reactors were not implemented for full scale systems until 1983 (Heijnen et al. 1989). In fluidized bed reactors the biomass grows on small particles (carriers) in the form of a bio-layer. This media helps to immobilize the biomass to a specific carrier (Chen et al. 1988). The carrier particle is in some cases sand or granular activated carbon (GAC). Zhang et al. (2007) found that the usage of GAC as a carrier particle poses some significant benefits such as faster biofilm formation and a significant increase in colonization of microbial species. Due to the high settling velocities, the reactor can operate at much higher superficial velocities. According to Fernandez et al. (2008), many factors inside an anaerobic fluidized bed reactor such as organic loading rate (OLR) and the fluidization level (FL) have a significant effect on the amount of biogas produced. A schematic representation of an anaerobic fluidized bed (AFB) reactor is shown in Figure 2-9.

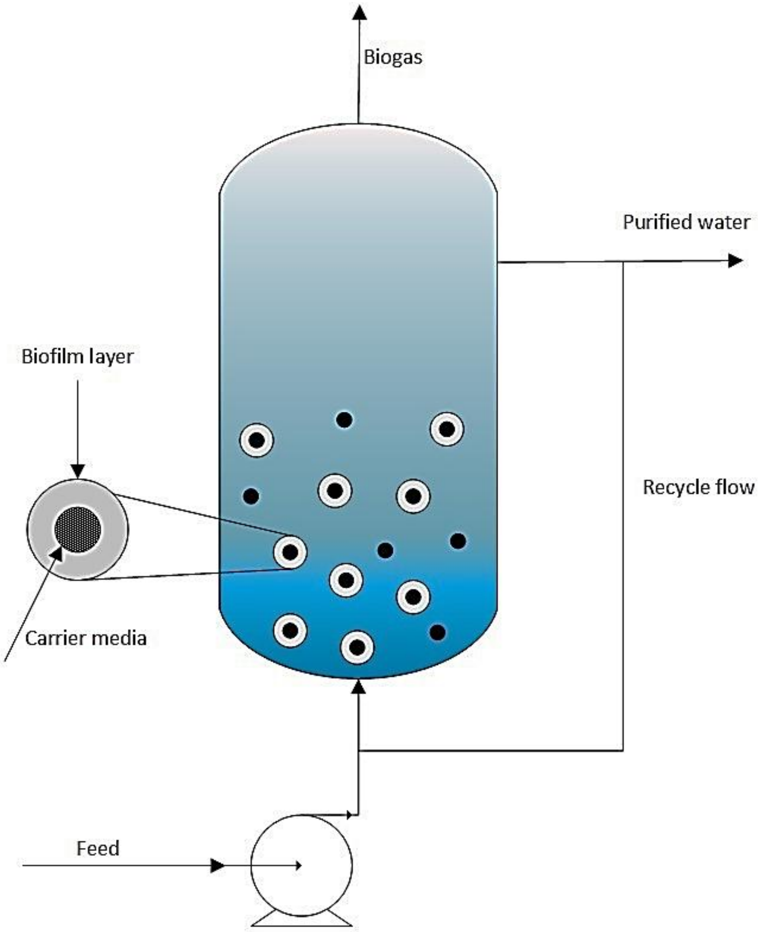


Figure 2-9: Anaerobic fluidized bed reactor (Heijnen et al. 1989).

When fluidized beds are operated at higher superficial velocities, a decrease in biofilm thickness is observed (Converti et al. 1990). The decrease in biofilm thickness reduces the diffusional limitations greatly in the reactor. Very high particle suspensions covered in a biofilm have also been reported, leading to higher conversion of substrate and higher methane/hydrogen yields. Heijnen et al. (1989) reported that higher settling velocities of the carrier particle help prevent wash-out of the attached biofilm. This is a problem in UASB systems, where sludge retention is considered problematic if complete granulation has not been reached. Some common disadvantages of anaerobic fluidized beds include high power consumption and biofilm controllability. Anaerobic fluidized bed reactors have high power consumption due to the high superficial velocities needed to fluidize the bed. In reality, it could also become difficult to control the thickness of the biofilm.

2.10.4 Typical reactor characteristics from various anaerobic reactors

The typical reactor characteristics (start-up time, loading rates, hydraulic residence time (HRT), volume) for various anaerobic reactors (CSTR, UASB, EGSB, IC, AFB) is shown in Table 2-3.

The implementation of an anaerobic fluidised bed (AFB) or internal circulation (IC) reactors would be favourable to treat paper and pulp effluent. These reactors are attractive anaerobic technologies in the paper and pulp industry due to the high loading rates and fast start-up periods compared to various other traditional anaerobic reactors.

Table 2-3: Characteristics of wastewater treatment anaerobic reactors

Reactor types	**Start-up period (Months)**	**Reactor loading rates (kg COD/m^3 day)**	**HRT(days)**	**Reactor volume (m^3/ton COD.day)**
CSTR-contact process	-	(0.25-3)[a] (1-5)[b]	(12-15)[a]	333[b]
UASB	(4-16)[a]	(10-30)[a] (5-15)[b]	(0.5-7)[a]	100[b]
EGSB	(3-4)[a]	(10-20)[b]	-	60[b]
IC	-	(20-30)[b]	-	40[b]
AFB	(3-4)[a]	(1-100)[a]	(0.2-5)[a]	-

[a] Rajeshwari et al. 2000 [b] Habets & Driessen 2007

2.10.5 Performance evaluation of different types of anaerobic reactors

In this section, the performance of various anaerobic reactors to treat paper and pulp effluent is evaluated. These reactors include upflow anaerobic sludge blanket (UASB) reactors, anaerobic baffled reactor (ABR), anaerobic membrane bioreactors (AnMBR) and anaerobic fluidized bed (AFB) reactors. The inlet COD, TSS and the type of effluent used in the studies is shown in Table 2-4.

Table 2-4: A performance summary of anaerobic biological reactors in the paper and pulp industry

Reactor type	Treated stream	Initial COD (mg/l)	TSS (mg/l)	COD removal (%)	HRT (hr)	Temperature (°C)	References
Upflow anaerobic sludge blanket (UASB) reactors							
UASB Lab-scale	Black Liquor	1300	n.a	80	30	30	Buzzini et al. (2006)
UASB Lab - scale	Paper and pulp mill wastewater	1133	1033	81	24	35	Turkdogan et al. (2013)
Anaerobic baffled reactors (ABR)							
ABR Lab-scale	Mill effluent form recycled paper plant	988	319	71	120	35	Zwain et al. (2013)
Membrane anaerobic bioreactors (MBR)							
Membrane reactors (UASB+M) Pilot plant	Kraft evaporator condensate	10,000	9000	97-99	20 - 77	55 and 37	Lin et al. (2009)
AnMBR Lab-Scale	TMP effluent	5100	550	83	32	35	Gao et al. (2016)
Anaerobic fluidized bed reactor							
Anaerobic fluidized bed (Full scale, France)	Paperboard effluent	3000	n.a	72.2	n.a	n.a	Pokhrel & Viraraghavan (2004)

2.10.6 Aerobic wastewater treatment technologies

The process in which microorganisms utilise carbon in the form of complex organics, together with oxygen and other trace elements to produce biomass and carbon dioxide is called aerobic digestion (Spellman 2013). Aerobic digestion involves two processes, where the first step involves the direct oxidation of biodegradable matter and secondly the oxidation of microbial cellular material (endogenous respiration) (Wang et al. 2007). These biological oxidation reactions are presented in Eq. 2-1 and 2-2 (Metcalf & Eddy et al. 2002).

Oxidation and synthesis:

$$Organic\ matter + O_2 + nutrients \rightarrow Cellular\ material + CO_2 + end\ products \tag{2-1}$$

Endogenous respiration:

$$Cellular\ material + O_2 \rightarrow Digested\ sludge + CO_2 \tag{2-2}$$

Aerobic treatment of municipal wastewater was implemented as early as 1950s with high efficiencies (Wang et al. 2007). Aerobic digestion is a common secondary wastewater treatment system which has been implemented in the paper and pulp industry (Tezel et al. 2001; Möbius 2006; Habets & Driessen 2007).

2.10.7 Advantages of aerobic wastewater treatment

Process stability

According to Chan et al. (2009), the typical aerobic wastewater system is less sensitive to changes in pH and temperature compared anaerobic wastewater systems. Lawrence & McCarty (1970) reported that aerobic processes have significantly higher reaction rates compared to anaerobic at the same temperature. Higher temperatures in anaerobic systems are therefore needed to ensure that the reaction rates stay practical and applicable. In most cases, no extra heating requirements were needed in aerobic wastewater treatment facilities. As a result, less strict control of pH and temperature in aerobic systems are needed in the long term. Aerobic wastewater systems are less likely to be affected by toxic chemicals (phenols and heavy metals) compared to anaerobic treatment methods (Eckenfelder et al. 1988). The robustness of aerobic wastewater systems makes it a very stable process and suitable to treat a variety of industrial wastewater.

Start-up time

The average start-up times for aerobic wastewater treatment facilities averages between 2-4 weeks (Eckenfelder et al. 1988) compared to 2-8 months in anaerobic treatment facilities (Lin et al. 2013). Consequently, no additional seeding of bacterial species is necessary since they spontaneously develop in aerobic treatment systems.

2.10.8 Aerobic reactor types and configurations

The most commonly implemented aerobic reactors in the paper and pulp industry are activated sludge tanks, aerated lagoons, moving bed and sequencing batch reactors (Pokhrel & Viraraghavan 2004).

Activated sludge tanks (AS)

Activated sludge tanks are one of most commonly implemented wastewater treatment systems in the paper and pulp industry (Möbius 2006). A schematic representation of an activated sludge tank (AS) is shown in Figure 2-10. Activated sludge tanks can be divided into two sections, the aeration tank and a settling tank. In activated sludge tanks, the wastewater is mixed with a various microbes under aerobic conditions to assist in the removal of dissolved organics. In activated sludge tanks, it is important to keep the microorganisms in a well flocculated state to ensure that the biomass settles in the clarifier to separate sludge from the clarified water (Biggs & Lant 2000).

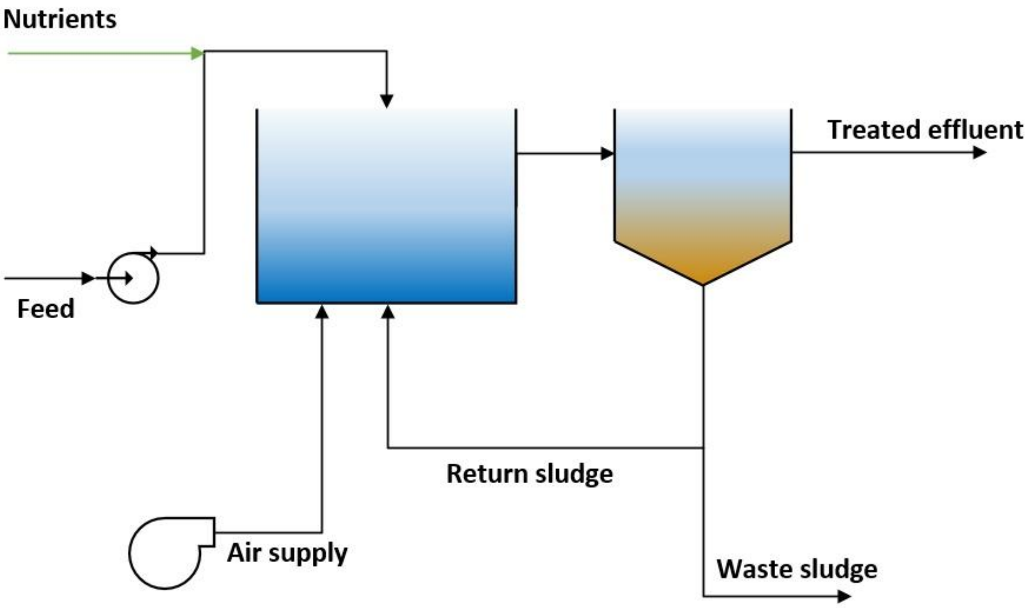


Figure 2-10: Activated sludge treatment process flow diagram (Gouveia & Pinto 2000).

Under adequate operating conditions high COD and BOD removal efficiencies of between 75-92% and 70-98% respectively have been reported in literature for paper mill effluent (Thompson et al. 2001).

The poor settlement of biomass in activated sludge tanks, also referred to as bulking sludge, has been a reoccurring problem in the wastewater treatment facilities (Thompson et al.

2001). There exist two forms of bacteria, filamentous bacteria and floc forming bacteria, in activated sludge tanks. Unlike filamentous bacteria, floc forming bacteria have a high settling quality measured by the sludge volume index (SVI) (Bagheri et al. 2015). Bulking sludge occurs when an excess of filamentous bacteria is present in the activated sludge tank (Möbius 2006). Various models have been developed to understand the behaviour of floc characteristics in activated sludge tanks in attempt to increase settling efficiencies. More recently the potential of artificial neural networks have realized to help predict the settlement (SVI) by using a couple of parameters which includes MLVSS, pH, DO, temperature, TSS, COD and total nitrogen (Bagheri et al. 2015).

Cingolani et al. (1994) conducted a survey at paper mills to isolate the factors that contribute to the development filamentous bacteria (bulking sludge). The survey concluded that poor aeration, nutrient deficiencies and low organic loadings are the main causes of bulking sludge.

Aerated Lagoons (AL)

The implementation of aerated lagoons has long been seen as the most economical alternative to effectively treat wastewater generated by the paper and pulp industry (Cocci et al. 1993). This alternative has become attractive due to the simplicity, minimal maintenance and low capital and operational costs (Nameche & Vasel 1998). In general, aerated lagoons can either be facultative or aerobic, depending on the extent to which these lagoons are aerated and the depth of the lagoons (Wolverton & McDonald 1979). Facultative lagoons tend to benefit from both aerobic and anaerobic systems.

Aerated lagoons host numerous complex microbial communities which reduce the dissolved organics and adsorable organic halides (AOX) present in paper mill wastewater (Pokhrel & Viraraghavan 2004). The efficiencies of aerated lagoons are influenced by various perturbations that include the variation in temperature, pH, organic loading rates (OLR), climate changes and toxicant levels (Yu & Mohn 2001). Colder climates are a limiting factor in organic and toxicity removals, which are influenced by ambient temperature (Cocci et al. 1993). Literature suggests that the efficiencies of aerated lagoons in the paper and pulp industry have COD removal ranges between 30-65% (Chamorro et al. 2009; Welander et al. 1997; Hagelqvist 2013).

The distinctive stumbling block of aerated lagoons in the paper and pulp industry is the sheer size required to effectively treat wastewater (Pougatch et al. 2007). Consequently, this treatment technology can only be implemented in cases where large amounts of unused land are available.

Moving bed biofilm reactors (MBBR)

More recently the potential of moving bed biofilm reactors (Figure 2-11) was realised for the possible application in the paper and pulp industry (de Oliveira et al. 2014). Moving bed biofilm reactors incorporate factors from both activated sludge tanks and biofilm processes, which includes both suspended biomass and adhered biomass (Vaidhegi 2013).

Moving bed biofilm reactors contain numerous small polyethylene carriers (lengths ranging from 7-37 mm and diameters ranging from 10-46 mm) and these carriers are held in suspension by means of agitation encouraged by aeration and mechanical mixers in the tank (Jahren et al. 2002). These carries contains very large surface areas (200–500 m^2/m^3) which is ideal for the formations of biofilms on theses carries (Ødegaard et al. 2000).

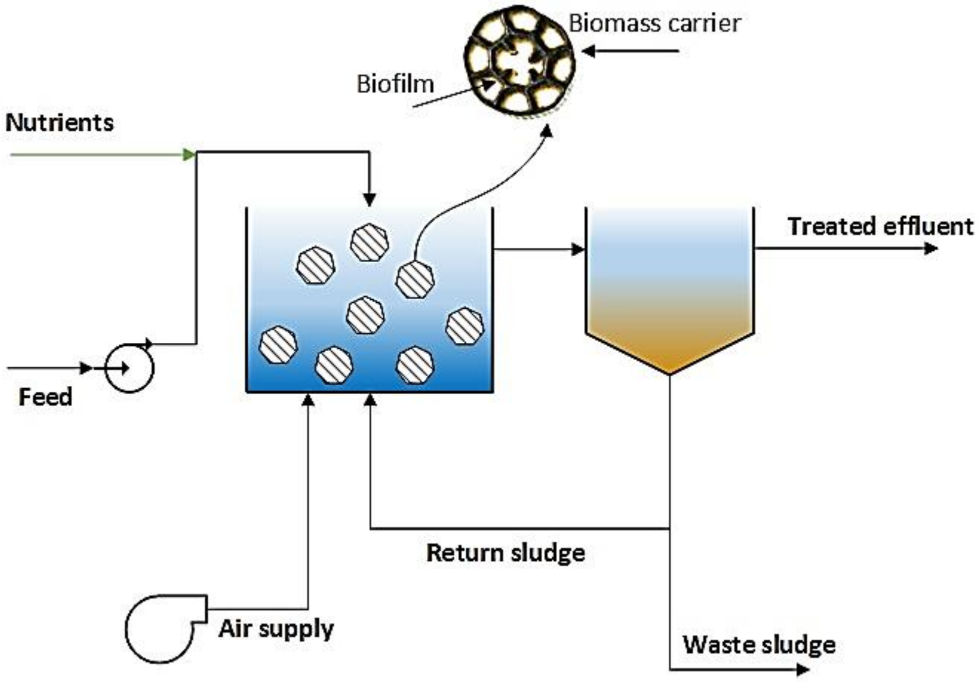


Figure 2-11: A typical arrangement of a moving bed biofilm reactor (MBBR) in the paper and pulp industry.

The reactor temperature configuration plays an important role in the effective operation of aerobic moving bed biofilm reactors (Jahren et al. 2002).The discharge temperature of wastewater from the paper and pulp industry is typically >45°C (Pozzi et al. 2014), subsequently it is important to consider thermophillic operation, which needs no cooling. Thermophillic (50-55°C) and mesophilic operating conditions are comparable (Barr et al. 1996). In thermophillic reactors, better settling of biomass was reported due to the decrease in the liquid viscosity at high temperatures (Jahren et al. 2002). Other factors such as the carrier geometry and size have been known to have some effect on the overall performance of moving bed reactors. Ødegaard et al. (2000) reports that the size and effective surface area have influenced the effectiveness of the moving bed biofilm reactors.

The COD and BOD removal efficiencies of various lab scale and pilot plant scale moving bed biofilm reactors (MBBR) treating paper/boards mill effluent ranged between 60-87% and 56-96% respectively (Broch-Due & Opheim 1997; Jahren et al. 2002; Vaidhegi 2013; de Oliveira et al. 2014; Pozzi et al. 2014). Microbial growth inside moving bed biofilm reactors are both suspended in the wastewater and attached to the carrier media. If the carriers are kept inside the reactor, no sludge recycling is necessary in moving bed biofilm reactors (MBBR) (Zafarzadeh et al. 2010), which ultimately saves cost through the elimination of large clarifiers that occupy space.

Sequencing Batch Reactors (SBR)

Treating wastewater from the paper and pulp industry using Sequencing Batch Reactors (SBR) yielded promising results (Dubeski et al. 2001; Khan et al. 2016; Khan et al. 2011). SBRs are characterised by sequence of phases which includes fill, react, settle, draw and idle where the duration of individual phase lasts for a distinct period (Tsang et al. 2007). The duration of the settling and draw phases is generally a fixed parameter in these types of reactors, which depend on the characteristics of the activated sludge (Vargas et al. 2000). In SBRs the reaction and settling takes place in the same vessel.

The effluent from the paper and pulp industry typically exists at high temperatures (>45°C), consequently operating at thermophillic reactor condition would prove most economical. Tripathi & Allen (1999) compared mesophillic and thermophillic operation of a SBR treating kraft pulp effluent. For optimal COD removal and settling capabilities the study suggested that the reactor operates at 45°C. Other factors that can greatly affect the efficiencies of SBRs are the durations of certain phases such as the reaction and settling phases. The ability to control duration of the reaction phase in SBRs can significantly improve the overall efficiency of the wastewater treatment system (Moreno 1997).

Various lab-scale results showed that the COD and BOD removal efficiencies for sequencing batch reactors (SBR) treating wastewater from the pulp and paper industry ranges between 60-93% and 80-94% respectively (Tripathi & Allen 1999; Tsang et al. 2007; Khan et al. 2011; Khan et al. 2016; Dubeski et al. 2001).

Aerobic membrane bioreactor (MBR)

In recent years, the application of aerobic MBRs as an alternative to the conventional activated sludge units (AS) for PPME treatment was investigated (Lerner et al. 2007; Dufresne et al. 1998; Galil et al. 2003).

As with AnMBRs, the main advantages of aerobic MBRs are smaller reactor volumes and excellent effluent qualities. The drawbacks of this treatment technology are primarily related to the high investment costs, fouling issues and complex maintenance. At high solid retention times (SRT) bio-recalcitrant organics and other inorganics could potentially build-up and inhibit microbial activity (Cicek et al. 1999).

Lab scale studies have demonstrated that aerobic MBRs treating PPME can achieve TSS and COD removal efficiencies ranging from 74 -100% and 87 - 89%, respectively (Lerner et al. 2007; Sheldon et al. 2012; Sitabule 2013). According to Lerner et al. (2007), aerobic MBRs treating PPME can produce excellent effluent qualities in terms of suspended solids (SS). However, the COD and BOD removal efficiencies of aerobic MBRs was found to be very similar to that of an activated sludge unit (AS).

2.10.9 Performance evaluation of different types of aerobic reactors

In this section; the performance of different aerobic reactors (activated sludge takes, aerated lagoons, moving bed biofilm reactor, sequencing batch reactors) treating wastewater originating from the paper and pulp industry is critically compared. The inlet chemical oxygen demand (COD), inlet total suspended solids (TSS), reactor hydraulic (HRT) and solid residence time (SRT) used in the various studies is shown in Table 2-5.

Table 2-5: Performance evaluation of aerobic reactors used to treat wastewater produced by the pulp and paper industry

Reactor Type	Treated stream	Initial COD (mg/l)	TSS (mg/l)	COD removal (%)	HRT (h)	SRT (h)	Reactor Temperature (^{o}C)	Reference
Activated Sludge Tanks(AS)								
AS Lab-scale	Anaerobic pre-treated pulp and paper mill effluent	2113	n.a	59 (SRT-20 days) 57 (SRT-15 days) 60 (SRT-10 days)	n.a	240-480	30	(Vogelaar et al. 2002)
			n.a	48 (SRT-20 days) 43 (SRT-15 days) 56 (SRT-10 days)	n.a	240-480	55	
AS Lab-scale	Kraft mill effluent	919	3031	63-72	8,12,16,20	n.a	25	(Peters 2001)
Aerated Lagoons(AL)								
AL Full- scale and pilot scale (Sweden)	Pulp and paper mill effluent	n.a	n.a	30-40 % (Full scale) 60-70 % (Pilot plant)	n.a	n.a	n.a	(Welander et al. 1997)
Moving bed biofilm reactors (MBBR)								
MBBR Lab-scale	Board mill effluent (Recycled Fibre)	4060-4680	12745-14380	78-86	36		55	(Pozzi et al. 2014)
MBBR Lab-scale	Pulp mill effluent (TMP white water)	2100-2800	n.a	61.6 (sCOD)	13.2-26.2		55	(Jahren et al. 2002)

Table 2-6: Performance evaluation of aerobic reactors used to treat wastewater produced by the pulp and paper industry

MBBR Lab-scale	Paper mill effluent (Bagasse Based)	3340	3204 (TS) 1024 (SS)	87	8		27	(Vaidhegi 2013)
MBBR-Pilot plant	Paper/Board mill effluent	1384 (sCOD)	21.2 (g/m^2)	35 (sCOD)	3.3		44	(de Oliveira et al. 2014)
Sequencing Batch Reactors (SBR)								
SRB Lab-scale	Board mill effluent (Recycled Fibre)	1200-1400	200-500	93.1 (0.5 hour settling period)	16-64		25	(Tsang et al. 2007)
SBR-Lab-scale	Pulp mill effluent	5980-6860	n.a	67-78 (4 hours settling time)	34.3		35	(Dubeski et al. 2001)
SBR Lab-scale	Recycled pulp and paper mill	7860	n.a	73.26 (24 hour HRT) 89.90 (72 hour HRT)	24-72		n.a	(Khan et al. 2016)
Aerobic membrane Bioreactor (MBR)								
MBR pilot scale	Tissue and fine effluent	910	300	89.00	33	744	n.a	(Lerner et al. 2007)

2.11 Tertiary treatment

Tertiary systems need to be incorporated in cases where the quality of biologically treated effluent is insufficient for disposal or reuse. Generally, tertiary systems are incorporated in wastewater that contains persistent substances which contribute to the remaining COD, AOX, TOC and colour after biological treatment (Catalkaya & Kargi 2007). In tertiary systems technologies such as membrane systems, advance oxidation processes (AOP), biofilters, chemical precipitation and flocculation are used (Möbius 2006). Membrane technologies are not discussed in the section below due to the high capital and operational cost, fouling, blocking and aging factors (Möbius 2006). Aerobic/anaerobic processes taking place in biofilters are discussed in the previous sections. Consequently, only chemical coagulation/precipitation and advance oxidation processes (AOP) are discussed in the section below.

2.11.1 Chemical coagulation and precipitation

The use of chemical precipitation and coagulation is widely used in the wastewater treatment industry (Henze et al. 2001). During chemical coagulation, colloid particles and small suspended particles form bigger aggregates which have the potential to adsorb dissolved organics (Jiang & Graham 1998). Aggregates can then be removed through clarifier or floatation units. Generally aluminum (Al^{3+}) and iron (Fe^{3+}) salts are used for the coagulation process (Stumm et al. 1962).

Chemical precipitation as a method of wastewater treatment is used to remove ionic constituents through the introduction of counter-ions which reduces the solubility of impurities and inherently causing solid formation (Wang et al. 2006). During chemical precipitation metals, phosphorus, oils and fats present in the wastewater is removed (EPA 2000). Commercial chemical agents conventionally used in precipitations systems include alum, $FeCl_3$, lime and polymers (EPA 1980).

Chemical precipitation and flocculation are generally considered a less expensive technology when compared to other advance treatment systems (Möbius 2006). Excess sludge is produced during chemical precipitation and flocculation; consequently, this may be a feasible solution depending on the discharge cost of sludge.

There are various lab scale studies done on the potential of chemical wastewater treatment on paper mill effluent (Ganjidoust et al. 1997; Rodrigues et al. 2008). A study done by Stephenson and Duff (1996) showed that coagulation and precipitation of paper mill effluent (BCTMP/TMP) reduced total carbon (TC), color and turbidity. The reductions reported were 88%, 90% and 98% respectively.

2.11.2 Advanced oxidation processes (AOP)

The principle of advanced oxidation processes (AOP) is based on the formation of hydroxyl radicals (OH*). These radicals prove to be very reactive species, rapidly reacting with contaminates to form harmless products such as CO_2, H_2O and other inorganics (Kumar et al. 2011; Andreozzi et al. 1999).

$$OH^* + Contaminants \rightarrow Intermidiates \rightarrow CO_2 + H_2O + end\ products \qquad 2\text{-}3$$

AOPs are implemented at wastewater treatment facilities to oxidize refractory organic constituents into more readily biodegradable end products (Metcalf & Eddy et al. 2002). The OH^* produced in the AOP technologies degrade organics by means of radical addition, hydrogen abstraction and electron transfer (Parsons 2004).

Table 2-7: Hydroxyl radical degradation reactions and mechanisms (Parsons 2004)

Degradation mechanism	**Reaction**	**Organics degraded**
Radical addition	$R + HO^* \rightarrow ROH \rightarrow hydroxylated\ radicals$	Aromatic and unsaturated aliphatic constituents
Hydrogen abstraction	$R + HO^* \rightarrow R^* + H_2O$	Saturated and unsaturated organics (Ketones, Aldehydes)
Electron transfer	$R^n + HO^* \rightarrow R^{n-1} + OH$	n.a

Hydroxyl radicals (OH^*) are primarily produced from oxidants such as ozone (O_3) and hydrogen peroxide (H_2O_2). The OH^* produced in the AOP treatment technologies have higher oxidation potentials (EV) than both O_3 and H_2O_2 as seen in Table 2-8. The paper and pulp industry has taken a keen interest in AOP technologies as a potential tertiary treatment process in recent years (Möbius 2006). Research have demonstrated Ozone and Fenton related treatment technologies are effective advanced oxidation processes for the treatment of paper and pulp mill effluents (PPMEs) (Ko et al. 2009; Cajal-Marinosa et al. 2012; Yeber et al. 1999; Catalkaya & Kargi 2007; M Perez et al. 2002; P. Kumar et al. 2011).

Table 2-8: The oxidation potential of various oxidants (Domènech et al. 2001; Legrini et al. 1993)

Oxidant	E°(V)
Fluorine ($\mathrm{F_2}$)	3.03
Hydroxyl radical ($\mathrm{OH^*}$)	2.80
Singlet oxygen ($\mathrm{O_2}$)	2.42
Ozone ($\mathrm{O_3}$)	2.07
Hydrogen peroxide ($\mathrm{H_2O_2}$)	1.78
Perhydroxyl radicals ($\mathrm{HO_2^*}$)	1.70
Permanganate ($\mathrm{MnO_4^-}$)	1.68
Hypobromous acid (HBrO)	1.59
Chlordioxide ($\mathrm{ClO_2}$)	1.57
Hypochlorous acid (HClO)	1.49
Chlorine ($\mathrm{Cl_2}$)	1.36
Bromine ($\mathrm{Br_2}$)	1.09
Iodine ($\mathrm{I_2}$)	0.54

Ozone (O_3) and Ultraviolet/Ozone (O_3/UV) systems

Ozone is a strong oxidizing agent that rapidly reacts with most organic compounds that contains electron-rich moieties (Liu et al. 2015). Ozone processes have been implemented in various municipal wastewater treatment systems globally (Hollender et al. 2009). The complex decomposition reaction of ozone is shown in the reactions below (Beltrán et al. 2005; Karat 2013).

$$O_3 + HO_2^- \rightarrow O_3^- * + HO_2 * \qquad 2\text{-}4$$

$$O_3 + O_2^- * \rightarrow O_3^- * + O_2 \qquad 2\text{-}5$$

$$O_3^{*-} \rightarrow HO_3^{*-} \qquad 2\text{-}6$$

$$HO_3^* \rightarrow OH^* + O_2 \qquad 2\text{-}7$$

The slow reaction between ozone (O_3) and certain organics such as saturated carboxylic acids and inactivated aromatics makes wastewater treatment with ozone (O_3) uneconomical (Beltrán et al. 2012; Beltrán et al. 2005). As result, catalysts are necessary to ensure high economic feasibility (Mehrjouei et al. 2015). In some cases, ultraviolet (UV) exposure is used in photocatalytic ozonation systems (Rivas et al. 2012; Mena et al. 2012). The ultraviolet irradiation assists in the formation of hydroxyl radical (OH*) and the simplified photocatalytic reactions occurring is shown below (Karat 2013).

$$O_3 + H_2O \rightarrow^{uv} O_2 + H_2O_2 \qquad 2\text{-}8$$

$$2O_3 + H_2O_2 \rightarrow 2OH^* + 3O_2 \qquad 2\text{-}9$$

Hydrogen peroxide and Ultraviolet (H_2O_2/UV)

The formation of hydroxyl radical when hydrogen peroxide is exposed to ultraviolet (UV) have also been investigated for the potential to be integrated into municipal wastewater system (Bhatti et al. 2011; Catalkaya & Kargi 2007). The formation reactions of hydroxyl radicals in H_2O_2/UV systems are shown below (Crittenden et al. 1999; Ogata et al. 1981).

$$H_2O_2 + uv \rightarrow 2OH^* \qquad 2\text{-}10$$

Peroxone (H_2O_2/O_3)

Hydrogen peroxide (H_2O_2) is frequently added to ozone (O_3) systems to increase the formation of hydroxyl radicals from the decomposition of ozone (O_3) (Catalkaya & Kargi 2007). The primary purpose of peroxone in wastewater treatment facilities is to remove the majority of compounds contributing to taste and odor as well as synthetic organics (EPA 1999). The formation of hydroxyl radicals in peroxone (H_2O_2/O_3) systems is shown in the reactions below (Glaze 1987):

$$H_2O_2 + H_2O \rightarrow HO_2^- + H_3O^+ \qquad 2\text{-}11$$

$$HO_2^- + O_3 \rightarrow OH^* + O_2^- + O_2 \qquad 2\text{-}12$$

Fenton (Fe^{2+}/H_2O_2) and Photo-Fenton (Fe^{2+}/H_2O_2/UV) systems

The organics in Fenton related technologies are removed by means of coagulation and oxidation steps (Wu et al. 2011). The oxidation steps are primarily influenced by the production of OH*. In the Fenton process, OH* are formed when electrons exchange between hydrogen peroxide (H_2O_2) and catalytic metallic ions (Fe^{2+}) (Lin et al. 1999). The reaction occurring in the Fenton process is shown below (Ashraf et al. 2006).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^* \qquad 2\text{-}13$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe(OOH)^2 + H^+ \qquad 2\text{-}14$$

$$Fe(OOH)^2 \rightarrow Fe^{2+} + HO_2^* \qquad 2\text{-}15$$

Also frequently described in literature is the addition of ultraviolet (UV) in the Photo-Fenton process which assist in the additional formation of hydroxyl radicals (Catalkaya & Kargi 2007). Aside from the above mentioned reactions an additional reaction takes place during UV exposure (Faust & Hoigné 1990).

$$Fe^{3+} + H_2O + uv \rightarrow Fe^{2+} + H^+ + OH^* \qquad 2\text{-}16$$

Fenton-like (Fe^{3+}/H_2O_2) and Photo-Fenton-like ($UV/Fe^{3+}/H_2O_2$) treatment systems

In the Fenton-like treatment system, hydroxyl radicals (OH*) are produced when H_2O_2 is catalytically converted by Fe^{3+} salts. The main set of reactions taking place in the Fenton-like oxidation of PPME are as follows (Wang 2008):

$$Fe^{3+} + H_2O_2 \rightarrow Fe(OOH^{2+}) \tag{2-17}$$

$$Fe(OOH^{2+}) \rightarrow HO_2^* + Fe^{2+} \tag{2-18}$$

$$Fe^{2+} + H_2O_2 \rightarrow OH^* + OH^- + Fe^{3+} \tag{2-19}$$

$$RH + OH^* \rightarrow R^* + H_2O \tag{2-20}$$

As with the Fenton oxidation systems, UV exposure have also been employed to assist in the removal of organics constituents. The addition of UV to the Fenton-like system assist in the additional formation of hydroxyl radicals (OH*) as seen in Eq. 2-16.

