IMPROVING WATER REUSE FOR A COMMERCIAL RECYCLED PAPER MILL

A thesis submitted in fulfilment of the requirements of the degree of Master of Engineering (Research)

By

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Abstract

The pulp and paper industry traditionally consumes high levels of water and energy and the reduction of fresh water use with emphasis on process water management and wastewater recycling are key factors for the growth of this industry.

The use of fresh water has reduced significantly during the last decades. The main reasons for this include increased environmental legislations relating to effluent discharge, and hefty costs arising from either the supply of fresh water or treatment of wastewater thus effecting the marketing potentials. Although using recovered paper as raw material has an advantage of saving energy, water and landfill space, attention needs to be paid to treating the wastewater due to discharge regulations and standards.

Wastewater sent to a treatment facility is regarded as waste. It is treated only with the purpose not to cause a negative impact to the environment. Although the level of impurities and toxic substances in treated wastewater satisfies the discharge standards, it often limits recycling potential because it adversely affects manufacturing processes and paper quality. Methods for removing these impurities and toxic substances include various physical and biological methods and the intended reuse of the water determines type and level of treatment required.

This study aims to explore the possibility of introducing advanced technologies such as enhanced coagulation and flocculation, and membrane separation to improve wastewater recycling in a commercial paper mill.

A commercial plant water circuit was first analysed and a water balance was proposed to reduce the water consumption from $10m^3$ to $6m^3$/tonne product.

The quality of treated wastewaters and associated parameters from commercial individual processes were analysed to forecast the plant influent flows and predict pollutants concentrations in wastewater.

Although organics in wastewater were mostly processed through biodegradation, non-biodegradable recalcitrant compounds limit its potential for reuse, thus a tertiary treatment is proposed.

Enhanced coagulation and flocculation yielded very promising results, especially for colour removal. The treatment was able to achieve the target colour value. The desirable COD output values were also achieved by varying coagulation/flocculant ratio.

For membrane separation, different units of operation and pollution parameters were examined. Results indicate that membrane technology produced higher colour removal efficiencies (96% for NF and 87% for UF) compared to enhanced coagulation and flocculation (61%). However, when it comes to removing COD, enhanced coagulation and flocculation was able to achieve a removal efficiency of 46% COD, compared to 43% for NF and 20% for UF. Amongst the three methods, UF, if used as a stand-alone method, failed to reduce the COD level to the target value. However, when feedwater was pre-treated with coagulant, UF was able to produce a similar COD removal rate to NF. Pre-treating feedwater also reduced fouling of membranes. Between the two membrane cleaning agents used, alkaline was shown to be more effective in reducing fouling. Backwashing was also investigated and found to be effective in prolonging membrane lifespan. However, despite the reduction in fouling, irreversible fouling still happened.

Although membrane technology performed better in the removal of colour, retrofitting a membrane system into an existing plant can be difficult, requires the implementation of appropriate pre-treatment technology to control fouling resulting in higher capital and operating costs compared to enhanced coagulation and flocculation.

Student Declaration

“I, Ngoc Bich Han, declare that the Master by Research thesis entitled “Improving water reuse for a commercial paper mill” is no more than 60,000 words in length including quotes and exclusive of tables, figures, appendices, bibliography, references and footnotes. This thesis contains no material that has been submitted previously, in whole or in part, for the award of any other academic degree or diploma. Except where otherwise indicated, this thesis is my own work”

“I have conducted my research in alignment with the Australian Code for the Responsible Conduct of Research and Victoria University’s Higher Degree by Research Policy and Procedures.”

Signature: [redacted] Date: 05/11/2021

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List of abbreviations

AS	Activated sludge
ACH	Aluminium chlorohydrate
AOX	Absorbable organic halides
BOD	Biological oxygen demand
BNR	Biological nutrient removal
COD	Chemical oxygen demand
DOC	Dissolved organic carbon
DAF	Dissolved air flotation
Poly-DADMAC	Polydiallyldimethylammonium chloride
DS	Dissolved solids
EDR	Electrodialysis
EGSB	Extended granular sludge bed
FTIR	Fourier transform infrared spectroscopy
GLSS	Gas–liquid–solid separation
HRT	Hydraulic retention times
HPLC	High performance liquid chromatography
IC	Internal circulation
ID	Inside diameter
IPS	Integrated purification system
LNF	Loose nanofiltration
LMW	Low molecular weight
MVR	Mechanical vapor recompression
MBR	Membrane bioreactor
NOM	Natural organic matter
NF	Nanofiltration
OTR	Oxygen transfer rate
OD	Outside diameter
PPE	Pulp and paper effluent
PSI	Polysilicato-iron
PES	Polyethersulphone
PVDF	Polyvinylidene fluoride
PAC	Polyaluminium chloride
PAM	Polyacrylamide
P&P	Pulp & paper
RO	Reverse osmosis
SS	Suspended solids
SBR	Sequencing batch reactor
SRT	Solid retention times
TMP	Trans-membrane pressure
TSS	Total suspended solids
UF	Ultrafiltration
UASB	Up-flow anaerobic sludge blanket
USSB	Up-flow staged sludge bed
VFA	Volatile fatty acid
ZLD	Zero liquid discharge

CHAPTER 1: INTRODUCTION

1.1. Background

Water plays several essential roles in paper manufacturing. It serves as a suspending medium and a swelling agent for the fibres, dispersing and forming them into a uniform sheet during the initial stage of the papermaking process. It also serves as the solvent for a variety of chemicals and additives to adjust product quality. Water reclamation has always been a momentous task in the pulp and paper (P&P) industry. The main driving forces for the adoption of process water and wastewater treatment technologies are environmental regulations, high costs of wastewater discharge and fresh water supply. Recent developments have made it possible to not only reduce water consumption and environmental impacts, but also to recover treated water and valuable compounds such as fibres, making water recycling technologies cost-efficient. Thus, the economic viability of these technologies has played an important role in their application. The technologies applied, the level of reduction in water consumption and the extent of water recycling are different for each mill, since the quality of whitewater and wastewater varies depending on the raw materials and products. The maintenance of a balance between partial equilibria of process variables such as water flowrates, pulp consistency, physiochemical, thermal and microbiological properties through water management is important for maintaining efficient water use and lowering the need for consumption of additional fresh water.

Global paper consumption in 2021 is expected to amount to more than 400 million tonnes with more than half of that production attributable to packaging paper (Tiseo, 2021). With the implementation of effluent regulations and internal water purifying processes, wastewater can either be discharged into the environment with permitted levels of pollutants, or be reused as process water. By recycling used water, fresh water consumption is reduced, lowering the cost for fresh water supply and wastewater treatment. On average, 5-80 m^3 of fresh water is needed for every tonne of paper manufactured, with the paper grade and the extent of water recycling being the influential factors (Olejnik, 2011)

In paper recycling, water with different qualities can be used for different processes. That creates opportunities for process water to be recycled back to the same process if it meets the influent requirements. In a modern mill there are two main water circuits that provide the opportunities for water recycling: short water loop and long water loop Hubbe et al. (2016). Figure 1.1 shows typical water circuits, which are made up of a short and long water loop, of a pulp and paper mill.

The short water loop, which is comprised of primary and secondary circuit, involved an internal treatment that allows instant whitewater recycling, the water that drains from a wet sheet of paper in the forming section, and fibre recovery (Blanco et al., 2015). Water used for paper machine can be recirculated back for the same process or pulp preparation through whitewater recycling.
When reusing process water, it is inevitable to experience build-up of suspended solids (SS), dissolved solids (DS) and increase temperature. While the increase in SS recovery can reduce the raw material losses and produce less sludge for wastewater, problems such as plugging of pipes and showers, dirt and spots in the final product, deposit formation, abrasion, fabric life reduction, tensile strength loss and possible modification of drainage capacity may arise. The accumulation of DS increases biological activity, colour, bad odour in the process and final product, the probability of scaling, deposit formation, corrosion, and lessens the stability in the wet-end. Heat rise due to process water reuse causes a reduction of the vacuum pump efficiency and increase and/or alteration of the microbiological activity.

Long water loop receives the excess water from the short loop and auxiliary waters. The tertiary circuit involving general treatment of wastewater is located on this loop. From this point, the recycling of water and short fibres into the manufacturing stage is organised depending on the quality of the paper produced. The wastewater treatment process generally includes a primary and a secondary process. A tertiary treatment is implemented when higher requirements for the effluent standards are required.

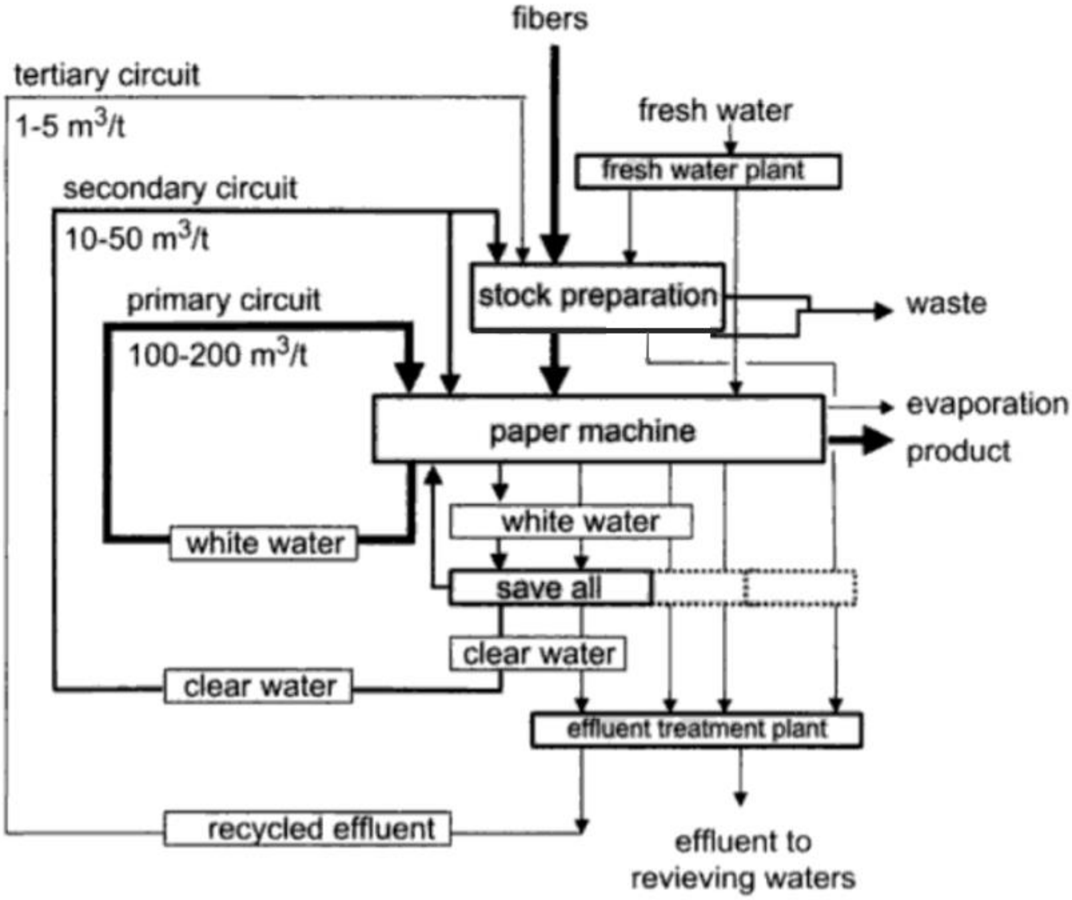

Figure 1.1. Simplified water system of a pulp and paper mill and its water recycling opportunities (Blanco et al., 2015).

By recirculating used water back to different parts of the pulp and paper making process, fresh water consumption is reduced, lowering the expense for fresh water supply and reducing the dependency on scarce environmental resources such as trees and water at the same time. Wastewaters in the recycled paper industry contain considerably less contaminants compared to the pulping process as recovered paper relies primarily on water with little chemical addition. Chemical substances found in wastewater from mills that use wood as a raw material include lignin, hemicellulose, cellulose, and wood extractives (Singh et al., 2019), all of which exist as residue from recovered materials in very small concentrations, which end up in recycled paper mill untreated effluents. As bleaching is not involved in the recycled paper making process, its wastewaters do not contain hazardous chemicals derived from lignin degradation such as formic acid, acetaldehyde, methanol, chlorophenols, dioxins, and furans. Despite having less contamination in the wastewater, recycled paper mill effluents still require treatment prior to disposal or recirculation to reduce contaminants (Fatta-Kassinos and Dionysiou, 2016). Therefore, a series of treatment technologies have been developed to address these problems. The design and structure of the treatment plant varies between mills depending on the quality of paper products, the type of raw materials utilised, the local discharge standards and the toxicity of the wastewater (Moo-young, 2007).

Primary and secondary treatments are part of a conventional wastewater treatment facility. Primary treatment is frequently used as a pre-treatment for subsequent treatment technologies, as its main purpose is to eliminate suspended solids. A coagulant and/or a flocculant coupled with sedimentation or dissolved air floatation (DAF) are often used in this stage to improve separation. Secondary treatment is a biological (anaerobic-aerobic or aerobic) treatment that removes excess colloidal particles, dissolved organic matter, and nitrogen, lowering COD, BOD, and colour (Englande et al., 2015). The rising demands in discharge quality require the implementation of tertiary treatment as a polishing step to achieve treated effluent that meets discharge requirements and is also appropriate for reuse. Some common techniques used in the recycled paper industry for the tertiary treatment are activated carbon, enhanced coagulation and flocculation, and membrane technology.
Besides wastewater treatment, these technologies also aid in water reclamation, reducing fresh water consumption thus liquid discharge. However, a reduction in liquid discharge as well as the need for fresh water, without proper water treatment and consideration, could cause detrimental effects to the plant's efficiency and the final products. The degree of contaminant reduction depends on the plant daily production rate, frequency of grade change, and especially the grade of paper product produced.

Victoria University and An Binh Paper Corporation Research Centre have identified an opportunity to reduce the water consumption rate for Khoi Nguyen paper mill, a new plant with a total liquid discharge of 4,000m^3/day, leading to financial support of this project.

1.2. Objectives

The aim of this dissertation is to evaluate the performance of individual processes for a commercial wastewater treatment plant and identify appropriate technologies for the tertiary treatment, enabling further water reuse and attainment of the wastewater discharge requirements, taking contaminants removal efficiency, retrofitting and financial feasibility into consideration.