2.11.3 Factors affecting AOP treatment

The main factors that can affect the performance of the Ozone and Fenton-related technologies are explained in this section.

Ozone related treatment technologies

Factors such as the pH, reactor pressure, ozone gas flow rate, UV exposure, H_2O_2 dosage and temperature are well-known to affect the oxidation of organics in ozone related systems.

The impact of pH on the performance of ozone treatment technologies are widely debated in literature. The performance of ozone treatment technologies are often increased at higher pH values (Amat et al. 2005; Bijan & Mohseni 2004) due to higher hydroxyl radical formation (Bijan & Mohseni 2005; Glaze et al. 1987). On the other hand, certain studies have demonstrated that the effect of pH is statistically insignificant (Merayo et al. 2013; Kreetachat et al. 2007). Nevertheless, it is often preferred to operate in neutral pH solution for economic purposes (Karat 2013).

The ozone flowrate also plays a key role in the oxidation rate of organics (Medeiros et al. 2008; Bijan & Mohseni 2005). The rate at which ozone dissolve in the wastewater can be given by the following equation (Prat et al. 1990):

$$\frac{dC_L}{dt} = k_L.a.(C_L^* - C_L) \tag{2-21}$$

where C_L is the concentration of O_3 in solution, C_L^* the saturation concentration of O_3 in the solution, $k_L.a$ the mass transfer coefficient. The increase in ozone gas flow rate generally increases the $k_L.a$ coefficient. As result increase in flowrate generally yields higher oxidation rates. However, the amount of O_3 in solution is primarily dependant the saturation concentration (C_L^*) on the on the partial pressure of ozone and the vessel temperature which follows Henry's Law (Karat 2013).

$$. C_L^* = P_{O_3}. \exp\left(22.3 - \frac{4030}{T}\right) \tag{2-22}$$

As a result, ozone reactors are often operated at higher partial pressures to increase the ozone saturation concentration (C_L^*) (Beltran 2003; Beiträn et al. 2000).

Certain studies have focused on the application of adding hydrogen peroxide to the solution to improve radical formation (Karat 2013; Ko et al. 2009; Catalkaya & Kargi 2007). The O_3/H_2O_2 generally have minimalistic effects on TOC and COD removal efficiencies (Catalkaya & Kargi 2007; Ko et al. 2009). However, the colour removal efficiency are often enhanced as a result.

The effectiveness of ozone treatment are often enhanced by UV exposure. Even though this treatment method was found to be a more effective for other types of wastewaters (Lucas et al. 2010; Mokrini et al. 1997), the treatment method only slightly improved COD removal in PPMEs (Yeber et al. 1999; Amat et al. 2005). The turbidity of the PPMEs are linked to the ineffectiveness of UV treatment methods which evidently hinders the penetration of UV irradiation into the solution (Amat et al. 2005; Karat 2013).

Higher temperatures generally leads to an increase in the organic oxidizing rate during ozone treatment (Lei & Li 2014; Kim et al. 2005). However, the solubility and stability of ozone in water also decreases with temperature (Perry & Green 1999). As a result, it is recommended that ozone reactors be operated between temperatures of 0°C and 30°C (Guendy 2007).

Fenton related technologies

The performance of the Fenton and Fenton-like treatment systems are mainly influenced by the Fe^{2+}/Fe^{3+} concentration, H_2O_2 concentration, UV exposure, pH and solution temperature.

The amount of iron catalyst (Fe^{2+}/Fe^{3+}) can have a significant impact on the performance of Fenton related treatment technologies. The addition of catalyst can have both positive and negative effects on the organic removal efficiency (Sevimli et al. 2014; Laiju et al. 2014). The increase in iron catalyst can evidently increase the organic removal efficiency due to the additional formation of hydroxyl radicals (OH*) (Laiju et al. 2014) and a higher coagulation potential (Irfan et al. 2013). This synergetic effect of oxidation and coagulation are the main mechanisms responsible for the reduction in organics. On the other hand, it was also reported that excessive Fe^{2+}/Fe^{3+} can reduce the organic removal efficiency of the Fenton process (Sevimli et al. 2014; Laiju et al. 2014). This phenomena is generally described by the scavenging of active OH^* by Fe^{2+}/Fe^{3+} ions.

The H_2O_2 dosage is a critical parameter for the production of hydroxyl radicals in Fenton related treatment systems. Even though the Fe^{2+}/Fe^{3+} addition alone removes a fraction of the organics by means of coagulation (Tambosi et al. 2006; Irfan et al. 2013), a significant fraction of the organics are primarily oxidized by hydroxyl radicals (Wu et al. 2011). The addition of H_2O_2 can have both positive and adverse effects on the organic removal efficiency. An increase in H_2O_2 can enhance OH^* production; however excessive H_2O_2 can also react with the active OH^* to form water (Ebrahiem et al. 2013).

The COD/H_2O_2 and Fe^{2+}/H_2O_2 ratios are often used to describe the complex relationship between COD, H_2O_2 and Fe^{2+} dosage in Fenton related technologies (Gulkaya et al. 2006; Hermosilla et al. 2012; Wang et al. 2011). These ratios vary greatly depending in the type of effluent and Fenton technology. A summary of the optimal ratios found in literature are presented in Table 2-9.

Table 2-9: Optimal COD/H_2O_2 and Fe^{2+} or Fe^{3+}/H_2O_2 ratios for the Fenton related oxidation of PPMEs.

Fenton technology	COD/H_2O_2	Fe^{2+} or Fe^{3+}/H_2O_2	Reference
Conventional Fenton process (Fe^{2+}/H_2O_2)	1.102[a] (wt/wt)	0.1 [*a] (molar ratio)	Wang et al. (2011b)[a]
	3.33[b] (wt/wt)	0.4 – 1[b,c] (wt/wt)	Sevimli (2005)[b]
	0.87[c] (wt/wt)	0.98[d] (wt/wt)	Sevimli et al. (2014)[c]
	0.33[d] (wt/wt)		Hermosilla et al. (2012)[d]
Photo-Fenton process ($UV/Fe^{2+}/H_2O_2$)	0.33[d] (wt/wt)	0.077[d] (wt/wt)	Rabelo et al. (2014)[e]
	0.6175[e] (wt/wt)	0.1[e] (wt/wt)	
Fenton-like process (Fe^{3+}/H_2O_2)	0.95[f] (wt/wt)	2.5[f] (wt/wt)	Tambosi et al. (2006)[f]

As with the ozone treatment systems, the addition of UV to the system can potentially be beneficial in Fenton oxidation processes. The addition of UV to the treatment system can enhance the production of hydroxyl radicals by catalytically converting H_2O_2 (Eq. 2-10) and

Fe^{3+} ions (Eq. 2-16). The photo-Fenton oxidation of PPMEs (Hermosilla et al. 2012) and other recalcitrant wastewaters have higher organic removal efficiencies compared to the conventional Fenton process (CFP) (Hansson et al. 2012; Miranzadeh et al. 2016 ; Lucas & Peres 2006). During the CFP, slowly degradable intermediate carboxylic acids are formed which evidently reduces the organic removal efficiency. However, these intermediate carboxylic acids and ferric carboxylates ($Fe(III)(RCO_2)$) are readily attacked under photo-Fenton conditions (Hermosilla et al. 2009; Hansson et al. 2012).

$$Fe(III)(RCO_2) + hv \rightarrow Fe^{2+} + CO_2 + R^* \qquad \text{2-23}$$

The efficiency of Fenton related oxidation of PPMEs are also greatly affected by the pH of the solution (Catalkaya & Kargi 2007; Wang et al. 2011; Sevimli et al. 2014). The optimal pH range for the Fenton oxidation of PPMEs are between 3 and 4 (Sevimli 2005). At higher pH values (>6), $Fe(OH)_2$ is formed which inherently reduces the free Fe^{2+} in the solution (Karat 2013). Consequently, a decline in organic removal efficiency can be noticed at higher pH values. At low pH values (<3), excessive H+ can react with the active hydroxyl radicals which in return also reduces the organic removal efficiency (Chiou et al. 2006).

The organic oxidizing rates generally increases at higher temperatures in Fenton related oxidation processes (Khamaruddin et al. 2011; Bahmani et al. 2013). However, the performance of Fenton related technologies can also decline at higher temperatures (50°C) due to the decomposition of H_2O_2 (Khamaruddin et al. 2011; Lin & Lo 1997). The optimal temperature range for Fenton-related treatment technologies are therefore between 30°C and 40°C (Lin & Lo 1997).

2.11.4 Performance evaluation of AOP and coagulation technologies

In this section, a summary of various AOP and coagulation technologies treating paper and pulp mill effluents are presented in Table 2-10. These tertiary treatment technologies are compared by their potential to remove recalcitrant organics (COD, colour and TSS).

Table 2-10: Summary of AOP and coagulation technologies used in the paper and pulp industry

Effluent type	Characteristics	Reagent dosage and conditions	Organic removal efficiency (%)	Reference
Chemical precipitation and coagulation				
Black Liquor	CODo = 28270 mg/L TSSo = 11455 mg/L	$FeCl_3$ = 1.2 g/L[a] $FeSO_4$ = 1.2 g/L[b]	COD_r = 16 %[a]; 12%[b] .TSS_r = 55%[a]; 48%[b] Colour = 20%[a,b]	Irfan et al. (2013)
Paper and pulp mill effluent	COD_o = 964 mg/L	$Fe_2(SO_4)_3$ = 400 mg/L	COD_r = 50% Colour = 100%	Tambosi et al. (2006)
Ozone (O_3)				
Bio-treated paper and pulp mill effluent	COD_o = 500 mg/L TOC_o = 110 mg/L AOX = 1.94 mg/L SS_o = 50 mg/L Phenol = 3.2 mg/L	O_3 = 4.7 g O_3/hr pH = 7	TOC_r = 29% AOX = 63% Colour = 91%	Catalkaya & Kargi (2007)
Recycle mill effluent (RME) AND Kraft mill effluent (KME)	RME COD_o = 2319 mg/L VFA_o = 347 mg/L KME CODo = 1749 mg/L VFA = 285 mg/L	O_3 = 3 g O_3/hr pH = 7 and 12	CODr = 35% (RME) CODr =60% (KME)	Merayo et al. (2013)

Table 2-11: Summary of AOP and coagulation technologies used in the paper and pulp industry

Photo-Ozone (O_3/UV)				
Paper and pulp mill effluents	Mill effluent A COD_o = 4500 mg/L VFA_o = 1100 mg/L Phenol = 22 mg/L Mill effluent B COD_o = 7100 mg/L VFA_o = 1300 mg/L Phenol = 42 mg/L Mill Effluent C COD_o = 11200 mg/L VFA_o = 3200 mg/L Phenol = 185 mg/L	O_3 = 8 g O_3/hr pH = 9	CODr = ± 40% (All effluents)	Amat et al. (2005)
Peroxone (O_3/H_2O_2)				
Bio-treated paper and pulp mill effluent	COD_o = 500 mg/L TOC_o = 110 mg/L AOX = 1.94 mg/L SS_o = 50 mg/L Phenol = 3.2 mg/L	O_3 = 4.7 g O_3/hr H_2O_2 = 5 mM pH = 11	TOC_r = 31% AOX = 95% Colour = 81%	Catalkaya & Kargi (2007)

Table 2-12: Summary of AOP and coagulation technologies used in the paper and pulp industry

Fenton process (Fe^{2+}/H_2O_2)				
Bio-treated paper and pulp mill effluent	COD_o = 500 mg/L TOC_o = 110 mg/L AOX = 1.94 mg/L SS_o = 50 mg/L Phenol = 3.2 mg/L	Fe^{2+}=2.5 mM H_2O_2 = 50 mM pH = 5	TOC_r = 88% AOX = 89% Colour = 85%	Catalkaya & Kargi (2007)
Bleaching Kraft mill effluent	COD_o = 1384 mg/L TOC_o = 441 mg/L	Fe^{2+} = 100 mg/L H_2O_2 = 5000 mg/L pH = 3	TOC_r = 50%	Perez et al. (2002)
Kraft mill effluent	DOC_o = 1000 mg/L AOX_o = 18.6 mg/L	Fe^{2+} = 206 mg/L H_2O_2 = 1278 mg/L pH = 4	DOC_r = 71% AOX_r = 84%	Cajal-Marinosa et al. (2012)
EFC Bleaching effluents	COD_o = 300 mg/L	Fe^{2+} = 206 mg/L H_2O_2 = 1278 mg/L pH = 3	COD_r = 82%	Wang et al. (2011b)
Photo-Fenton ($Fe^{2+}/H_2O_2/UV$)				
Bio-treated paper and pulp mill effluent	COD_o = 500 mg/L TOC_o = 110 mg/L AOX = 1.94 mg/L SS_o = 50 mg/L Phenol = 3.2 mg/L	Fe^{2+} = 2.5 mM H_2O_2 = 50 mM pH = 5 UV intensity = 4.98 × 10^{-6} einstein/s	TOC_r = 83% AOX = 94% Colour = 83%	Catalkaya & Kargi (2007)
Kraft Mill Effluent	COD_o = 1235 mg/L	Fe^{2+} = 10 mg/L H_2O_2 = 1000 mg/L UV intensity = 475±188 W.m^{-2}	COD_r = 62% TOC_r = 24.4% AOX_r = 19.1%	Rabelo et al. (2014)

Table 2-13: Summary of AOP and coagulation technologies used in the paper and pulp industry

Fenton-like (Fe^{3+}/H_2O_2)				
Paper and pulp mill effluent	COD_o = 964 mg/L TSS_o = 264 mg/L	Fe^{3+}= 400 mg/L H_2O_2 = 500 mg/L pH = 2.5 Coagulation pH = 5.0	COD = 75% Colour = 98%	Tambosi et al. (2006)
Black Liquor	COD_o = 4800 mg/L	Fe^{3+}= 700 mg/L H_2O_2 = 2472 mg/L pH = 4	COD_r = 83%	Lal & Grag (2015)
Photo-Fenton-like ($Fe^{3+}/UV/H_2O_2$)				
Bleaching effluents	COD_o = 1510 mg/L	Fe^{3+}= 1000 mg/L H_2O_2 = 3000 mg/L pH = 6.9	COD_r = 20%	Eskelinen et al. (2010)
Photo-Hydrogen peroxide (UV/H_2O_2) and Hydrogen peroxide (H_2O_2) treatment				
Bio-treated paper and pulp mill effluent	COD_o = 500 mg/L TOC_o = 110 mg/L AOX = 1.94 mg/L SS_o = 50 mg/L Phenol = 3.2 mg/L	H_2O_2 = 50 mM pH = 11 UV intensity = 4.98×10^{-6} einstein/s	TOC_r = 5.1%^{c}, 11.1%^{d} AOX = 34%^{c}, 18.5%^{d} Colour = 24%^{c}, 41%^{d}	Catalkaya & Kargi (2007)

^{a} FeCl3 coagulation; ^{b} FeSO4 coagulation; ^{c} H_2O_2 treatment; ^{d} H_2O_2/UV treatment

2.12 References

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Chapter 3. Technology identification and selection process

The biological and advanced oxidation processes (AOP) technologies used for the treatment of paper and pulp mill effluents were identified in Chapter 2. The logic behind the technology selection process is explained in this section. As discussed in the in Section 1.1, both Mill X and Mill Y require a wastewater treatment plant containing biological and AOP technologies to achieve their individual goals. Both mills already contain primary treatment stages (clarifier, dissolved air floatation units). Consequently, the investigation only looked at the usage of secondary and tertiary treatment systems. The technology selection diagram is shown in Figure 3-1. The definitions of the individual processes are also given in Table 3-2.

Secondary biological processes are required to remove the majority of the biochemical oxygen demand (BOD) from the paper and pulp mill effluents. In this study, an aerobic digestion processes (P-2) was chosen as the secondary treatment stage. Generally anaerobic digestion processes are preferred due to the formation of valuable biogas that could be used for energy recovery. However, anaerobic digestion systems have significantly slower microbial growth rates, inferior effluent qualities and are more sensitive to fluctuations in temperature, pH and other toxic chemicals (Chan et al. 2009; Leitão et al. 2006). Anaerobic digestion processes are known to be inhibited by terpenes, phenols, tannins, resin acids and sulphur constituents found in PPMEs (Sandberg 2008; Jahren et al. 2002; Sierra-Alvarez & Lettinga 1990; Sierra-Alvarez & Lettinga 1991; Vidal & Diez 2005; Klinke et al. 2004).

Table 3-1: A comparison between aerobic and anaerobic treatment technologies (Chan et al. 2009).

Feature	Aerobic	Anaerobic
Organic removal efficiency	High	High
Effluent quality	Excellent	Moderate to poor
Organic loading rate	Moderate	High
Sludge production	High	Low
Nutrient requirement	High	Low
Alkalinity requirement	Low	High
Energy requirement	High	Low to moderate
Temperature sensitivity	Low	High
Start-up time	2-4 weeks	2-4 months
Odour	Less opportunity for odours	Potential odour problem
Bioenergy and nutrient recovery	No	Yes
Mode of treatment	Total treatment	Predominantly pre-treatment

As a result, it was decided to investigate aerobic digestion technologies. Aerobic digestion technologies such as activated sludge (AS), sequencing batch reactors (SBR), moving bed biofilm reactors (MBBR) and membrane biological reactors (MBR) are often implemented at paper and pulp mills. Based upon the literature survey (Chapter 2) both the moving bed biofilm reactor (MBBR) and the membrane bio-reactor (MBR) showed the most promising results. The membrane bio-reactors (MBR) in general produce excellent effluent qualities that are low in BOD and TSS (Attiogbe 2013). However, one of the major drawbacks of MBRs is related to fouling issues which are caused by microbial growth or fillers used in the process (Lerner et al. 2007; Attiogbe 2013). More complex maintenance for the MBRs is therefore required when compared to MBBRs. The COD and BOD removal in MBRs are also similar to that of other biological processes such as activated sludge (Lerner et al. 2007). One crucial advantage of MBBRs is that they can recover quickly after toxic loadings since a large fraction of the bacteria stays protected within the biofilm carrier matrix. Consequently, it was decided to use an aerobic MBBR as the secondary treatment stage for both Mill X and Mill Y.

The primary purpose of tertiary treatment technologies is to remove the remaining bio-recalcitrant organics and colour by means of advanced oxidation processes (AOP), membranes, chemical addition or precipitation processes. For Mill X, membranes will eventually be required as the final purification step to remove excessive total dissolved solids (TDS) to close the water network. Membrane filtrations processes such as ultrafiltration (UF) and reverse osmosis (RO) generally produce excellent water qualities which are suitable for reuse. As with the case of MBRs, nano filtration (NF) and reverse osmosis (RO) membrane processes suffer from fouling issues along with highly concentrated retentated streams containing bio-recalcitrant organics (Kamali & Khodaparast 2015). Both of these problems could be addressed by the implementation of advanced oxidation processes (AOP). By using AOP technologies as a pre-treatment technique, membrane fouling can be greatly reduced (Oh et al. 2009). AOP technologies can also be used to treat the bio-recalcitrant organics in the concentrated retentate streams prior to disposal (Hermosilla et al. 2012). At Mill Y, NF or RO will not be required for treating to discharge for irrigation purposes. The BOD/COD ratios for the NSSC effluents are relatively low (0.22-0.35). The low ratios indicate that the effluent after biological treatment will still contain a large fraction of bio-recalcitrant COD. AOP technologies could therefore be used at Mill Y to lower the bio-recalcitrant COD concentrations in order to comply with environmental legislation.

It is evident that the implementation of AOP technologies as a tertiary treatment system at both mills would be necessary. As a result, the main focus of this project is on tertiary AOP treatment of BTMEs. These AOP technologies primarily include ozone (O_3) and Fenton (Fe^{2+}/H_2O_2; Fe^{3+}/H_2O_2) related treatment technologies. Literature suggests that both of these AOP technologies are able to remove bio-recalcitrant organics and colour (Karat 2013; Kazmi & Thul 2007; Catalkaya & Kargi 2007). However, various studies have found that Fenton related technologies are more efficient, economical and less complex to operate than ozone technologies (Sevimli 2005; Canizares et al. 2009; Kazmi & Thul 2007; Catalkaya & Kargi 2007). The potential of the Fenton related technologies as an effective AOP technology for BTME treatment was therefore chosen for this investigation. The applicability of combining an aerobic MBBR and Fenton related process for the Mill X and Mill Y will therefore be investigated throughout this dissertation.

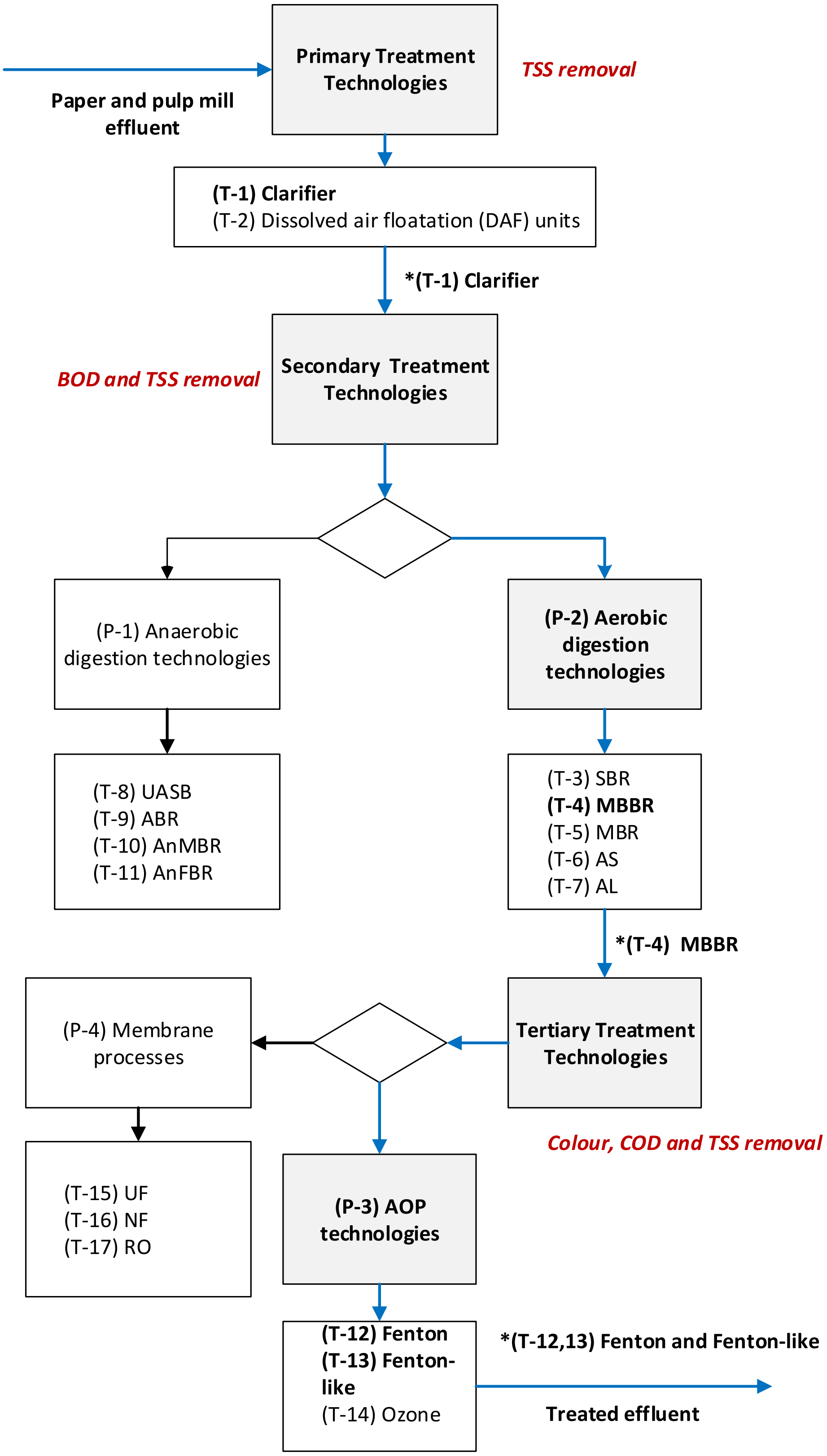

Figure 3-1: Schematic representation of the technology selection process

Table 3-2: *The description of various wastewater treatment technologies*

Technology	Description
T-1	Clarifiers
T-2	Dissolved air floatation (DAF) units
T-3	Sequencing batch reactor (SBR)
T-4	Moving bed biofilm reactor (MBBR)
T-5	Membrane biological reactor (MBR)
T-6	Activated sludge (AS)
T-7	Aerated Lagoon (AL)
T-8	Upflow anaerobic sludge blanket (UASB)
T-9	Anaerobic baffle reactor (ABR)
T-10	Anaerobic membrane bio-reactor (AnMBR)
T-11	Anaerobic fluidized bed reactor (AnFBR)
T-12	Fenton treatment process
T-13	Fenton-like treatment process
T-14	Ozone treatment
T-15	Ultrafiltration (UF)
T-16	Nanofiltration (NF)
T-17	Reverse osmosis (RO)

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Chapter 4. A kinetic study of a mesophilic aerobic moving bed biofilm reactor (MBBR) treating paper and pulp mill effluents: The impact of phenols on biodegradation rates

A. Brink; C. Sheridan; K. Harding

The aim of this Chapter was to investigate the potential of an aerobic mesophilic MBBR for the treatment of wastewater originating from Mill X and Y. A kinetic study was conducted in order to assess the applicability of different kinetic models and to differentiate between the biodegradation for the various effluents.

This article was submitted to the *Journal of Water Process Engineering* for peer review and publication. The co-authors of this article contributed by means of supervision while the write-up and experiments were conducted by the author of this dissertation.

4.1 Abstract

This study investigated the impact that phenols have on the biodegradation rate of paper and pulp mill effluents in a bench-scale aerobic moving bed biofilm reactor (MBBR). Paper and pulp mill effluents were collected from recycle and neutral sulfite semi-chemical mills. The phenol concentrations of the four-individual paper and pulp mill effluents were 4.61, 29.1, 42.65 and 60.6 mg/L. The removal of chemical oxygen demand (COD) was continuously monitored for individual effluents during the experiments. The hydraulic residence time (HRT) and organic loading rates (OLR) in the experiment were varied between 5 – 45 hours and 2 – 6 kg COD/m^3.day, respectively. The biodegradable chemical oxygen demand (COD) removal efficiency at a hydraulic residence time (HRT) of 16 hours was 86, 65, 60 and 46% for individual mill effluents. The Kincannon-Stover, first order and Grau second order kinetic models were evaluated to describe the removal of organics in a mesophilic aerobic MBBR. The highest correlation coefficients (r^2) were found for the Kincannon-Stover model. According to the Kincannon-Stover model, the maximum substrate removal rates were 15.06, 9.81, 6.77 and 4.62 gCOD/L.day for mill effluents containing 4.61, 29.1, 42.65 and 60.6 mg/L phenols, respectively. The trend indicated that phenols inhibited the biodegradation rates of paper and pulp mill effluents in a mesophilic aerobic MBBR. Additional intermediate or pre-treatment may be required to remove excessive phenols to ultimately increase the performance of MBBRs in the paper and pulp industry.

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Keywords: phenols; aerobic moving bed biofilm reactor (MBBR); neutral sulfite semi chemical (NSSC) effluent; recycle mill effluent; chemical oxygen demand (COD)

4.2 Introduction

The paper and pulp industry produces large volumes of organic-rich wastewater. These organic compounds can include cellulosic material, phenols, solvents, chlorinated complexes and sulfide complexes (Carg 2012). The direct discharge of mill effluents to the surrounding environment can impact the terrestrial and aquatic ecosystems. The growth, maturation, mortality and metabolism of various fish species can be altered due to the direct discharge of mill effluents (McMaster & Hewitt 2011). Excess nutrients and biodegradable organics in discharged mill effluents can deplete dissolved oxygen, cause slime and scum growth in surrounding waterbodies (Garg & Tripathi 2011; Lacorte et al. 2003). As a result, the implementation of biological treatment systems is generally required to meet environmental discharge legislation.

Paper and pulp mill effluents often contain toxic and inhibitory constituents which can complicate the bioremediation process (Chaparro & Pires 2011; Pessala et al. 2004). The inhibitory effect caused by some of the mill effluents can potentially be linked to the phenolic content. According to Hussain et al. (2015), the growth rate of activated sludge (AS) can be severely inhibited by high phenol concentrations. The alkylphenols such as cresols and xylenol present in mill effluents are considered to be 5 to 34 times more toxic to mixed bacterial cultures than pure phenol (Acuña-Argüelles et al. 2003). Bacterial cultures generally adapt and acclimatise in high phenolic wastewaters in order to increase specific growth and substrate removal rates (Lim et al. 2013; Agarry et al. 2009). However, the rate at which the effluent composition fluctuates within the paper and pulp industry often exceeds the rate of microbial adaptation (Liss & Allen 1992).

Aerobic moving bed biofilm reactors (MBBR) yielded promising results for the treatment of paper and pulp mill effluents (Jahren et al. 2002; Ødegaard et al. 1994). Various studies investigated the performance of aerobic moving bed biofilm reactors (MBBR) treating paper and pulp mill effluents (Pozzi et al. 2014; Oliveira et al. 2014). However, there are a lack of studies investigating the kinetics and the potential impact of phenols on this bioremediation process. Consequently, the primary objectives of this study are to assess:

(i) the applicability of different kinetic models to describe organic removal in a MBBR

(ii) the potential impact that phenols have on the biodegradation rate of paper and pulp mill effluents.

4.3 Materials and Methods

4.3.1 Paper and pulp mill effluent characteristics

Clarified mill effluents were collected from two separate paper mills. Mill X utilised mainly recycled material as a feedstock whilst Mill Y used a combination of virgin fibre and recycled material as feed. Effluent A, was produced in Mill X while Effluent B and C were produced in Mill Y. Effluent D was a blend containing 57% (v/v) of Effluent B and 43% (v/v) of Effluent C. Effluent B and C were blended to evaluate the impact of lower COD and phenol loadings on the performance of the MBBR. The blending ratio was estimated with historical mill production data. The process characteristics of the individual mill effluents are presented in Table 4-1.

Table 4-1: The process specifications for each mill effluent type

Parameter	Effluent A	Effluent B	Effluent C
Recycle material (%)	95	50 – 55	25
Broke (%)	5	5 – 7	5
NSSC (%)	0	40 – 42	70
Hardwood (%)	-	60	100
Softwood (%)	-	40	-

All the samples were collected from the supernatant stream exiting the primary clarifiers. After collection, all the samples were stored at 4°C. The wastewater characteristics of the mill effluents are presented in Table 4-2.

Table 4-2: Wastewater characteristics of untreated clarified mill effluent A, B and C

Parameter	Effluent A	Effluent B	Effluent C
COD (mg/L)	1892	4850	7447
Volatile organic acids (mg/L)	1150	1115	1682
Phenolic content (mg/L)	4.61	29.1	60.6
TSS (mg/L)	121	429.6	803.42
pH	6.6	6.39	7.34
Conductivity (µS/cm)	1374	4060	4760
TDS (mg/L)	879	2600	3050
Carbohydrates (mg/L)	74	278	521

The wastewater characteristics of Effluent D are expected to be a combination of Effluent B (57%) and C (43%).The various effluent samples were tested at an external lab for volatile and semi-volatile organics. The detected semi-volatile organic constituents for effluent A, B, C are presented in Table 4-3. These semi-volatile organic screening results indicate that phenols, organic acids and other solvents are present in the mill effluents.