Pulp and paper wastewaters vary in characteristics and contain different contaminant loads depending on the pulping and papermaking process. For commercial paper mills that utilise recovered materials, the wastewater is characteristically high in colour due to the presence of dyes and inks in raw materials and addition of colouring agents during the production process. Therefore, discharged wastewater is required to meet the local discharge regulations, whereas recycled wastewater, if any, is expected to achieve industrially quality requirements such as hardness, corrosion and scaling ability.

This project was carried out at An Binh Paper and Khoi Nguyen Paper commercial recycling paper mills in Vietnam. The An Binh mill currently consumes approximately 10 m^3 of water for every tonne of product. Due to the similarity of the manufacturing process, Khoi Nguyen's wastewater treatment plant is based on the design of An Binh wastewater treatment plant with some improved features.

The study looks at various method of wastewater treatments, including enhanced coagulation and flocculation, and membrane technologies for tertiary treatment that enable water recycling in a commercial paper plant. Although there has been extensive research on these technologies, the main objective of this work was to investigate the interactive effects of the experimental factors, viz. the initial contaminant inputs, process conditions, chemical dosages as process parameters for process optimisation. For this purpose, wastewaters from An Binh commercial paper mill were selected as a case study to investigate the applicability in terms of technical and economic feasibility. The contribution of this dissertation is organised according to the following specific objectives:

- Determine the characteristics of the wastewater in terms of contaminant loads including COD, BOD, colour and total suspended solids (TSS) to identify parameters of concern,
- Assess and compare the removal efficacy of contaminants of concern by various treatment technologies including enhanced coagulation and flocculation, and membrane technologies, and
- Assess suitable technology in terms of performance and economic viability for contaminant removal to meet the discharge standard and enable reuse of wastewater.

CHAPTER 2: LITERATURE REVIEW

2.1. Water consumption in recycled paper mills

Water is used extensively in the papermaking process, including raw material preparation, chemical make-up, fibre property development, transportation, pulp dilution, paper web formation, equipment cleaning, and lubricating, cooling, and heating in the form of steam (Olejnik, 2011). As a result, a traditional papermaking plant's economics are based on the use of water (Olejnik, 2011). For every tonne of paper created, 5–80 m^3 of fresh water is required, with the paper grade and level of water recycling being the determining factors (Olejnik, 2011)

Improvements in water efficiency in P&P industry have been made possible by various techniques such as establishing more effective wastewater treatment and narrowing or closing water circuits through the reuse of clarified process water (Man et al., 2018). The water consumption varies in each mill, based on the raw material used, the paper grade produced, and the size and structure of the plant (Ramezani et al., 2011). It has been demonstrated that when recovered papers are used as raw materials, 9–25% less water and 28–70% less energy are consumed (Ramezani et al., 2011).

The deinking process also has an impact on water consumption rates (Jung and Kappen, 2014). The process water can be easily cleaned for recirculation in mills that do not require deinking as chemicals for bleaching are not required. Depending on the system, a volume of freshwater ranging from 5.5 to 75 m^3/tonne of pulp is necessary for the deinking process. Mills that generate high-quality goods but have small paper machines, limited production rates, and frequent grade changes are frequently confronted with rising effluent volumes (Jung and Kappen, 2014).

2.2. Contaminants in recycled paper mills

Closing the water system to reduce freshwater use could have a detrimental impact on various unit operations. According to Fatta-Kassinos and Dionysiou

(2016), reduced fresh water usage can cause a continuous increase in problems due to an increased presence of harmful compounds in water loops. In recent years, many attempts have been made to improve the recycling ratio of process water by treating suspended particles and organic dissolved solids. However, the treatment of dissolved inorganics, which include salts and metal ions, has yet to be fully explored. It has been suggested that metal ion chelating agents based on aminopolycarboxylate-based molecules can be used (Chauhan et al., 2015). Metal ion chelating agents, however, would be unsuitable for a completely closed, zero discharge system due to the high cost of removing the metal complexes.

Because each mill's process water has a different composition, the amount of these contaminants varies. Due to the diverse nature of recovered paper, contamination during its recovery and storage, and additives in the stock preparation stage such as chemicals used for dispersion fibres, recovered paper, despite being environmentally friendly, still produces a wide range of pollutants in the water stream. The wastewater would have significant suspended and dissolved solids loads, requiring frequent treatment chemical adjustments such as oxidising agents, polyelectrolytes, and/or pH-controlling compounds (Miranda et al., 2009).

Starch (native starch or cationic starch), volatile fatty acids (VFA) from bacteria on recovered paper contaminated during its use, storage, and recovery. These can be measured by chemical oxygen demand (COD) (Hubbe, 2007). Salts include calcium carbonate from filler and coating pigments, silicates from deinking and adhesives, and aluminium sulphate from the sizing process are all common detrimental substances found in recycled paper mills' water circuits (Stetter, 2006). Detrimental compounds, as the name implies, produce complications in the papermaking process, such as reduced additive efficacy, paper appearance and strength qualities, sizing efficiency, foul odour, drainage, and drying issues, all of which slow down the paper machine speed (Stetter, 2012). Deposits and foam development can result in paper flaws and web breakage.

The paper appearance is dictated by the removal of ink from recovered sheets. Although ink removal is not required for all paper grades, the lack of such a process result in a greyish tint in the water, which transfers onto the paper products (Zhao et al., 2004). Deinking is required for grades that demand a high level of whiteness, such as tissues, printing, and writing paper. Chemicals such as hydrogen peroxide, chelating agents, chlorinated compounds and absorbable organic halides (AOX), among others, are used to strip colour from paper and are then washed away and treated as pollutants in the water.

Salts are also regarded harmful to the process since their accumulation can corrode machine parts and reduce the strength of paper products. Due to the increased osmotic pressure of the fluid, high salt concentrations limit the swelling potential of fibres (Hubbe, 2007a). These contaminants are particularly prevalent in whitewater systems that employ recycled or low-quality mixed recovered paper as raw materials (Hubbe, 2007a). Because calcium carbonate from filler and coating pigment is found in recycled materials, the accumulation of calcium ions (Ca^{2+}) in the processing water is usually significant (Mittal et al., 2006).

Besides Ca^{2+}, other dissolved inorganics can also be found in the process and wastewater of recycled paper mill. There are two types of dissolved inorganics: large ion size with low charge density (Ti, Si, Fe, Al) and small ion size with high charge density (Na, Ca, Mg, K), both of which are easily hydrated (Mittal et al., 2006). Despite the high recycling ratio of processing water, ions of the first group are rarely detected in considerable quantities because they are normally absorbed into paper products through high ionic attraction to cellulose fibre (Mittal et al., 2006). When the water is recycled, the latter group, on the other hand, accumulates in the whitewater (Mittal et al., 2006). In most cases, calcium ions make up more than 50% of all dissolved inorganics (Kim et al., 2003). As it adsorbs on the cellulose fibre surface, Ca^{2+} sorption competes with polymer additives used as retention aids and lowers their efficacy. The sorption capacity of fibres is determined by the starting cation concentration and pH. The Ca^{2+} binding strength and sorption capacity both increase as pH rises. This pH effect is due to increased pH increasing fibre charge, resulting in more adsorption sites available for Ca^{2+} sorption (Duong et al., 2006). Furthermore, at high temperatures, solid calcium carbonate deposits can form, leading to scaling (Kim et al., 2003). Hard water also shortens the life of equipment and raises the expense of unclogging pipes (Kim et al., 2003). The more salt in the water or the presence of simple ions, the more corrosive it is (Kim et al., 2003).

Due to the use of aluminium sulphate (alum) for the retention of additives and in the sizing process, wastewaters from recycled paper mills can be classified as sulphate-rich wastewaters (Pol et al., 1998). Excess aluminium sulphate can cause a number of problems (Minami et al., 1991), including:

- Formation of sulfuric acid as a result of excess alum on the finished product reacting with moisture in the air, resulting in degradation of paper fibre and thus paper quality.
- Increased plant maintenance costs since alum build-up causes corrosion in papermaking equipment.
- Floc development in fibre suspension, which promotes sheet formation deformity.
- When sulphur-reducing bacteria are present and anaerobic conditions are present, H_2S and other sulphur-containing chemicals are produced, resulting in a foul odour.

Stickies, which come from hot melts, pressure sensitive adhesives, and coated binders, are also common in paper recycling facilities (Cathie, 1994). Even after pulping, these stickies do not disintegrate in the process water and can be recycled into paper. These particles fragment into smaller particles that are easily distorted under heat and pressure, becoming trapped in the papermaking machinery and resulting in low quality paper or paper sheet breakage during the drying process. Therefore, the presence of stickies diminishes the paper machine's reliability.

2.3. Water circuits of a recycled paper mill

The primary circuit, secondary circuit, and tertiary circuit are the three main water circuits of a recycled paper mill. Figure 1.1 depicts a generalised water and stock circuit layout. The aqueous solution that drains from a wet sheet of paper in the forming section is referred to as ‘‘whitewater," also known as process water (NCSU, n.d.). Dilution of stock is accomplished in the primary circuit, also known as the short circulation of process water, by reusing whitewater derived from the wire section's sheet-forming zone, which is heavy in fibre fines and filler. As the whitewater is recirculated, these components tend to accumulate. The majority of the water in this water circuit is used, and the overflow is transferred to the save-all unit. The save-all serves as a separator for solids and liquids. It uses unit operations including filtration, sedimentation, and flotation to remove fibres and fillers, allowing for fibre reclamation and easier wastewater treatment (Olanrewaju and Gustavo, 2014). Disc filters are the most often used process equipment in all sorts of paper production, and they may generate three different types of filtrates: cloudy, clear, and super clear (Stetter, 2012). For further separation, the cloudy filtrate is frequently looped back to the disc filter's input. The clear filtrate, which typically includes fewer than 50 ppm solids, is sent to the whitewater tower and used in the stock preparation system for stock dilution and consistency control. Water is utilised mostly for pulp mixing and preventing the mixture from becoming too thick or thin at this stage, therefore it is not required to maintain a very low solids content. The super clear water, which contains less than 20 ppm suspended solids, can be utilised as fresh water in high-pressure showers connected with the wire and press roll operations. This water stream was shown to be less prone to clog or cause product contamination. The disc filter's recovered stock is returned to the pulp stream. Disc filters are chosen over flotation methods such as dissolved air flotation (DAF) because they produce higher-quality filtrates without the use of chemicals and take up less space. As a result, DAF is frequently linked with older process designs, but it is still considered when fillers and particles need to be removed. The secondary circuit consists of the recirculation of treated whitewater to stock preparation, as well as cleaning water (Blanco et al., 2015; Olanrewaju and Gustavo, 2014). Excess water from the secondary circuit, as well as other non-reusable water from processes such as plant cleaning, boiler blowdown water, and used residential water, are handled in the tertiary circuit.

While a save-all unit is adequate for eliminating coarse and suspended sediments, dissolved solids that make up the COD and BOD are still present in clarified water (Pulp and Paper Technology, 2019). Further treatment of the water stream is required due to chemical build-up from recirculating process water (Blanco et al., 2015). Depending on the effluent requirements, wastewater treatment may include primary, secondary, and tertiary treatment (Blanco et al., 2015). The tertiary circuit's treated wastewater can be recycled back to the stock preparation process.

2.4. Trends in water reduction

The paper industry has been under social and regulatory pressure for many years to minimise the volume and toxicity of its industrial waste (Karthik et al., 2011). As a result, the idea of a closed water system is gaining attraction in the industry. The closure of the water system could result in a significant reduction of liquid discharges, if not total closure, and reduction in fresh water consumption through reusing treated process water and wastewater enables a reduction in production costs. These opportunities have fuelled the development of new and innovative zero liquid discharge (ZLD) technologies (Rathoure, 2019). When installed, this system will recover effluent, convert it to clean process water, and recycle it back to the mill. Industrial waste is frequently complex with inorganic and organic solutes, demanding a combination of technologies with specific functions for clarification (Bajpai et al., 2016). As a result, concerns such as identifying appropriate wastewater treatment technology, waste sludge disposal, and the presence and accumulation of undesired contaminants in the water loop are unavoidable obstacles to any closed-loop plant's implementation (Alexandersson, 2003).

Furthermore, freshwater use is the primary source of wastewater (Allender et al., 2010). In most cases, the save-all unit is used to implement whitewater reuse (Moslehi, 2018). The initial goal of an internal whitewater treatment system with the save-all units was to keep fibre and filler from being wasted. However, since the high-quality clear filtrate from the save-all could be used as shower water for the paper machine's wire section, an integrated purification system (IPS), which is a combination of other treatment technologies and the save-all, was developed to further improve the treated process water quality and water reuse rate. A thorough understanding of the process and the impact of the raw materials and additives used in the plant provides a solid foundation for selecting an appropriate treatment system. The integrated purification system/s would replace the wastewater treatment system if a complete closure of the water loop is to achieve, as there would not be any liquid waste and all treated liquid would be recirculated into different parts of the paper making operations (Ngoc et al., 2021). Figure 2.1 shows a simplified closed water system using IPS. This is more achievable for mills that manufacture low-grade paper products, as the recycled water stream is of lesser quality (Batista et al., 2020). Corrosion and bacterial development are the major potential problems in the paper machine because the clear whitewater contains organic compounds that act as carbon sources for bacterial growth or slime (Batista et al., 2020). Spray nozzles can become clogged as a result of bacterial development. Chemicals, biocides, dispersants, or raising the system's temperature over 50°C or maintaining a pH of 8.5–9 can all be employed to overcome microbe or slime production. On the other hand, in mills where a complete water loop closure is unattainable, effluent treatment becomes the priority.

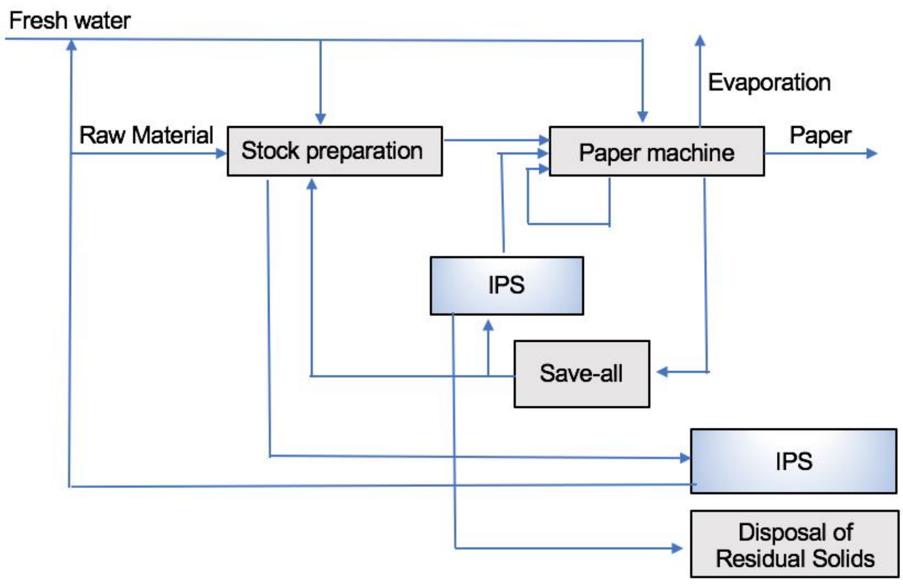

Figure 2.1. An example of a completely closed process water loop with integrated purification systems (IPSs). (Adapted from Hamm and Schabel, 2007).

An example of a mill that has successfully achieved a zero-effluent system is Zulpich Mill of Kappa Paper (Hamm and Schabel, 2007). They used primary clarification before up-flow anaerobic sludge blanket (UASB) reactors followed by two aerobics units, secondary clarification to treat excess sludge produced from the aeration tanks followed by a sand filter to minimise the solids content below 20 mg/L. The treated water is then used for cleaning and stock dilution.

Visy's Tumut paper mill is another example. They employed a sequencing batch reactor (SBR) with biological nutrient removal (BNR) activated sludge process. The same reactors are used for all unit processes, eliminating the need for a secondary clarifier and sludge recycle system. The treated wastewater from the mill is reused in the process with any excess discharged on-site for agricultural purposes (Otto, 2006).

Oji Paper operating in Nanjing, China implemented an ozone-coupled biofilter that removes COD, integrated membrane system of UF and RO, electrodialysis (EDR) concentration system and mechanical vapor recompression (MVR) system. Purified water is recirculated to power plant desalination and water production. Waste salt is supplied to the Transportation Bureau to be used as snowmelt agent and raw materials (Jiuwu, 2020).

2.5. Consequences of closing the water loop without treatment

For a smooth operation, maintaining the dynamic balance between partial equilibria of process variables such as water flowrate, pulp consistency, and the physiochemical, thermal, and microbiological water characteristics is critical (Miranda et al., 2009). These partial equilibria are interconnected, and any disturbance in one of them will have a direct impact on the others, resulting in a system imbalance (Miranda et al., 2009). Any reduction in fresh water consumption (water equilibrium) often increases pulp content in circulating water (mass equilibrium), solute concentration (physicochemical equilibrium), and circulating water temperature (thermal equilibrium) (Paris, 2000). The type and amount of microorganisms in the system will change due to the increase in temperature, shifting the described equilibria (Paris, 2000). As the temperature rises, the dewatering of the paper web also becomes easier, altering fibre retention in the wire section and product quality (Paris, 2000). As a result of the circulating water containing a varied proportion of pulp particles and dissolved chemicals, the pulp and physicochemical equilibrium would be further disrupted (Paris, 2000). Thus, as the circulating water now contains a different concentration of pulp particles and dissolved chemicals, the pulp and physicochemical equilibrium would be further disrupted (Paris, 2000).

Consequently, closing the water loop without proper treatments can result in high water temperature and increased suspended and dissolved solids content in the water system, causing paper defects, product quality loss, and paper machine reliability issues. Specifically, materials that did not maintain the created paper web, such as soluble colloids and fine solid particles, accumulate in whitewater as a result of repeated recirculation (Tsai et al., 2011). Thus, water reduction disturbs the balance of partial equilibriums, resulting in repercussions such as:

- Paper machine wire furnish retention reduction
- Equipment corrosion
- Deposit precipitation
- Pulp foaming
- Circulating water temperature increase (up to 60–70°C)
- Microorganism growth in the system
- Paper machine reliability issues such as web breaking
- Additive efficiency reduction
- Wastewater treatment complications
- Lower product quality.

2.6. Discharge standards and environmental performance of a paper mill

The design and structure of the treatment plant varies between mills depending on the quality of paper products, the type of raw materials utilised, and the toxicity of the wastewater (Moo-young, 2007). Primary and secondary treatment are all part of a conventional wastewater treatment facility. Primary treatment is frequently used as a pre-treatment for subsequent wastewater treatment. It usually consists of an equalisation basin for regulating pH and temperature, as well as a sedimentation or flotation tank for separating solids and precipitating hardness from the water (Englande et al., 2015). A coagulant and/or a flocculant are often used in this process to improve separation. As a result, the sedimentation or flotation mechanism is separate from the save-all unit, preventing chemicals used for this process from re-entering the primary and secondary water circuits and polluting the recovered fibre by the save-all unit (Bratby, 2016). Subsequent treatment includes biological (anaerobic and aerobic) treatment as well as a secondary settling tank. Its purpose is to remove suspended particles, colloidal, and dissolved organic matter, and lowering COD, BOD, and colour (Englande et al., 2015). Although biological treatments are more cost-effective and environmentally friendly than physicochemical treatment, biological processes have been shown to perform badly when it comes to eliminating colour and recalcitrant chemicals. Contaminants such as unsaturated fatty acids, alcohols, and chlorinated hydrocarbons are also a challenge for biological treatments.

Suspended solids can be removed by the primary treatment, dissolved biodegradable organic matter can be removed by the secondary treatment, and chemicals with limited biodegradability, such as refractory bleaching compounds and inorganic salts, can be removed by the tertiary treatment. Because of this, tertiary treatment is required to obtain treated effluent that complies with discharge regulations while being appropriate for reuse within the recycled paper mill. Advanced oxidation by Fenton reagent, activated carbon, enhanced coagulation and flocculation, or membrane technology are all possibilities for tertiary treatment.

Where the complete closure of the water system is implemented, these treatments would be coupled with a save-all unit/s for both water and fibre reclamation as depicted in Figure 2.1.

The effluent treatment circuit also includes sludge treatment, as sludge is generated during the treatments and must be removed or reused. Water removal is an important aspect of sludge treatment. While primary sludge from primary treatment is relatively easy to dewater, secondary sludge from biological treatment, also known as bio-sludge or biosolids, has low dewaterability due to the presence of high concentrations of extracellular polymeric molecules. Mechanical dewatering followed by composting for landfilling and mechanical dewatering followed by incineration and ash deposition are currently the two most popular sludge management options (Meyer et al., 2018). Mechanical dewatering is accomplished using machines that work on various solid content ranges, such as a gravity table or rotary thickener, followed by a belt or screw press (Hagelqvist, 2013). While composting with windrows or reactors is simple, the finished product is often nutrient-deficient and unsuited as fertiliser. Sludge incineration is desirable because it creates thermal energy, allowing for biofuel generation, and produces ash that is easier to dispose of. For this application, sludge must be dried up to 65% solids content in order to burn properly, but mechanically dewatered sludge can only contain up to 35% solids. To promote dewaterability, thermal drying and mixing of primary and bio-sludge are considered (Hovey, 2016). In addition, a small amount of primary sludge can be utilised to create low-grade paper products and bio-sludge can be partially recycled into biological treatment units to maintain the biological activity (Hovey, 2016).

Plant capacity, effluent quality requirements for treated wastewater, and site-specific variables are all taken into account for the design of treatment plants. The treatment's goal is to either recycle some or all of the treated wastewater back into the industrial process (closed circuit) or to be disposed of. Treated wastewater may be reintroduced to the process in part, depending on the quality of the output and the demands of the facility (Allender et al., 2010). As a result, paper mills that use recovered fibres to make corrugating medium have a better chance of attaining a closed water circuit.

When it comes to recycling, the pollutants in the wastewater fluctuate from one mill to the next. Mills that employ 100% recovered paper, for example, have a higher BOD load, colour, TSS, chemicals, and fillers in their effluent than mills that use both recovered papers and virgin pulp. Meeting local or national effluent discharge requirements is a requirement for all mills. Depending on where the treated effluent will be discharged, these criteria differ from country to country and even state to state. In some countries, treated wastewater can be discharged into a receiving water system (urban drainage systems, rivers, or coastal water) or routed to an external system for further treatment, depending on their quality. Table 2.1 shows the various legal criteria for treated industrial wastewaters in Vietnam, depending on where the treated water would be used (Ministry of Natural Resources & Environment, 2011). Standards for effluents discharged into receiving water systems are listed in column A, while standards for effluents discharged into a central wastewater treatment system for further treatment are included in column B.

Table 2.1. Effluent discharge standards in Vietnam (Ministry of Natural Resources & Environment, 2011). Limits shown in column A refer to treated water discharged to the environment and column B values to water discharged to a central wastewater treatment system. C refers to the values of industrial wastewater parameters.

No.	Parameter	Unit	Value (C)	
			A	B
1	Temperature	°C	40	40
2	Colour	Pt-Co	50	150
3	pH	-	6-9	5.5-9
4	BOD_5	mg/l	30	50
5	COD	mg/l	75	150
6	Suspended solids	mg/l	50	100

2.7. Primary treatment

Primary treatment can be accomplished using a simple liquid and solid separation approach, such as gravity separation (clarifiers) or flotation, with flotation being the more popular option.

Dissolved air flotation (DAF) is the most prevalent type of flotation (Manago et al., 2016). At the bottom of a shallow tank containing paper mill process water, the device introduces a pressurised stream of water saturated with air. The release of the injected water into the tank creates air bubbles as the pressure is lessened. As the bubbles rise, solid particles are stuck to them and are brought to the water surface. The solids are then skimmed from the top of the water. DAF is a cost-effective method for treating big water flows that produce a wide range of solids content in the flotation concentrate (300 to 5000 mg/L) (Ackermann et al., 2000).

Due to high solid concentration of recycled paper mill effluent, chemical coagulation followed by sedimentation is a recommended method for removing suspended solids, particularly those with colloidal characteristics. It is possible to remove finely distributed and colloidal organic particles larger than 0.2µm (Ackermann et al., 2000). Because starch (Kadwe et al., 2019) and stickies (Chakrabarti et al., 2011) are insoluble substances, they can be removed by a coagulant and/or a flocculant utilising liquid and solid separation procedures. The supernatant is biologically treated to eliminate organic contaminants.

When the correct concentration is dosed, coagulation can remove suspended particles, certain toxins, colour, COD, and BOD, which makes subsequent treatment more cost-effective and efficient (Tetteh and Rathilal, 2018). The most commonly used compounds are alum, ferrous salts, and polyelectrolytes. Tetteh and Rathilal (2018) discovered that coagulants with a high valence, such as aluminium sulphate, are frequently used because the concentration of metal ions for coagulation is reduced with increasing charge of cation, further cutting cost. Aluminium sulphate, on the other hand, has a number of drawbacks. The addition of alkalinity to the effluent is typically necessary to reach the ideal coagulation pH. However, the quantity of sulphate ion in the effluent is increased, affecting subsequent biological treatments. and the alum floc formed are very brittle, limiting the rate of the floc separation process.

Because amino acids, proteins, and long chain fatty acids are eliminated during the coagulation process with aluminum-based coagulants, the effluent becomes less biodegradable (Birjandi et al., 2016). Furthermore, residual alum and ferric-based coagulants obstruct downstream biological treatment by lowering microorganism respiration rates and organic matter removal rates (Birjandi et al., 2016). Birjandi et al. (2016) also found that biological wastewater treatment plants have increased predatory growth. Polysilicato-iron (PSI) was created to replace the use of aluminium coagulant. PSI has been shown to be more efficient than poly-aluminium chloride (PAC) due to its strong bridging feature, which enables the formation of flocs that settle more quickly allowing a smaller sedimentation tank to be used (Tran et al., 2006). PSI can help maintain nutritional bioavailability (Tran et al., 2006), however it is not widely employed. Chemical coagulation sludge is frequently toxic because it contains hydroxides and has a high pH. Despite having a similar valence as alum and being less expensive, iron salts such as ferric chloride and ferrous sulphate are highly coloured. As a result, iron products are not recommended as a coagulant in the recycling of pulp and paper wastewater.

Coagulants based on polymeric aluminium with the general formula $(Al_n(OH)_mCl_{(3n-m)})_x$ are currently commonly employed. PAC (n = 2 and m = 3) and aluminium chlorohydrate (ACH, n = 2 and m = 5) are two of them. Various monomeric and polymeric species are produced during hydrolysis, with $Al_{13}O_4(OH)_{24}{}^{7+}$ being the most significant cation. The basicity of poly-aluminium coagulants is an important feature. This is the ratio of hydroxyl to aluminium ions in the hydrated complex; as a result, poly-aluminium coagulants use far less alkalinity than alum, lowering the pH of treated water and reducing the need for pH adjustment (Brandt et al., 2017). As a result, poly-aluminium coagulants are more effective than alum over a wider pH range. Cationic inorganic polymers like PAC, according to Cai et al. (2019), have the advantages of being affordable, a fast sedimentation rate, achieving low turbidity, and are suitable for treating starchy wastewater. In the recycled paper mill water stream, starch, which is utilised for surface sizing and coating pigment, works as a source of microbial growth, odour, and colour. Adding a biocide to the pulp slurry to prevent bacteria from degrading the starch, resulting in the creation of volatile fatty acid (VFA), and employing cationic starch in the papermaking process to enhance fixation to fibre are the two most important steps in regulating starch content (Maurer, 2009). During web breakage events, recovered papers are returned for processing, and cationic starches will remain linked to the cellulose and, if dispersed, will combine with anionic materials to create large particles that can be retained in paper, lowering starch level in the effluent (Maurer, 2009).

Furthermore, highly cationic organic polymers may be chosen over inorganic coagulants for usage with flotation due to their ability to densely agglomerate and settle fast (Gray and Ritchie, 2005; Bolto and Xie, 2019; Cai et al., 2019). The creation of smaller flocs from suspended materials flocculation utilising polymers such as polydiallyldimethylammonium chloride (poly-DADMAC) has been shown to be successful as a flocculant for pulp and paper mill wastewater (Razali et al., 2011). Some polymeric flocculants, on the other hand, can only be partially biodegraded, resulting in odourous compounds such as trimethylamine (Dentel et al., 2002). A patented treatment for stickies control uses poly-DADMAC in combination with acrylamide. Stickies found in broken and recovered paper, such as starch, are dispersed into colloidal form during the pulping process in recycled paper mills to prevent fibre clumps from being incorporated into new paper products. Stickies are frequently removed from the pulp slurry using a screen or dissolved air flotation before the paper production stage to limit the likelihood of disposition in the paper machine (Chakrabarti et al., 2011). Flotation can remove up to 70% of stickies when performed after the dispersion process (Chakrabarti et al., 2011). The remaining stickies remain in the slurry as dissolved or colloidal components that require cationic coagulants for either stimulating fixation on fibres (and hence removal with the paper sheet) or encouraging agglomeration for easy discharge from the wastewater stream.