Table 4-3: Semi-Volatile organic screening results for Effluent A, B and C

Effluent A	Effluent B	Effluent C
Butyl glycol	Furfural	Butanoic acid
p-Cresol	Butanoic acid, -2 methyl-	Butanoic acid, -2 methyl-
Ethylhexanoic acid	Phenol	Phenol
Benzoic acid	2-Methylphenol	2-Metylphenol
1-(2-Butoxyethoxy) ethanol	3/4-Methylphenol	3/4-Methylphenol
Benzeneacetic acid	Benzoic acid	1,2-Benzenediol, 3-methoxy
Benzenepropanoic acid	Phenol, 2,6-dimethoxy-	Phenol, 2,6-dimethoxy
1,4-Diisobutyl-1,4-dimethylbutynediol	2(3)-Furanone,dihydro-5-pentyl-	1,4-Diisobutyl-1,4-dimethylbutynediol
4-(1,5-Dimethyl-3-oxohexyl)-1-cyclohexene-1-carboxyllic acid	1,4-Diisobutyl-1,4-dimethylbutynediol	Ethanone
Octadecanoic acid	Ethanone	Homovanillyl alcohol
Bisphenol A	Homovanillyl alcohol	Phenol,3,4,5-trimethoxy-
Callitrisic acid	Phenol,3,4,5-trimethoxy-	Di-n-butyl phthlate
Dibenzylbutyrolactone	Phthalic acid	Cis-13-Octadecenoic acid
	Di-n-butyl phthlate	

4.3.2 Mesophilic aerobic moving bed biofilm reactor (MBBR)

A laboratory scale 10 L moving bed biofilm reactor (MBBR) was used in this study. The MBBR had a reactor carrier media filling ratio of 30% (v/v). The total surface area of the carrier media inside the reactor was 340 m^2/m^3. The temperature of the supernatant exiting the clarifiers at the mills was 35°C. Consequently, the temperature inside the reactor was maintained at a constant 32°C using a ViaAqua heater to try to reproduce field conditions. Two 2 L/min Sonic 9905 air pumps were used to supply air to the MBBR, where each airline was equipped with air stones. The dissolved oxygen (DO) concentrations inside the reactor ranged between 3.0 – 3.5 mg/L. A peristaltic pump (Watson Marlow 120S) was used to vary the feed flow rates according to need.

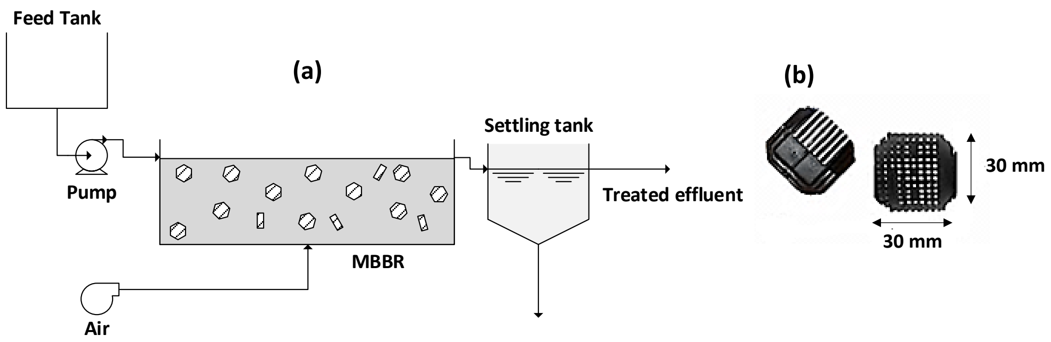

Figure 4-1: Schematic illustration of (a) the experimental set-up and (b) the biomass carrier media

4.3.3 Reactor start-up period

The moving bed biofilm reactor (MBBR) was inoculated with activated sludge which was collected from a local wastewater treatment plant. Effluent A was used as a feedstock for the maturation of the reactor over a 30 day period. The concentration of the paper and pulp mill effluent was gradually increased during this maturation period to acclimatise it to full strength. The attached and suspended biomass had significantly increased during the start-up period. The experiments were initiated after this 30 day maturation period.

4.3.4 Chemical analysis

The COD, VOA and phenolic measurements were determined with calorific methods and measured on a Merck Spectroquant®. A Merck COD cell test (100 – 1500 mg/L) (Code: 114539), volatile organic acid cell test (50 – 3000 mg/L) (Code: 101809) and phenol test (0.002 – 5 mg/L) (Code: 100856) were used to characterise the effluent. The modified Anthrone method was used to determine the carbohydrate content of the effluent (Mu & Plummer 1988). The pH, conductivity and dissolved oxygen (DO) were monitored using a handheld IP67 Combo pH/COND/D.O. (8603) meter. The amount of suspended solids (SS) was measured according to standard methods described by Skrentner (1988).

4.4 Mathematical models: Biological kinetics

4.4.1.1 First order kinetic model

In well-agitated systems, the substrate (C_F) removal according to first order kinetics can be given by the following expression (Esmaeilirad et al. 2015; Metcalf & Eddy et al. 2002):

$$\frac{dC_F}{dt} = \frac{Q.C_o}{V} - \frac{Q.C_F}{V} - k_x.X.C_F \qquad 4\text{-}1$$

The rate of substrate removal (dC_F/dt) at steady state conditions is considered to be insignificant and subsequently Eq. 4-1 can be simplified to yield Eq. 4-2:

$$\frac{C_o - C_F}{HRT} = k_{x1}.X.C_F = k_1.C_F \tag{4-2}$$

where C_o and C_F are the initial and effluent substrate COD concentrations (mg/L), *HRT* the hydraulic residence time (hr), *X* the active bacterial concentration (mg VSS/L), k_x the first order kinetic constant (L/mg VSS.hr) and k_{x1} the lumped first order kinetic parameter (hr^{-1}).

4.4.2 Second order kinetic model (Grau model)

According to Grau et al. (1975), the rate of substrate removal (dC_F/dt) which follows second order reaction kinetics is given by the following equation:

$$\frac{dC_F}{dt} = \frac{Q.C_O}{V} - \frac{Q.C_F}{V} - k.X.\left(\frac{C_F}{C_o}\right)^2 \tag{4-3}$$

when Eq. 4-3 is integrated and linearized which yields Eq. 4-4.

$$\left(\frac{C_o.HRT}{C_o - C_F}\right) = HRT + \frac{C_o}{k.X} \tag{4-4}$$

if the term ($C_o/k.X$) in Eq. 4-4, is accepted to be a constant (*a*) the following expression can be obtained:

$$\left(\frac{C_o.HRT}{C_o - C_F}\right) = bHRT + a \tag{4-5}$$

where C_o and C_F represents the initial and effluent substrate COD concentrations (mg/L), HRT the hydraulic residence time (hr) and a (hr) and *b* are the Grau kinetic model constants.

4.4.3 Kincannon-Stover model

The Kincannon-Stover kinetic parameters were initially used to describe the removal of substrate in rotary biological contactors (RBC) which took the film surface area (*A*) into account. Hosseiny & Borghei (2002) modified this equation by replacing the area (*A*) of the film with the reactor volume (*V*). This modified Kincannon-Stover kinetic model is frequently used to describe the substrate removal in moving bed biofilm reactors (MBBR) (Esmaeilirad et al. 2015; Babaei et al. 2013). The Kincannon-Stover model describing the substrate removal is given by the following expression:

$$\frac{dC_F}{dt} = \frac{Q}{V}.(C_o - C_F) = \frac{U_{max}.\left(\frac{Q.C_o}{V}\right)}{K_B + \frac{Q.C_o}{V}} \qquad 4\text{-}6$$

Eq. 4-6 can be linearised which yields the following equation:

$$\frac{V}{Q.(C_o - C_F)} = \frac{K_B}{U_{max}}.\left(\frac{V}{Q.C_o}\right) + \frac{1}{U_{max}} \qquad 4\text{-}7$$

where C_o and C_F are the influent and effluent substrate COD concentrations (mg/L); V represents the reactor volume (L); Q is the flow rate (L/d); U_{max} signifies the maximum substrate removal rate (g COD/L.d) and K_B represents the saturation constant (g COD/L.d).

4.5 Biodegradability and inhibition assessment

In order to assess the biodegradability and inhibitory effects of paper and pulp mill effluents, it is important to differentiate between the biodegradable and non-biodegradable COD fractions. The Kincannon Stover model can be manipulated to create a model that can estimate biodegradable and non-biodegradable COD fractions. The fractional COD removal in the MBBR, according to the Kincannon-Stover model, is given by the following expression:

$$COD\ removal\ \ fraction = \left(\frac{1}{C_o}\right)\left(\frac{U_{max}.C_o}{K_B + (C_o/HRT)}\right) \qquad 4\text{-}8$$

where C_o represents the initial substrate COD concentration (mg/L), U_{max} and K_B the Kincannon-Stover kinetic parameters (gCOD/L.day) and HRT the hydraulic residence time (day). The biodegradable COD fraction (*f_b*) can be calculated using Eq. 4-8, by assuming that the maximum COD removal in the MBBR is reached at an infinite hydraulic residence time (HRT). The biodegradable COD fraction (f_b) is given by the following equation:

$$\lim_{HRT\to\infty} COD\ removal\ fraction = f_b = \left(\frac{1}{C_o}\right)\left(\frac{U_{max}.C_o}{K_B}\right) = \frac{U_{max}}{K_B} \qquad 4\text{-}9$$

4.6 Results and Discussion

4.6.1 COD removal results

The organic loading rate (OLR) for Effluent A was varied from 2 to 5 kg COD/m^3.day, for Effluent B from 3 to 5.2 kg COD/m^3.day, for Effluent C from 2.5 to 4 kg COD/m^3.day, for Effluent D from 2.4 to 6 kg COD/m^3.day. The average COD removal for the various mill effluents at various hydraulic residence times (HRT) are presented in Table 4-4. The maximum COD removal efficiency (%) obtained during the experiments for effluent A, B, C and D were 55, 52, 34 and 32 %, respectively.

Table 4-4: COD removed (mg/L) at various hydraulic residence times (HRT) for the various mill effluents

HRT (hr)	Effluent A	Effluent B	Effluent C	Effluent D
5	813 (43%)	1276 (26%)	-	804 (13%)
16	927 (49%)	2231(46%)	1562 (21%)	1704 (28%)
21	-	2552 (52%)	2009 (27%)	-
24	1040 (55%)	-	-	1968 (32%)
45	-	-	2529.94 (34%)	-

The COD removal efficiency cannot be used as a direct indicator for the rate of biodegradation since a certain fraction of the COD value is considered to be bio-recalcitrant, which varies for each individual effluent. The biological oxygen demand (BOD) parameter is often used as an indicator of the biodegradability, which essentially excludes the bio-recalcitrant constituents. However, the BOD/COD ratios of paper and pulp mill effluents can occasionally be misleading and give faulty ratios, since non-specialised bacterial cultures are used in the conventional BOD tests (Kumar et al. 2010). The bacterial growth in an acclimatised MBBR is more specialised and adapted for aromatic specific biodegradation. Hence, the actual BOD/COD ratios for specialised growth are found to be higher than that of non-specialised growth.

Biological kinetic models are generally used for design and optimisation of industrial scale applications, but can also be used as an indirect approach to calculate the biodegradable and bio-recalcitrant COD. Consequently, the applicability of several kinetic models, which can ultimately be used to determine the biodegradability of the various mill effluents are evaluated in the following sections.

4.6.2 First order kinetic model

To determine the first order kinetic parameter (k_1), the experimental values for the $(C_o-C_F)/HRT$ and C_F terms were calculated and plotted (Figure 4-2). The trend line for individual effluents A, B, C and D are labelled as yA, yB, yC and yD, respectively. The correlation coefficients (r^2) for Effluent A, B ,C and D were 0.65, 0.85, 0.82 and 0.98, respectively. The slightly lower correlation coefficients (r^2) indicate that the COD removal in the MBBR is less likely to follow first order COD removal. The first order kinetic constants (k_1) for effluent A, B, C and D are 6.67, 1.80, 1.19, 0.61 /hr, respectively.

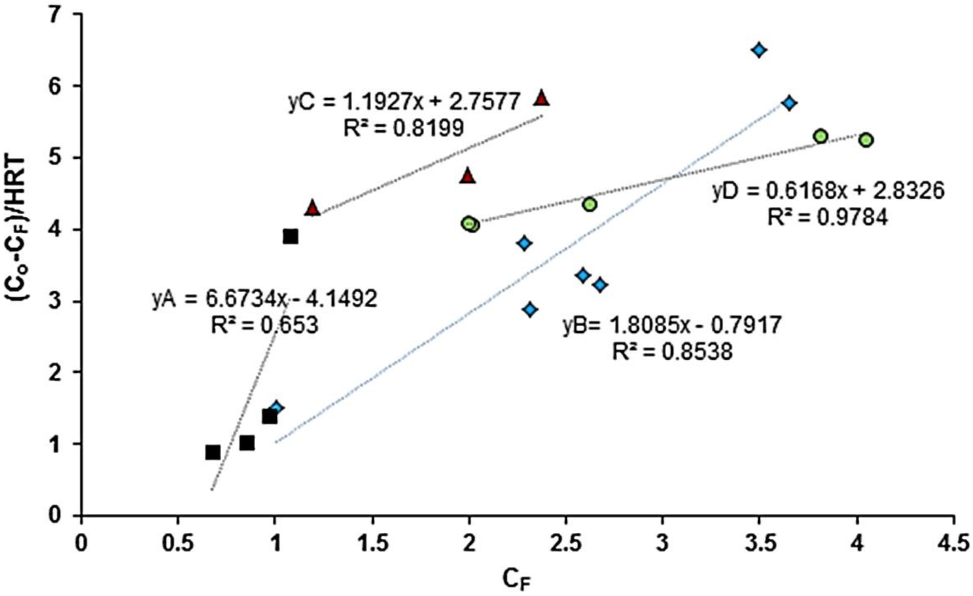

Figure 4-2: First order kinetic model plot for various paper and pulp mill effluents (■Effluent A; ♦ Effluent B; ▲ Effluent C; ● Effluent D)

4.6.3 Grau second order kinetic model

The Grau second order kinetic parameters (*a*,*b*) were obtained by plotting $C_o.HRT/ (C_o-C_F)$ and *HRT*. The intercept and gradient of the trend line represents the a and *b* kinetic parameters, respectively (Figure 4-3). The correlation coefficients (r^2) for effluent A, B, C and D were found to be 0.99, 0.94, 0.98 and 0.99 respectively. High correlation coefficients (r^2) for the mill effluents indicate that the second order model can accurately predict the removal of organics. The kinetic parameter (*a*) for Effluent A, B, C and D are -0.17, 0.56, 1.61 and 1.14 hr^{-1}, respectively. Similarly the kinetic parameter (*b*) for Effluent A, B, C and D is given by 2.43, 1.21, 2.06 and 1.87, respectively.

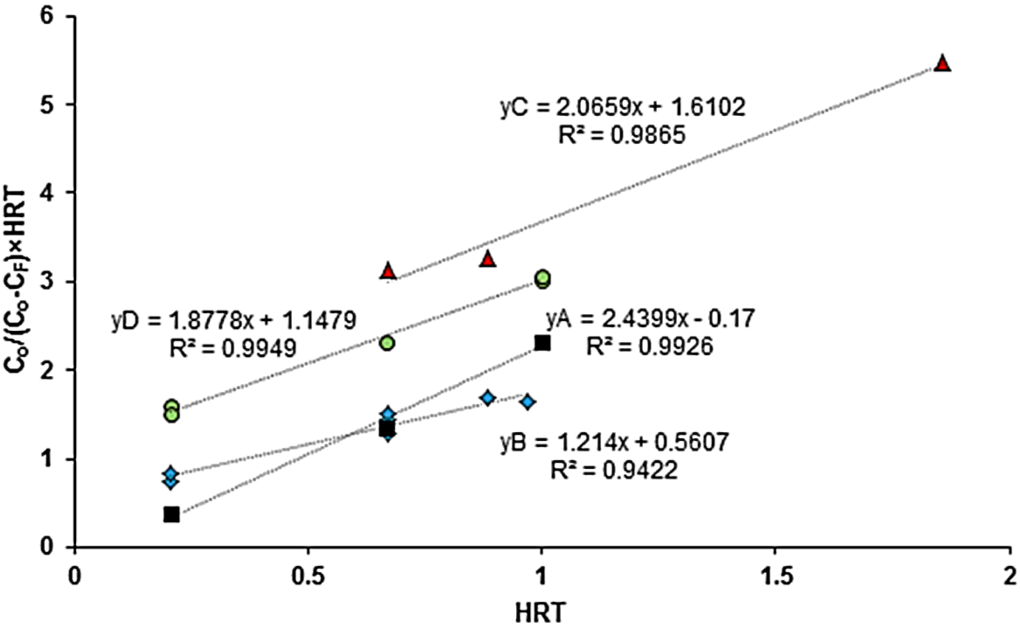

Figure 4-3: Second order kinetic model plot for various paper and pulp mill effluents (■Effluent A; ♦ Effluent B; ▲ Effluent C; ● Effluent D)

4.6.4 Kincannon-Stover kinetic model

To obtain the kinetic parameters K_B and U_{max}, $V/Q.(C_o\text{-}C_F)$ was plotted against $V/Q.C_o$ (Figure 4-4). The intercept of the trend line represents $1/U_{max}$ while the gradient represents K_B/U_{max}. The correlation coefficients (r^2) for all of the effluents were 0.99. Consequently, accurate biodegradable organic removal predictions can be made with this model. The maximum utilisation rates (U_{max}) for mill Effluent A, B, C and D are 15.06, 9.81, 4.62 and 6.77 gCOD/L.day, respectively. The saturation constant (K_B) for mill Effluents A, B, C and D is given by the following values 26.37, 13.95, 10.10, 14.53 gCOD/L.day, respectively.

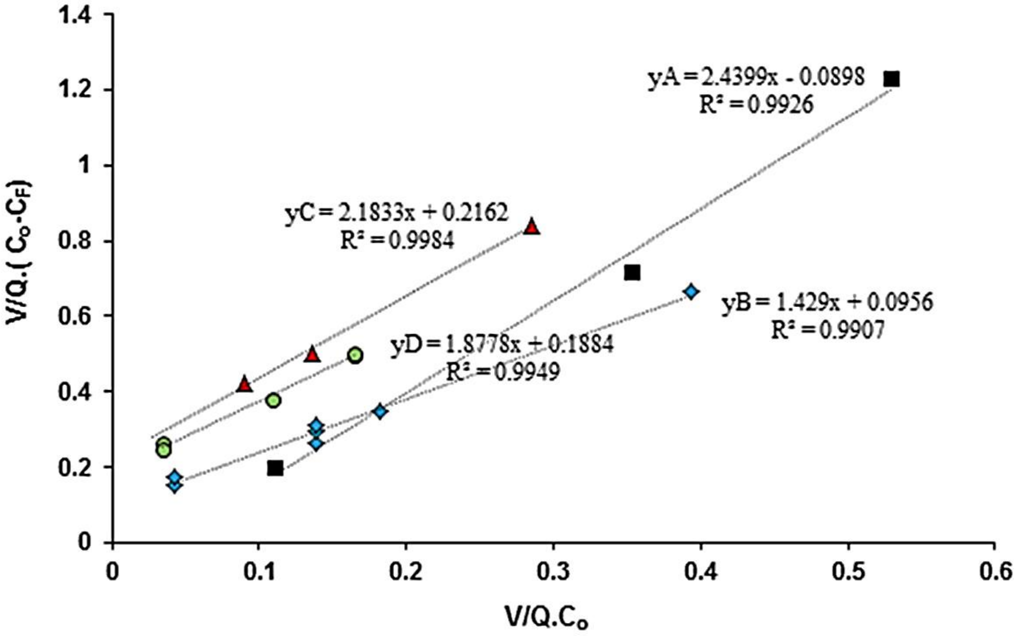

Figure 4-4: Kincannon-Stover model plot for the various paper and pulp mill effluents (■Effluent A; ♦ Effluent B; ▲ Effluent C; ● Effluent D)

The effluent substrate COD concentration (C_F) for individual mill effluents exiting the MBBR at various hydraulic residence times (HRT) is given by the following expression:

$$C_F = C_o - \frac{U_{max}.C_o}{K_B + \left(\frac{QC_o}{V}\right)} \qquad 4\text{-}10$$

4.7 Biodegradability and inhibition assessment

The experimental COD removal efficiency for the various effluents, along with the corresponding Kincannon-Stover models, is presented in Figure 4-5. The Kincannon-Stover model values were determined using Eq. 4-10. Figure 4-5 illustrates that the COD removal of the mill effluents increases until an asymptote is reached, which is generally lower than 100%. The bio-recalcitrant organics present in the effluent streams is responsible the remainder of the COD fraction. Using Eq. 4-9, the biodegradable COD fraction (f_b) of each individual effluent can be calculated using the predetermined Kincannon-Stover kinetic parameters (U_{max}, K_B). The biodegradable COD fractions for effluent A, B and C are presented in Table 4-5.

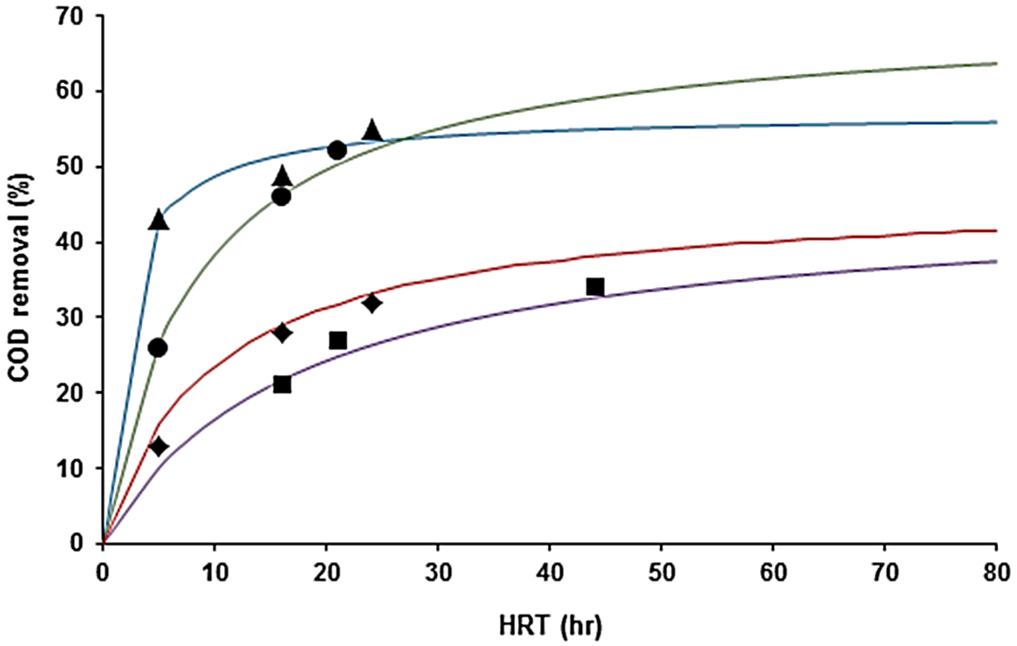

Figure 4-5: The Kincannon-Stover kinetic model (lines) for the various paper and pulp mill effluents treated by the MBBR (▲ Effluent A experimental data; ● Effluent B experimental data; ■ Effluent C experimental data; ♦ Effluent D experimental data)

Table 4-5: Estimations on the biodegradable COD fractions of the effluent

	Effluent A	**Effluent B**	**Effluent C**
U_{max} (g COD/L.day)	15.06	9.81	4.62
K_B (g COD/L.day)	26.37	13.95	10.10
Biodegradable COD fraction (f_b)	0.57	0.70	0.46
Initial COD value (mg/L)	1892	4850	7447
Biodegradable COD amount (mg/L)	1080	3411	3406

The biodegradable COD fractions (f_b) of effluent B and C differ significantly as seen in Table 4-5, however the quantity of biodegradable COD are very similar. This suggests that Effluent C contains a significantly larger fraction of bio-recalcitrant COD when compared to Effluent B. The amount of biodegradable COD can be an indicator of the BOD_5 value of the effluent. Samples of effluent B and C were sent away for conventional (non-specialised seeding) BOD_5 analysis, which revealed that the BOD_5 was 1650 mg/L and 1710 mg/L for Effluent B and C, respectively. These BOD_5 values are lower than that of the biodegradable COD values (Table 4-5). This difference in biodegradable COD and BOD_5 values is due the difference in microbial cultures used for testing. The BOD_5 estimates were determined using non-specialised cultures whereas the biodegradable COD content were determined using specialised microbial cultures. According to Kumar et al. (2010), the BOD_5 values that were determined using non-specialised seeding methods, will be significantly lower than the BOD_5 values obtained from specialised cultures. The BOD_5 and biodegradable COD values differ, however both values indicate that the biodegradable content of both Effluent B and C are very similar. The removal of biodegradable COD at various hydraulic residence times (HRT) are presented in Table 4-6.

Table 4-6: The biodegradable COD removal efficiencies (%) for the various mill effluents.

HRT (hr)	Effluent A	Effluent B	Effluent C	Effluent D
5	75	37	-	29
16	86	65	46	60
21	-	75	59	-
24	96	-	-	70
45	-	-	74	-

The results in Table 4-6 indicate that Effluent A is degraded at a much faster rate in comparison with the other mill effluents. Similar results were obtained in Merayo et al. (2013) which found that recycle mill effluent (RME) was more readily biodegradable compared to that of Kraft mill effluent. The majority of the COD in Effluent A consisted of volatile organic acids (VOA). The VOA/COD ratio for Effluent A, B and C was 0.62, 0.22 and 0.22, respectively. According to Metcalf & Eddy et al. (2002), the majority of volatile fatty acids are readily biodegraded. The high VOA/COD ratios can potentially explain the high removal efficiencies of biodegradable material for Effluent A. At a hydraulic residence time (HRT) of 24 hours, the amount of VOA removed from effluent A, B and C were 708, 659 and 512 mg/L, respectively.

The biodegradable COD removal efficiency results in Table 4-6 suggest that Effluent C might have been inhibited during the treatment process. The calorific phenol test revealed that total phenols present in Effluent C were almost double that of Effluent B. The semi-volatile organic analysis data (Table 4-3) illustrated that the concentration of 3/4-Methylphenol for Effluent C was almost double that of Effluent B. According to Hussain et al. (2015), high phenol concentrations can have a negative effect on the specific growth rate of activated sludge (AS). The inhibitory effects of phenol on specific growth and substrate removal rate of some bacterial cultures can be noticed at concentrations as low as 30 mg/L (Agarry et al. 2009). The inhibitory effect of alkyl phenols present in these mill effluents can even be more severe than phenol (Acuña-Argüelles et al. 2003).

The higher phenol concentration found in Effluent C can be linked to the type of feed stock that was utilised in the process. The feedstock for Effluent C contained a significantly larger fraction of virgin fibre (hardwood and softwood) (Table 4-1). Hard and softwood contain approximately 23-34% lignin (Amaral et al. 2014), whereas recyclable materials such as waste paper and cardboard contain approximately 14.8 % lignin (Francou et al. 2008; ElNawawy et al. 1994). It can be expected that the lignin content of Effluent C will be significantly higher in comparison to Effluent A and B, as a direct result of type of feedstock. According to Servos (1996), the majority of phenols present in the mill effluents are generally lignin-derived. Subsequently it can also be expected that Effluent C will contain more phenols, due to the higher lignin content. The correlation between the maximum substrate removal rate (U_{max}) for the various mill effluents and the phenol concentrations is illustrated in Figure 4-6. This illustrates that an increase in phenol concentration leads to a decrease in the biodegradation rate. In a study by Pessala et al. (2004), a direct correlation was found between the toxicity of the effluent and the quantity of lignin present in the paper mill effluent. This corresponds well with the findings of this study, since most of the phenols are generally lignin-derived (Servos 1996).

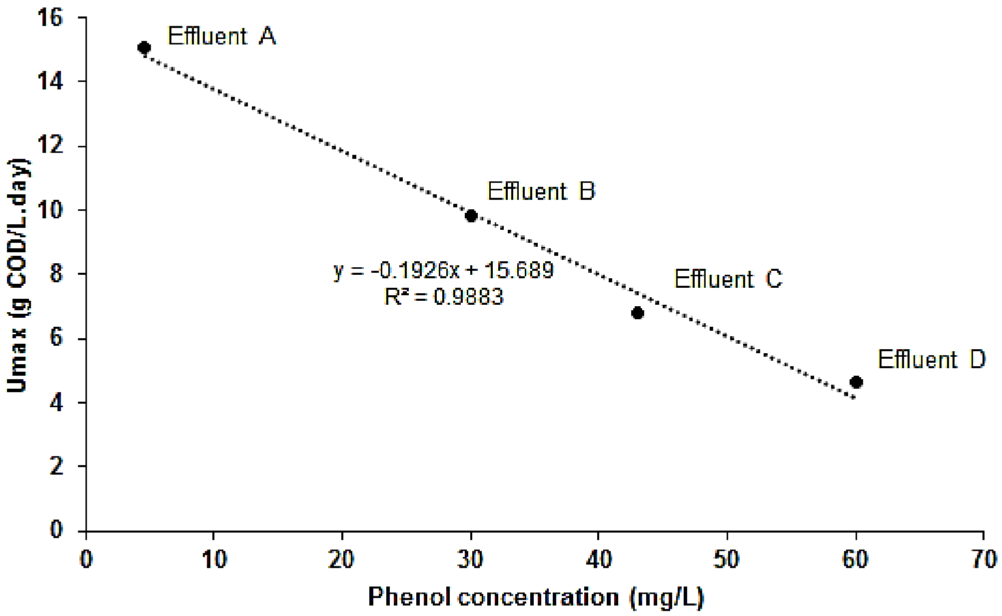

Figure 4-6: The maximum substrate removal rate (U_{max}) for the various mill effluents

4.8 Kinetic model summary and comparison

The high correlation coefficients (r^2) obtained for both the Kincannon-Stover and second order models indicate that these models are applicable for predicting the removal of biodegradable organics in a lab scale mesophilic MBBR. In a study done by Yilmaz et al.

(2008), simulated paper mill wastewater was treated using an anaerobic filter. The simulated paper mill effluent was prepared by adding waste paper into a pulper and filtering the pulp mixture. The real life effect of inhibitory substances such as biocides, phenols and resin acids are not necessarily taken into account in such simulated scenarios. The Kincannon-Stover and Grau second order kinetic constants were found to be comparable with the results from Yilmaz et al. (2008). The maximum substrate utilization rate (U_{max}) for effluent A, B and D were generally higher than that of the simulated mill effluent. The higher substrate utilization rates (U_{max}) may be due to the rate differences between aerobic and anaerobic microbial digestion at mesophilic temperatures or effluent composition. Aerobic reactors exhibit higher COD and VSS removal capabilities compared to that of anaerobic reactors (Chan et al. 2009). The saturation constant (K_B) of all the effluents were found to be higher than that of the simulated effluent. The biodegradable COD fraction (U_{max}/K_B) of the simulated mill effluent was calculated to be 1.09 according to Eq. 4-9. Consequently, a complete removal of COD can be achieved in the anaerobic filter. This suggests the presence of minimal bio-recalcitrant COD in the simulated paper and pulp mill effluent. The comparison between this study and Yilmaz et al. (2008) is presented in Table 4-7.

Table 4-7: Comparison between Kincannon-Stover and second order parameters

Kinetic model	Substrate	COD_o (mg L^{-1})	HRT (hr)	Kinetic parameters		Reactor	Reference
				U_{max}(g/L.d)	K_B(g/L.d)		
Kincannon-Stover	Simulated paper mill wastewater	2000	10.6,7.9,6	6.71	6.14	AnFilter	(Yilmaz et al. 2008)
Kincannon-Stover	Recycle mill effluent (RME) (Effluent A)	1892	5,16,24	15.06	26.37	MBBR	This study
Kincannon-Stover	Recycle mill effluent and NSSC (Effluent B)	4850	5,16,24	9.81	13.95	MBBR	This study
Kincannon-Stover	NSSC effluent (Effluent C)	7447	16,24,48	4.62	10.10	MBBR	This study
				a	***b***		
Grau second order kinetics	Simulated paper mill wastewater	2000	10.6,7.9,6	0.468	0.92	AnFilter	(Yilmaz et al. 2008)
Grau second order kinetics	Recycle mill effluent (RME) (Effluent A)	1892	5,16,24	-0.17	2.43	MBBR	This study
Grau second order kinetics	Recycle mill effluent and NSSC (Effluent B)	4850	5,16,24	0.56	1.214	MBBR	This study
Grau second	NSSC effluent	7447	16,24,48	1.61	2.06	MBBR	This study

order kinetics	(Effluent C)

4.9 Conclusions

The primary objectives of this study were to (i) assess the applicability of various kinetic models and (ii) investigate the impact that phenols have on the biodegradation rates of paper and pulp mill effluents.

The first order, Grau second order and Kincannon-Stover kinetic models were evaluated in this study. The highest correlation coefficients (r^2) were found for the Kincannon-Stover kinetic model, which suggests that this model is best suited to describe the removal of organics in a mesophilic aerobic MBBR when treating paper and pulp mill effluents. According to the Kincannon-Stover model, the maximum substrate removal rates for Effluent A, B, C and D were found to be 15.06, 9.81, 4.62 and 6.77g COD/L.day, respectively.

The kinetic study indicated that the maximum substrate removal rate generally decreased with an increase in effluent phenol concentration. This trend suggests that phenols potentially inhibited the biodegradation rates of paper and pulp mill effluents in a mesophilic aerobic MBBR. As a result, mill effluents high in phenols may require additional intermediate or pre-treatment such as advanced oxidation processes (AOP) to reduce the initial phenol loadings prior to the biological treatment step.

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Chapter 5. The Fenton oxidation of biologically treated paper and pulp mill effluents: A performance and kinetic study

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The aim of this Chapter was to investigate the potential of the Fenton process to remove bio-recalcitrant organics from the biologically treated mill effluents (BTME). The performance and kinetic mechanisms were extensively studied in this Chapter.

This article was submitted to *Process Safety and Environmental Protection (PSEP)* for peer review and publications. The co-authors of this article contributed by means of supervision while the write-up and experiments was conducted by the author of this dissertation.

5.1 Abstract

The Fenton oxidation (Fe^{2+}/H_2O_2) of bio-recalcitrant organics, which are present in biologically treated paper and pulp mill effluents (BTME), were investigated in this study. This study primarily focused on the performance and kinetics involved in the Fenton oxidation of BTMEs. A biologically treated recycle mill effluent (RME) and a neutral sulfite semi-chemical (NSSC) mill effluent were used for the experiments. The impact of $FeSO_4.7H_2O$ and H_2O_2 dosages on chemical oxygen demand removal (COD) was evaluated. The maximum COD removal was found at a Fe^{2+}/H_2O_2 ratio of 2.22 and 0.32 for the RME and NSSC effluents, respectively. The optimal COD/H_2O_2 for the RME and NSSC effluents was found to be 0.96 and 1.19 respectively. After a 60 minute reaction, the maximum COD removal efficiency for the NSSC and RME effluents were found to be 44% and 63%, respectively. The maximum reaction rates obtained for the RME and NSSC effluents were 18 mg COD.L^{-1}.min^{-1} and 48 mg COD.L^{-1}.min^{-1}, respectively. The experimental results demonstrated that bio-recalcitrant organics, such as phenols and lignin, were readily degraded into organic acids. The applicability of the first order, second order, Behnajady–Modirshahla–Ghanbery (BMG) and a newly developed two staged first-order (TSF) kinetic model were evaluated. Both the BMG and TSF models yielded high correlation coefficients (r^2). For extended reaction times, it was found that the TSF model best described the COD removal. In addition, the TSF kinetic constants (k_{12}, k_{13}) revealed that a rapid initial degradation reaction is followed by a slower secondary degradation reaction. This performance and kinetic study demonstrated that the conventional Fenton process can effectively remove bio-recalcitrant organics that are found in BTMEs.

Keywords: Fenton process; Recycle mill effluent; Neutral sulfite semi chemical mill effluent; chemical oxygen demand

5.2 Introduction

One of the more pressing environmental concerns related to the paper and pulp industry is the production of organic rich wastewaters. Paper and pulp mill effluents generally contain cellulosic material, lignin, phenols, chlorinated and sulfite complexes (Carg 2012). The biodegradable matter present in these mill effluents are generally removed by anaerobic and aerobic digestion processes (Meyer & Edwards 2014; Singh 2007). However, certain mill effluents still contain a large fraction of bio-recalcitrant aromatic/phenols organics such as lignin and humic acids (Thompson et al. 2001; Teresa et al. 2011; Archibald et al. 1998). The direct discharge of biologically treated mill effluents (BTME) can therefore still have a significant impact on surrounding waterbodies.

The toxicity of BTMEs are primarily caused by lignin derivatives such as phenols, resins, lignosulphonic acids and other hydrocarbons (Garg & Tripathi 2011; Raj et al. 2007). The phenols present in BTMEs are extremely toxic to aquatic ecosystems, even at low concentrations (Alver et al. 2015). Certain alkyl phenols originating from the paper and pulp industry can be considered toxic to the aquatic environment at concentrations as low as 1-20 mg/L (Staples et al. 2002). In addition, resin acids can accumulate in sediment and are responsible for chronic and acute toxicity in fish species (Liss et al. 1997). The dark colour of certain BTMEs lowers the aesthetic water quality of waters and hinders natural photosynthesis in aquatic systems (Murugesan 2003; Kannan & Oblisami 1990). Consequently, the treatment of bio-recalcitrant organics is considered to be an important aspect for future environmental preservation.

Recently, advanced oxidation processes (AOP), such as the Fenton process, yielded promising results for the treatment of recalcitrant organics that are present in paper and pulp mill effluents (Rabelo et al. 2014; Zahrim et al. 2007; Perez et al. 2002). The Fenton process have shown to be an effective treatment technology to remove phenols and lignin from Kraft mill effluents (Arantes & Milagres 2007). This AOP technology is favoured since it is associated with high organic removal rates, as well as low capital and operational costs (Alver, et al., 2015). The efficiency of Fenton related processes is generally based upon the catalytic formation and equilibrium concentration of hydroxyl radicals (OH*) (Maezono et al. 2011). The conventional Fenton process is primarily described by reactions 5-1 to 5-7 (Wu et al. 2010):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^* + OH^- \tag{5-1}$$

$$Organics + OH^* \rightarrow H_2O + CO_2 + products \tag{5-2}$$

$$OH^* + H_2O_2 \rightarrow H_2O + HO_2^* \tag{5-3}$$

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HO_2^* + H^+ \quad 5\text{-}4$$

$$Fe^{3+} + HO_2^* \rightarrow Fe^{2+} + O_2 + H^+ \quad 5\text{-}5$$

$$Fe^{2+} + HO_2^* \rightarrow Fe^{3+} + OH^- \quad 5\text{-}6$$

$$OH^* + Fe^{2+} \rightarrow OH^- + Fe^{3+} \quad 5\text{-}7$$

Various studies have investigated the removal of organics from raw paper and pulp mill effluents using Fenton related oxidation processes (Perez et al. 2002; Torrades et al. 2003; Rabelo et al. 2014; Zahrim et al. 2007). However, only a few studies evaluated the performance of Fenton oxidation processes treating biologically treated paper and pulp mill effluents (Catalkaya & Kargi 2007; Ginni et al. 2014). There are also a shortage of studies investigating the mechanisms and kinetics involved in the Fenton oxidation of BTME (Wang et al. 2011a). As a result, the aim of this study was to investigate the performance, degradation pathways and kinetics involved in the Fenton oxidation of BTMEs. The primary objectives of this study are to assess (i) the influence of Fe^{2+} and H_2O_2 dosages on organic removal efficiencies and (ii) to investigate the applicability of several kinetic models.

5.3 Material and Methods

5.3.1 Paper and pulp mill effluent characterisation

Recycle (RME) and neutral sulfite semi-chemical (NSSC) mill effluents were collected from separate mills. After collection, the samples were stored at 4°C. The samples were treated in a lab scale aerobic moving bed biofilm reactor (MBBR) to resemble biologically treated mill effluents. The MBBR removed 32% and 55% of the COD from the untreated NSSC and RME effluent at a hydraulic residence time (HRT) of 24 hours. The characteristics of the biologically treated paper and pulp mill effluents are shown in Table 5-1.

Table 5-1: The wastewater characteristics of the biologically treated RME and NSSC effluents

Parameters	Recycle mill effluent (RME)	Neutral sulfite semi chemical effluent (NSSC)
COD (mg/L)	436 ± 11.00	3756 ± 92.00
VOA (mg/L)	221 ± 6.00	951 ± 26.00
Phenols (mg/L)	6.9 ± 0.12	90 ± 1.59
Lignin (mg/L)	35 ± 7.00	1840 ± 92.15
TSS (mg/L)	45 ± 2.25	278 ± 13.90
pH	7.67 ± 0.10	8.09 ± 0.10
Conductivity (µS/cm)	1374 ± 13.47	4060 ± 40.60

5.3.2 Fenton reagents and chemical analysis

The $FeSO_4.7H_2O$ (Merck) (Code: 103965) and H_2O_2 (Merck, 30% w/v) (Code: 107209) were used as the Fenton's reagent. The pH of the solution was altered using analytical grade H_2SO_4 (Merck) (Code: 100731). MnO_2 (Merck) (Code: 105957) was immediately added to the samples taken directly from the original reaction batch to remove excess H_2O_2 prior to sample analysis. The absence of residual H_2O_2 was confirmed using an MQaunt test strips (0.5 – 25 mg/L H_2O_2) (Code: 110011). The COD, volatile organic acids (VOA) and phenolic measurements were determined with calorific methods and measured on a Spectroquant®. A Merck COD cell test (100-1500 mg/L) (Code: 114539), volatile organic acid cell test (50-3000 mg/L) (Code: 101809) and phenol test (0.002-5 mg/L) (Code: 100856) were used to characterise the effluent. The equivalent lignin content was measured using UV-methods. A calibration curve was obtained at 267 nm using Kraft lignin (Sigma-Aldrich) (Code: 370959) (Wang et al. 2014). The pH values of the samples were measured using a handheld IP67 Combo pH/COND/D.O. (8603) meter. The total suspended solids (TSS) were measured according to standard methods (Skrentner 1988). The colour content of the effluent was measured at 485 nm on a Merck Spectroquant ®.

5.3.3 Experimental procedures

The untreated recycle (RME) and neutral sulfite semi chemical (NSSC) mill effluents were initially treated using an aerobic moving bed biofilm reactor (MBBR). The MBBR was operated at a hydraulic residence time (HRT) of 24 hours. After biological treatment the samples were stored at 4°C.

In the experiments the effect of $FeSO_4.7H_2O$ and H_2O_2 were investigated. In the first set of experiments, H_2O_2 dosages of 450 mg/L, 3150 mg/L and 6300 mg/L was used for both the RME and NSSC effluents. The generally accepted theoretical H_2O_2/COD ratio is 2.125 g H_2O_2/g COD to fully oxidize organics. However, optimal reaction rates are often found at H_2O_2/COD ratios significantly lower than this theoretical ratio due to side reactions occurring (Sevimli et al., 2014; Ertugay and Acar, 2013; Barbusi and Pieczykolan, 2010). Consequently, H_2O_2/COD ratios lower than the theoretical amount was also evaluated in this study. In the experimental work the initial H_2O_2/COD ratios for the RME effluent ranged between 1.03 (g/g) and 14.45 (g/g). For the NSSC effluent, the H_2O_2/COD ratios were varied between 0.12 (g/g) and 1.68 (g/g). For each individual H_2O_2 dosage three different $FeSO_4.7H_2O$ dosages were evaluated. The corresponding $FeSO_4.7H_2O$ dosages were 50 mg/L, 500 mg/L and 1000 mg/L. The initial pH value of the solution was adjusted to 3.81 using H_2SO_4. All the experiments were carried out in a 250 mL Erlen Meyer flask at room temperature (25°C) and constant agitation (3000 rpm). The reaction time for all these experiments was 60 minutes.

In a separate set of experiments, the reaction time was increased from 60 to 240 minutes for the NSSC effluents to evaluate the impact of extended reaction times on COD removal. The H_2O_2 dosages were 3150 mg/L and 6300 mg/L, respectively. The corresponding $FeSO_4.7H_2O$ dosages for each individual H_2O_2 dosage were 500 mg/L and 1000 mg/L, respectively.

5.4 Kinetic models

5.4.1 First order kinetic model

The rate of organic removal (COD) in terms of first order rate laws can be described by the following expression (Khamaruddin et al. 2011; Wang 2008):

$$\frac{dC_{COD}}{dt} = -r_{COD} = -k_2 C_{COD}.C_{OH^*} = k_{app,1}.C_{COD} \tag{5-8}$$

According to Wu et al. (2010), hydroxyl radicals (OH^*) only have a lifetime of a few nanoseconds and is present in low concentrations. Hence, it can be assumed that the concentration of the hydroxyl radicals (C_{OH^*}) is constant. When Eq. 5-9 is integrated, the following equation is derived:

$$\ln\left(\frac{C_{COD}}{C_{COD_o}}\right) = -k_{app,1}.t \tag{5-9}$$

where C_{CODo} and C_{COD} are the initial and effluent COD concentrations (mg/L), $k_{app,1}$ the apparent first order rate constant (min^{-1}) and t the reaction time (min). To obtain the apparent first order kinetic parameter ($k_{app,1}$), $ln(C_{COD}/C_{CODo})$ value was plotted against the time (t). The gradient of this line represents the apparent first order kinetic parameter ($k_{app,1}$).

5.4.2 Second order kinetic model

The rate of substrate removal (r_{COD}) described by second order reaction kinetics can be given by Eq. 5-10 (Guedes et al. 2003):

$$\frac{dC_{COD}}{dt} = -r_{COD} = -k_{app,2}\,.\,C_{COD}^2 \tag{5-10}$$

Eq. 5-10 can be simplified by means of integration to yield the following linear expression:

$$\frac{1}{C_{CODo}} - \frac{1}{C_{COD}} = -k_{app,2}.t \qquad 5\text{-}11$$

where C_{CODo} and C_{COD} represents the initial and effluent COD concentration (mg.L^{-1}), $k_{app,2}$ the second order rate constant (L.mg^{-1}.min^{-1}). The second order kinetic parameter ($k_{app,2}$) is obtained by plotting the ($1/C_{CODo}$ - $1/C_{COD}$) value against the time (*t*). The slope of Eq. 5-11 will represent the second order kinetic parameter ($k_{app,2}$).

5.4.3 Behnajady–Modirshahla–Ghanbery (BMG) model

A mathematical model was developed by Behnajady et al. (2007) to describe the rate of substrate removal during Fenton oxidation. This model is given by the following expression:

$$\frac{C_{COD}}{C_{COD_o}} = 1 - \frac{t}{m + bt} \qquad 5\text{-}12$$

where C_{CODo} and C_{COD} represents the initial and effluent COD concentrations (mg/L), *t* the reaction time (min), *m* (min) and *b* are the kinetic parameters. The graphical meanings of *m* and *b* are shown in Figure 5-1. These values can theoretically be determined by taking the derivative of Eq. 5-12, which yields the following expression:

$$\frac{d\left(\frac{C_{COD}}{C_{COD_o}}\right)}{dt} = -\frac{m}{(m + bt)^2} \qquad 5\text{-}13$$

When the time (t) is short or approaching zero, Eq. 5-13 can be manipulated to give the following equation:

$$\frac{d\left(\frac{C_{COD}}{C_{COD_o}}\right)}{dt} = -\frac{1}{m} \qquad 5\text{-}14$$

The 1/b value represents the maximum substrate removal and can be calculated by the following expression:

$$\frac{1}{b} = 1 - \frac{C_{COD\,\infty}}{C_{COD_o}} \qquad 5\text{-}15$$

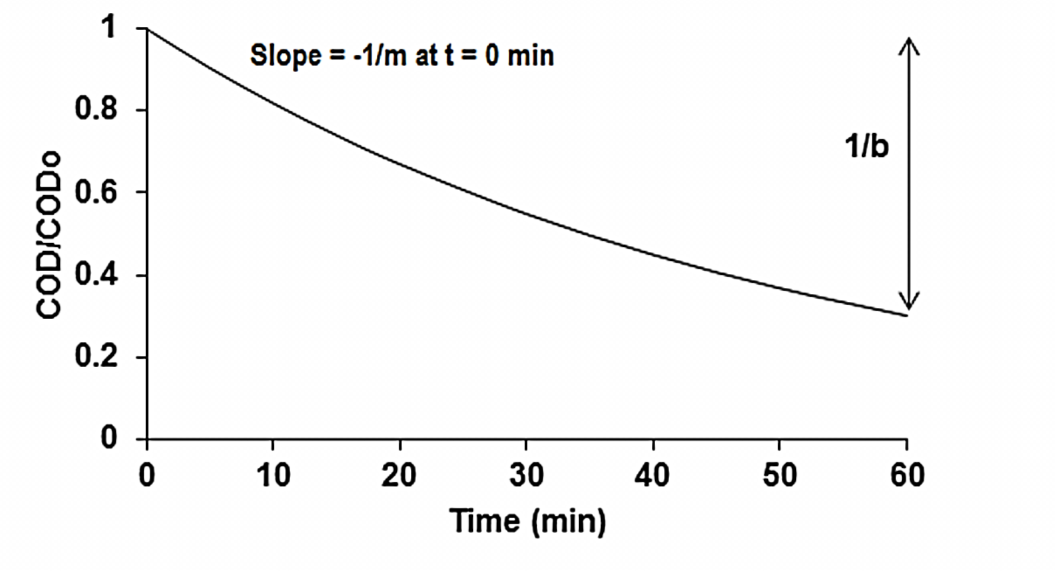

Figure 5-1: Graphical illustration of the BMG model

5.4.4 Two staged first order kinetic (TSF) model

A study conducted by Lei and Li (2014), demonstrated that the COD removal during the ozonation of Kraft mill effluent exhibited a two staged first order behaviour. Unfortunately, the two staged first order (TSF) kinetic model was not developed and evaluated in Lei and Li (2014). As a result, this study develops and assesses the applicability of the TSF model. In the TSF model, it was assumed that the chemical oxygen demand (COD) can be divided into a rapid degradable (COD_{rd}) and a slowly degradable (COD_{sd}) fraction. The rapidly degradable COD (COD_{rd}) are assumed to be aromatic constituents such as lignin and phenols, while the slowly degradable COD (COD_{sd}) are generally carboxylic acids (Lopez et al. 2004). Literature have shown that the Fenton oxidation of lignin, phenols and carboxylic acids follow first order rate laws (Zazo et al. 2005; Passauer et al. 2011; Makhotkina et al. 2008). Subsequently, it is expected that the kinetics describing COD removal will reflect this same first order behaviour. The model further assumes that organic type A contributes to the readily degradable COD (COD_{rd}), while organic type B primarily contributes to the slowly degradable COD (COD_{sd}). The oxidising reactions for both organic type A and B are presented in Eqs. 5-16 and 5-17.

$$C_A + OH^* \xrightarrow{k12} C_B \quad \text{5-16}$$

$$C_B + OH^* \xrightarrow{k13} CO_2 + H_2O \quad \text{5-17}$$

The differential equations describing the removal of type A and type B organics are presented in Eqs. 5-18 and 5-19.

$$\frac{dC_A}{dt} = -k_{12}.C_A \tag{5-18}$$

$$\frac{dC_B}{dt} = k_{12}.C_{AO}.\mathrm{e}^{-k_{12}.t} - k_{13}.C_B \tag{5-19}$$

The analytical solution for C_A and C_B is given by Eqs. 5-18 and 5-19, respectively. The mathematical derivation for Eq. 5-19 is given in **Error! Reference source not found.**. Where C_{AO} and C_{BO} represent the initial concentrations of organic type A and B (mg/L), t the reaction time (min), k_{12} and k_{13} the first order rate constants (min^{-1}). The individual COD values of organic A and B can be calculated using Eqs. 5-20 and 5-21.

$$C_{COD_{rd}} = x.C_A \tag{5-20}$$

$$C_{COD_{sd}} = y.C_B \tag{5-21}$$

where x and y represent the COD conversion constants (mg COD/mg A or B), C_{CODsd} and C_{CODrd} the slowly and rapidly degradable COD concentrations (mg/L), respectively. The total COD concentration can be given as a function of the rapidly (A) and slowly (B) degradable organics as seen in Eqs. 5-22 and 5-23.

$$C_{COD_o} = C_{COD_{sd},o} + C_{COD_{rd},o} = x.C_{AO} + y.C_{BO} \tag{5-22}$$

$$C_{COD} = C_{COD_{sd}} + C_{COD_{rd}} = x.C_A + y.C_B \tag{5-23}$$

If the analytical solutions for C_A and C_B are substituted into Eq. 5-23, the COD concentration can be given by Eq. 5-24 which is a function of time (t) and the initial concentrations of organic type A and B.

$$C_{COD} = x.C_{AO}.\mathrm{e}^{-\mathrm{k}_{12}.t} + \left(\frac{y}{e^{k_{13}.t}}\right)\left[C_{BO} + (k_{12}.C_{AO})\left[\frac{e^{t.(k_{13}-k_{12})}}{k_{13}-k_{12}} - \frac{1}{k_{13}-k_{12}}\right]\right] \tag{5-24}$$

By substituting C_{AO} from Eq. 5-22 into Eq. 5-24, the following equation can be obtained which represents the TSF model.

$$C_{COD} = (COD_o - y.C_{BO}).e^{-k_{12}.t} + \left(\frac{y}{e^{k_{13}.t}}\right)\left[C_{BO} + \left(\frac{k_{12}(COD_o - y.C_{BO}}{x(k_{13} - k_{12})}\right)\left[e^{t.(k_{13}-k_{12})} - 1\right]\right] \quad \text{5-25}$$

The initial concentration of the slowly degradable constituents was assumed to be negligible ($C_{BO} \approx 0$). The y/x ratio, k_{12} and k_{13} parameters were obtained by fitting the experimental data to the TSF model given by Eq. 5-25. The equations were solved using the solver function in Microsoft Excel.

5.5 Results and Discussion

5.5.1 The effect of pH on the COD removal efficiency

The impact that the pH value has on the COD removal efficiency is shown Figure 5-2 and Figure 5-3.

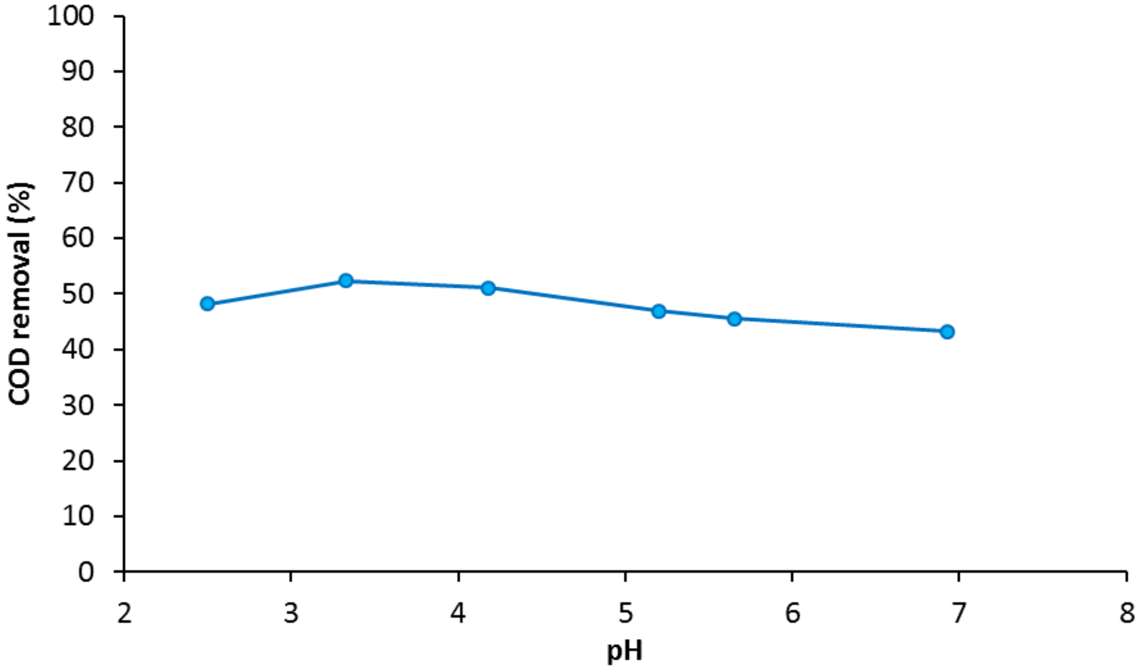

Figure 5-2: Effect of pH on COD removal in the Fenton process treating the RME effluent (250 mg/L $FeSO_4$; 2686 mg/L H_2O_2; 30 min reaction time)

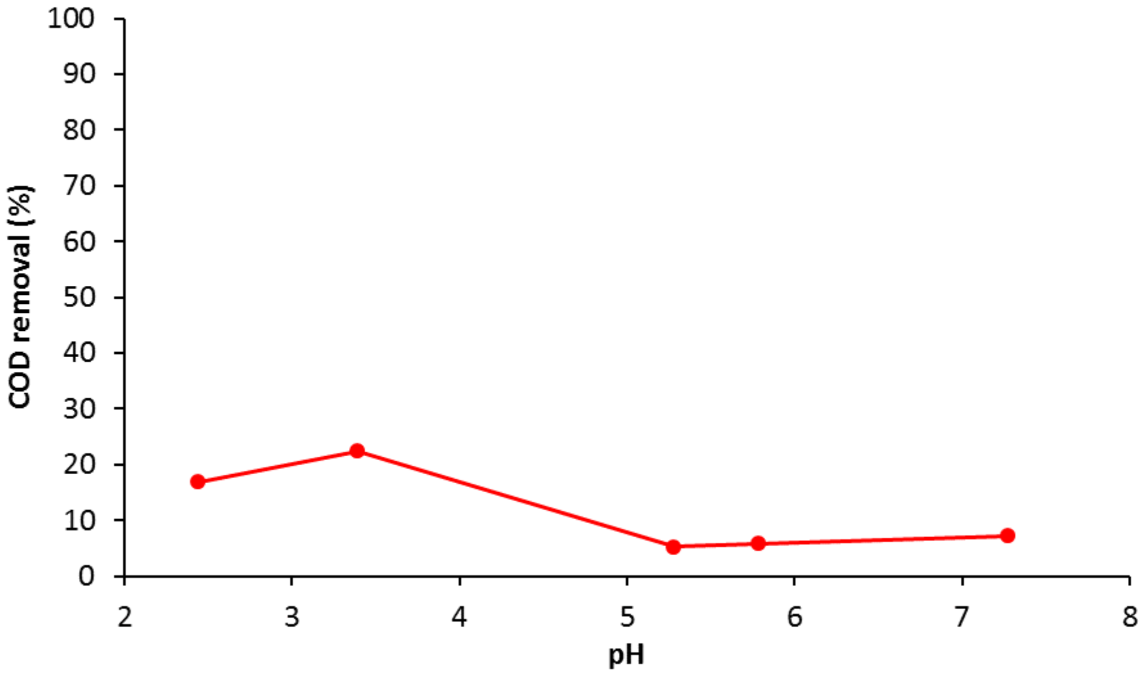

Figure 5-3: Effect of pH on COD removal in the Fenton process treating the NSSC effluent (250 mg/L $FeSO_4$; 2686 mg/L H_2O_2; 30 min reaction time)

The optimal pH range lies between a value of 3 and 4. The drop in COD removal with increasing pH values can be elucidated by the $Fe(OH)_3$ precipitate forming at higher pH values (Lu et al. 2010). Subsequently, the removal of Fe^{2+} from Eq. 5-1 coincides with the rapid drop in the COD removal rate at a higher pH values. Below a pH of 3, excessive H^+ will react with hydroxyl radicals (OH^*) to form water. This reaction is shown in Eq. 5-26 (Chiou et al. 2006).

$$OH^* + H^+ \rightarrow H_2O \qquad 5\text{-}26$$

As a result, an optimum pH should be maintained during the reaction to ensure that there is a sufficient production of OH^* and to evade scavenging of OH^*.

5.5.2 Effect of H_2O_2 and $FeSO_4.7H_2O$ dosages on COD removal efficiency

The effect of H_2O_2 and $FeSO_4.7H_2O$ dosages on the COD removal was evaluated in this section. The optimal pH was found to be between 3 and 4, which corresponds with values found in literature (Badawy et al. 2006; Sevimli et al. 2014). Consequently, an initial pH value of 3.8 was used for the experiments. The COD removal results for the Fenton oxidation of NSSC and RME effluents are illustrated in Figure 5-4 and Figure 5-5, respectively.

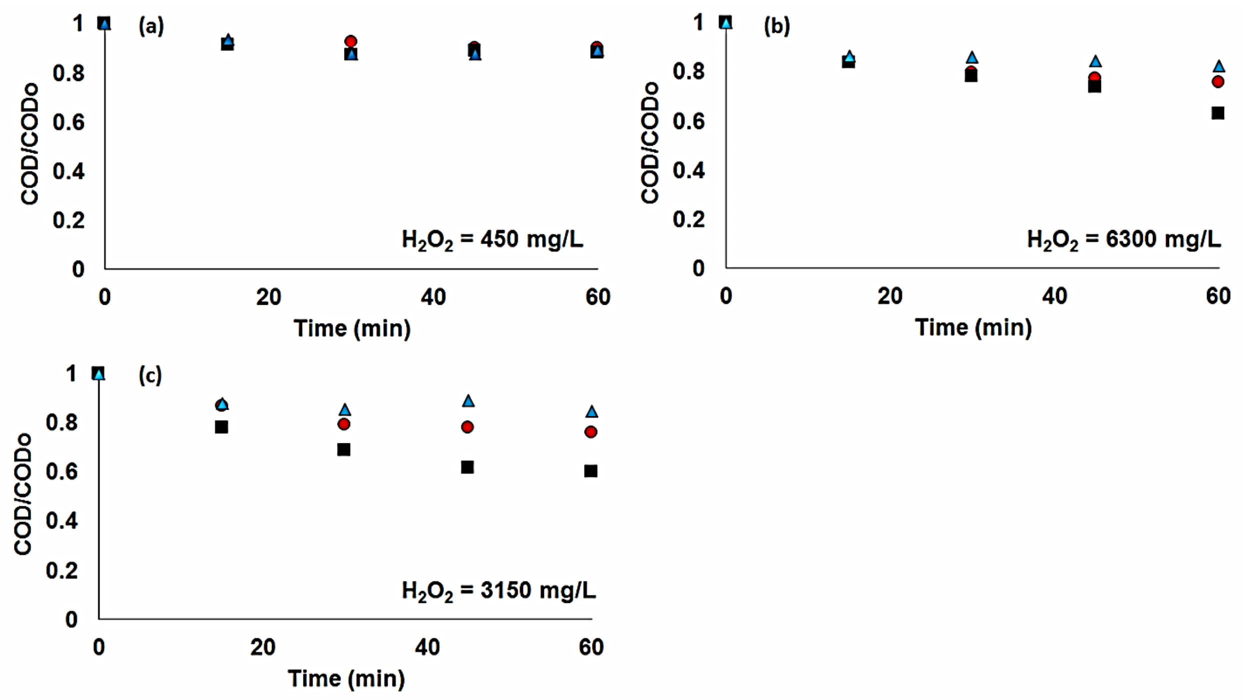

Figure 5-4: The effect of various H_2O_2 and $FeSO_4.7H_2O$ dosages on the COD removal efficiency for the NSSC effluent at pH = 3.8 (▲ = 50 mg/L $FeSO_4.7H_2O$; ● = 500 mg/L $FeSO_4.7H_2O$; ■ = 1000 mg/L $FeSO_4.7H_2O$)

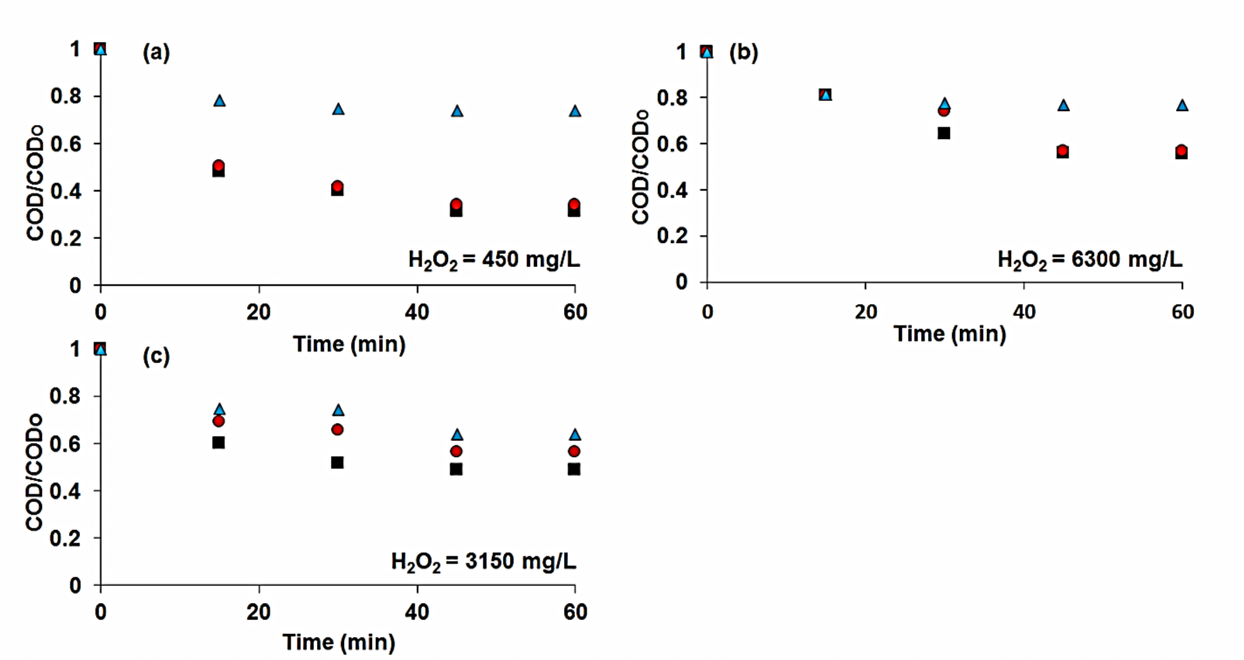

Figure 5-5: The effect of various H_2O_2 and $FeSO_4.7H_2O$ dosages on the COD removal efficiency for the RME effluent at a pH = 3.8 (▲ = 50 mg/L $FeSO_4.7H_2O$; ● = 500 mg/L $FeSO_4.7H_2O$; ■ = 1000 mg/L $FeSO_4.7H_2O$)

The optimum COD removal for the NSSC effluent was found at a $FeSO_4.7H_2O$ and H_2O_2 dosage of 1000 mg/L and 3150 mg/L, respectively. For the RME effluent, the optimum COD removal was found to be at a $FeSO_4.7H_2O$ and H_2O_2 dosage of 1000 mg/L and 450 mg/L, respectively. At optimum conditions, the phenol degradation was greater than 85% for both effluents.