It's worth noting that the cationic polymer chitosan, which can be extracted from marine biomass, has piqued industry attention (Song et al., 2018). The use of chitosan-based compounds as coagulants and flocculants is becoming more common in wastewater treatment research. They can remove both inorganic and organic suspended solids, as well as organic compounds that have dissolved. Dense sludge is generated when a chitosan-based substance is used as a coagulant, suggesting potential high efficiency, especially when paired with DAF (Song et al., 2018).

Chemical precipitation is also used to reduce the amount of chloride-based coagulants in the system, which can cause corrosion. Although cost-effective, it has significant disadvantages, such as sludge generation and disposal (Chaudhari et al., 2010). Plus, as sludge are produced, the anions become free, resulting in a decrease in pH (Altmayer, 2008). The suspended solids collect at the bottom of the tank as they cluster and settle.

For pulp and paper industry effluent, Sahu and Chaudhari (2013) noticed a varied effect on COD and colour removal by coagulation at pH 4, 5, and 6, which are the optimum values for $AlCl_3$, $CuSO_4$, and poly-aluminium chloride, respectively. PAC achieved maximum COD and colour removal of 84% and 92%, respectively. $AlCl_3$ reduced COD by 72% and colour by 84%. $CuSO_4$ was able to remove 74% of COD and 76% of colour. Due to their acidic nature, the pH level drops as the dose of coagulants increases. $AlCl_3$ had the greatest pH drop, followed by PAC, and finally $CuSO_4$. As a result, pH is critical to coagulation efficacy, and an acid or a base must be added to ensure pH is at the ideal range for the coagulant in use. Overall, PAC was determined to be the most effective coagulant, removing more contaminants while producing less sludge.

Polyacrylamide (PAM) is a commonly used flocculant that forms big agglomerates from smaller particles due to its high molecular weight (Teng et al., 2014). Because of their lengthy chains, flocculants can adsorb on two particles at the same time. Through ionisation or hydrolysis in water, the structural units of these polyacrylamides can carry charges. As a result, there are different types, such as cationic, anionic, and non-ionic (Teng et al., 2014). By electrostatic attraction, cationic polyacrylamide adsorbs negatively charged colloidal particles on its chain, transforming scattered tiny particles into bigger particles (Gregory and Barany, 2011). Similarly, anionic polyacrylamide serves as a ‘‘bridge" between numerous positively charged colloidal particles, allowing them to combine to form larger particles (Sharma et al., 2006). Anionic PAM is appropriate for effluents with a high concentration of positively charged inorganic suspensions or suspended particles ranging in size from 0.01 to 1 mm. Cationic PAM functions best at neutral or alkaline pH levels, making it ideal for wastewater treatment with high levels of negatively charged suspended particles and organic materials. To prevent wasting the expensive flocculants, it is recommended to utilise an optimal amount of an affordable coagulant to drive surface charge decrease (Leiknes, 2009). The inclusion of bigger aggregates increases the settling rates of flocs when combined with a coagulant. When treating effluent high in inorganic salts such as aluminium sulphate or calcium carbonate, which is similar to recycled paper effluent, Stephenson and Duff (1996) observed reduction of colour and turbidity of 90% and 98%, respectively.

2.8. Secondary treatment

One of the most widely utilised strategies in paper wastewater treatment is activated sludge (AS). However, combining anaerobic treatment with an aerobic biological technique has become more common in recent years (Thompson et al., 2001).

Aerobic treatment, also known as activated sludge, is one of the oldest secondary treatment procedures. It comprises aeration and recirculation of a part of aerobic sludge back to the system's input. The system is divided into two parts: an aeration basin and a sedimentation basin (Thompson et al., 2001). Wastewater is fed activated sludge, which is a high-concentration suspension of cultured microorganisms, resulting in a mixed liquor. The oxygen in the aerated liquid aids biomass respiration, providing the energy it needs to absorb and metabolise nutrients such as carbonaceous compounds, which contributes to the BOD level. After that, the liquor is transferred to a sedimentation tank, where the biomass settles and the treated wastewater is purified. To keep the biosolids concentration constant in the activated sludge process, a tiny percentage of the concentrated biomass at the bottom of the sedimentation basin is removed (Englande et al., 2015). The aeration basin reuses the majority of the settled biomass. According to Cabrera (2017), activated sludge can remove between 85 and 98% of BOD and 20 to 50% of COD from pulp mill wastewater. Because VFAs are highly biodegradable, aerobic treatment is the primary method of elimination (Markis, 2003). When used after primary treatment, the removal of suspended particles is typically 85%–90%. (Cabrera, 2017). Most pulp and paper mills favour this treatment because it produces reliable results, is easy to monitor, and requires a modest plant footprint (Ashrafi et al., 2015). However, with the activated sludge process, increased sludge formation and thickening difficulties cause efficiency loss. Bulking difficulties, particularly filamentous bulking sludge, with abundant extracellular polymeric compounds generating bulking, tiny floc formation, and distributed biomass, make it difficult to maintain a low suspended material concentration in the effluent (Mehmood et al., 2019). Another disadvantage of the activated sludge process is its low phosphate removal rate.

Colour and refractory chemicals contained in paper wastewater are difficult to remove with only aerobic treatment. Anaerobic treatment, on the other hand, has been shown to remove 70%–90% COD and up to 90% AOX (Toczyłowska - Maminska, 2017). Bacterial hydrolysis initiates the anaerobic digestion process, which breaks down insoluble organic polymers such as carbohydrates, hemicellulose, and chlorinated chemicals into soluble and simpler derivatives that are more biodegradable (Ahammad and Sreekrishnan, 2016). In the second stage, acidogenesis, commonly known as fermentation, sugars and amino acids are transformed into carbon dioxide (CO_2), hydrogen, ammonia, and organic acids. Following that, organic acids are converted to acetic acid during acetogenesis, releasing additional ammonia, hydrogen, and CO_2. Finally, methanogenesis converts these compounds into methane and more CO_2. Methane and CO_2 can be collected for disposal or repurposed as a renewable energy source or as a heat source for high-temperature activities (Weiland, 2010). Aside from the enormous cost savings, this treatment produces substantially less sludge than its aerated biological alternative. Because there is no need for an air pump, the energy cost is cheaper (Weiland, 2010). As a result, anaerobic treatment may be used instead of or in addition to aerobic treatment. The generation of hydrogen sulphide from sulphate ions in the presence of sulphate reducing bacteria that break down sulphates into sulphides is one of the major drawbacks of anaerobic treatment (Khan et al., 2013). These bacteria receive their energy by converting elemental sulphur to hydrogen sulphide, which can obstruct the synthesis of methane because H_2S is exceedingly poisonous to the microbes responsible for methane production (Khan et al., 2013). Moreover, degradation of organic contents is low for anaerobic digestion process, producing wastewater that is still high in COD and aesthetically unpleasant, which requires further treatment (Toczyłowska - Maminska, 2017).

Many recycled paper mills have been using anaerobic biological treatment followed by aerobic treatment to eliminate contaminants in recent years. While anaerobic treatment reduces sludge formation and creates biogas that may be collected and utilised as energy in other areas of the mill, it is not capable of eliminating all organic compounds. However, it aids in making refractory compounds more biodegradable. As a result, further aerobic treatment aids in the elimination of any remaining organic matter from the anaerobically treated effluent (Marwaha et al., 1998). The aerobic system, in general, aids in the removal of excess VFAs, digested refractory compounds, and dissolved sulphides from anaerobic effluents (Khan et al., 2013). Micro-aeration can be utilised to oxidise sulphides back to elemental sulphur in addition to sulphide purging, making the system even more cost effective (Khan et al., 2013). Toczyłowska -Maminska (2017) demonstrated that such a strategy is effective in meeting the regulations for pulp and paper mill wastewater discharge. Combining these treatments with a membrane filtration stage makes it possible to reuse the treated wastewater (Marwaha et al., 1998). Despite the fact that successive anaerobic and aerobic treatment reduces the organic content and toxicity of effluents, Kortekaas et al. (1998) found that the combination treatment employed to treat hemp thermomechanical pulping effluent had some unfavourable impacts. The colour of the wastewater following aerobic treatment increased.

Due to its low cost and ease of construction, UASB reactors have been the most popular and commonly utilised anaerobic treatment method to date. It requires a tank with settleable sludge granules and a three-phase gas–liquid–solid separation (GLSS) equipment in the shape of a reverse funnel. Nonetheless, UASB reactors have certain drawbacks, such as low suspended solid removal, susceptibility to biomass washout under high influent flow, low gas output, and possible scaling, all of which have an impact on COD degradation and removal (Sevilla-Espinosa et al., 2010). The use of a second pH raising unit utilising the CO_2 stripping procedure helps prevent scaling caused by calcium carbonate precipitates (Kim et al., 2003). Because the pH of the UASB reactor is too low for calcium carbonate production, a pH elevation step is necessary. The pH of the CO_2 stripping unit is raised through aeration, which encourages the development of calcium carbonate and, as a result, it precipitates. These precipitates are subsequently thrown in the settler as sludge waste. Furthermore, to address low SS removal and biomass washout issues, an up-flow staged sludge bed (USSB) reactor with compartments was devised, in which the reactor was separated longitudinally into a number of compartments by the use of baffles (Sevilla-Espinosa et al., 2010). High solids retention and minimal biomass washout are achieved by baffles running the length of the reactor. As residual solids travel through the system, the compartments encourage the separation of distinct phases of anaerobic degradation, resulting in optimal conditions for their decomposition (Sevilla-Espinosa et al., 2010).

The extended granular sludge bed (EGSB) and internal circulation (IC) reactors are the most current generations of biological processes (van Lier et al., 2015). Because they use granular sludge with high settling rates and methanogenic activity but at a significantly greater volumetric loading rate and upward flow velocities, the extended bed systems can be regarded an upgrade over conventional UASB reactors. Due to biogas holdup in the granules, large loading rates impair sludge settleability. Because sludge has a high natural settleability, surface flow velocities of more than 6 m h^{-1} can be achieved by using a tall reactor or recycling effluent, which, when combined with gas lifting in the bed, partially extends the sludge bed. As a result, there is more contact between sludge and wastewater, which improves loading potentials when compared to standard UASB reactors. Different EGSB suppliers have their own GLSS design with unique features for EGSB reactors that aren't compatible with standard GLSS devices (van Lier et al., 2015). As a result, many types of wastewater with varying BOD concentrations can be treated. The EGSB has a unique version called the IC. The IC contains an integrated GLSS device that separates the produced biogas from the liquid midway through the reactor, allowing the gas to flow upwards to a de-gasifier or expansion unit via a conduit. The sludge–water mixture is then returned to the reactor's bottom via a different pipe, while the separated gas is evacuated from the system. Following that, the lifting action of the biogas is used to recirculate liquid and granular sludge over the lowest part of the reactor, improving sludge and wastewater contact. The Biopaq® IC-reactor created by PAQUES was used to produce superficial flow velocities of 25–30 m h^{-1} caused by the movement of liquid and gas (van Lier et al., 2015). The reactor medium was almost thoroughly mixed with the biomass by the surface flow velocities. Despite COD fluctuations, which are frequent in the paper recycling sector, Driessen et al. (1999) found that the IC reactor's performance remained stable utilising effluent from three separate recycled paper mills. Visy is currently using this technology (Aquatec Maxcon, 2020).

2.9. Tertiary treatment

2.9.1. Enhanced coagulation and flocculation

The term "enhanced coagulation" refers to increasing the amount of coagulant used in the traditional coagulation treatment of water while maintaining the desired turbidity removal effect (Cui et al., 2020). The concept of improved coagulation is based on increasing the amount of coagulant used or controlling the coagulation process with reaction pH settings. Optimised coagulation is based on enhanced coagulation, which is a coagulation process with multiple goals: maximisation of particulate matter and turbidity removal, maximisation of COD removal, minimisation of residual coagulant content, minimisation of sludge production, and minimisation of production costs. Increases in efficiency are influenced not only by the coagulant's dose and pH, but also by the nature and distribution of organic matter and particle matter in the water, as well as temperature, hydraulic conditions, and coagulant morphology, according to previous researches (Cui et al., 2020; Yu et al., 2006; Xue et al., 2014).

Another way to enhance coagulation is to add a flocculant to further agglomerate tiny particles and colloids into bigger particles in order to reduce turbidity, soluble organic and inorganic pollutants (Macczak et al., 2020). This procedure consists of two stages: strong agitation from rapid mixing of dispersed coagulant with water to be treated, and flocculation for agglomeration of tiny particles into well-defined flocs. During the process, coagulation acts as to destabilise a suspension, resulting in aggregates while flocculation creates bigger aggregates. The flocs formed are allowed to settle and are then removed as sludge, while the supernatant is recycled or discharged. Coagulation and flocculation have been effectively used in a variety of sectors due to its ease of operation, comparatively simple construction, and low energy consumption. Due to the versatility of the treatment process, coagulation and flocculation can be employed as a pre-treatment, post-treatment, or even as the primary treatment of wastewater.

2.9.2. Membrane technology

Membranes are classified according to their pore diameters, which determine their capacity to efficiently exclude pollutants such organic materials, including AOX, salts, and ions (Adnan et al., 2010). The broad use of membrane technology is hampered by a persistent problem: fouling. Contaminants accumulated on the membrane surface or lodged in the membrane pores foul the membrane, impeding water flow (Jepsen et al., 2018). This has an impact not only on filtration productivity, but also on the amount of energy required. Cleaning is necessary on a regular basis to prevent fouling, which raises maintenance costs and diminishes membrane longevity, resulting in higher replacement costs (Jepsen et al., 2018). Membranes, however, have gotten more economical in terms of space, energy, and capital cost throughout time as their application in diverse industries has grown (Ezugbe and Rathilal, 2020). The majority of the cost would be for capital expenditure, such as the membrane system's initial installation (Chellam et al., 1998). Samcotech (2017) revealed that a complete UF system capable of treating 2,000 m^3 per day might cost up to AUD $1.5 million. When all additional costs, such as maintenance and replacement are factored in, the cost can be prohibitively high, especially for small-scale facilities. Due to high energy demand and a lack of industrial application, both energy and capital costs rise as the pore size shrinks (Jepsen et al., 2018). As a result, membrane technology is currently not recommended for pulp and paper effluent treatment as a stand-alone method for retrofitting purposes.

Pressure-driven membrane processes are by far the most widely used systems in wastewater treatment (Ezugbe and Rathilal, 2020), and they rely on hydraulic pressure to achieve separation (as the name suggests). Table 2.2 lists the four basic categories and their characteristics (Adapted from Ezugbe and Rathilal, 2020). In the pulp and paper industry, UF has been gaining attention due to its capability of excluding some metals. Iron, magnesium, and calcium compounds are complexed by the addition of polyelectrolytes, allowing them to be retained during the clarifying process (Barjoveanu and Teodosiu, 2006).