The experimental results suggest that an increase in catalyst (Fe^{2+}) dosage generally leads to increased COD removal efficiency. The increase in catalyst (Fe^{2+}) concentrations coincides with the increase in the formation of active hydroxyl radicals (OH^*), as seen in Eq. 5-27. Higher oxidation rates of organic constituents (R-H) will consequently be the direct result of higher hydroxyl radicals (OH^*) concentrations.

$$Fe^{2+} + H_2O_2 \rightarrow OH^* + OH^- + Fe^{3+} \qquad 5\text{-}27$$

$$RH + OH^* \rightarrow R^* + H_2O \qquad 5\text{-}28$$

However, excessive catalyst (Fe^{2+}) dosages can decrease COD removal efficiency as seen in Figure 5-4 a. According to Sevimli et al. (2014), excessive Fe^{2+} catalyst can react with the hydroxyl radicals (OH^*), which evidently decreases the COD removal efficiency as seen in Eq. 5-29.

$$Fe^{2+} + OH^* \rightarrow Fe^{3+} + OH^- \qquad 5\text{-}29$$

The increase in H_2O_2 concentrations can also have both positive and negative implications on the COD removal efficiency. An increase in H_2O_2 can lead to an increase in COD removal efficiency due to the additional formation of hydroxyl radicals (OH*) as seen in Eq. 5-27. However, excessive H_2O_2 concentrations can have negative implications on the COD removal efficiency as seen in Figure 5-4 and Figure 5-5. This rather unique behaviour can be explained by the fact that H_2O_2 in excess can react with the active hydroxyl radicals (OH*) to form water and perhydroxyl radicals (OH_2^*). The scavenging of active OH* is shown in 5-30.

$$H_2O_2 + OH^* \rightarrow HO_2^* + H_2O \qquad 5\text{-}30$$

Consequently, the COD removal efficiency will drop due to the scavenging of OH*. The most efficient and economical solutions for the Fenton oxidation of wastewaters can be determined using the Fe^{2+}/H_2O_2 and COD/H_2O_2 ratios. The ratios vary greatly in literature, likely due to the dependency on the type of contaminant treated in the Fenton process. In a study done by El Haddad et al. (2014) on the Fenton treatment of azo dyes, the optimal Fe^{2+}/H_2O_2 ratio was found to be 0.1. In another study conducted by Ponuwei (2009) on the treatment of paper and pulp mill effluents using Fenton oxidation processes, the optimal ratio Fe^{2+}/H_2O_2 ratio was measured as 0.82. This study showed that the optimal Fe^{2+}/H_2O_2 ratio for the NSSC and RME effluents were 0.32 and 2.22, respectively. In a study conducted on white liquor by Sevimli et al. (2014), an optimal COD removal was found at a COD/H_2O_2 ratio of 0.865. Similar results was obtained by Jarpa et al. (2016), where a maximum amount of COD was removed from Kraft mill effluent at a COD/H_2O_2 ratio of 1.12. In this study, the optimal COD/H_2O_2 ratio for the RME and NSSC effluents was found to be 0.96 and 1.19 respectively.

Due to the complexity of Fenton reactions, polynomial multiple regression models are frequently used to predict the removal of contaminants (Mojtaba & Soghraa 2014; Lak et al. 2012). In this study, a reduced cubic polynomial model was used to graphically illustrate the impact $FeSO_4$ and H_2O_2 dosages. The graphical illustrations depicting the COD removal efficiencies (%) are shown in Figure 5-6 and Figure 5-7 for the NSSC and RME effluents, respectively. The graphical illustrations were generated using Stat-Ease Design Expert ®.

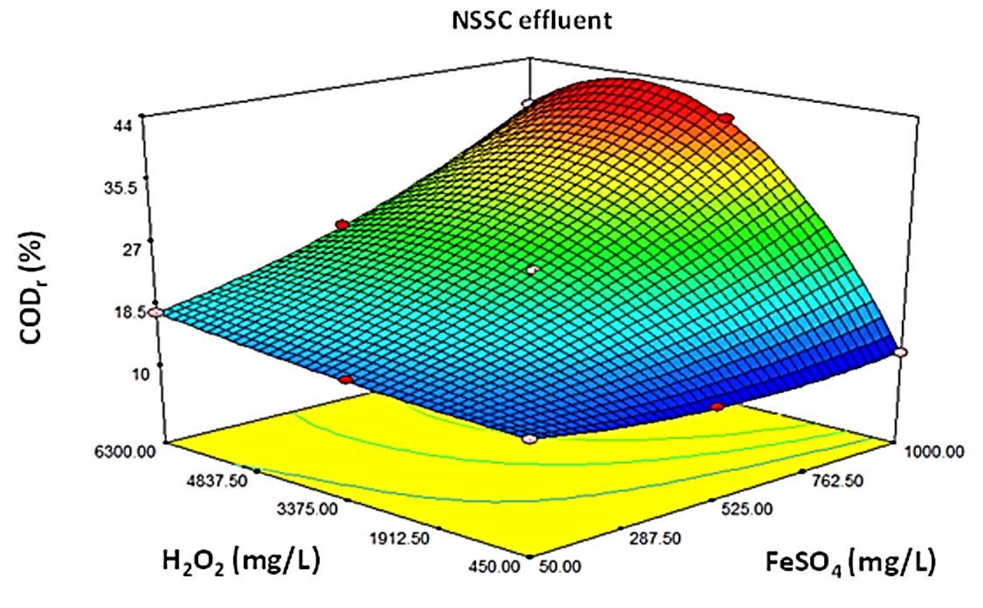

Figure 5-6: The COD removal efficiency (%) at various H_2O_2 and $FeSO_4.7H_2O$ dosages (NSSC effluent; 60 minute reaction time, pH = 3.8)

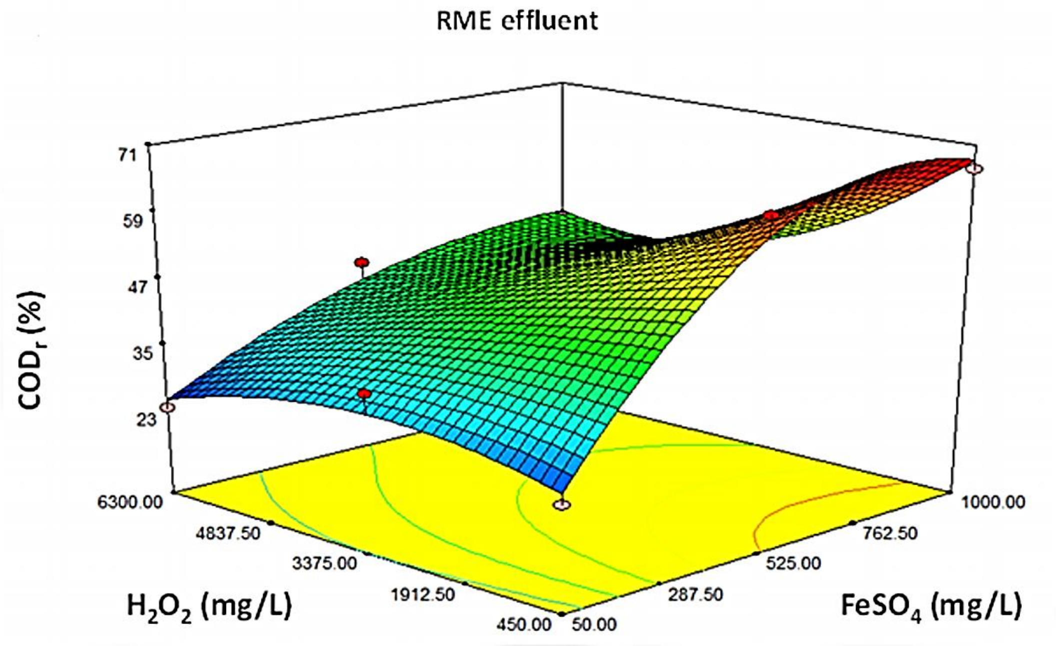

Figure 5-7: The COD removal (%) at various H_2O_2 and $FeSO_4.7H_2O$ dosages (RME effluent; 60 minute reaction time, pH = 3.8)

The maximum COD removal efficiency can be predicted for a specific $FeSO_4.7H_2O$ and H_2O_2 dosage which can be calculated according to Eq. 5-31, where x_1 and x_2 represent the $FeSO_4.7H_2O$ and H_2O_2 dosages, respectively. The predicted values represent the COD removal efficiencies after a 60 minute reaction period. The constant values (A_i, B_i, C_i, D_i, E_i, F_i, G_i, H_i) for the RME and NSSC effluents are listed in Table 5-2.

$$COD_R(\%) = A_i + B_i.x_1 + C_i.x_2 + D_i.x_1.x_2 + E_i.x_1^2 + F_i.x_2^2 + G_i.x_1^2.x_2 + H_i.x_1.x_2^2 \qquad 5\text{-}31$$

These models are applicable for a H_2O_2 dosage between 450 mg/L - 6300 mg/L and a $FeSO_4.7H_2O$ dosage between 50 mg/L - 1000 mg/L. The absolute values for B_i were found to be significantly higher than that of the C_i values, for both effluents. Consequently, the amount of catalyst (Fe^{2+}) has a greater effect on the overall COD removal than the amount of H_2O_2. Other studies have also demonstrated that the impact of catalyst (Fe^{2+}) dosage have a more pronounced effect on contaminant removal in the Fenton process (Molina et al., 2006; Tony and Bedri, 2014).

Table 5-2: Individual factorial design parameters for the NSSC and RME effluents

Polynomial parameters	**NSSC effluent**	**RME effluent**
A_i	15.10	20.04
B_i	-0.02	0.12
C_i	-8.82E-04	5.32E-03
D_i	1.78E-05	-2.50E-05
E_i	9.80E-06	-7.12E-05
F_i	1.83E-07	7.77E-07
G_i	-	7.78E-09
H_i	-2.05E-09	1.97E-09

5.5.3 Colour removal during Fenton oxidation

The measurement of the change in colour content was only important for the Mill X (As discussed in Section 1.1) for recycling purposes. There is no legislation on the colour limits for irrigation for Mill Y. As a result, this section only focused on the biologically treated RME (Mill X). As seen in Figure 5-8, the colour reduction after the Fenton process is approximately 74%. The Fenton treated effluent was neutralised with slaked slime ($Ca(OH)_2$ = 1000 mg/L). After a 60 minute precipitation period the colour reduction was increased to 97%.

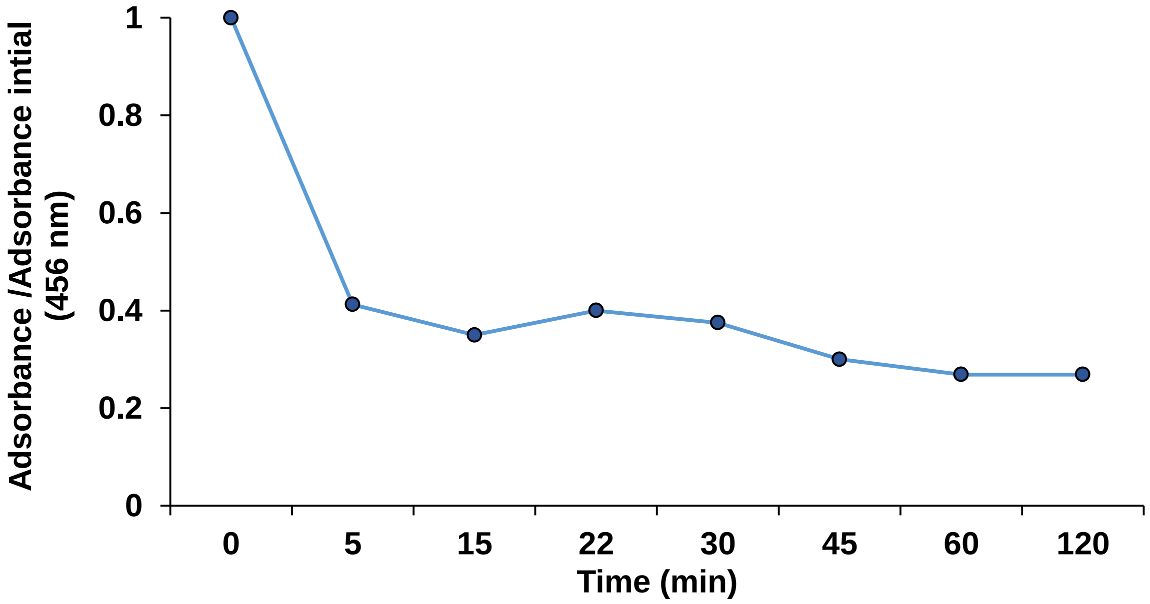

Figure 5-8: The change in colour (measured as absorbance at 456 nm) during the Fenton oxidation of the biologically treated RME effluent (pH=3.8; H_2O_2=450 mg/L; $FeSO_4$=1000 mg/L)

5.5.4 Kinetic model evaluation

The mechanisms and kinetic models behind the Fenton oxidation of paper and pulp mill effluent are discussed in this section. The first order, second order and BMG model are well-known models used to describe the removal of organics in the Fenton process (Tunc et al. 2012; Cui et al. 2014). The kinetic parameters and corresponding correlation coefficients (r^2) for these models are presented in Table 5-3 and Table 5-4. The high correlations (r^2) found for the BMG model would suggest that this model is best suited to describe the COD removal rate during the Fenton oxidation of biologically treated paper and pulp mill effluents.

Table 5-3: The kinetic parameters for various kinetic models for Fenton process treating the bio-treated neutral semi sulfite chemical (NSSC) effluent (Reaction time = 60 minutes)

		First-order		Second-order		Behnajady-Modirshahla-Ghanbery (BMG)		
$FeSO_4.7H_2O$ (mg/L)	H_2O_2 (mg/L)	k_1 (min^{-1})	r^2	k_2 ($L.\ mg^{-1}.\ min^{-1}$)×1000	r^2	m (min)	b	r^2
50	450	0.0018	0.74	0.0008	0.85	60.2612	7.1818	0.93
50	3150	0.0035	0.58	0.0010	0.61	27.2010	6.6083	0.92
50	6300	0.0038	0.64	0.0011	0.67	27.6752	5.7460	0.98
500	450	0.0024	0.61	0.0007	0.62	55.5804	8.8173	0.94
500	3150	0.0055	0.83	0.0017	0.87	29.9547	4.1503	0.96
500	6300	0.0057	0.69	0.0017	0.75	24.3546	4.0736	0.90
1000	450	0.0026	0.65	0.0007	0.71	22.6154	8.4676	0.95
1000	3150	0.0099	0.91	0.0034	0.95	19.5849	2.5121	0.96
1000	6300	0.0074	0.94	0.0023	0.96	42.0774	2.6779	0.91

Table 5-4: The kinetic parameters for various kinetic models for Fenton process treating the bio-treated RME effluent (Reaction time = 60 minutes)

		First-order		Second-order		Behnajady-Modirshahla-Ghanbery (BMG)		
$FeSO_4.7H_2O$ (mg/L)	H_2O_2 (mg/L)	k_1 (min^{-1})	r^2	k_2 ($L.\ mg^{-1}.\ min^{-1}$)×1000	r^2	m (min)	b	r^2
50	450	0.0065	0.59	0.0172	0.67	7.94	3.86	0.99
50	3150	0.0088	0.81	0.0244	0.87	20.52	2.71	0.95
50	6300	0.0057	0.64	0.0150	0.71	12.29	4.24	0.99
500	450	0.0209	0.83	0.0805	0.93	6.59	1.52	0.99
500	3150	0.0154	0.79	0.0498	0.89	5.81	1.96	0.99
500	6300	0.0114	0.94	0.0355	0.97	19.24	2.24	0.87
1000	450	0.0233	0.78	0.0948	0.90	2.56	1.44	0.99
1000	3150	0.0110	0.81	0.0334	0.88	13.03	2.30	0.98

1000	6300	0.0098	0.97	0.0289	0.99	31.01	2.32	0.87

The lower correlation coefficient (r^2) values found for the first and second order plots can be explained by a two staged degradation of paper and pulp mill effluents. The first order kinetic plot in Figure 5-9 illustrates the typical two staged degradation behaviour. The correlation coefficient for the complete 240 minute Fenton oxidation reaction might be relatively low (r^2 = 0.44), however the correlation coefficient for the α (r^2 = 0.98) and β (r^2 = 0.99) regions are high. This suggests that two separate first order degradation pathways may be responsible for the COD removal. The α and β regions represents rapid and slow first order reactions, respectively.

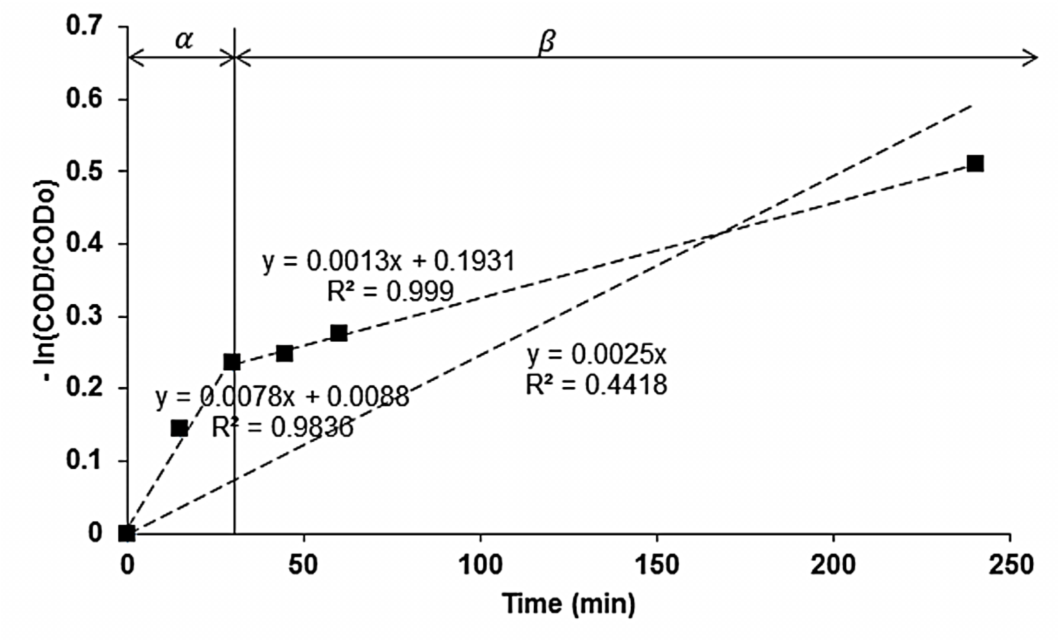

Figure 5-9: First order kinetic plot for the NSSC effluent ($FeSO_4.7H_2O$=500 mg/L; H_2O_2=3150 mg/L)

Similar findings were reported in Lei and Li (2014), where the ozonation of Kraft mill effluent illustrated that a two staged first-order model can potentially be used to describe the COD removal. Another study conducted by Wang (2008) on the Fenton oxidation of azo dyes illustrated that the degradation pathways followed combined first order kinetics, which were dependent on two different initial dye concentrations.

According to Oturan et al. (2008), the degradation of aromatic constituents during Fenton oxidation resulted in the formation of slowly degradable short chained carboxylic acids. Subsequently, the first rapid reaction step is mainly responsible for the reduction of aromatic molecules (α), followed by the slower degradation of carboxylic acids (β). The aromatic constituents in paper and pulp mill effluents are generally lignin and phenolic derived compounds. The initial step in lignin and phenol oxidation include the hydroxylation of the aromatic ring, followed by the formation of mono and dicarboxylic acids (Zazo et al. 2005; Passauer et al. 2011). Intermediate carboxylic acids can include muconic acid, maleic acid, fumaric acid, oxalic acid, acetic acid and formic acid (Zazo et al. 2005). A separate Fenton oxidation experiment was conducted to confirm the degradation pathways of aromatic constituents present in the NSSC mill effluents. The change in phenols, lignin and acids (measured as pH) concentrations are illustrated in Figure 5-10. The drop in pH during the course of the reaction could indicate that lignin and phenols are converted into intermediate organic acids. The lignin and phenols removal efficiency was found to be 78% and 87%, respectively. The results from Figure 5-10 indicate that lignin and phenols are potentially converted into organic acids, since a pH drop is noticed. Other studies have also attributed the drop in pH to the formation of intermediate organic acids during the fractionation of aromatic and aliphatic constituents (Basu et al. 1997).

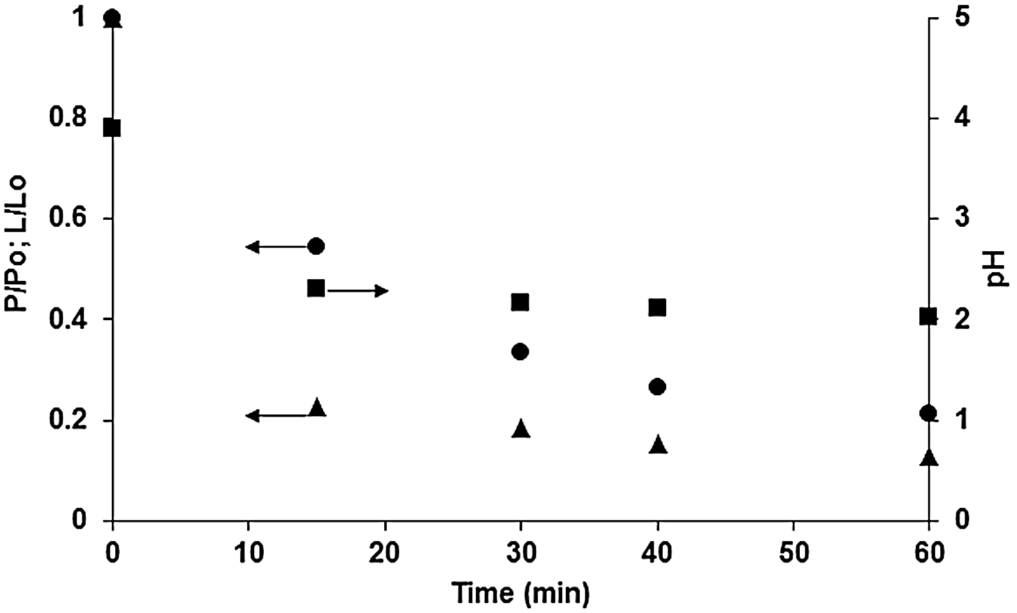

Figure 5-10: The change in lignin (L/Lo) ●, phenol (P/Po) ▲ and pH value ■ during Fenton oxidation ($FeSO_4.7H_2O$ = 500 mg/L; H_2O_2 = 3150 mg/L)

The kinetic parameters for the TSF model, first order kinetic model and BMG model are presented in Table 5-5. The kinetic parameters for the first order and BMG model differ from that of Table 5-3, due to extended reaction times (240 minutes). The TSF model takes the transformations of lignin and phenols into intermediate organic acids into account. As a result, the TSF model was only evaluated on the biologically treated NSSC effluent due to the high aromatic content (1840 mg/L lignin, 90 mg/L phenols) of the effluent. The reaction times were extended from 60 to 240 minutes to demonstrate that a slower secondary reaction is more dominant at final stages of the reaction. The kinetic results in Table 5-5 indicate that the TSF model had the highest correlation coefficients (r^2). As a result, the TSF model would be best suited to describe the COD removal rate during the extended Fenton oxidation of bio-treated mill effluents.

Table 5-5: Comparison between a one-step first-order, BMG and TSF kinetic model for the complete 240 minute reaction time (NSSC mill effluent)

		First-order model		TSF model				BMG model		
$FeSO_4.7H_2O$ (mg/L)	H_2O_2 (mg/L)	$k_{app,1}$ (min^{-1})	r^2	y/x	k_{12} (min^{-1})	k_{13} (min^{-1})	r^2	m	b	r^2
500	3150	0.0025	0.79	0.79	0.07107	1.23E-03	0.99	78.12	2.5	0.95
500	6300	0.0020	0.51	0.79	0.13430	6.17E-04	0.99	42.87	3.20	0.97
1000	3150	0.0032	0.40	0.57	0,04588	1.18E-04	0.99	26.076	2.25	0.97
1000	6300	0.0022	0.66	0.74	0.06326	7.63E-04	0.99	50.98	2.68	0.98

The kinetic parameters (k_{12}, k_{13}) for the TSF model indicated that the initial degradation reaction is fast which is simultaneously followed by a slower reaction. According to Babuponnusami and Muthukumar (2012), the first order constant (k) for phenol degradation by means of Fenton oxidation are 0.0067 min^{-1} at Fe^{2+} and H_2O_2 dosages of 4 mg/L and 800 mg/L, respectively. Other Fenton related treatment systems yielded a first order rate constant (k) of 0.0934 min^{-1} for phenol degradation. In Wang et al. (2014), the first order rate constant for lignin degradation via a Fenton process was 0.0498 min^{-1}. In this study the first order rate constant for lignin and phenol degradation was found to be 0.0349 min^{-1} and 0.0652 min^{-1} respectively at a dosage of 500 mg/L $FeSO_4$ and 3150 mg/L H_2O_2. The lignin and phenol first order rate constant found in the experiments are comparable with k_{12} found in Table 5-5 for the same dosage conditions.

Experimental data from Centi et al. (2000) illustrated that the combination of zeolite and Fe^{2+} type catalysts for the Fenton oxidation of intermediate organic acids, such as formic acid and acetic acid, yielded first order constants of 0.0072 min^{-1} and 0.0018 min^{-1} respectively. At a dosage of 500 mg/L $FeSO_4$ and 3150 mg/L H_2O_2, the change in volatile organic acids (VOA) yielded a first order rate constant (k) of 0.0011 min^{-1}, which is comparable with k_{13} in Table 5-5 for the same dosage conditions.

At a dosage condition of 500 mg/L $FeSO_4$ and 3150 mg/L H_2O_2, the y/x ratio was found to be 0.79 as seen in Table 5-5. The y/x ratio found can possibly indicate the type of organic transformation taking place during the Fenton oxidation process. The hydroxylation of lignin and phenolic structures generally yields y/x ratios close to 0.79. The breakdown of aromatic derived muconic acid into acetic acid will also result in y/x ratios close to 0.79. The change in total COD, readily COD_{rd} and slowly degradable COD_{sd} can be seen in Figure 5-11.

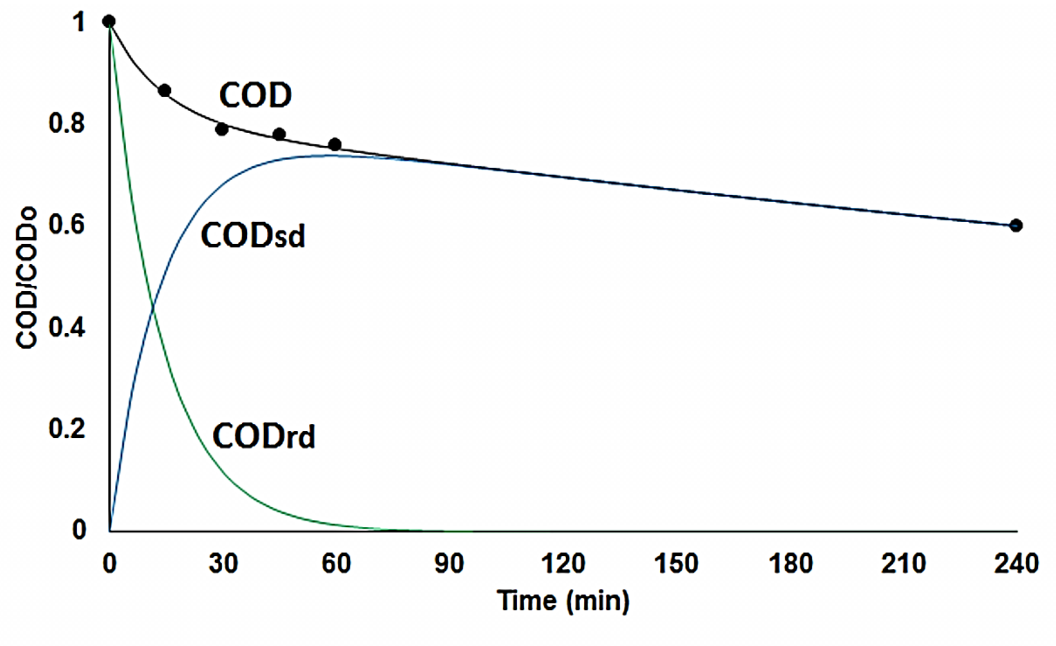

Figure 5-11: The TSF model illustrating the change in the overall COD, COD_{rd} and COD_{sd} for the NSSC effluent with a $FeSO_4.7H_2O$ and H_2O_2 dosage of 500 mg/L and 3150 mg/L (● experimental COD values)

5.6 Conclusion

This study investigated the treatment performance, degradation pathways and kinetics involved in the Fenton oxidation of biologically treated mill effluents (BTME). One of the primary objectives was to evaluate the impact of Fe^{2+} and H_2O_2 dosages on the COD removal efficiency. It was found that the optimal Fe^{2+}/H_2O_2 and COD/H_2O_2 ratio for the NSSC effluent was 0.32 and 1.19, respectively. Whereas the optimal Fe^{2+}/H_2O_2 and COD/H_2O_2 ratios for the RME effluent were found to be 2.22 and 0.96, respectively. The constants in the reduced cubic polynomial models revealed that the influence of catalyst dosage (Fe^{2+}) appears to have a more pronounced effect on COD removal efficiencies. After a 60 minute reaction time, the maximum COD removal efficiency for the NSSC and RME effluents were found to be 44% and 63%, respectively.

The second objective of this study was to assess the applicability of various kinetic models to describe the organic removal rates. The first order, second order, BMG and newly developed TSF model were evaluated. Both the BMG and TSF model generally had high correlation coefficients (r^2). However, during extended Fenton oxidation reactions the TSF model yielded the highest correlation coefficients ($r^2 = 0.99$). The TSF kinetic model constants k_{12} and k_{13} were found to be comparable to the first order kinetic constants that described the degradation of aromatics and of carboxylic acids, respectively. The kinetic results for the TSF model revealed that the k_{12} value is significantly higher than the k_{13} value. Hence, rapidly degradable aromatic constituents such as lignin and phenols are converted into slowly degradable carboxylic acids. The readily biodegradable organic acids formed during the Fenton oxidation of PPMEs can be removed with tertiary biological systems in future studies. The performance and kinetic results of this study demonstrates that the Fenton process can effectively treat bio-recalcitrant organics present in BTMEs.

5.7 References

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Chapter 6. Combined biological and advance oxidation processes for paper and pulp effluent treatment: Fenton-like oxidation

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The aim of this Chapter was to investigate the potential of the Fenton-like process to remove bio-recalcitrant organics from the biologically treated RME (Mill X). Additional Fenton-like experiments were conducted on the RME effluent primarily for the economic assessment (Chapter 7).

Certain sections that were discussed in earlier Chapters were removed from the original manuscript to avoid repetition. The work of this paper was presented at the Water Institute of Southern Africa (WISA) 2016 Biennial Conference and exhibition in Durban. The work of this article was also presented at the TAPPSA 2016 Conference and Exhibition in Durban. The article was peer reviewed and accepted for publication in the TAPPSA journal. The co-authors of this article contributed by means of supervision while the write-up and experiments was conducted by the author of this dissertation.

6.1 Abstract

The Fenton-like experiments were carried out in batch runs on the biologically treated RME effluent. The optimal pH, $Fe_2(SO_4)_3$ and H_2O_2 dosage was investigated. Maximum COD removals were found to be at a pH of 3.33, Fe^{3+} dosage of 1000 mg/L and H_2O_2 of 528 mg/L. First order reaction kinetics was used to describe the kinetic characteristics of the Fenton-like treatment system. The calculated first order kinetic constant k_{COD} (min^{-1}) was 0.0095 min^{-1} at a pH of 3.24, Fe^{3+} dosage of 215 mg/L and a H_2O_2 dosage of 900 mg/L. The kinetic results demonstrated that the rate of organic removal in the Fenton process is much faster in comparison with the Fenton-like process.

Keywords: Fenton-like system, recycle mill effluent (RME)

6.2 Fenton-like reactions

The main set of reactions taking place in the Fenton-like process is given as follows (Wang 2008):

$$Fe^{3+} + H_2O_2 \rightarrow Fe(OOH^{2+}) \qquad 6\text{-}1$$

$$Fe(OOH^{2+}) \rightarrow HO_2^* + Fe^{2+} \qquad 6\text{-}2$$

$$Fe^{2+} + H_2O_2 \rightarrow OH^* + OH^- + Fe^{3+} \qquad 6\text{-}3$$

$$RH + OH^* \rightarrow R^* + H_2O \qquad 6\text{-}4$$

6.3 Materials and methods

6.3.1 Wastewater Characteristics

The wastewater characteristics of the RME effluent used in this Chapter are presented in Table 5-1.

6.3.2 Chemical analysis

The chemical analysis used for this Chapter are described in Section 5.3.2.

6.3.3 Fenton-like oxidation procedure

The potential of a Fenton-like process (Fe^{3+}/H_2O_2) as a tertiary treatment system was investigated in this study. Biologically treated effluent from the moving bed biofilm reactor (MBBR) was used in the Fenton-like experiments. The Fenton-like batch experiments were carried out in 250 mL Erlenmeyer flasks at ambient temperature (25°C).

Ferric sulfate hydrate ($Fe_2(SO_4)_3.xH_2O$, Merck) was used to supply the Fe^{3+} catalyst. A 30% (w/v) hydrogen peroxide solution (Merck) was used as the oxidizing agent. The pH of the solution was adjusted with concentrated H_2SO_4 and NaOH. Mangenese (IV) oxide (MnO_2, Merck) was used to remove residual hydrogen peroxide prior to analysis. Before COD analysis, MQaunt peroxide test strips (Merck) was used to determine if the hydrogen peroxide (H_2O_2) concentration was lower than 10 mg/L.

6.3.4 First order reaction kinetics

The first order kinetics explained in Section 5.4.1 was used in this Chapter.

6.4 Results and discussion

6.4.1 Fenton-like treatment systems

The performance of the Fenton-like treatment system was evaluated to remove the remaining refractory COD. The main influencing factors involved in the Fenton-like treatment systems are the pH, H_2O_2 and Fe^{3+} dosages, temperature and UV exposure (Eskelinen et al. 2010; Mesquita et al. 2012; Wang 2008). In this study the effect of pH, reaction time, Fe^{3+} and H_2O_2 dosages were investigated.

6.4.2 Effect of pH on COD removal

The effectiveness of the Fenton-like process was evaluated at a pH ranging from 2.50 to 6.93. The H_2O_2 and Fe^{3+} dosages were held constant at 2686 mg/L and 250 mg/L. An initial drop in pH was noticed when ferric sulphate was added to the solution. The solution was then further adjusted to the designated pH values using sulphuric acid. The maximum removal of refractory COD was determined at a pH ranging from 3.33 and 4.18 as seen in Figure 6-1. At a pH of 3.33, the COD removal was 51 % after a reaction time of 30 min. The drop in COD removal with increasing pH values can be elucidated by the $Fe(OH)_3$ precipitate forming at higher pH values (Lu et al. 2010). Subsequently, the removal of Fe^{3+} from Eq. 6-1 to 6-4 coincides with the rapid drop in the COD removal rate at a higher pH values.

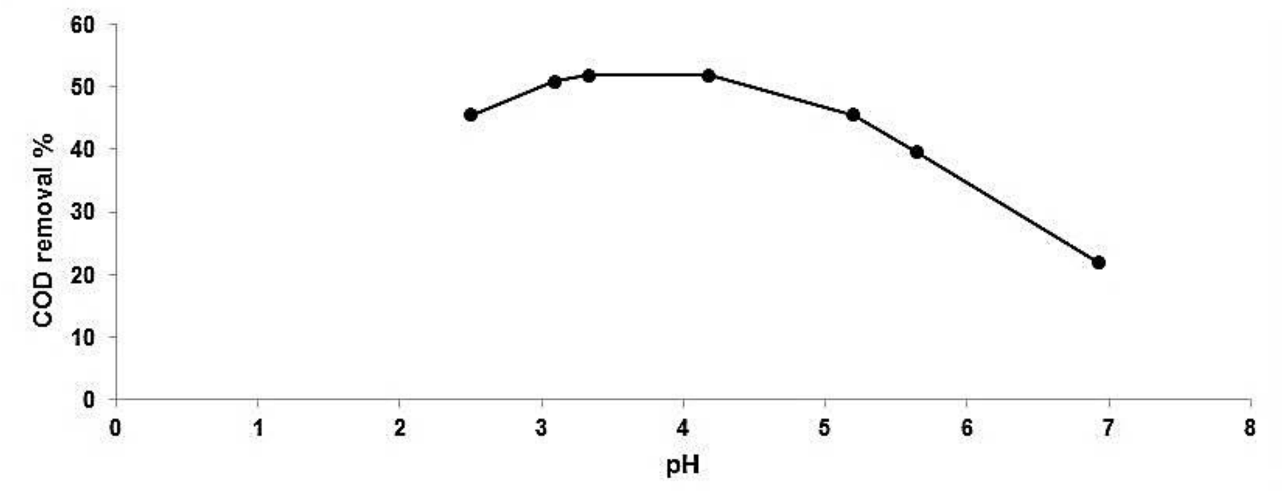

Figure 6-1: Effect of pH on the COD removal in the Fenton-like treatment (30 min reaction time, 250 mg/L $Fe_2(SO_4)_3$, 2686 mg/L H_2O_2)

Below a pH of 3, excessive H^+ will react with hydroxyl radicals (OH^*) to form water. This reaction is shown in Eq. 6-5 (Chiou et al. 2006).

$$OH^* + H^+ \rightarrow H_2O \qquad 6\text{-}5$$

As a result, an optimum pH should be maintained during the reaction to ensure that there is a sufficient production of OH^* and to evade scavenging of OH^*. During the reactions, a drop in pH was noticed. The drop in pH can be explained by the formation of organic acids during the reaction when hydroxyl radicals (OH^*) react with reluctant aromatic and phenolic structures (Thakare 2004; Nakagawa & Yamaguchi 2012).

6.4.3 Effect of ferric sulfate concentration on COD removal

The ferric sulfate ($Fe_2(SO_4)_3$) concentration was varied between 64 and 1000 mg/L to evaluate the effect of the Fe^{3+} concentration on COD removal. During the experiments the pH and H_2O_2 dosages were 3.33 and 2686 mg/L respectively. The highest COD removal was obtained at 1000 mg/L $Fe_2(SO_4)_3$. The COD removal rapidly increased from 64 mg/L to 250 mg/L $Fe_2(SO_4)_3$ as illustrated in Figure 6-2. The rapid increase in COD removal efficiency can be explained by the increase in hydroxyl radical (OH^*) formation as the Fe^{3+} dosage increases. The slope from Figure 6-2 gradually decreases after 250 mg/L. It is important to determine the optimum Fe^{3+} dosage to reduce sludge formation.

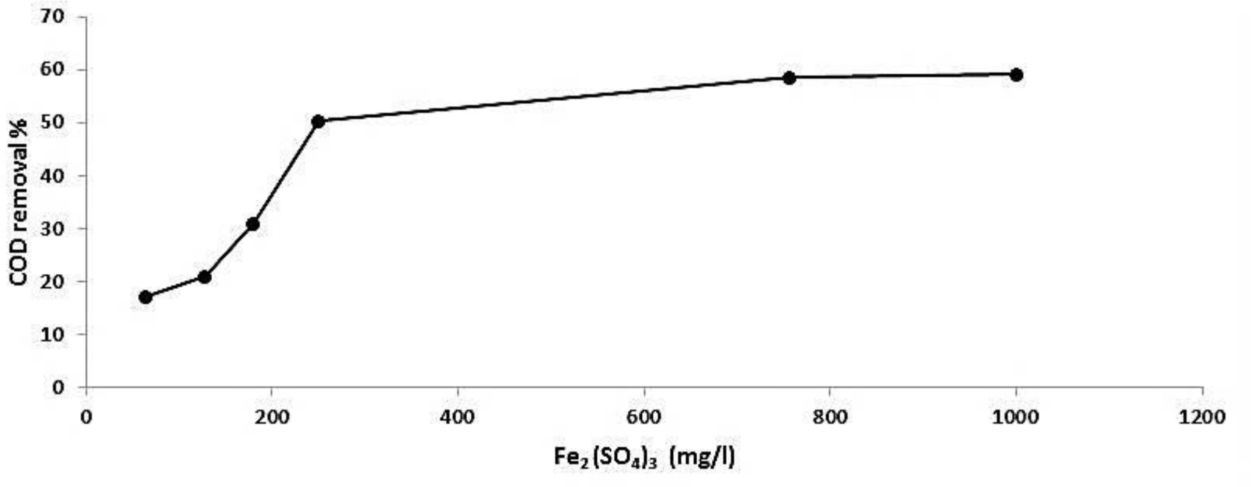

Figure 6-2: Effect of $Fe_2(SO_4)_3$ concentrations on COD removal in a Fenton-like treatment system (30 min reaction time, 2686 mg/L H_2O_2, pH = 3.33)

6.4.4 Effect of hydrogen peroxide dosage on COD removal

The H_2O_2 concentration was varied between 224 and 2686 mg/L. The pH and $Fe_2(SO_4)_3$ was 3.33 and 250 mg/L, respectively. At 528 mg/L H_2O_2, the COD removal was 55.43 %, which represents the optimum dosage of H_2O_2. The COD removal initially increased with increasing H_2O_2 concentrations due to the additional formation of hydroxyl radicals (OH*).

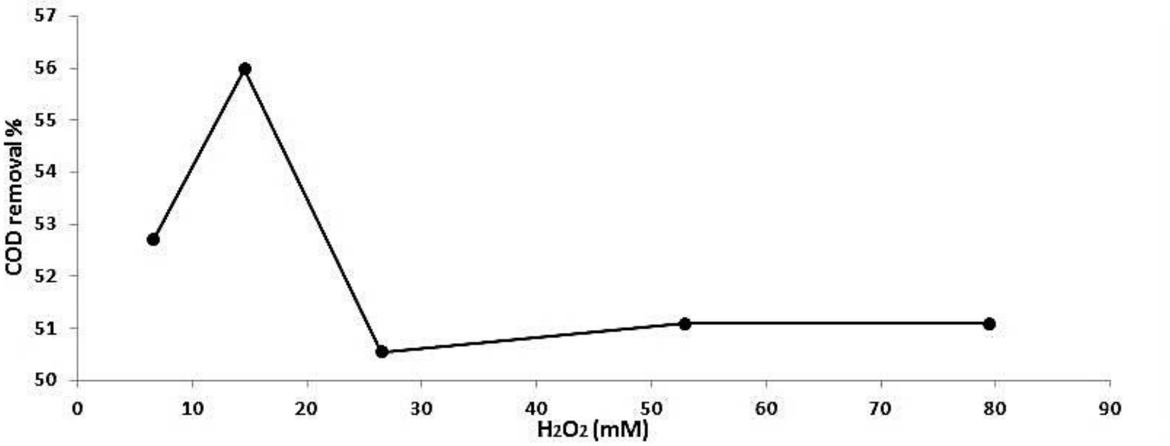

Figure 6-3: Effect of H_2O_2 concentrations on COD removal in a Fenton-like treatment system (30 min reaction time, 250 mg/L $Fe_2(SO_4)_3$, pH = 3.33)

The COD removal decreased after 528 mg/L H_2O_2, as seen in Figure 6-3. This unique behaviour can be explained by the scavenging of active hydroxyl radicals as it reacts with the excess H_2O_2, as shown in Eq. 6-6 (Ebrahiem et al. 2013).

$$H_2O_2 + OH^* \rightarrow HO_2^* + H_2O \qquad 6\text{-}6$$

Because the hydroxyl radical (OH^*) formation is such an important aspect of the overall COD removal, it is essential to determine the optimum $Fe_2(SO_4)_3$ to H_2O_2 ratio. In this study the optimum $Fe_2(SO_4)_3$ to H_2O_2 ratio was found to be 1:1.76.

6.4.5 The effect of reaction time on COD removal

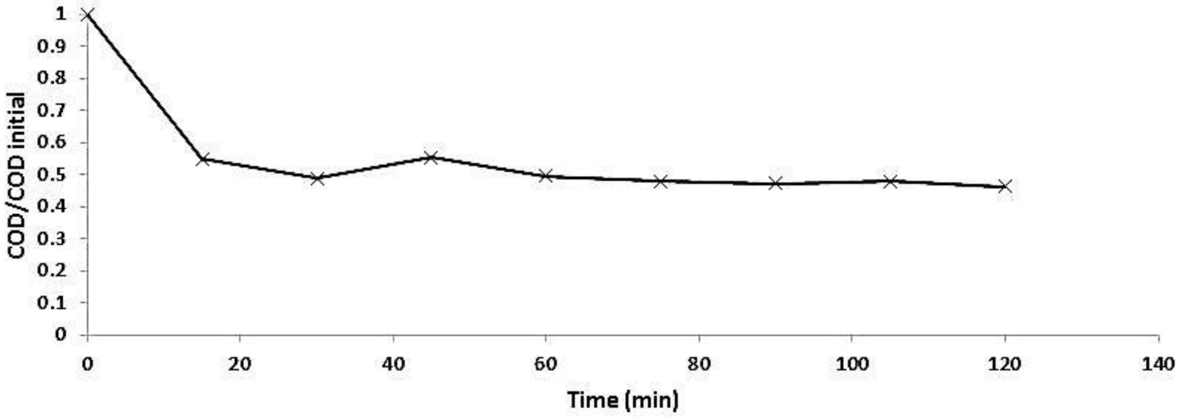

Figure 6-4: Effect of reaction time (min) on COD removal in a Fenton-like treatment system (pH=3.24, $Fe_2(SO_4)_3$ = 250 mg/L; H_2O_2 = 2686 mg/L)

The COD removal was monitored over a 120 minute reaction period. As seen in Figure 6-4, 46% of the COD was removed within the first 15 minutes. Similar results were obtained in Nieto et al. (2011) where Fenton-like systems were also evaluated. Although there is no significant change in the COD after 15 minutes, there can be a substantial drop in toxicity if the reaction time is increased. According to Barbusiński (2005), the change in COD is not proportional to the change in toxicity. This suggests that the toxicity of the effluent is largely dependent on intermediates produced during the Fenton-like reaction. Longer reaction times may therefore be used in processes where lower toxicity levels are required. The first order kinetic constants (k) obtained for both the Fenton and Fenton-like experiments are shown in Table 6-1. It is evident that the rate of oxidation in the Fenton process is higher than that of the Fenton-like experiments.

Table 6-1: A comparison between the first order rates constants of the Fenton and Fenton-like oxidation of RME (Mill X)

Parameters	Fenton process (Fe^{2+}/H_2O_2)	Fenton-like process Fenton process (Fe^{2+}/H_2O_2)
H_2O_2 (mg/L)	900	900
Fe^{2+}; Fe^{3+} (mg/L)	215	215
pH	3.5	3.5
k (min^{-1})	0.0215	0.0095

6.5 Conclusion

The results demonstrated that the Fenton-like process can remove bio-recalcitrant COD from the biologically treated RME effluent (Mill X). The performance of the Fenton-like treatment was affected by the pH, Fe^{3+} and H_2O_2 dosages. The highest COD removal was established at a pH of 3.33, Fe^{3+} dosage of 1000 mg/L and a H_2O_2 dosage of 528 mg/L. The Fenton-like treatment system removed 53.73 % of the COD after a 60 minutes reaction time.

6.6 References

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Chapter 7. Economic Evaluation

The economic feasibility of combining an aerobic MBBR with different AOP technologies for Mill X was evaluated in this Chapter. The economic analysis was only done on the Mill X since the data obtained in this project can be used in conjunction with previous water optimization work done at the mill (Vurdiah 2015).

7.1 Mass balance and design specifications

The previous water optimization work at the Mill X was mainly focusing on the water network of Board mill 3 (BM3) (Vurdiah 2015). As a result, this economic assessment will only be conducted on BM3. In the mass balance models used in Vurdiah (2015), the COD and TSS water quality parameters were the main constraints that restricted the amount of water that could be reused in the water network. Consequently, the COD and TSS water quality parameters were taken into consideration for this economic analysis. The schematic diagram of the complete water network that was used in Vurdiah (2015) is shown in Appendix E. As the water network is closed, it can be noticed that the contaminants will build-up in the water network. The internal COD and TSS limit for the mill was 2000 mg/L and 25 mg/L, respectively.

The simplified process flow diagram of BM3 and WWTP used is illustrated in Figure 7-1. The description of the various streams is presented in Table 7-1. The majority of the total suspended solids (TSS) are initially removed with a primary clarification process. The clarifier supernatant and underflow are given by streams F39 and F35, respectively. Prior to the recycling of the clarifier supernatant (F39) to the high pressure showers (MU5a, MU6a), a WWTP is required to remove the COD, TSS and colour. The WWTP utilized both aerobic MBBR and Fenton related technologies to achieve the desired water quality parameters. The treated effluent is then recycled to the high pressure showers (MU5a, MU6a), which consequently reduces the freshwater demand (F18, F43). The volumetric flow rate of the recycling stream F44 is dependent on the performance of the WWTP. Mass balance calculations were done on the BM3 to determine the desired effluent quality parameters that the WWTP should be able to achieve in order to comply with the internal COD limit (2000 mg/L). The WWTP should lower the COD concentration to approximately 250 mg/L in order to close the water network. According to Vurdiah (2015), the critical TSS concentrations are 25 mg/L. It was assumed that both secondary and tertiary clarifiers in the proposed WWTP would be able to reduce the TSS concentration below 25 mg/L. The addition of $FeSO_4$ and slaked lime will also act as coagulant which will be able to reduce the TSS concentrations smaller than 25 mg/L (Meyer & Edwards 2014; Chowdhury et al. 2013). No strict colour requirements were stated in Vurdiah (2015) for the closure of the water network. The batch experiments demonstrated that the Fenton oxidation and lime addition removed 97% of the colour content of the BTME. As long as the reaction time for the Fenton process was larger than 30 minutes, it was assumed that the WWTP would be able to comply with the colour restrictions. By closing the water network, the fresh water demand of the Mill X could be further decreased from 569 m^3/day to 249 m^3/day.

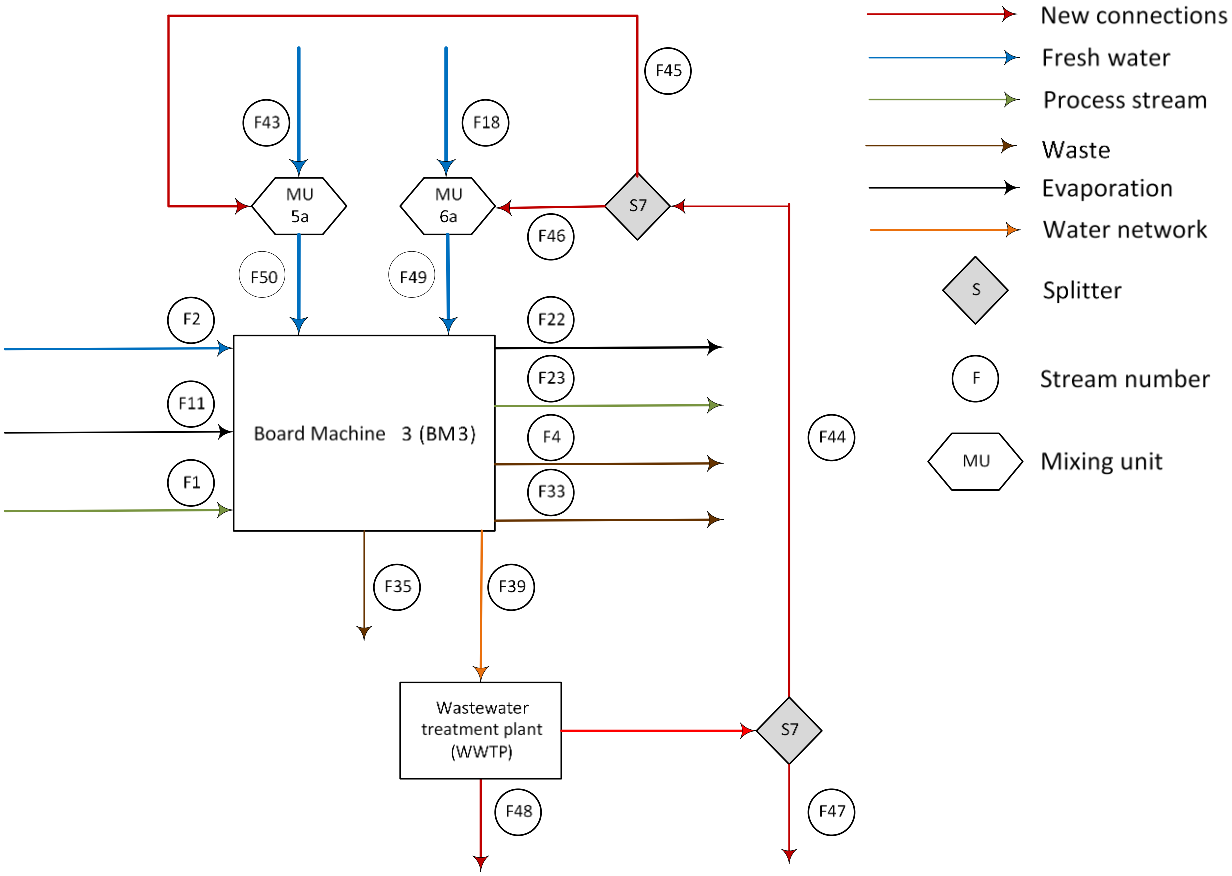

Figure 7-1: General flow diagram for Board machine 3 (BM3) and the WWTP

Table 7-1: The stream numbers and corresponding stream descriptions

Stream number	Description
F1	Raw material
F2	Steam
F4	Rejects
F11	Chemicals
F18	High pressure shower
F22	Evaporation
F23	Product
F33	Recovered fibre

F35	Sludge
F39	Clarifier supernatant
F43	High pressure shower
F44	Treated effluent main return stream
F45	Treated effluent return stream 1
F46	Treated effluent return stream 2
F47	Treated effluent waste stream
F48	Sludge

The proposed MBBR-Fenton WWTP is presented in Figure 7-2. The supernatant from the primary clarifier is initially treated using an aerobic MBBR (T-1) to remove the majority of the biodegradable material. A certain fraction of the suspended bacterial and particulate matter is recycled (W5) back into the MBBR, whereas the remaining sludge (W4) is removed for disposal. The MBBR (T-1) is operated at mesophilic temperatures (32°C) and dissolved oxygen (DO) concentrations larger than 3 mg/L. The supernatant (W7) from the secondary clarifier (T-2) flows into the Fenton reactor (T-3) where the remaining fraction of the bio-recalcitrant organics and colour are removed. The Fenton reagents (H_2O_2, $FeSO_4.7H_2O$; H_2SO_4) (W15) are continuously added to the Fenton reactor (T-3) and are operated at a pH value between 3 and 4. The Fenton treated effluent (W8) is neutralised with slaked lime (W9). The neutralised effluent is aerated (T-4) to oxidize the calcium and iron in the solution into more insoluble complexes that could be removed in the tertiary clarifier (T-5). The design specifications for the WWTP are presented in Table 7-2.

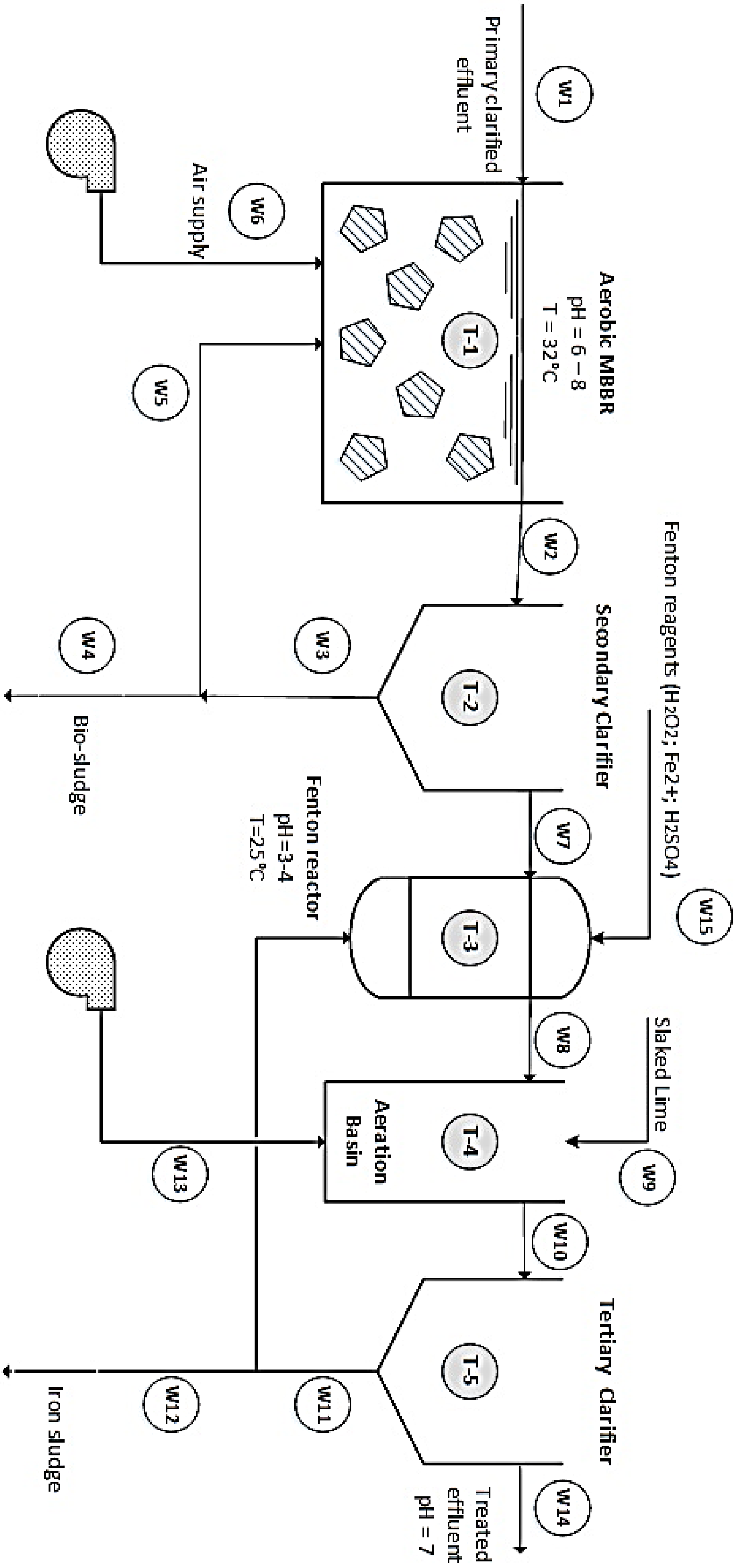

Figure 7-2: Proposed wastewater treatment plant for Mill X

Table 7-2: Design specifications for the wastewater treatment plant (WWTP)

Parameters	Value	Units
Flowrate	395	m^3/day
COD inlet	1993	mg/L
COD outlet	250	mg/L
TSS outlet	<28	mg/L
TSS inlet	148	mg/L

7.2 Reactor sizing

The results obtained in Chapter 4-6 were used to determine the reactor sizes for both biological and AOP technologies.

For the aerobic MBBR, the Kincannon-Stover kinetic model and the corresponding kinetic parameters found in Chapter 4 were used to predict the reactor performance at various hydraulic residence times (HRT). The MBBR reactor volume was predicted using Eq. 4-10 (Chapter 4). The results suggest that at a HRT of 24 hours the reactor could remove approximately 97% of the biodegradable COD. The Fenton and Fenton-like oxidation results presented in Chapter 5 and 6 were used to determine the corresponding reactor volumes. The first order batch kinetic parameters (*k*) obtained during the experimental work were used to model the continuous Fenton and Fenton-like reactors. The reactor volume for a continuous Fenton related reactor set-ups can be calculated using the following expression:

$$V = \frac{Q(COD_o - COD_e)}{k.COD_e} \tag{7-1}$$

Experimental results demonstrated that the addition of lime for effluent neutralization (pH = 7) can remove another 25% of the COD. The drop in COD is linked to the coagulation and flocculation effect of lime and $FeSO_4$. After the effluent neutralization and aeration steps, a 60 minute settling time was required to precipitate the oxidized iron and calcium complexes out of the solution. The volume of the settling tank was also taken into account. The treatment of the BTMEs using ozone (O_3) was not part of the scope of this dissertation. However, kinetics obtained from literature on the ozonation of paper and pulp mill effluents were used to compare the capital & operational costs to that of the Fenton related technologies in this study (Lei & Li 2014). The kinetic data from (Lei & Li 2014) was used for all the ozone calculations. At a pH of 8.0 and an ozone dosage of 2.88 $gO_3.L^{-1}.hr^{-1}$, the first order kinetic constant (k) was found to be 0.00751 min^{-1}. Additional ozone experiments were conducted on the RME to confirm that the first order rate constants found in Lei & Li (2014) were applicable. The ozone (O_3) results demonstrated that similar first order rate constants (k = 0.00753 min^{-1}) can be achieved with the RME at an ozone dosage of 6 $gO_3.L^{-1}.hr^{-1}$ and pH = 8.5. The additional results obtained during the ozone experiments can be found in Appendix D. The corresponding ozone reactor volume was also calculated with Eq. 7-1. The calculated volumes for the biological and AOP technologies are presented in Table 7-3.

Table 7-3: Specifications for the biological and AOP reactors

	Biological Treatment	**Advanced oxidation processes (AOP)**		
Parameter	MBBR	Fenton (Fe^{2+}/H_2O_2)	Fenton-like (Fe^{3+}/H_2O_2)	Ozone (O_3)
Feed flowrate (m^3/day)	395	395	395	395
Reactor volume (m^3)	395	33	36	80
Filling ratio	30	-	-	-
Air feed supply	158	-	-	-
COD/H_2O_2	-	0.96	0.96	-
Catalyst/H_2O_2	-	1	1	-
gO_3/L.hr	-	-	-	2.88

7.3 Total capital investment

The main factors considered for the total capital investment calculations are presented in Table 7-4. The table presents each individual item as a percentage of the delivered equipment cost. The total capital investment cost for the different biological and AOP technologies were estimated using the estimations of (Awad & Abuzaid 1997).

Table 7-4: Capital investment items for a wastewater treatment plant (WWTP) (Awad & Abuzaid 1997)

Item	**% of delivered equipment**
Equipment and machinery	100
Purchased equipment installation	47
Instrumentation and controls (installed)	18
Piping (installed)	66
Electrical (installed)	11
Building (including services)	18
Yard improvements	10

Service facilities	70
Land	6
Total direct plant cost	**346**
Engineering supervision	33
Construction expenses	41
Total direct and indirect cost	**420**
Contractor fees	21
Contingency	42
Fixed capital investment	**483**
Working capital	86
Total capital investment	**569**

The chemical engineering plant cost index (CEPCI) was used in this study to estimate the equipment cost for the specified year (2016). The cost indexes were incorporated in the following expression to determine current equipment costs (Seider 2006).

$$C_C = C_B \cdot \left(\frac{I}{I_B}\right) \tag{7-2}$$

where C_C signifies the current cost (R), C_B the base cost (R), I the current cost index and I_B the base cost index. The chemical engineering plant cost index (CEPCI) used in this study is presented in Table 7-5.

Table 7-5: The chemical engineering plant cost index (CEPCI) values used in the calculations (Seider 2006)

Year	CEPCI values
1990	358
1995	381
1998	391
2006	500
2016	556

The six tenths factor was used to predict the cost of larger equipment. The following expression correlates the variation in capacity with the difference in equipment cost (Seider 2006):

$$\frac{Cost_a}{Cost_b} = \left(\frac{Capacity_a}{Capacity_b}\right)^{0.6} \qquad 7\text{-}3$$

The cost of biological and AOP treatment equipment was based upon cost correlations which are presented in Table 7-6. The cost correlations for the Fenton, Fenton-like and ozone technologies were given as bare module costs (Canizares et al. 2009).