Table 2.2. Classification and features of different pressure driven membrane types (Ezugbe and Rathilal, 2020).

Membrane types	MWCO (kilo Dalton)	Retained Diameters (µm)	Pressure required (kPa)	Average Permeability (L/m^2 h bar)	Solutes Retained
MF	100-500	10^{-1}-10	1-3	500	Bacteria, fat, oil, grease, colloids, organics, micro-particles
UF	20-150	10^{-3}-1	2-5	150	Protein, colour, oils, sugar, organics, microplastics
NF	2-20	10^{-3}-10^{-2}	5-15	10-20	Colour, sulfates, divalent cations and anions, lactose, sucrose, sodium chloride
RO	0.2-2	10^{-4}-10^{-3}	15-75	5-10	All contaminants including monovalent ions

When tiny molecules must be retained from permeates, NF is an excellent choice. It is effective at removing metals, colour, and even organic substances in wastewater that are difficult to decompose. The design and operation of the NF and RO are extremely similar (Liu et al., 2008). However, the pore size of the NF membrane is slightly greater than that of the RO membrane, requiring a lower supply pressure. Because its small pores reject divalent ions preferentially over monovalent ions, NF is sometimes referred to as the "softening membrane." It's commonly used to reduce hardness from water. However, this could only be done with water that has a low concentration of total dissolved solids; otherwise, scaling could impair membrane performance. NF and RO both provide high-quality treated water that can be reused (Liu et al., 2008). NF, on the other hand, was thought to be better suitable for large-scale operations since it runs at lower pressure and has a larger permeate flux. Furthermore, for colour removal, NF is the recommended membrane. Loose NF (LNF), which has a pore size that is halfway between NF and UF, is utilised to effectively remove organic macromolecules but not salts (Abdel-Fatah, 2018). LNF has a higher permeability than tight NF, which allows for faster filtration at lower pressure, saving energy and money. As a result, LNF is gaining traction in the pulp and paper business, particularly in the paper recycling industry, as a means of removing natural organic matter (NOM) and thereby lowering colour (Abdel-Fatah, 2018). Different NF manufactured with different source materials have been studied to boost NF applicability (Abdel-Fatah, 2018). To improve the membrane's chemical resistance, polymers such as cellulose acetate and polyamide are utilised. The two-step fabrication procedure of conventional NF involves an interfacial polymerisation reaction on a UF flatsheet membrane (Thong et al., 2018). Thong et al. (2018) used a hollow fibre structure using polyethersulphone (PES) to construct a loose outer-selective NF with high packing density and no spacer, allowing for more investigation into its removal efficiency. Ceramic NF membranes are also available to boost high temperature resistance, lowering maintenance and replacement costs.

Among these membranes, the RO membrane is well-known for its ability to separate monovalent ions such as sodium and chloride ions. It has been at the forefront of wastewater treatment and desalination for water recovery (Ezugbe and Rathilal, 2020). The Lucart paper mill, which uses recycled paper as a raw material and produces bleaching effluent, was able to achieve a COD of 25 ppm and ion rejections of 96–99.9% by using RO (Pizzichini et al., 2005). MF and UF membranes are still chosen due to their lower construction and operational costs, notwithstanding the positive outcomes for RO. Furthermore, when comparing MF with UF, the latter is more generally utilised because it has a higher rate of colour and COD removal. For UF and MF, the average colour removal rate was 84% and 75%, respectively, while the average COD removal rate was 84.3% and 80% (Neves et al., 2017). Furthermore, UF can remove up to 82.5% lignin, whereas MF can only remove 76.5%. Although both membranes reduced turbidity by 99%, the UF membrane had a better removal of COD, colour, and lignin (Neves et al., 2017).

2.9.3. Membrane bioreactor (MBR)

A MBR is a combination of traditional activated sludge treatment and physical separation by membrane filtration, suitable for the removal of both suspended particles and organic materials. In comparison to conventional biological treatment, this treatment provides higher volumetric loading rates, shorter hydraulic retention times (HRT), longer solid retention times (SRT), less sludge production, and opportunities for simultaneous nitrification/denitrification associated with long sludge retention times (Izadi et al., 2018). Furthermore, the use of MBR reduces the need for secondary clarifiers. This, combined with shorter HRT, results in a smaller plant footprint. Despite the energy cost, fouling tendency, and cost of membrane replacement, MBR has gained favour in the pulp and paper sector for its advantages over conventional biological treatment when used with the appropriate pre-treatment and fouling reducer (Izadi et al., 2018). MBR continues to suffer from fouling. It not only reduces the membrane's energy efficiency and lifespan, but it also raises its maintenance and operating costs. Fouling is caused by suspended particles such as bacteria and cell debris, colloids, solutes, and sludge flocs. These materials deposit on the membrane's surface and into the pores, clogging and lowering the membrane's permeability. Due to the heterogeneous nature of suspended solids and active microorganisms in mixed liquid suspended solids, this is unavoidable, making long-term MBR application challenging. As a result, one of the most important areas of research in order to improve wastewater treatment and encourage membrane application has been fouling reduction.

External, submerged/immersed, and airlift side-stream configurations are the three options for MBR (Izadi et al., 2018). Membrane modules of the external design are positioned outside of the bioreactor, allowing for more direct hydrodynamic control of membrane fouling, easier membrane replacement, and higher flux operation (Le-Clech et al., 2006). This arrangement has the disadvantage of requiring high trans-membrane pressure (TMP) and cross flow velocities, which raises energy expenditures. The concept of submerging membranes in the bioreactor was conceived and tested in 1989. (Liao et al., 2004). Membrane modules are submerged in mixed liquor and put within the bioreactor, with a driving force across the membrane produced by a negative pressure on the permeate side. As a result, submerged membranes are the least energy-intensive MBR arrangement, with an energy requirement up to two times lower than its side-stream counterpart. In this design, coarse bubble aeration is used to mix and restrict fouling by retaining suspended materials, cleaning the membrane surface, and supplying oxygen to the biomass, encouraging biodegradability and cell production.

MBR reactors are available in aerobic or anaerobic mode (Izadi et al., 2018). Anaerobic MBRs provided more advantages than aerobic MBRs in terms of sludge output, energy recovery, and operational costs (Izadi et al., 2018). If excellent effluent quality in terms of SS is not required, replacing activated sludge with MBR would be unreasonable because the removal rates for organic matter, phosphorus, and nitrogen compounds are equivalent (Lerner et al., 2007). Mills that want to reuse effluent should utilise MBR to remove as many pollutants and SS as possible. Paper mills might theoretically accomplish 100% water recycling and zero liquid discharge using MBR with the combination of appropriate pre-treatments, fouling control and treatment. However, a closed water system has one detrimental problem, which is the build-up of inorganics. While MBR is efficient in rejecting organic matters and heavy metals, the rejection rate for monovalent ions such as chloride, sodium and potassium is low (Yazdi et al., 2019). These ions interact with other ions when recycled, precipitating into salts. For RO membranes, the precipitation of salts occurs mostly on the membrane surface as their smaller pore size allows for better rejection of monovalent ions (Yazdi et al., 2019). Nonetheless, traces of monovalent ions still end up in the permeate stream for reuse. Therefore, a post MBR salt removal step would be required.

Fouling can be avoided by lowering the load. A larger membrane area, on the other hand, is necessary. As a result, it is more environmentally friendly to utilise coagulants to aid in the development of big flocs, hence improving membrane filtering (Johansson, 2012). Lee et al. (2001) claimed that alum, ferric chloride, and ferric sulphate could increase filterability. Because of their ability to limit gel layer formation, inhibit the growth of fouling layers, and eliminate stable foulants from membrane surfaces, these coagulants and polymeric coagulants lowered the initial transmembrane pressure and fouling rate. Because of their ability to limit gel layer formation, inhibit the growth of fouling layers, and eliminate stable foulants from membrane surfaces, these coagulants and polymeric coagulants lowered the initial transmembrane pressure and fouling rate. Ferric sulphate was found to be the most efficient of the three coagulants, with a lower optimal dose.

Another study by Zhang et al. (2008) examined the ability of ferric chloride to slow membrane fouling. Ferric chloride, at 1.2 mM Fe(III), provided positive charges for charge neutralisation of soluble macromolecular compounds and sludge flocs, resulting in improved filterability. Furthermore, ferric chloride performed somewhat better than aluminium sulphate (Mishima and Nakajima, 2009). During a 40-day trial, the MBR reactor with 4.52 g/L coagulant added was cleaned just five times, while reactors with less and zero coagulant added were cleaned nine and eight times, respectively. This suggests that the inclusion of a coagulant significantly lowered the fouling rate.

Coagulant addition to the MBR mixed liquor, on the other hand, may result in a pH drop (Ngo and Guo, 2009). The biological activity of the MBR mixed liquor can be affected by a drop in pH. As a result, pH correction using a base such as NaOH is required. Over-dosing can also result in the deposition of excess coagulant on the membrane surface. As a result, more research is needed to find long-term doses and control strategies for membrane fouling without reducing the pH.

2.10. Summary

As the use of water is fundamental in paper manufacturing, water recycling is highly implemented in mills to reduce expenses related to fresh water supply, wastewater discharge fees, and fines if the discharge does not satisfy environmental regulations. Therefore, wastewater treatment technologies are constantly being innovated to help the P&P achieve the goal. Furthermore, a typical wastewater treatment system in a recycled paper mill involves a primary and secondary treatment. The first treatment often is a pre-treatment for subsequent treatments that follow by reducing the majority of SS and colloidal particles. The later treatment is tasked with the removal of more SS and colloidal substances, and DS, further reducing COD, BOD and colour of wastewater. Thus, secondary treatment relies on biological methods such as aerobic and anaerobic treatments. Depending on the target discharge quality and/or the insensitivity of water reuse, a tertiary treatment that specialises in removing even more colour and the left-over recalcitrant compounds from the previous treatments might be required.

Enhanced coagulation and flocculation, and membrane filtration are two promising technologies as part of the tertiary treatment system. Both have excellent colour removal efficiency, but enhance coagulation and flocculation is more widely used due to its ease of application and affordability. However, since the chemicals involve are pH and temperature sensitive, either optimisation of wastewater prior to application or using appropriate types of coagulant and flocculant is required. Dosage of the two chemicals can also influence the efficiency of the floc formation, thus needing further consideration. Also, the type of contaminants contained in the wastewater could affect the coagulation and flocculation process, as different types of coagulant and flocculant react distinctively with organic and inorganic matter of different molecular weight. Therefore, more studies could be conducted focusing on the efficiency of various coagulants and flocculants on recycled paper mill wastewater.

Membrane filtration, on the other hand, despite having a higher recalcitrant compounds removal rate, is less considered due to its tendency to foul. Since fouling is inevitable due to contaminant accumulation on the membrane surface and/or inside membrane pores, appropriate fouling management and control are of interest to many researchers from a variety of industries where membrane filtration is applicable. Since recycled paper mill wastewater is high in organic materials that result in fouling, the chemical and/or physical cleaning and pre-treatment of feed should be investigated. With proper cleaning and pre-treatment, membranes would be viable for treating wastewater. Moreover, recent developments in membrane technology have introduced new membranes on the market that are more resistant to fouling while still able to remove certain contaminants such as hollow fibre NF for colour removal.

The emergence of advanced technologies is rapid due to the importance of treating pulp and paper mill wastewater. Contaminants can be reduced, and water reused through the combination of existing processes or hybrid technology, and novel technology such as biosorption, photo-catalysis, advanced oxidation via Fenton reagent, Filtration Assisted Crystallisation Technology (FACT), which are still in their initial stages of development. As these technologies are new, more research would be of interest to determine their applicability to paper recycling effluent and compatibility to other wastewater treatment processes. Thus, as mentioned, retrofitting is difficult for established plants due to space limits and potentially high capital expense. Therefore, it would be more reliable and lower risk to use well-researched technologies, technologies that are widely used commercially by pulp and paper plants such as enhanced coagulation and flocculation, or membrane filtration. As this thesis focused on these two promising technologies and comparing their performance and economic feasibility, this thesis could be used to plan a design for tertiary treatment specifically for the paper mill involved.

CHAPTER 3. MATERIALS AND EXPERIMENTAL METHODS

3.1. Wastewater samples

In this project, experiments were conducted in both Vietnam and Australia. Enhanced coagulation and flocculation using wastewater from the recycled paper mills was carried out in Vietnam. Due to Australia's border protection regulations, wastewater samples from Vietnam are not allowed into Australia, membrane related experiments were conducted in Australia on samples of untreated effluent obtained from a similar local commercial recycled paper mill.

Simulated biologically treated wastewater was produced by mixing the Australian mill wastewater with deionised water to reduce colour and COD values to 300-350 Pt-Co and 200-250 mg/L respectively, which are estimated values for Khoi Nguyen mill.

3.2. Wastewater characterisation and materials

3.2.1. Recycled paper mill wastewater and treated wastewater analysis

In this study, the influent flow rate, and the influent pollutants including TSS, COD and colour for individual processes were monitored against discharge standards and predicted for short-term and long-term changes, thus providing information to efficiently operate the treatment process.

Sample water were collected from various points from the wastewater treatment plant: (1) untreated wastewater from a collection tank; (2) after coagulation and flocculation; (3) after DAF; (4) after anaerobic treatment (UASB); (5) after aerobic treatment; and (6) after clarifier or final treated wastewater. The samples were monitored for colour, COD, TSS, hardness and temperature. All samples are assessed against the industry-specific standards given by the National Technical Regulation for industrial wastewater discharge outlined in Table 3.3. The final treated wastewater is categorised into two distinct grades, A and B. If the result is the same as the given value for grade A or B, the recorded parameter is classified accordingly. If the result is higher than the value given for grade A but still lower than of grade B, that parameter of the treated wastewater is classified as B. All investigated parameters need to achieve the same grade in order to be classified as that grade. For example, the effluent is classified as A grade when the final treated wastewater achieves all parameters achieve grade A values. If one out of all parameters were to achieve a different grade, for instance, colour falls under B grade, but all other parameters achieved grade A, the wastewater would be classified as grade B. If the value of a specific parameter for treated effluent is higher than the value given for grade B, the wastewater is deemed unsafe for discharge and further treatment is required by onsite treatment or by sending to a centralised treatment plant.

Hardness, colour and COD of wastewater were tested using various Hanna instruments as listed in Table 3.1 below. All test kits were supplied by Hanna Instruments unless stated otherwise.

Table 3.1. Equipment used for daily analysis of wastewater

Equipment	Use
HI 3812	Hardness
HI 96727	Colour
HI 83214	COD (0-1500 mg/L)
HI 839800	COD reactor and Test tube heater at 150 °C for 2 hours

The characterisation of wastewater with regard to the organic content is important from the standpoint of modelling, process design, control and prediction of treated effluent quality. Analytical parameters such as Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) are routinely used to reflect the total organics in wastewater.

3.2.2. Colour source identification

The system analysis revealed that colour is the biggest problem for An Binh paper. As mentioned above, wastewater samples from Vietnam are not permitted into Australia because of biosecurity concerns, experiments presented in this study were conducted in Australia on samples of untreated wastewater obtained from a similar commercial recycled paper mill. Information on the manufacturer and wastewater treatment processes regarding this commercial sample was asked to be kept confidential.

High performance liquid chromatography (HPLC) was used to detect traces of dye chemicals to ensure the same dyes were used in both mills. Untreated wastewater, UF permeate and NF permeate were analysed by size exclusion chromatography fitted with a TSKgel column. Instrument parameters are described in Table 4.2.

Table 3.2. HPLC parameters

Mod	Flowrate	UV wavelength	Total run time
Isocratic flow	1 mL/min	245	15 minutes

3.2.3. <u>Coagulant (PAC)</u>

Poly-aluminium chloride was preferred over other coagulants for various reasons. According to Gebbie (2001), PAC is non-disruptive to the pH. Variation in pH could affect the subsequent treatments in the system. This is because PAC consumes less alkalinity, especially compared to alum. PAC is also effective against a broader range of pH from 5-8 while other coagulants are pH sensitive. Another benefit provided by PAC is its ability to lower sulphate residues in the water. This reduces the colour and odour formation in the anaerobic treatment. PAC is also widely used across multiple industry, hence its commercial value at very affordable cost compared to its counterparts.

A commercial poly-aluminium chloride called PAC31 with the general formula $(Al_n(OH)_mCl_{(3n-m)})x$, containing 30wt% Al_2O_3 was used. A solution of 2.5% PAC31 was made by mixing 25 kg of PAC31 powder with water to make up 1 m^3 coagulation solution and used as coagulant. This solution was used in order to recreate its usage in An Binh and Khoi Nguyen mill.

3.2.4. Flocculant (PAM^-)

Although cationic polymers are good options for the flocculation of negatively charged fine particles, PAM (-) was chosen for its many advantages. Compared to PAM (+), PAM(-) is more appropriate as a flocculant for negatively charged particles due to the intramolecular electrostatic repulsion between the polymers, forcing the polymer chains to adopt a more extended conformation, increasing the efficiency of bridging flocculation (Vajihinejad et al., 2018). Polymer chains having nowhere to bind to, adsorb onto the neutral sites of the organic matters. The same PAM chains continue to adsorb onto surface of other particles, forming large aggregates. When organics' negative charge is neutralised by PAC, PAM chains have more particles to adsorb onto. PAM(-) was chosen because of its environmental friendliness over PAM(+). PAM(+) has a severely higher toxicity to aquatic life as it has a tendency to stick to fish gills (Kerr et al., 2014).

A commercial anionic polyacrylamide $(C_3H_5NO)_n$ called "Snowflake X1" supplied by Aquaplustech with solid content > 90%, charge density of 30 wt%, and molecular weight of 20 $x10^6$ g/mol was used. A solution of 0.1 wt% was made by mixing 1kg of PAM with water to make up 1 m^3 flocculation solution and used as flocculant. This solution was used in order to recreate its usage in An Binh and Khoi Nguyen mill.

3.3. Enhanced coagulation and flocculation experiments

As PAC adsorbs the colour or contaminants and PAM aids in building larger flocs from the PAC, improving the settling time, thus the PAC and PAM doses are optimised this way.

The effect of PAM(-) on PAC was firstly investigated in order to determine the optimal PAM(-) concentration for PAC. Various concentrations of 0.1 wt% PAM (-) were added after the coagulation with PAC. PAC concentration was kept constant. The experimental conditions are shown in Table 3.3.

Table 3.3. Experimental conditions for coagulation and flocculation experiment.

Samples	1	2	3
Sample size (mL)		1000	
PAC (2.5%) (mg/L)	25	25	25
Stirring time (min.)		5	
PAM (0.1wt%) (mg/L)	0.5	1	2
Stirring time (min.)		3	

The coagulation and flocculation experiments were carried out with 1 L wastewater at room temperature for each sample. The sample pH was adjusted from pH 6.5 to 7 by adding NaOH solution. Different ratios between PAC and PAM were examined with PAC added and stirred to initiate coagulation before the addition of PAM. In order to obtain the optimum amount of coagulant dosage, 1 mL to 10 mL of the 2.5% PAC31 solution, correlating to 25 mg/L to 250 mg/L PAC31 powder were used. The sample was stirred at a constant speed of 900 rpm for 5 minutes. This represents the residence time in a 14 m^3 commercial processing tank, which is used in An Binh and Khoi Nguyen mills. Optimal PAM(-) concentration was determined to be 1 mL/L of the 0.1 wt% PAM(-), correlating to 1 mg/L PAM(-) powder, from the previous experiment, which was added and stirred at 300 rpm for 3 minutes immediately after the 5 minutes of PAC stirring. This represents the residence time in an 8.5 m^3 commercial flocculation tank used in An Binh and Khoi Nguyen mills. The treated wastewater was then settled for 30 minutes and samples were taken from the water level around 5 cm below the surface for COD and colour analysis. Table 3.4 below shows the experimental conditions used in this study.

Table 3.4. Experimental conditions for the determination of the PAC concentration.

Samples	1	2	3	4	5	6	7	8	9	10
Sample size (mL)	1000									
PAC (2.5%) (mg/L)	25	50	75	100	135	150	175	200	225	250
Stirring time (min.)	5									
PAM (0.1wt%) (mg//L)	1									
Stirring time (min.)	3									

3.4. Membrane study

In this study, UF and NF were investigated for colour and COD removal. The membrane material, indicative pore size and direction of flow are shown in Table 3.5.

Table 3.5. Types, pore sizes and mode of action of membranes

Membrane types	Membrane material	Membrane pore sizes (μm)	Mode of operation
Scinor UF	Polyvinylidene fluoride (PVDF), hollow fibre	0.1	Outside-inside, dead end
Memcor UF	PVDF, hollow fibre	0.04	Outside-inside, dead end
Pentair NF	Polyethersulfone (PES), hollow fibre	0.0013	Inside-outside, cross flow

Membrane modules were built with membrane hollow fibres, nylon tubes as housing and pneumatic fittings. Membrane area was calculated based on outside diameter (OD) for both UF, and on inside diameter (ID) for NF.

Since NF fibres were visibly thinner than both UF, by identifying how many NF fibre would fit in the tube, the number of fibres needed for both UF can be worked out to create the same membrane area to NF. Membrane areas for both UF and NF were kept similar for easy comparison. With the same membrane area of 0.004 m^2, starting flux for all membrane modules was 15 LMH. The NF membrane test was performed under constant pressure mode (300 kPa pressure) in a cross-flow filtration configuration. On the other hand, the UF membrane test was conducted in a constant flux mode in a dead-end configuration.

The starting permeate flowrate was also kept similar between the membrane modules for fouling evaluation comparison. Thus, in order to obtain the desired starting flowrate, the starting pressures of each module were adjusted to achieve a permeate flowrate of 1mL/min. This permeate flowrate was chosen mainly because of the high pressure required for NF (300 kPa) to achieve such a flowrate. While NF can tolerate up to 700 kPa, during testing the maximum pressure allowed by the FMI "Q" pump was 400 kPa and this did not dislodge the pneumatic fittings and connecting tubing. Hence, the maximum operating pressure used was 400 kPa to work within the maximum operating pressure of the pump, and to ensure the fittings were leak tight.

For UF, since they required much lower pressure compared to NF, the required pressure to achieve 1 mL/min permeate flowrate was considerably less. For Scinor membrane, the starting pressure was 3 kPa while the starting pressure for Memcor was 7 kPa as Memcor pore size is slightly smaller than that of the Scinor membranes.

Each membrane module was then connected to data logging equipment for filtration data collection. Schematic drawings of the membrane testing systems are provided in Figures 3.1 and 3.2, in which the blue lines indicate feed and permeate flow, and the green lines show the flow of pressure and permeate weight information.

Preliminary tests were conducted to compare the performance of the different types of membranes used. Feed water was deionised water mixed with colour powder to produce feed water with colour value of 300 – 350 Pt-Co. To avoid influence from fouling, the initial 10 mL of permeate was collected from each test for colour measurement. Fouling can block off some pores and reduce permeability, hence would alter the true result of colour removal.

Untreated wastewater obtained from an Australian recycled mill with biocide added to prevent bacterial growth was diluted with deionised water to simulate biologically treated wastewater with colour ~ 300 – 350 Pt-Co. This wastewater was used as the feed for membrane colour and COD removal tests. This feed may contain more SS and DS compared to that from An Binh mill as it is directly diluted from untreated wastewater, thus may impact the membrane fouling.

As 70% of treated wastewater from Khoi Nguyen was contracted to be sent to a centralised treatment facility, the water recovery rate for the experiment was set for 30%. Briefly, for each filtration test, 200 mL of wastewater was used as the feed and the experiment would run until 60 mL of permeate was collected. The feed and permeate samples were collected and analysed for colour and COD.

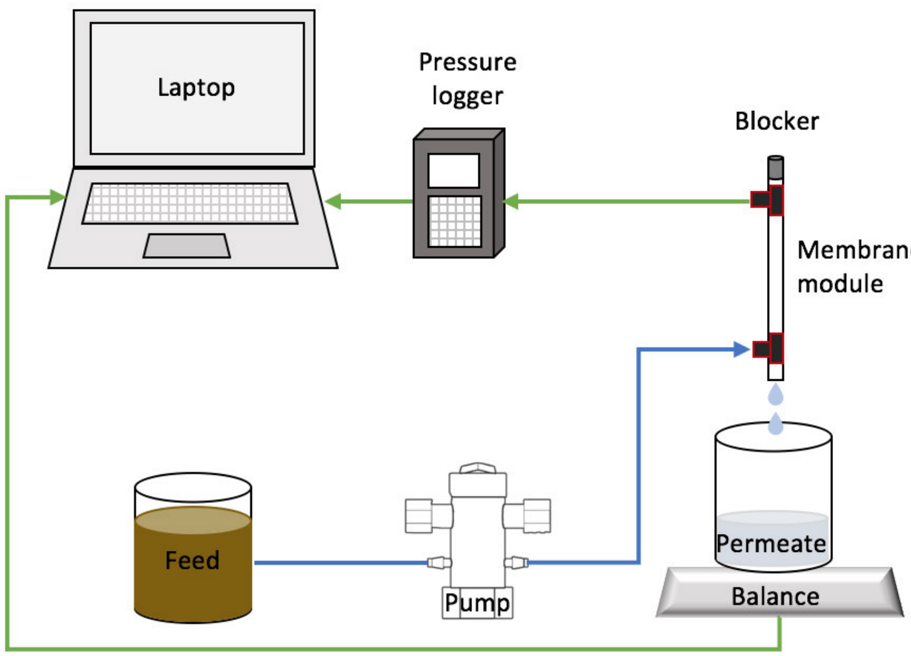

Figure 3.1. UF membrane rigs in outside-inside and dead-end mode.

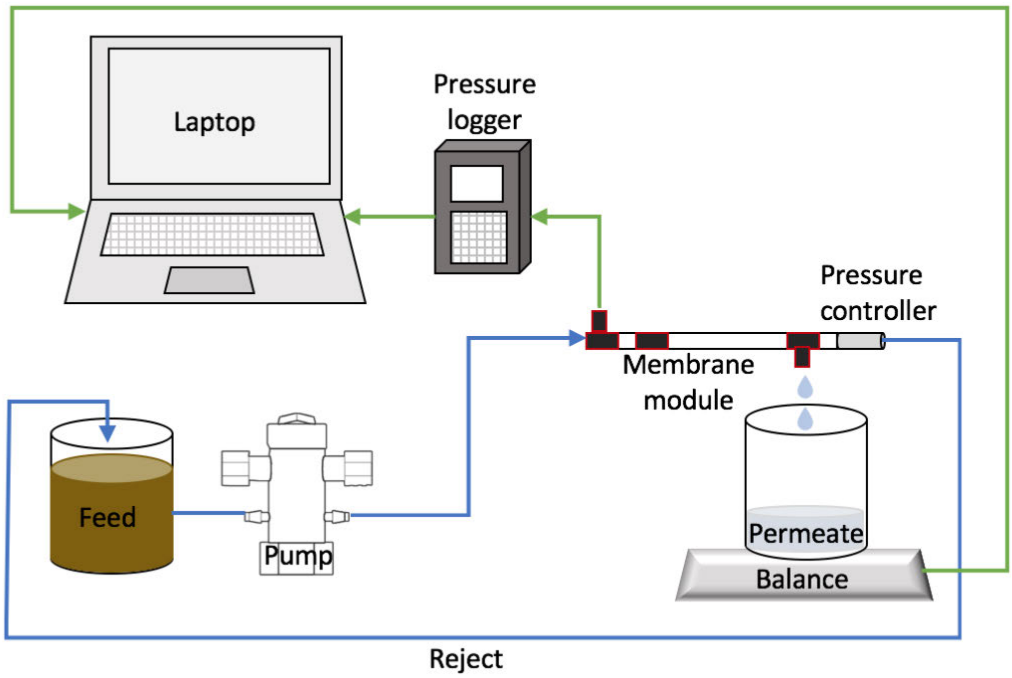

Figure 3.2. NF membrane rig in inside-outside and crossflow mode.

3.5. Membrane fouling study

One of the major drawbacks for membrane processes in wastewater treatment is its tendency to foul. Since UF and NF were used with different modes of filtration, fouling in UF was determined by the increase in pressure (kPa) with constant flux, while NF by the flux (LMH) decrease under constant pressure. Therefore, both UF and NF were tasked to filtrate 1 L of feed water until UF reached the maximum pressure allowed by the pressure pump (400 kPa) or NF experienced approximately 80% reduction of flux.

3.5.1. Membrane fouling identification

Fourier transform infrared spectroscopy (FTIR) Frontier by Perkin Elmer was used to verify the presence of foulants in UF and NF by comparing the fresh and fouled membrane FTIR spectra. Wavelength used was 500 nm ~ 4,000 nm.