Table 7-6: Individual items and cost correlations[1]

Unit	Description	Cost correlation	Currency	Reference
Moving bed biofilm reactor (MBBR)				
MBBR- aeration unit	Concrete base Concrete wall	$356.95 \times \left(\frac{\pi}{4} D^2\right)$ $466.8 \times \pi . D . H$	Can$ (1995)	(Fels et al. 1997)
MBBR- aeration equipment	Air diffusers and blowers	$8590. OC^{0.433}$	€ (1998)	(Gillot et al. 1999)
MBBR-agitation	Open vessel propeller mixers	$2300. S^{0.34}$	US$ (CE=500)	(Seider 2006)
MBBR carrier media	Biomass carriers	$255. V_{carrier}$	US$ (2016)	Supplier
Clarifier	Clarifier steel Mechanical equipment	$3050. A_1{}^{0.58}$ $60{,}000. \left(\frac{A_2}{220}\right)^{0.6}$	US$ (CE=500) Can$ (1990)	(Seider 2006) (Wright & Woods 1993) (Wright & Woods 1994)
Pumping station	Concrete Screws Screens	$2334. Q_1{}^{0.637}$ $2123. Q_1{}^{0.540}$ $3090. Q_1{}^{0.349}$	€ (1998)	(Gillot et al. 1999)
Sludge pump	Electromechanical equipment	$5038. Q_2{}^{0.304}$	€ (1998)	(Gillot et al. 1999)
Ozone (O_3) treatment technology				
Ozone equipment	Reactor and ozone generator	$1719.5 \cdot q^{0.6143}$	€ (2006)	(Canizares et al. 2009)
Fenton (Fe^{2+}/H_2O_2) treatment system				
Fenton equipment	Reactor and settler	$20804 \cdot V^{0.3596}$	€ (2006)	(Canizares et al. 2009)

Fenton-like (Fe^{3+}/H_2O_2) treatment system				
Fenton-like equipment	Reactor and settler	$20804 \cdot V^{0.3596}$	€ (2006)	(Canizares et al. 2009)

[1] The description, range and units of each symbol used for the cost correlations (Table 7-6) are presented in Table 7-7. The cost of equipment delivery was estimated to be 5% of the total equipment cost (Seider 2006).

Table 7-7: The description of the various symbols used for the biological and AOP cost correlations

Symbol	Description	Units	Ranges
D	Tank diameter	m	-
H	Tank height	m	-
OC	Oxygen capacity	$kg\ O_2/hr$	30 - 630
S	Motor power	hp	1 - 8
$V_{carrier}$	Volume of biomass carriers	m^3	-
A_1	Clarifier surface area	ft^2	80 - 8000
A_2	Clarifier surface area	m^2	175 - 1250
Q_1	Volumetric flow rate	m^3/hr	250 - 4000
Q_2	Volumetric flow rate	m^3/hr	35 - 2340
V	Reactor and settler volume	m^3	-
q	Required ozone production	$g\ O_3/hr$	-

The capital investment for the MBBR, Fenton, Fenton-like and ozone treatment technologies are presented in Table 7-8. It can be seen that the capital investment of the ozone treatment technologies are significantly greater than that of the MBBR and Fenton related technologies. (Canizares et al. 2009) also demonstrated that the ozone treatment technology have the higher capital costs than the Fenton treatment technologies. The total capital investment cost of the proposed WWTP (Figure 7-2) was calculated to be R 28,5 million.

Table 7-8: The capital investment (ZAR) of the various wastewater treatment technologies (2016)

Item	**Biological Treatment**	**Advanced oxidation processes (AOP)**		
	MBBR	Fenton process	Fenton-like process	Ozone treatment

Equipment and machinery	3,626,000	1,385,000	1,505,000	36,941,000
Purchased equipment installation	1,704,000	651,000	707,000	17,363,000
Instrumentation and controls	653,000	249,000	271,000	6,649,000
Piping	2,393,000	914,000	993,000	24,381,000
Electrical	399,000	152,000	166,000	4,063,000
Building	653,000	249,000	271,000	6,649,000
Yard improvements	363,000	139,000	151,000	3,694,000
Service facilities	2,538,000	970,000	1,054,000	25,858,000
Land	218,000	83,000	91,000	2,216,000
Total direct plant cost	**12,546,000**	**4,792,000**	**5,207,000**	**127,815,000**
Engineering supervision	1,197,000	457,000	497,000	12,190,000
Construction expenses	1,487,000	568,000	617,000	15,146,000
Total direct and indirect cost	**15,229,000**	**5,817,000**	**6,321,000**	**155,151,000**
Contractor fees	761,000	291,000	316,000	7,758,000
Contingency	1,523,000	582,000	632,000	15,515,000
Fixed capital investment	**17,513,000**	**6,690,000**	**7,269,000**	**178,423,000**
Working capital	3,118,000	1,191,000	1,294,000	31,769,000
Total capital investment	**20,632,000**	**7,881,000**	**8,564,000**	**210,192,000**

7.4 Operational costs

This section evaluates the operational costs of the various wastewater treatment technologies. The main factors that influence the operational costs (OC) of WWTPs are discharge fees, electricity cost, chemical cost, staff cost, maintenance and replacement cost, sludge disposal and transport, and administration cost (Scheepers et al. 2009). The cost of chemicals/reagents and electricity are the only factors that will be taken into account for this operational cost assessment. The operational cost (OC) was calculated using Eq. 7-4:

$$OC = C_E + C_R \tag{7-4}$$

where C_E and C_R signifies the cost of electricity and reagents (R/m^3), respectively. In this study it was assumed that operational cost of an aerobic MBBR will be similar to that of an activated sludge (AS) unit. The power consumption of an activated sludge (AS) plant smaller than 500 m^3/day will consume approximately 0.5906 kWh/m^3 (Scheepers et al. 2009). The cost of electricity was taken as R0.80/kWh. According to (Scheepers et al. 2009), the power and chemicals contributes approximately 20% and 13% of high end activated sludge (AS) units in South Africa. The average price for the H_2O_2, $FeSO_4$ and $Fe_2(SO_4)_3$ used were taken as R11.00/kg H_2O_2, R3.33 /kg $Fe_2(SO_4)_3$ and R2.96/kg $FeSO_4$, respectively.

The cost of changing the pH was also added to the operational cost estimations. The cost of H_2SO_4 and $CaCO_3$ were taken as R1.68/kg H_2SO_4 and R0.74/kg $CaCO_3$, respectively. The cost of sludge disposal was not added to these calculations. The power requirements for the conventional Fenton process were estimated to be 0.192 kW/m^3 (Pérez et al. 2013). The following empirical relationship can was used to calculate the energy requirement of the Fenton treatment plant (Yasar & Yousaf 2012):

$$E\left(\frac{kWh}{m^3}\right) = \frac{P.t}{V.\log\left(\frac{C_o}{C_t}\right)} \qquad 7\text{-}5$$

where E represents the energy requirement for the Fenton process (kWh/m^3), P the power usage of equipment (kW), V the volume of the effluent (m^3), t represents the reaction time (h), C_o the influent COD concentration and C_f the effluent COD concentration (mg/L). In Pérez et al. (2013), 0.192 kW/m^3 was required for the Fenton reactor. The 0.192 kW/m^3 represents P/V in Eq. 7-5. The actual power consumption was then found to be 0.48 kWh/m^3. This power consumption for the Fenton-like treatment system was found to be 0.55 kWh/m^3. The power consumption of air fed ozone generator range between 22.24 and 25 kWh/kg O_3 (Sevimli 2005). The amount of ozone required was taken as 2.88 kg O_3/m^3 (Lei & Li, 2014). The corresponding energy consumption was calculated to be approximately 64 kWh/m^3.

The operational cost results in Table 7-9 indicated that the Fenton process was the cheapest AOP technology. Based upon the operational & capital cost results it is recommended that the aerobic MBBR should be used in combination with a Fenton process for effluent treatment. The cost of fresh water and discharge for Mill X is R15.40/m^3 and R4.60/m^3, respectively. The total operational cost of a MBBR-Fenton treatment plant was approximated to be a R12.21/m^3.

Table 7-9: Operational cost of the various treatment technologies

Items	**Biological Treatment**	**Advanced oxidation processes (AOP)**		
	MBBR	Fenton	Fenton-like	Ozone
Chemicals/Reagents (R/m^3)	0.31	11.05	13.35	-
Electricity (R/m^3)	0.47	0.38	0.44	51.25
Total cost (R/m^3)	**0.78**	**11.43**	**13.79**	**51.25**

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Chapter 8. Conclusions

The primary aim of this dissertation was to investigate the technical and economic feasibility of combining biological and advanced oxidative processes (AOP) for the treatment of paper and pulp mill effluents at Mill X and Y. The following conclusions were made:

1. In Chapter 2, an extensive literature study was conducted in order to identify suitable biological and AOP technologies for the treatment of paper and pulp mill effluents. In the technology identification and selection process (Chapter 3), it was concluded that aerobic MBBRs and Fenton related technologies should be used as secondary and tertiary treatment stages, respectively.

2. The performance and kinetics of an aerobic MBBR treating paper and pulp mill effluents was evaluated in Chapter 4. The bench scale aerobic MBBR was able to effectively remove the biodegradable COD from recycle and neutral sulfite semi-chemical (NSSC) paper and pulp mill effluents. At a hydraulic residence time (HRT) of 16 hours, the aerobic MBBR was able to remove 49, 46 21 and 28% of the total COD from Effluent A, B, C and D, respectively. The maximum biodegradation rates of the RME effluent were found to be higher than that of pure NSSC effluents. The biodegradation rates in an aerobic mesophilic MBBR were best described by the Kincannon-Stover model ($r^2>0.99$). The kinetic results demonstrated that the phenols present in the effluents might act as inhibitors which might result in decreased performances. The negative effect of phenolic inhibition had on the bench-scale studies therefore suggest that that industrial scale aerobic MBBRs might need longer acclimatization periods to grow specialized cultures. Despite the limitations, aerobic MBBR technologies are still recommended for both mills as a secondary biological treatment system.

3. The potential of the Fenton and Fenton-like oxidation processes to treat biologically treated mill effluents (BTME) was investigated in Chapter 5 and Chapter 6. Both the Fenton (Fe^{2+}/H_2O_2) and Fenton-like (Fe^{3+}/H_2O_2) oxidation processes were able to effectively remove bio-recalcitrant organics and colour from biologically treated recycle and neutral sulfite semi-chemical (NSSC) effluents. Preliminary tests demonstrated that the oxidizing rates of the Fenton process were found to be superior to that of the Fenton-like process. In terms of the performance results it will be better to use the Fenton process for such applications in the paper and pulp industry. The optimal conditions of the Fenton process were largely dependent on the type of BTME treated. Optimal COD removal was obtained between a pH value of 3 and 4. The

optimal COD/H_2O_2 and Fe^{2+}/H_2O_2 ratios for the RME effluent were found to be 0.96 and 2.22, respectively. The optimal COD/H_2O_2 and Fe^{2+}/H_2O_2 ratios for the NSSC effluent were found to be 1.19 and 0.32, respectively. The conversion of H_2O_2 during the reactions was not measured, which evidently poses some limitations to this work. The applicability of the first order, second order, BMG and newly developed TSF model were evaluated to describe the Fenton oxidation of BTMEs. Both the TSF and BMG model were found to be applicable to describe the removal of bio-recalcitrant organics from BTMEs. The kinetic results revealed that the NSSC effluent is degraded at much faster rates than the RME effluent (Chapter 4). It was concluded that the Fenton process is an effective tertiary treatment technology applicable for both mills. The Fenton process and lime treatment can effectively remove the colour content of the RME effluent (97%).

4. The economic feasibility of combining MBBR and AOP technologies primarily for the purpose of water network closure was investigated. The MBBR-Fenton treatment process was found to be the most economical treatment solution for Mill X. The total cost of treatment was calculated to be R12.21/m^3, whereas the total cost of fresh water and discharge was found to be R20/m^3.

5. Based upon the technical and economic phases of this dissertation, it can be concluded that a MBBR-Fenton treatment combination will be suitable for the treatment of PPMEs.

8.1 Recommendations

The limitations and recommendations of the work done in this project are given as follows:

1. In this dissertation, the effluent was primarily characterised based upon COD, phenols, lignin, volatile organic aids (VOA), carbohydrate content and semi-volatile organic constituents. A more detailed compositional analysis is required before simulation programs such as AspenTech® can be used.

2. During the Fenton process, complex bio-recalcitrant organics present in paper and pulp mill effluent can be transformed into more readily degradable organic matter (BOD) (Ginni et al. 2014). Using this partial oxidation principle, various studies have already combined ozone oxidation with tertiary bio-filters to reduce the operational costs (Merayo et al. 2013; Möbius 2006). This study showed that ozone is still much more expensive in comparison to the Fenton process. The problem with the Fenton process is that the solution is at a low pH value (2 - 3) after treatment and the

remaining ferrous (Fe^{2+}) sulphate is still in solution. By using iron bacteria such as *Thiobacillus Ferrooxidans* with which flourishes in acid solutions high Fe^{2+} content, the fractionated complex organics can now be further biodegraded by these bacteria. (Mandal et al. 2010) demonstrated that the concept of combining the Fenton process with *Thiobacillus Ferrooxidans* yielded very promising results for the treatment of leather industrial effluents. Another advantage of the biological treatment by *Thiobacillus Ferrooxidans* is that the ferrous salts are converted into less soluble ferric salts as seen in reactions below:

$$FeSO_4 + H_2SO_4 + O_2 + T.ferrooxidans \rightarrow Fe^{3+} + H_2O$$

The derived ferric salts (Fe^{3+}) can be precipitate out of solution much more easily than the ferrous salts (Fe^{2+}), therefore yielding cleaner effluents. The implementation of Fenton partial oxidation techniques are relatively unexplored for the paper and pulp industry.

3. In this project, the impact of the total dissolved solids (TDS) was not taken into account. This parameter can severely limit the amount of treated process water that can be recycled back into the paper and pulp mill (Chapter 7). Excessive amounts of TDS in the process water can cause scale deposits which can cause clogging of equipment, pipes and showers as well as that the pH value downgrade the quality of the product (Sitholé 2001). According to (Aguinaldo 2009), in industrial applications the total dissolved solids (TDS) is generally removed by lime softening, reverse osmosis (RO), microfiltration (MF), ultrafiltration (UF) and nano filtration (NF). Both reverse osmosis (RO) and nano-filtration are excellent technologies to reduce the TDS (Schoeman & Steyn 2003); Izadpanah & Javidnia 2012). However, in some cases where high TDS is found lime softening is a preferred (Aguinaldo 2009). Lime softening can be used in conjunction with the Fenton process (Fe^{2+}/H_2O_2). Both the calcium and iron is removed in this process. Calcium is generally precipitated out as $CaCO_3$ (pH>9.5), whereas the iron is precipitated as $Fe(OH)_3$. Additional oxygen is might be required as seen in reaction no. 4 to convert $Fe(OH)_2$ into $Fe(OH)_3$. After sludge removal, the pH of the supernatant is then altered by carbonation processes. However, future studies are required to do a technical and economical assessment on the potential of lime softening and membrane processes (MF, UF, NF and RO) to remove the excessive TDS concentrations after MBBR-Fenton treatment steps.

8.2 References

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Appendix A MBBR experimental data

Appendix A.1. COD calibration curve

***Note:** Certain samples initially tested with the 500 – 10 000 mg/L COD test kit. The calibration curves for these COD (500 – 10 000 mg/L) test kit was already build-in the Merck Spectroquant ®. However, the 100 – 1000 mg/L COD refill test kits required a separate calibration curve (Table A-). Different dilutions of sucrose were used to determine the calibration curve. The theoretical COD of the sucrose ($\mathrm{C_{12}H_{22}O_{11}}$) was calculated according to the following equation:

$$ThCOD = \frac{8(4n + a - 2b - 3c)}{(12n + a + 16b + 14c)} \left(\frac{gCOD}{gC_nH_aO_bN_c}\right) \qquad \text{A-1}$$

The 100 – 1500 mg/L COD test and 500 – 10 000 mg/L test kits yielded the same COD value for randomly tested samples. As a result, the sucrose calibration curve was found to be accurate.

Table A-1: COD calibration curve

Sucrose concentration (g/L)	**Theoretical COD (mg/L)**	**Absorbance (585 nm)**
1.12	1261.92	0.806
0.56	623.58	0.430
0.30	333.19	0.237
0	0	0.052

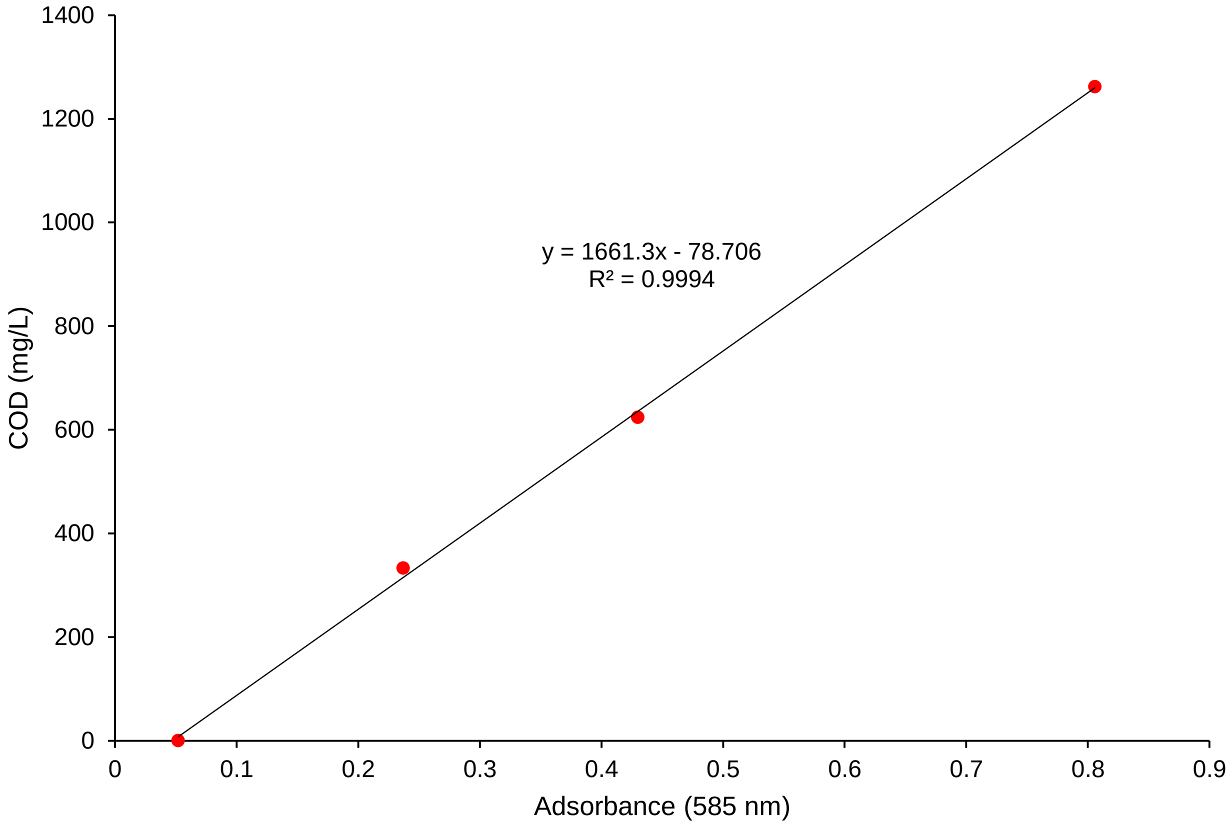

Figure 8-1: COD calibration curve

Appendix A.2. Volatile and semi-volatile organic screening results

Analytical methods:

The samples were extracted and analysed for semi-volatile organic compounds using an in-house method. They were also analysed by purge and trap GC-MS to determine volatile organic compounds. No VOC were detected in samples.

***Note**: It is important to note, that the estimated concentrations from the CSIR results are lower than that of the calorific method determinations (e.g phenols). A possible explanation could be attributed to the liquid – liquid extraction methods used prior to GC-MS. Generally the concentration of organics in the solvent-extract differs to that in the original wastewater sample. As a result, the exact quantity of the organics present in the original wastewater sample is unknown. The VOC and sVOC screening results are mainly used to identify specific organic compounds rather than specific quantities.

Table A-2: Semi-volatile organic screening results (Effluent A = Mill X)

Compounds	Retention time (min)	CAS number	Estimated conc (ppb)
2-Fluorophenol	3.857	Surrogate	-
*Unknown	3.987	N/A	88
Butyl glycol	4.081	111-76-2	77
Phenol-d6	4.587	Surrogate	-
1,4-Dichlorobenzene-d4	4.904	Internal standard	-
p-Cresol	5.251	106-44-5	140
Nitrobenzene-d5	5.393	Surrogate	-
Ethylhexanoic acid	5.551	149-57-5	126
Benzoic acid	5.922	65-85-0	219
1-(2-Butoxyethoxy) ethanol	5.975	54446-78-5	60
Naphthalene-d8	6.069	Internal standard	-
Benzeneacetic acid	6.346	103-82-2	57
Benzenepropanoic acid	6.887	501-52-0	213
2-Fluorobiphenyl	7.098	Surrogate	-
1,4-Diisobutyl-1,4-dimethylbutynediol	7.228	126-86-3	51
*Unknown	7.316	N/A	86
Acenaphthene-d10	7.769	Internal standard	-
*Unknown	8.487	N/A	114
2,4,6-Tribromophenol	8.545	Surrogate	-
*Unknown	8.710	N/A	54
Phenanthrene-d10	9.234	Internal standard	-
Dibutyl phthalate	9.781	84-74-2	80
*Unknown	9.945	N/A	191
4-(1,5-Dimethyl-3-oxohexyl)-1-cyclohexene-1-carboxyllic acid	10.210	6753-22-6	114
Octadecanoic acid	10.545	57-11-4	42
*Unknown	10.681	N/A	40
Bisphenol A	10.710	80-05-7	96
P-Terphenyl-d14	10.804	Surrogate	-
Callitrisic acid	11.828	5155-70-4	222
Chrysene-d12	12.051	Internal standard	-
*Unknown	12.269	N/A	42
Perylene-d12	14.404	Internal standard	-
Dibenzylbutyrolactone	16.233	34444-37-6	169

*These compounds did not match the any of the NIST library compounds with a minimum confidence of 80 %.

Table A-3: Semi-volatile organic screening results (Effluent B from Mill Y)

Compounds	Retention time (min)	CAS number	Estimated conc (ppb)
Furfural	3.528	98-01-1	<50
*Unknown	3.681	N/A	150
Butanoic acid, 2-methyl-	3.769	116-53-0	53
2-Fluorophenol	3.846	Surrogate	
*Unknown	4.063	N/A	220
Phenol-d6	4.593	Surrogate	
Phenol	4.604	108-95-2	190
1,4-Dichlorobenzene-d4	4.887	Internal standard	
2-Methylphenol	5.122	95-48-7	170
3/4-Methylphenol	5.281	106-44-5	2500
Nitrobenzene-d5	5.381	Surrogate	
Benzoic acid	5.893	65-85-0	150
Naphthalene-d8	6.057	Internal standard	
Phenol, 2,6-dimethoxy-	6.940	91-10-1	390
2(3)-Furanone, dihydro-5-pentyl-	7.016	104-61-0	99
2-Fluorobipheny	7.092	Surrogate	
1,4-Diisobutyl-1,4-dimethylbutynediol	7.228	126-86-3	130
*Unknown	7.440	N/A	<50
Ethanone, 1-(4-hydroxy-3-methoxy…	7.698	498-02-2	250
Acenaphthene-d10	7.763	Internal standard	
Homovanillyl alcohol	7.892	2380-78-1	100
Phenol,3,4,5-trimethoxy-	8.239	642-71-7	<50
2,4,6-Tribromophenol	8.545	Surrogate	
Ethanone, 1-(4-hydroxy-3,5-dimet…	8.863	2478-38-8	350
Phenanthrene-d10	9.228	Internal standard	
Phthalic acid, butyl isohexyl ester	9.398	1000309-03-6	<50
Di-n-butyl phthlate	9.792	84-74-2	90
13-octadecenal'(Z)	9.939	58594-45-9	<50
P-Terphenyl-d14	10.804	Surrogate	
Chrysene-d12	12.039	Internal standard	
Perylene-d12	14.363	Internal standard	

*These compounds did not match the any of the NIST library compounds with a minimum confidence of 80 %.

Table A-4: Semi-volatile organic screening results (Effluent C from Mill Y)

Compounds	Retention time (min)	CAS number	Estimated conc (ppb)
Butanoic acid	3.457	107-92-6	1000
*Unknown	3.687	N/A	250
Butanoic acid, 2-methyl-	3.775	116-53-0	56
2-Fluorophenol	3.846	Surrogate	
*Unknown	3.940	N/A	56
*Unknown	4.075	N/A	300
Phenol-d6	4.587	Surrogate	
Phenol	4.599	108-95-2	490
1,4-Dichlorobenzene-d4	4.887	Internal standard	
2-Methylphenol	5.122	95-48-7	430
3/4-Methylphenol	5.298	106-44-5	5300
Nitrobenzene-d5	5.387	Surrogate	
Naphthalene-d8	6.057	Internal standard	
1,2-Benzenediol, 3-methoxy-	6.463	934-00-9	68
Phenol, 2,6-dimethoxy-	6.957	91-10-1	1300
2-Fluorobipheny	7.093	Surrogate	
1,4-Diisobutyl-1,4-dimethylbutynediol	7.228	126-86-3	170
*Unknown	7.440	N/A	95
Ethanone,1-(4-hydroxy-3-methoxy…	7.698	498-02-2	360
Acenaphthene-d10	7.763	Internal standard	
Homovanillyl alcohol	7.892	2380-78-1	140
Phenol,3,4,5-trimethoxy-	8.245	642-71-7	180
2,4,6-Tribromophenol	8.545	Surrogate	
Ethanone,1-(4-hydroxy-3,5-dimet…	8.863	2478-38-8	740
Phenanthrene-d10	9.228	Internal standard	
Di-n-butyl phthlate	9.792	84-74-2	85
Cis-13-Octadecenoic acid	10.486	13126-39-1	200
P-Terphenyl-d14	10.798	Surrogate	
Chrysene-d12	12.039	Internal standard	
Perylene-d12	14.363	Internal standard	

*These compounds did not match the any of the NIST library compounds with a minimum confidence of 80 %

Appendix A.3. MBBR experimental data

Table A-5: Moving bed biofilm reactor (MBBR) experimental data for Effluent A (RME)

Hydraulic residence time HRT,(hour)	**Volumetric flowrate Q, (L/day)**	**Reactor Volume V_r, (L)**	**COD initial, (mg/L)**	**COD effluent, (mg/L)**	**COD removal (%)**
24.00	10.00	10.00	1.89	0.85	55.07
24.00	10.00	10.00	1.89	0.81	57.19
24.00	10.00	10.00	1.89	0.87	54.02
16.00	15.00	10.00	1.89	0.96	49.26
16.00	15.00	10.00	1.89	0.97	48.68
16.00	15.00	10.00	1.89	0.98	48.47
5.00	48.00	10.00	1.89	1.07	43.45
5.00	48.00	10.00	1.89	1.10	41.86
5.00	48.00	10.00	1.89	1.05	44.45

Table A-6: Moving bed biofilm reactor (MBBR) experimental data for Effluent B (NSSC)

Hydraulic residence time HRT,(hour)	**Volumetric flowrate Q, (L/day)**	**Reactor Volume V_r, (L)**	**COD initial, (mg/L)**	**COD effluent, (mg/L)**	**COD removal (%)**
23.26	10.32	10.00	2.47	1.01	59.23
23.26	10.32	10.00	2.47	1.05	57.47
21.19	11.33	10.00	4.85	2.32	52.27
16.13	14.88	10.00	4.85	2.29	52.80

16.13	14.88	10.00	4.85	2.59	46.60
16.13	14.88	10.00	4.85	2.67	44.87
5.00	48.00	10.00	4.85	3.50	27.92
5.00	48.00	10.00	4.85	3.65	24.74
5.00	48.00	10.00	4.85	3.51	27.63

Table A-7: Moving bed biofilm reactor (MBBR) experimental data for Effluent C (NSSC)

Hydraulic residence time HRT,(hour)	**Volumetric flowrate Q, (L/day)**	**Reactor Volume V_r, (L)**	**COD initial, (mg/L)**	**COD effluent, (mg/L)**	**COD removal (%)**
45.00	5.33	10.00	6.81	4.45	34.65
45.00	5.33	10.00	6.81	4.50	33.92
45.00	5.33	10.00	6.81	4.52	33.63
21.00	11.43	10.00	7.48	5.48	26.74
21.00	11.43	10.00	7.48	5.55	25.80
21.00	11.43	10.00	7.48	5.42	27.54
16.00	15.00	10.00	7.48	5.90	21.12
16.00	15.00	10.00	7.48	5.80	22.46
16.00	15.00	10.00	7.48	5.75	23.13

Table A-8: Moving bed biofilm reactor (MBBR) experimental data for Effluent D (NSSC)

Hydraulic residence time HRT,(hour)	**Volumetric flowrate Q, (L/day)**	**Reactor Volume V_r, (L)**	**COD initial, (mg/L)**	**COD effluent, (mg/L)**	**COD removal (%)**

24.00	10.00	10.00	6.09	4.10	32.71
24.00	10.00	10.00	6.09	4.15	31.89
24.00	10.00	10.00	6.09	4.09	32.87
16.00	15.00	10.00	6.09	4.43	27.29
16.00	15.00	10.00	6.09	4.30	29.43
16.00	15.00	10.00	6.09	4.35	28.61
5.00	48.00	10.00	6.09	5.30	13.01
5.00	48.00	10.00	6.09	5.26	13.67
5.00	48.00	10.00	6.09	5.34	12.36

Appendix A.4. Biodegradable COD fraction derivation

The derivation of the biodegradable COD fraction as a function of kinetic constants is given below. The equation below is the Kincannon-Stover model used in literature (Esmaeilirad et al. 2015; Babaei et al. 2013):

$$\frac{Q}{V}(C_o - C_F) = U_{max} \cdot \frac{\left(\frac{Q.C_o}{V}\right)}{K_B + \frac{Q.C_o}{V}} \qquad \text{A-2}$$

If V/Q =HRT then Eq. (1) can be modified to give the following equation:

$$\frac{(C_o - C_F)}{HRT} = U_{max} \cdot \frac{\left(\frac{C_o}{HRT}\right)}{K_B + \frac{C_o}{HRT}} \qquad \text{A-3}$$

Then the concentration of COD removed (C_o-C_F) can be given as:

$$(C_o - C_F) = U_{max} \cdot \frac{C_o}{K_B + \frac{C_o}{HRT}} \qquad \text{A-4}$$

The fraction of COD removed can then be given by:

$$\frac{C_o - C_F}{C_o} = \frac{U_{max}}{K_B + \frac{C_o}{HRT}} \qquad \text{A-5}$$

A maximum amount of COD will be removed in the reactor due to biodegradation at a maximum hydraulic residence time of ∞.

$$Biodegradable\ COD\ fraction = \lim_{HRT \to \infty} \frac{C_o - C_F}{C_o} = \lim_{HRT \to \infty} \frac{U_{max}}{K_B + \frac{C_o}{HRT}} = \frac{U_{max}}{K_B} \qquad \text{A-6}$$

Appendix B Fenton experimental data

Appendix B.1. Preliminary Fenton and Fenton-like experiments

A preliminary experiment primarily conducted to show the applicability of the Fenton and Fenton-like oxidation techniques for biologically treated mill effluent (BTME) treatment. The Fenton and Fenton-like experiments was conducted on the bio-treated recycle mill effluent (Mill X). The hydrogen peroxide (H_2O_2) and catalyst dosages ($FeSO_4.7H_2O$ and $Fe_2(SO_4)_3.xH_2O$) was 900 mg/L and 1000 mg/L respectively. A Iron test kit (Merck) was used to test for the amount of iron in the catalysts ($FeSO_4.7H_2O$ and $Fe_2(SO_4)_3.xH_2O$). The amount of Fe^{2+} and Fe^{3+} used in the experiments were 212 mg/L and 217.67 mg/L, respectively. The initial pH value was 3.5 for both experimental runs. The change of COD concentration (C_{COD}/C_{CODo}) over a 60 minute reaction period is presented in Figure B-8-2. The maximum COD removal for the Fenton and Fenton-like treatment systems after the 60 minute reaction period was 50.87% and 72.32% respectively. It is evident that the Fenton process (Fe^{2+}/H_2O_2) is more efficient than Fenton-like process (Fe^{3+}/H_2O_2) for the removal of bio-recalcitrant organics. According to Bautista et al. (2014), the rate of the reactions for the Fenton (Fe^{2+}/H_2O_2) and Fenton-like processes (Fe^{3+}/H_2O_2) are given by Equation 8-2 and 8-3, respectively.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^* + OH^- \qquad k = 76\, L.mol^{-1}.s^{-1} \tag{8-2}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^* + H^+ \qquad k = 0.01\, L.mol^{-1}.s^{-1} \tag{8-3}$$

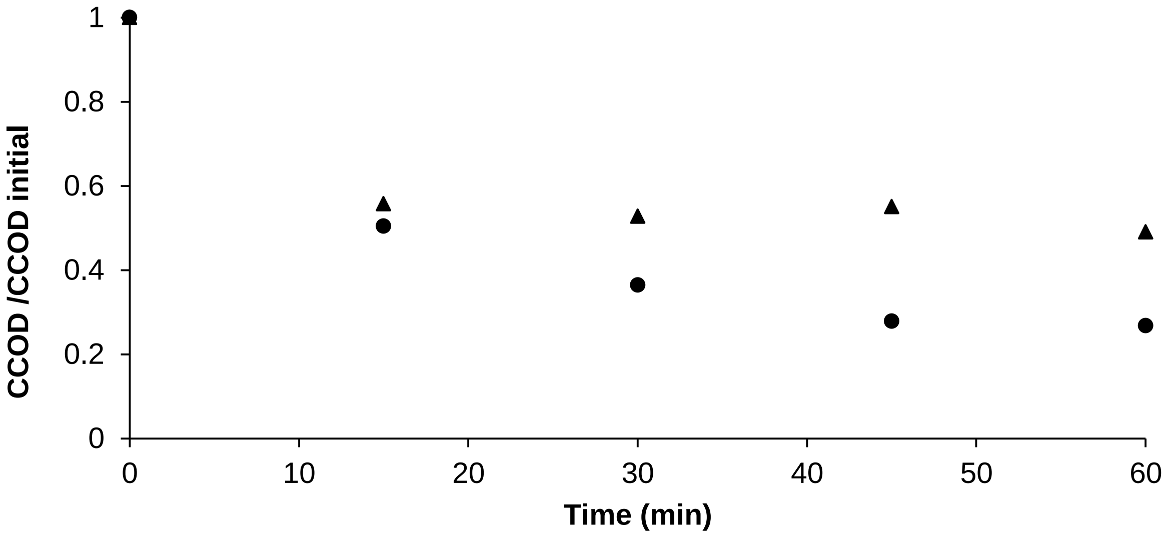

Figure B-8-2: The removal of bio recalcitrant COD using Fenton (●) and Fenton-like (▲) treatment systems (pH=3.5; H_2O_2 =900 mg/L; $FeSO_4.7H_2O$ and $Fe_2(SO_4)_3.xH_2O$ =1000 mg/L)

The oxidizing potential (EV) of the hydroxyl radicals (OH*) (EV = 2.80 V) are higher than that of the perhydroxyls (HO_2^*) (EV = 1.70 V). Based upon the first order rate constants (*k*) and oxidizing potentials (EV) it is expected that the rate of organic removal of the Fenton process will surpass that of the Fenton-like process. This preliminary experiment also demonstrated that this difference in degradation rates is prominent. As a result, the primary focus of this dissertation will mainly be on the Fenton oxidation of BTMEs. However, additional Fenton-like experiments were also done in Chapter 6 for comparison purposes in the economic assessment (Chapter 7).