3.5.2. Membrane cleaning

3.5.2.1. Chemical cleaning

In these experiments, UF and NF were cleaned with NaOH and citric acid to evaluate foulant removal efficiency of such chemicals. As recommended by literatures, 1,000 mg/L NaOH and citric acid were used in attempt to clean the membrane modules. New modules were used for each chemical. Thus, 2 UF and 2 NF modules were cleaned with NaOH and citric acid separately. Each test had 3 cycles where

1) Deionised water was run through the module first to establish a baseline for flux and pressure
2) Feed water was added and filtrated until 30% recovery rate was reached with the permeate collected and measured for colour and COD
3) Continue the filtration until the module reaches critical flux or maximum pressure allowed by the pump
4) Clean membrane with NaOH or citric acid for 15 minutes using Clean-In-Place (CIP) technique, which is soaking the membrane in the cleaning solution
5) Flush the module with deionised water for 10 minutes to remove excess cleaning solution and foulants
6) Run deionised water to re-establish baseline for flux and pressure
7) Repeat from step 2 to 6 (second cycle)
8) Repeat from step 2 to 5 (third cycle)

Similar tests using the same steps were carried out using 500 mg/L NaOH and Citric Acid, and 1,500 mg/L NaOH and citric acid to determine the effect of low and high concentration of alkaline and acid cleaning on membrane performance.

3.5.2.2. Mechanical cleaning – Backwashing

In this study backwashing was used as an alternative for fouling control. Two UF modules were used. The first one was run with deionised water first followed by filtrating until a critical pressure was reached (400 kPa). This process was repeated once using the same method without backwashing to distinguish any difference in the fouling rate. The fouling point (80 kPa) where the pressure starts to increase drastically was determined during this test. The second module was used for the backwashing test using these steps:

1) Filtration with DIW to establish baseline pressure
2) Filtration with feed water until the pressure reaches the fouling point (80 kPa) and record the pressure changes
3) Backwash with permeate for 3 minutes
4) Repeat steps 2 to 3 nine times

3.5.3. Feed pre-treatment

As an attempt to control fouling, an investigation on whether pre-treatment would prevent or reduce the fouling was made. A commercial Fast Floc was used instead of PAC31 from Vietnam, as it could not be brought into Australia. Consequently, 20 µl was used to treat 1 L of wastewater as recommended on the label since no other information regarding PAC strength or Al2O3 concentration was provided.

A 3L sample of wastewater was split into 3 equal 1 L beakers. HCL and NaOH were used to adjust pH to 7 before the addition of different doses (40 µL, 20 µL, 10 µL) of Fast Floc in labelled beakers. The dosed samples were then stirred for 3 minutes. Once the flocs had settled, filter 20 mL from each beaker to measure colour and COD. The wastewater dosed with 20 µL was then used as feed water for a UF filtration. Permeate was collected and measured for colour and COD once 30% water recovery was reached, but filtration continued until the module reaches the maximum pressure allowed.

CHAPTER 4. WATER CIRCUIT ANALYSIS AND WASTEWATER TREATMENT OF AN BINH AND KHOI NGUYEN COMMERCIAL RECYCLED PAPER PLANT

An Binh paper mill produces less paper but uses more fresh water compared to its newly established sister mill – Khoi Nguyen. With the increase in production, Khoi Nguyen processes almost double the amount of wastewater a day. However, with the increasing price of fresh water supply and demand in conserving the precious water resource, Khoi Nguyen aim to further reduce their fresh water consumption. Hence, the objective of this Chapter is to provide background information on the two paper mills and identify opportunities for water recycling for Khoi Nguyen based on An Binh's existing wastewater treatment plant.

The reuse of wastewater for different steps in the overall production process depends on the quality of the treated water as well as the treatment cost that would bring great economic benefits to the company. In a typical paper mill, the cost for fresh water supply and wastewater discharge accounts for about 10% of production cost. With acceptable technology, the reduced cost of fresh water consumption and effluent discharge fees could help save up to 35% of process water cost in the long run. In order to achieve this, a series of elements at the mill such as the design of the wastewater treatment system, points of water input and output, the quality of treated water and the local discharge standards for effluents were taken into consideration.

4.1. Khoi Nguyen plant water circuit

Khoi Nguyen, despite being a newly established sister factory of An Binh, has a bigger production capacity, processing up to 4,000 m^3 of wastewater per day. Khoi Nguyen's water circuits are shown in Figure 4.1.

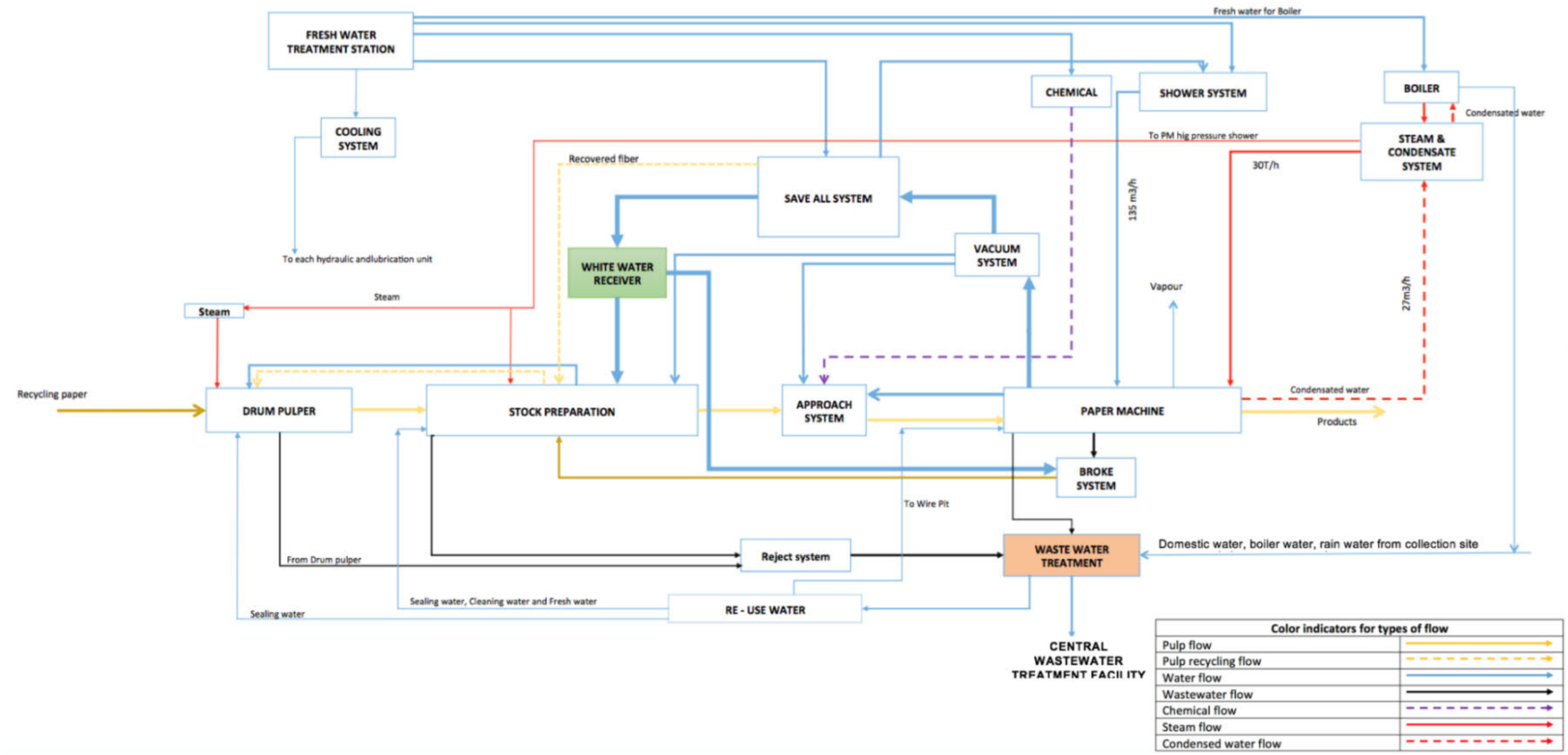

Figure 4.1. Khoi Nguyen water circuits. Illustration by courtesy of Khoi Nguyen Paper Ltd.

Compared to the water circuits proposed by Blanco et al. (2015) in Figure 4.1, Khoi Nguyen water circuits bare many similarities. The primary circuit can be depicted through the water (blue arrows) exiting the paper machine and being sent directly to the system for pulp consistency and flow control. The yellow arrows show the stock stream, which describes the collection of recovered paper, pulping, stock preparation, pulp transformation into final paper products after going through the paper machine, and a fibre recovery stage (yellow dotted arrow) occurs at the save-all system. The fresh water is supplied from the fresh water station to the paper machine. The whitewater drains from a wet sheet of paper in the forming section and is subsequently treated at the save-all unit and reused for stock preparation along with the fibre recovery step and the shower system. These streams make up the secondary water circuit. The tertiary water circuit includes used process water from all stages of paper production including pulping, stock preparation, reject system, blowdown water from boiler and water for domestic use. These streams are sent to a wastewater treatment system. The reuse of treated wastewater makes up the tertiary water circuit.

The wastewater treatment system design is similar to that of An Binh with some enhanced modifications. The difference is that Khoi Nguyen considers a tertiary treatment process as an option to further remove colour, which is a main concern for Khoi Nguyen. This will be discussed in the subsequent water balance analysis section to achieve a reduction of fresh water consumption from 10 m^3 to around 6 m^3/tonne product

4.2. Wastewater treatment systems of the two recycled paper mills

With a manufacturing capacity of 75,000 tonnes per year, An Binh Paper produces around 2,000 m^3/day wastewater. Along with increased productivity, An Binh has also managed to reduce their fresh water usage by having an effluent treatment plant on-site to treat and recycle some of the wastewater. Their treatment system flowsheet, which is shown in Figure 4.2, is comprised of primary and secondary treatment, implementing coagulation and flocculation treatment, DAF, anaerobic and activated sludge treatment.

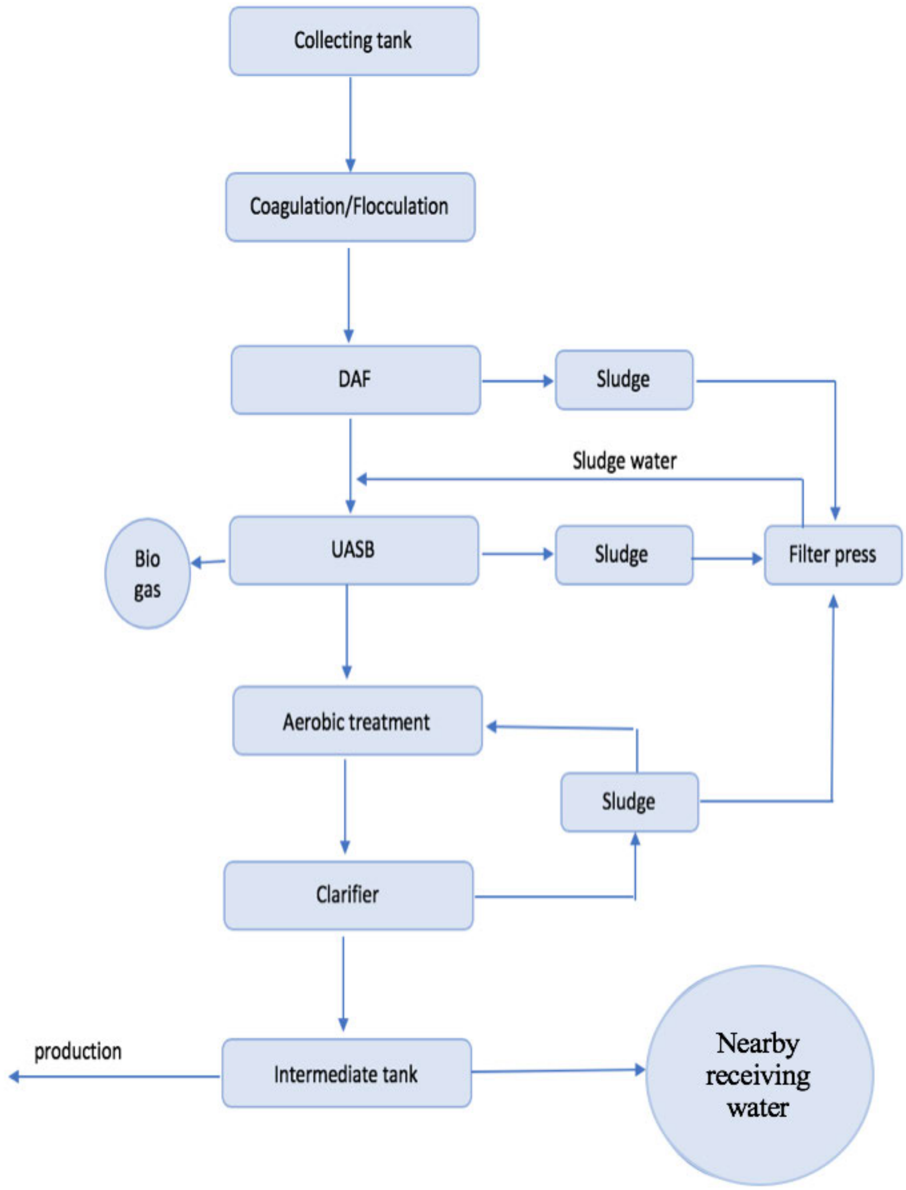

Figure 4.2. An Binh's wastewater treatment system

Compared to An Binh's wastewater treatment system, Khoi Nguyen has some improvements. A screen and equalisation basin are added before the coagulation and flocculation step to increase the efficiency of the treatments. The screen aids in pre-treating the wastewater, and removing any visible contaminants that are large in size. The equalisation basin performs pH and temperature control, maintaining the optimal condition for coagulant and flocculant in the chemical treatment process, and microbes in the biological treatment process. Due to colour being a concern for the An Binh mill, as their wastewater treatment plant fails to consistently meet the discharge standard for colour, an enhanced or tertiary treatment process is to be implemented after the biological treatment for Khoi Nguyen wastewater treatment system to ensure the same problem will not happen for this plant. The wastewater treatment system of Khoi Nguyen is outlined in Figure 4.3.