Appendix B.2. Lignin calibration curve

Table B-1: Lignin (Kraft = Water soluble lignin) calibration curve data

Lignin concentrations (g/L)	Absorbance (267 nm)
1.27	0.083
0.64	0.060
0.42	0.051
1.95	0.113

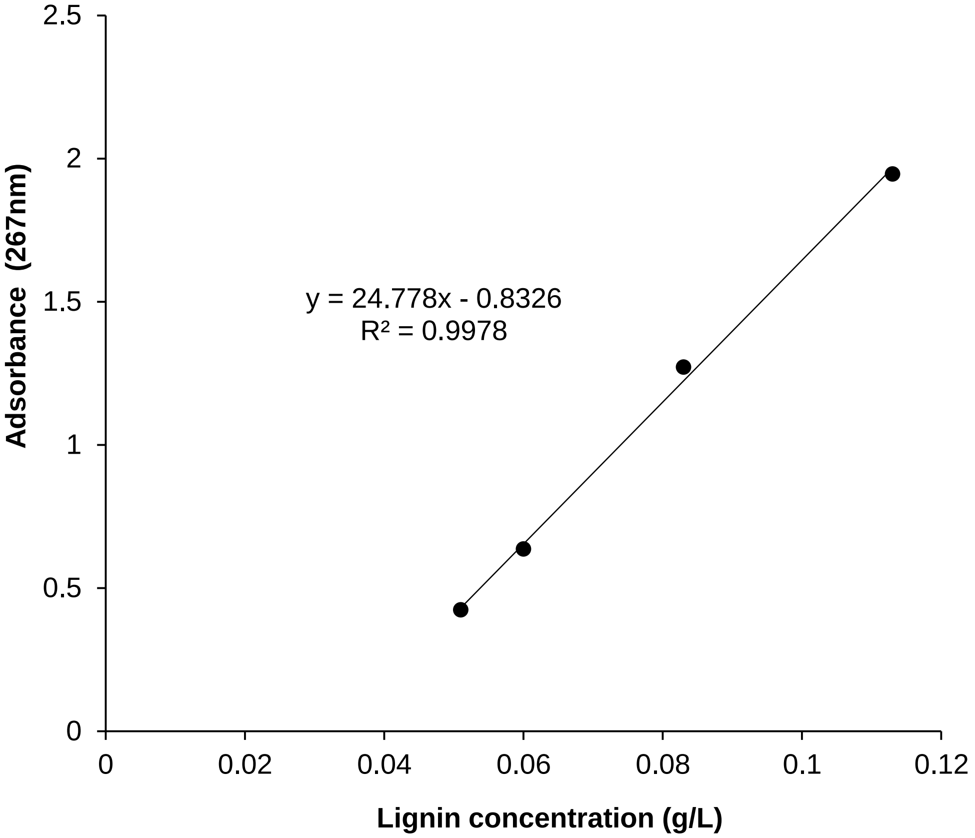

Figure B-8-3: Lignin calibration curve at 267 nm

Appendix B.3. Fenton oxidation results of bio-treated NSSC effluent (Mill Y)

Table B-2: Fenton oxidation of the biologically treated NSSC effluent ($FeSO_4$ =500 mg/L; H_2O_2 = 6300 mg/L)

Time (min)	COD (mg/L)	COD/COD_o	COD removal (%)
0	3756	1,00	0,00
15	3048	0,81	18,85
30	2994	0,80	20,29
45	2899	0,77	22,82
60	2834	0,75	24,55
240	2580	0,69	31,31

Table B-3: Fenton oxidation of the biologically treated NSSC effluent ($FeSO_4$ =1000 mg/L; H_2O_2 = 6300 mg/L)

Time (min)	COD (mg/L)	COD/COD_o	COD removal (%)
0	3950	1,00	0,00
15	3300	0,84	16,46
30	3083	0,78	21,95
45	2909	0,74	26,35
60	2475	0,63	37,34
240	2559	0,65	35,22

Table B-4: Fenton oxidation of the biologically treated NSSC effluent ($FeSO_4$ =500 mg/L; H_2O_2 = 3150 mg/L)

Time (min)	COD (mg/L)	COD/COD_o	COD removal (%)
0	3756	1,00	0,00
15	3252	0,87	13,42
30	2968	0,79	20,98
45	2934	0,78	21,88
60	2851	0,76	24,09
240	2254	0,60	39,99

Table B-5: Fenton oxidation of the biologically treated NSSC effluent ($FeSO_4$ =1000 mg/L; H_2O_2 = 3150 mg/L)

Time (min)	COD (mg/L)	COD/COD_o	COD removal (%)
0	3756	1,00	0,00
15	2929	0,78	22,02
30	2585	0,69	31,18
45	2321	0,62	38,21
60	2261	0,60	39,80
240	2089	0,56	44,38

Table B-6: Fenton oxidation of the biologically treated NSSC effluent ($FeSO_4$ = 50 mg/L; H_2O_2 = 3150 mg/L)

Time (min)	COD (mg/L)	COD/COD_o	COD removal (%)
0	3950	1,00	0,00

15	3471	0,88	12,13
30	3372	0,85	14,63
45	3527	0,89	10,71
60	3352	0,85	15,14
240	3463	0,88	12,33

Table B-7: Fenton oxidation of the biologically treated NSSC effluent ($FeSO_4$ = 50 mg/L; H_2O_2 = 6300 mg/L)

Time (min)	COD (mg/L)	COD/COD_o	COD removal (%)
0	3950	1	0
15	3416	0.86	13.20
30	3402	0.86	13.87
45	3337	0.84	15.51
60	3263	0.83	17.40
240	3371	0.85	14.67

Table B-8: Fenton oxidation of the biologically treated NSSC effluent ($FeSO_4$ = 1000 mg/L; H_2O_2 = 450 mg/L)

Time (min)	COD (mg/L)	COD/COD_o	COD removal (%)
0	3755	1	0
15	3432	0.91	8.62
30	3272	0.87	12.87
45	3332	0.89	11.28

60	3312	0.88	11.81
240	3259	0.87	13.23

Table B-9: Fenton oxidation of the biologically treated NSSC effluent ($FeSO_4$ = 500 mg/L; H_2O_2 = 450 mg/L)

Time (min)	COD (mg/L)	COD/COD_o	COD removal (%)
0	3755	1	0
15	3427	0.91	8.76
30	3467	0.92	7.70
45	3387	0.90	9.82
60	3387	0.90	9.82
240	3328	0.89	11.39

Table B-10: Fenton oxidation of the biologically treated NSSC effluent ($FeSO_4$ = 50 mg/L; H_2O_2 = 450 mg/L)

Time (min)	COD (mg/L)	COD/COD_o	COD removal (%)
0	3950	1	0
15	3691	0.93	6.55
30	3456	0.87	12.51
45	3461	0.88	12.38
60	3521	0.89	10.86
240	3505	0.88	11.26

Appendix B.4. Fenton oxidation of bio-treated RME effluent (Mill X)

Table B-11: Fenton oxidation of the biologically treated RME effluent ($FeSO_4$ = 500 mg/L; H_2O_2 = 6300 mg/L)

Time (min)	**COD (mg/L)**	**COD/COD$_o$**	**COD removal (%)**
0	436.30	1	0
15	344.93	0.79	21
30	280.13	0.64	36
45	243.59	0.56	44
60	241.92	0.55	45

Table B-12: Fenton oxidation of the biologically treated RME effluent ($FeSO_4$ = 1000 mg/L; H_2O_2 = 450 mg/L)

Time (min)	**COD (mg/L)**	**COD/COD$_o$**	**COD removal (%)**
0	436.29	1	0
15	175.47	0.40	60
30	143.91	0.33	67
45	137.26	0.31	69
60	132.27	0.30	70

Table B-13: Fenton oxidation of the biologically treated RME effluent ($FeSO_4$ = 500 mg/L; H_2O_2 = 450 mg/L)

Time (min)	**COD (mg/L)**	**COD/COD$_o$**	**COD removal (%)**
0	436.29	1	0

15	220.32	0.50	50
30	182.12	0.42	58
45	178.80	0.41	59
60	148.89	0.34	66

Table B-14: Fenton oxidation of the biologically treated RME effluent ($FeSO_4$ = 50 mg/L; H_2O_2 = 450 mg/L)

Time (min)	**COD (mg/L)**	**COD/COD$_o$**	**COD removal (%)**
0	436.29	1	0
15	341.60	0.78	22
30	326.65	0.75	25
45	324.99	0.74	26
60	323.33	0.74	26

Table B-15: Fenton oxidation of the biologically treated RME effluent **(**$FeSO_4$ = 50 mg/L; H_2O_2 = 6300 mg/L**)**

Time (min)	**COD (mg/L)**	**COD/COD$_o$**	**COD removal (%)**
0	436.29	1	0
15	354.89	0.81	19
30	339.94	0.78	22
45	334.96	0.77	23
60	328.31	0.75	25

Table B-16: Fenton oxidation of the biologically treated RME effluent ($FeSO_4$ = 1000 mg/L; H_2O_2 = 6300 mg/L)

Time (min)	**COD (mg/L)**	**COD/COD$_o$**	**COD removal (%)**
0	436.29	1	0
15	353.23	0.81	19
30	323.33	0.74	26
45	276.81	0.63	37
60	248.57	0.57	43

Table B-17: Fenton oxidation of the biologically treated RME effluent ($FeSO_4$ = 1000 mg/L; H_2O_2 = 3150 mg/L)

Time (min)	**COD (mg/L)**	**COD/COD$_o$**	**COD removal (%)**
0	436.29	1	0
15	301.73	0.69	31
30	286.78	0.66	34
45	261.86	0.60	40
60	246.91	0.57	43

Table B-18: Fenton oxidation of the biologically treated RME effluent ($FeSO_4$ = 500 mg/L; H_2O_2 = 3150 mg/L)

Time (min)	**COD (mg/L)**	**COD/COD$_o$**	**COD removal (%)**
0	436.29	1	0
15	261.86	0.60	40

30	225.31	0.52	48
45	215.34	0.49	51
60	213.68	0.49	51

Table B-19: Fenton oxidation of the biologically treated RME effluent ($FeSO_4$ = 50 mg/L; H_2O_2 = 3150 mg/L**)**

Time (min)	**COD (mg/L)**	**COD/COD$_o$**	**COD removal (%)**
0	436.29	1	0
15	326.65	0.75	25
30	324.99	0.75	25
45	295.09	0.68	32
60	280.13	0.64	36

Appendix B.5. TSF model derivation

The analytical solution of the Eq. 5-19 was determined using integrating factors (Kreyszig 2010).

$$\frac{\partial}{\partial C_B}(FP) = \frac{\partial}{\partial t}(FQ) \tag{B-1}$$

$$Q = k_{app,10}.C_{AO}.\exp(-k_{app,10}.t) - k_{app,11}.C_B \tag{B-2}$$

$$P = 1 \tag{B-3}$$

$$F^*(C_B) = exp \int R^*(C_B)\, dC_B \tag{B-4}$$

$$R^* = \frac{1}{P}\left(\frac{\partial Q}{\partial t} - \frac{\partial P}{\partial C_B}\right) \tag{B-5}$$

$$\frac{\partial Q}{\partial C_B} = k_{11} \tag{B-6}$$

$$\frac{\partial P}{\partial t} = 0 \tag{B-7}$$

$$R^* = k_{11} \tag{B-8}$$

$$F^*(C_B) = e^{k_{11}.t} \tag{B-9}$$

$$(1)dC_B + \left(k_2 C_B - k_1 C_{AO} e^{-k1*t}\right)dt = 0 \tag{B-10}$$

$$e^{k_1.t}dC_B - \left(k_2.C_B.e^{k_2.t} - k_1.C_{AO}.e^{-k_1.t}.e^{k_2.t}\right)dt \tag{B-11}$$

$$u = \int e^{k_2.t}dC_B = e^{k_2.t}.C_B + z(y) \tag{B-12}$$

$$\frac{du}{dt} = k_2.C_B.e^{k_2.t} + \frac{dz}{dt} = k_2.C_B.e^{k_2.t} - k_1.C_{AO}.e^{-k_1.t}.e^{k_2.t} \tag{B-13}$$

$$\frac{dz}{dt} = -k_1.C_{AO}.e^{-k_1.t}.e^{k_2.t} = -k_1.C_{AO}.e^{(k_2-k_1).t} \tag{B-14}$$

$$z = -(k_1.C_{AO}.e^{(k_2-k_1).t})/(k_2 - k_1) + W* \tag{B-15}$$

$$u(t, C_B) = e^{k_2.t}.C_B - \frac{k_1.C_{AO}.e^{t.(k_2-k_1)}}{k_2 - k_1} = W \tag{B-16}$$

$$W = C_{BO} - \frac{k_1.C_{AO}}{k_2 - k_1} \tag{B-17}$$

$$e^{k_2.t}.C_B - \frac{k_1.C_{AO}.e^{t.(k_2-k_1)}}{k_2 - k_1} = C_{BO} - \frac{k_1.C_{AO}}{k_2 - k_1} \tag{B-18}$$

$$C_B = \left(\frac{1}{e^{k_2.t}}\right)\left[C_{BO} + \frac{k_1.C_{AO}.e^{t.(k_2-k_1)}}{k_2 - k_1} - \frac{k_1.C_{AO}}{k_2 - k_1}\right] \tag{B-19}$$

*Kreyszig, E., 2010. *Advanced engineering mathematics*, John Wiley & Sons.

Appendix C Fenton-like experimental data

Table C-1: The effect of H_2O_2 dosage on the COD removal in the Fenton like oxidation of BTME (Bio-treated Mill Effluent A) (Reaction time = 30 min; $Fe_2(SO_4)_3$ = 250 mg/L; pH = 3.3)

H_2O_2 (mg/L)	**COD removal efficiency (%)**
224.74	52.71
528.7	55.97
899.98	50.54
1799.96	51.08
2686	51.08

Table C-2: The effect of pH on the COD removal in the Fenton like oxidation of BTME (Bio-treated Mill Effluent A) (Reaction time = 30 min; $Fe_2(SO_4)_3$ = 250 mg/L; H_2O_2 = 2686 mg/L)

pH	**COD removal efficiency (%)**
2.5	45.45
3.09	50.80
3.33	51.87
4.18	51.82
5.2	45.45
5.65	39.57
6.93	21.92

Table C-3: The effect of $Fe_2(SO_4)_3$ on the COD removal in the Fenton like oxidation of BTME (Bio-treated Mill Effluent A) (Reaction time = 30 min; H_2O_2 =2686 mg/L; pH = 3.3)

$Fe_2(SO_4)_3$ (mg/L)	COD removal efficiency (%)
64	17.12
128	20.99
180	30.94
250	50.27
756	58.56
1000	59.11

Appendix D Ozone experimental data

Table D-1: Ozone data obtained from the ozonation of biologically treated mill effluent A (6 gO_3/L.hr at pH=8.5)

Time (min)	**COD/COD_{intial}**	**Adsorbance/Adsorbance initial (456 nm)**
0	1.00	1.00
20	0.86	0.39
35	0.81	0.26
50	0.66	0.26
65	0.64	0.25
80	0.58	0.26
95	0.47	0.25

* First order kinetic constant **k=0.007531 $\mathbf{min^{-1}}$ (COD).**

Appendix E Water network research at Mill X

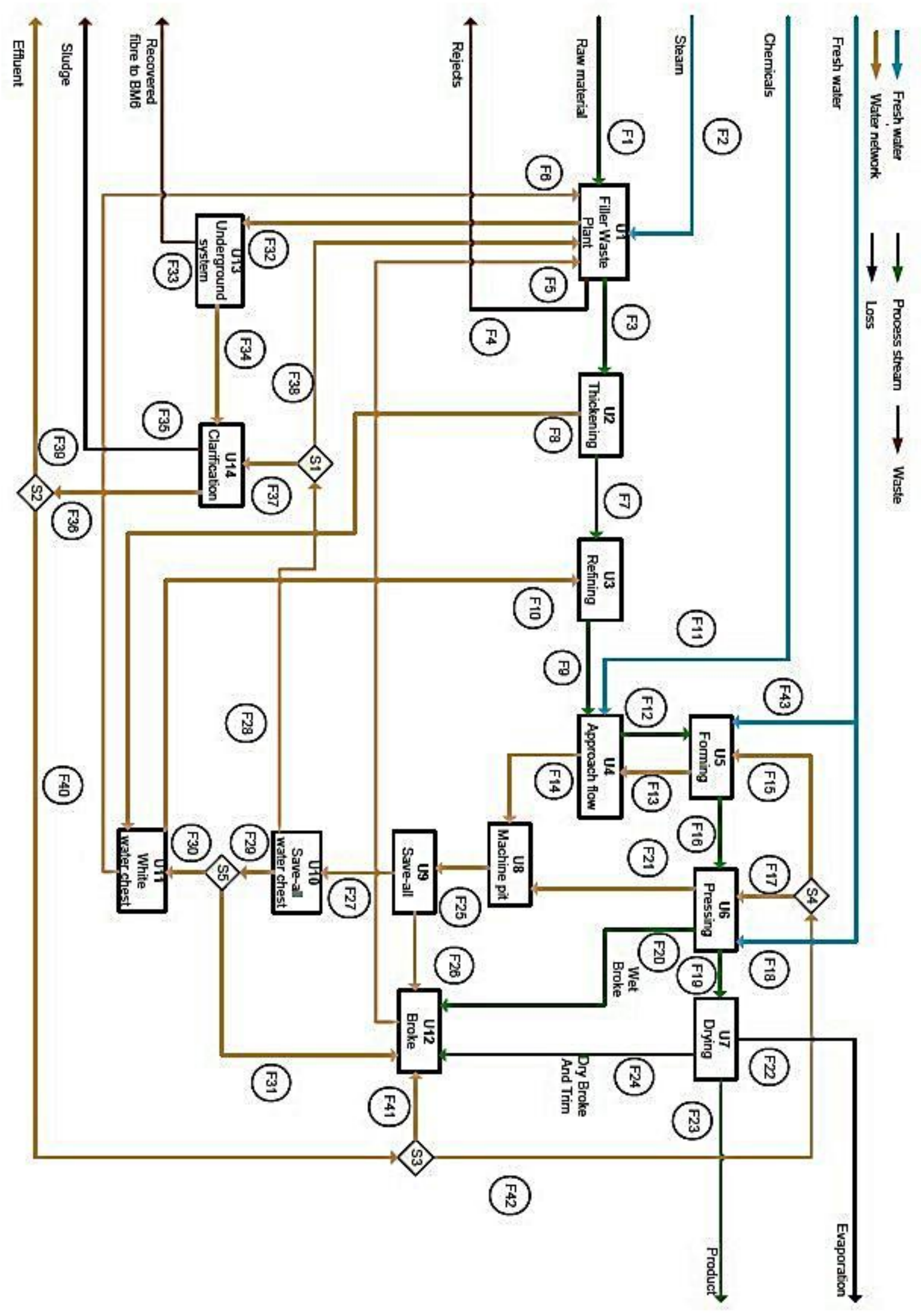

Figure 8-4: Process flow diagram of Board mill 3 (BM3) (Vurdiah 2015)

Table E-1: Results from previous water network optimization work done at Mill X (Vurdiah 2015)

Total Flow*			**Composition**			
TSS			**COD**			
Stream Name	**Stream Number**	**tons/day**	**weight fraction [g TSS / g Stream]**		**weight fraction [g COD / g Stream]**	
Raw material	F1	106	x1	0.88	y1	2.95E-02
Steam	F2	50	x2	0	y 2	0
Cleaned stock	F3	12 670	x3	9.00E-03	y 3	1.47E-03
Rejects	F4	16	x4	0.2	y 4	1.47E-03
Broke	F5	3 298	x5	8.23E-03	y 5	1.42E-03
Dilution	F6	10 889	x6	1.03E-03	y 6	1.46E-03
Thick stock	F7	2 444	x7	0.042	y 7	1.47E-03
Thickener water	F8	10 226	x8	1.12E-03	y 8	1.47E-03
Refined stock	F9	2 947	x9	0.035	y 9	1.47E-03
Dilution	F10	504	x10	1.03E-03	y 10	1.46E-03
Chemicals	F11	202	x11	0	y 11	5.97E-02
Board Machine feed	F12	14 270	x12	9.00E-03	y 12	1.52E-03
Forming return water	F13	14 452	x13	2.67E-03	y 13	1.49E-03
Surplus water	F14	3 331	x14	4.00E-03	y 14	1.52E-03
Low pressure shower	F15	533	x15	1.50E-04	y 15	1.43E-03
Formed fibre mat	F16	599	x16	1.50E-01	y 16	1.52E-03
Low pressure shower	F17	646	x17	1.50E-04	y 17	1.43E-03
High pressure shower	F18	369	x18	0	y 18	0
Pressed fibre mat	F19	158	x19	0.53	y 19	1.52E-03
Wet broke	F20	8.3	x20	0.53	y 20	1.52E-03
Pressing water	F21	1 448	x21	1.31E-03	y 21	1.09E-03
Evaporation	F22	68	x22	0	y 22	0
Product	F23	81	x23	0.93	y 23	1.79E-02
Dry broke and Trim	F24	9	x24	0.93	y 24	1.79E-02
Machine water	F25	4 779	x25	3.18E-03	y 25	1.39E-03

Recovered fibre	F26	114	x26	0.12	y 26	1.39E-03
Save-all water	F27	4 665	x27	3.26E-04	y 27	1.39E-03
Save-all water	F28	2 332	x28	3.26E-04	y 28	1.39E-03
Save-all water	F29	2 332	x29	3.26E-04	y 29	1.39E-03
Save-all water	F30	1 167	x30	3.26E-04	y 30	1.39E-03
Dilution	F31	1 167	x31	3.26E-04	y 31	1.39E-03
Drains and water purge	F32	1 989	x32	7.33E-03	y 32	1.47E-03
Recovered fibre	F33	416	x33	0.0315	y 33	1.47E-03
Underground water	F34	1 573	x34	9.27E-04	y 34	1.47E-03
Sludge	F35	4.5	x35	0.35	y 35	1.43E-03
Clarifier overflow	F36	3 568	x36	1.50E-04	y 36	1.43E-03
Clarifier feed	F37	2 000	x37	3.26E-04	y 37	1.39E-03
Dilution	F38	332	x38	3.26E-04	y 38	1.39E-03
Effluent	F39	389	x39	1.50E-04	y 39	1.43E-03
Return water	F40	3 179	x40	1.50E-04	y 40	1.43E-03
Dilution	F41	2 000	x41	1.50E-04	y 41	1.43E-03
Shower water	F42	1 179	x42	1.50E-04	y 42	1.43E-03
High pressure shower	F43	248	x43	0	y 43	0

* Vurdiah, L., 2015. Application of water network optimization at Mpact Ltd, Springs mill. (March)

Appendix F Experimental error calculations

The error calculations on COD measurements were estimated using the following equation:

$$95\%\ confidence\ level = 1.96\left(\frac{\sigma}{\sqrt{n}}\right) \quad \text{F-1}$$

where the standard deviation can be calculated as follows:

$$\sigma = \sqrt{\frac{\sum(x - x_{mean})^2}{n-1}} \quad \text{F-2}$$

The experimental % error was calculated as follows:

$$Error\ (\%) = \frac{(2 \times Confidence\ Level)}{x_{mean}} \times 100 \quad \text{F-3}$$

Table F-1: Experimental error calculations

Sample 1 measurement	**Sample 2 measurement**	x_{mean}	σ	**Confidence Level**	**Error (%)**
7163.10	7153.13	14.10	19.54	39.07	0.55
5917.12	5867.28	70.48	97.68	195.37	3.33
5249.28	5209.41	56.39	78.15	156.30	3.00
4043.18	4102.98	84.58	117.22	234.44	5.71
				Average error (%)	3.14

Appendix G Environmental legislation

The environmental legislation for irrigation with industrial effluents are shown in the Table below. The water quality parameters differ based upon the irrigation area (National water act 36 of 1998- Regulations and Notices- Government notice R665).

Table G-1: Environmental legislation on irrigation limit with industrial effluents in South Africa

Parameters	**Irrigation area (m^2)**		
	2000 m^2	**500 m^2**	**50 m^2**
pH	$5.5 < pH < 9.5$	$5.5 < pH < 9$	$6 < pH < 9$
EC	<70 mS/m	<200 mS/m	<200 mS/m
COD	<75 mg/L	<400 mg/L	<5000 mg/L

Appendix H Material mass Balance results (Mill X)

The primary goal of the mass balance on BM3 was to estimate the required performance of the wastewater treatment plant (WWTP) to achieve complete water network closure. An internal COD limit of approximately 2000 mg/L (≈2190 mg/L according to mass balance) was the imposed limits. The previous mass balance data (Table E-1)**Table E-** obtained from Vurdiah (2015) was used in the calculations.

In the calculations, the sum of the total influent contaminants ($\sum F.x_{COD}$) (TSS, COD, water, total flow) was taken as a constant. Using the previous data (Table E-1) for a semi-closed circuit, the relative distribution (fractions y_i) of contaminants in the exiting/out streams were estimated. During water network closure the contaminants build-up, however it was assumed that the relative contaminant distribution (fraction y_i) for each stream would stay constant. As a result, the contaminant concentration for each exiting/out streams could be calculated. In this iterative mass balance calculations, the desired effluent COD concentrations for the WWTP could be specified in order to comply with the internal COD limits.

$$y_1(Out) = \frac{x_1.F_1}{x_1.F_1 + x_2.F_2 \ldots \ldots .} \tag{H-1}$$

$$\sum F.x(in) = \sum F.x_{in}(out) = y_1.\left(\sum F.x(in)\right) + y_2.\left(\sum F.x(in)\right) \ldots . \tag{H-2}$$

The mass balance calculation results obtained are presented in Table H-1 and the graphical illustration of the simplified BM3 is presented in Figure 8-5. The WWTP should be able to reduce the COD and TSS concentrations to 250 mg /L and 25 mg/L, respectively. The influent of the WWTP is estimated to be 395 m^3/day.

Table H-1: The stream results obtained from mass balance calculations for closed water network system (Effluent quality of WWTP: COD = 250 mg/L; TSS = 25 mg/L)

Stream number	Total flow (ton/day)	TSS concentration (mg/L)	COD concentration (mg/L)
F1	106	9723756.91	325966.85
F2	50	0	0
F4	16.24	246066.84	2814.94
F11	202	0	4716.07
F18	149.28	0	0

F22	69.23	0	0
F23	81.90	17537171.84	525360.97
F33	423.60	32002.58	2324.45
F35	4.56	530182.66	3371.48
F39	396.31	**147.60**	**2190**
F43	100.32	0	0
F49	385.75	15.32	153.23
F50	259.24	15.32	153.23

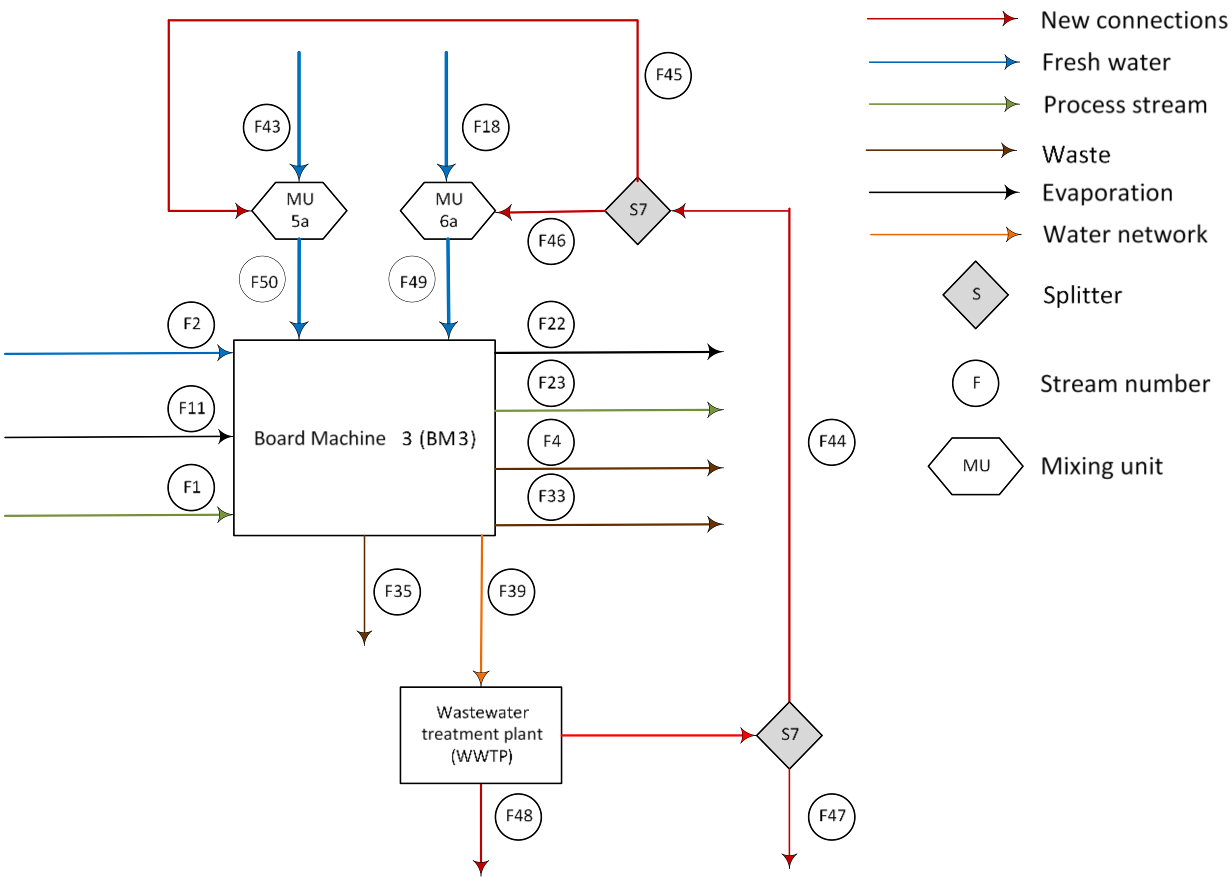

Figure 8-5: Simplified process flow diagram of Board Mill 3 (BM3)