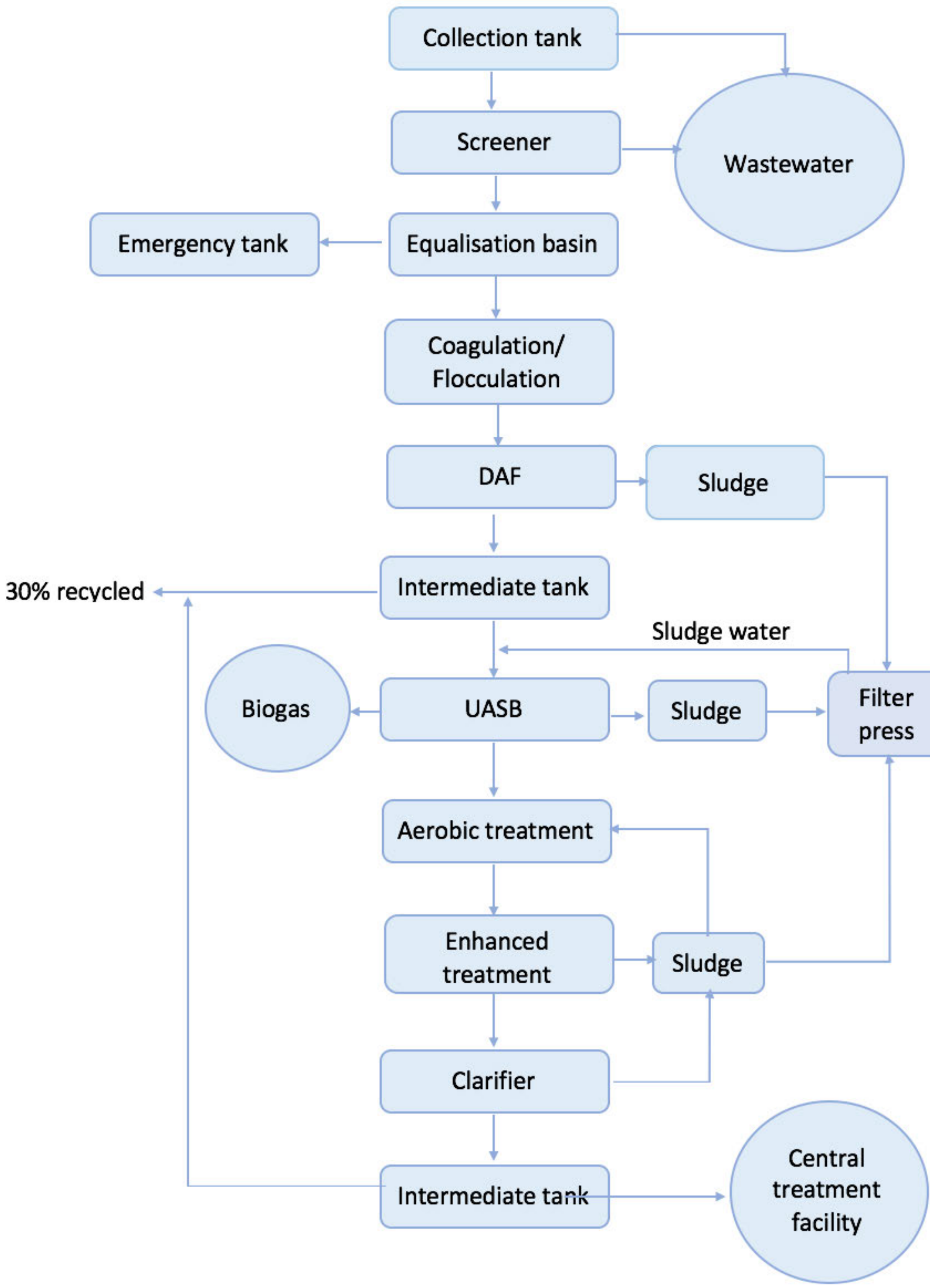

Figure 4.3. Khoi Nguyen's proposed wastewater treatment system

4.3. Individual processes for wastewater treatment plant

4.3.1. Operation units for physical/chemical treatment

Screens: screens with a uniform in size are equipped to remove large floating materials and suspended particles. The process of screening can be carried out by passing wastewater through different types of screens with different opening sizes.

Equalisation basin: provides a consistent influent flow downstream by regulating the flow, pH and temperature of wastewater. It is designed to store the volume of water generated during peak hours or when the system needs to stop for repair and maintenance. The basin has a submersible aeration system to avoid settlement of sediment and anaerobic processes causing odours, and to stabilise the concentration of wastewater before passing it through to the next treatment stages

Coagulation-Flocculation: Wastewater from the equalization basin is pumped to the coagulation tank, where a coagulant such as poly-aluminium chloride (PAC), is dosed in through a metering pump. PAC has a higher coagulation efficiency than alum, does not cause fluctuations in pH, produces less sludge, reduces TDS and leaves no residual sulphate in the water treatment system. Effluent from the coagulant tank then continues onto the flocculant tank. The chemical used in this process is polyacrylamide (PAM). The coagulation/flocculant process forces suspended solids to form larger particles, improving the efficiency of the next treatment stages.

Dissolved Air Flotation (DAF): DAF separates the flocs produced in the previous process from the wastewater. Small air bubbles are introduced into the system to form bubble-particle agglomerates with density less than water. This mechanism causes the particles to float to the surface for collection, and pumped to a sludge collecting tank. Particles with higher densities will settle to the bottom and are removed after intermittently for further treatment.

Intermediate tank: provides an option for reuse of wastewater treated by DAF.

4.3.2. Biological treatment

Upflow Anaerobic Sludge Blanket (UASB): Wastewater is distributed into the tank from the top of the UASB. The wastewater then moves upwards through the sludge. The dense sludge layer allows handling of organic matter at high loads, and in addition the biomass content also remains high. An outstanding feature of the UASB is that the system is capable of gas-liquid-solid phase separation. The treatment begins when the effluent flows through the sludge layer. Sludge-bearing wastewater, combined with gas bubbles rises above into the three phases separator from which the sludge will fall back into the sludge layer and the gas is collected, and the treated wastewater flows to the next process. Biogas is collected and burned, residual sludge is pumped to the sludge collecting tank.

Aerobic Treatment Tank: Air is provided to mix activated sludge and wastewater, and to give oxygen to aerobic bacteria to encourage the digestion of organic compounds. Aerobic microorganisms are added prior to treatment to create a healthy concentration of bacteria to process the residual organic materials from the anaerobic stage. Part of the biomass is retained to keep the balance of bacteria and organic loads while the rest is transferred to a sludge collection tank. These aerobic microbes would need nutrients, primarily nitrogen and phosphorous to reproduce and function. Anaerobic bacteria require less nutrients as they produce less sludge than their aerobic counterparts.

4.3.3. Operation units for tertiary treatment

Enhanced treatment: as will be discuss later, the most viable option is enhanced coagulation and flocculation.

Clarifier/ Settling tank or Sedimentation tank: Holds and separates the mixture of sludge and treated wastewater by letting the sludge settle to the bottom. Parts of the biomass will be recirculated to the aerobic tank to maintain the biomass level while the rest is pumped to a sludge collection tank, where it will be sent to the filter press for dewatering. Dewatered sludge is sent for disposal while sludge water is introduced to UASB for further treatment. The treated water will then go on to another intermediate tank, either to be reused or discharged.

As mentioned, treated wastewater from various points of the treatment system is recycled back into production. Currently, effluents after coagulation and flocculation process and DAF will be reused. Treated water is transferred to an intermediate tank as the final step either to be reused as cleaning water or sealing water for hydraulic press machines, drum pulpers, stock preparation and paper machines, or released into the receiving water body, which is shown in Figure 4.2.

4.3.4. Discharge requirements

It is a common requirement for all mills to meet the local or national effluent discharge standards. These standards vary from country to country and even state to state, depending on where the treated effluent would be discharged. In Vietnam, depending on the quality of treated waters, they can be discharged into a receiving water system (drainage system of urban areas, rivers or coastal water), or can be sent to an external system for further treatment.

The National Technical Regulation (Ministry of Natural Resources & Environment, 2011) is specific for every industry and depends on the discharge rate (K_f) coefficient and the receiving waters coefficient (K_q). Contaminant targets for An Binh and Khoi Nguyen treated wastewater against discharge standards are depicted in Table 4.3.

The maximum value for industrial wastewater discharge permitted can be calculated following the formula $C_{max} = C \times K_q \times K_f$

- C_{max} is the maximum permissible value for effluent being discharged into receiving waters
- C is a pollution parameter value given in Table 4.3.
- K_q is the receiving waters coefficient which indicates the flow rate the receiving waters. (For Khoi Nguyen, $K_q = 0.9$)

- K_f is the receiving waters flow rate coefficient which indicates the total flow rate of wastewater being discharged in receiving waters (For Khoi Nguyen, K_f = 1)

K_q and K_f can be determined following criteria given in Table 4.1 and 4.3.

Table 4.1. Kq value for different receiving waters flowrates.

Flowrate of the receiving water body (Q) (m^3/s)		K_q
$Q \leq 50$		0.9
$50 < Q \leq 200$		1
$200 < Q \leq 500$		1.1
$Q > 500$		1.2

Table 4.2. Kf value for different discharge water flowrates

Volume of discharged water (m^3/24h)	K_f
$F \leq 50$	1.2
$50 < F \leq 500$	1.1
$500 < F \leq 5000$	1
$F > 5000$	0.9

When measuring temperature, colour, pH, coliform, gross alpha activity and gross B activity, Kq and Kf are not applicable so Cmax = C.

Table 4.3. Values of parameters for wastewater discharge (C) of An Binh and Khoi Nguyen.

No.	Parameter	Unit	Value (C)	
			An Binh (Grade A)	Khoi Nguyen (Grade B)
1	Temperature	^oC	40	40
2	Colour	Pt-Co	50	150
3	pH	-	6-9	5.5-9
4	BOD_5	mg/L	27	45
5	COD	mg/L	65.5	135
6	Suspended solids	mg/L	45	90

4.4. Daily analysis of An Binh wastewater

In this study, the influent flow rate, the influent pollutants including TSS, COD and colour for individual processes are monitored against discharge standards and predict for short-term and long-term changes thus providing information to efficiently operate the treatment process. Although the quality of treated effluent is monitored daily by the factory, the measurements only include the parameters according to discharge standards. Industrial wastewater treatment plants do not usually measure the water quality parameters of their influents for individual processes. Thus, in this research the quality of treated wastewaters and associated parameters from individual processes were monitored in this study to make data suitable for analysis. The methods are described in Chapter 3, including:

- Monitoring and predicting the pollutants in wastewater to provide information to select physical/chemical and biological control strategy.
- Forecasting the plant influent flows to provide useful influent flow information to plant management.
- Pollutants, such as total suspended solids (TSS), colour and COD in the wastewater are correlated to the influent flow. The treatment process is then be adjusted accordingly to the pollutant concentrations in the influent.

Wastewater treatment involves complex physical, chemical, and biological processes, understanding the relationships among the parameters of the individual process is an important step to identify problems and improve system performance. An analysis of the wastewater system was conducted as the primary experiment, showing the input and output of individual processes used in the wastewater treatment plant. The influent flow rate, the influent pollutants including TSS, COD and colour for individual processes were monitored against discharge standards and were used to predict short-term and long-term changes thus providing information to efficiently operate the treatment process. This allows for identification of water recycling or lack thereof according to the analytical results. Thus, in order to further improve the treatment process, various technologies are implemented into the current wastewater treatment system, enabling the assessment of their efficiency and financial viability. Suitable technology is then determined based on its performance in treating the wastewater, hence its wastewater quality, and the economic benefits it brings.

4.4.1. Effluent quality

4.4.1.1. COD

The BOD_5/COD ratio for An Binh wastewater was approximately 0.7, indicating high biodegradability.

Figure 4.4 presents average COD values at each point of the wastewater treatment process monitored for a period of 5 days. The yellow dotted line in Figure 4.4, 4.5 and 4.6 represents grade B target (target grade for Khoi Nguyen) while green dotted line displays the target for grade A (target grade for An Binh). Depending on the requirement of the paper products and recovered materials, chemical dosing and dyes added vary from time to time, resulting in a large variability for influent readings seen in Figure 4.4. Since coagulation and flocculation work by forming flocs of contaminants instead of physically removing them, COD slightly increased and the variability remained large during the coagulation and flocculation process. The variability for stage (3) where solids are separated from liquid was small, indicating the performance of PAC and PAM used in stage (2) was stable and often produced similar results. The liquid from DAF is then anaerobically treated (stage 4). The majority of COD removal occurred at this step of the wastewater treatment system. Aerobic treatment (stage 5) succeeded in further reducing the COD value from stage (4) to grade B with COD < 135 mg/L. From stage (4) to stage (5), there was a 94.5% COD reduction. At the final stage (6), COD was well below the target for grade A.

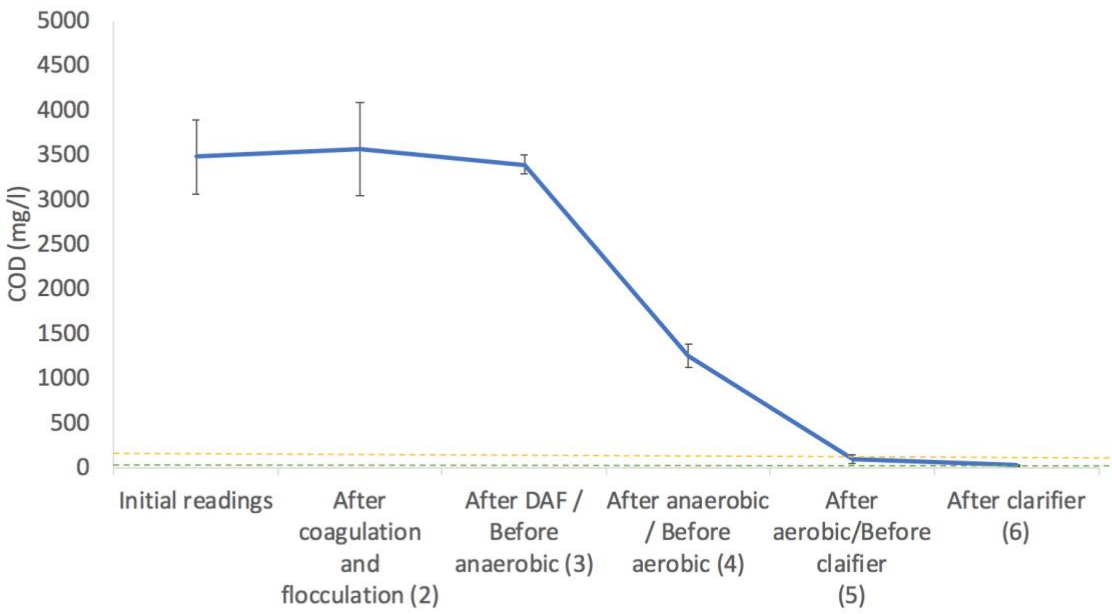

Figure 4.4. COD values at each point of the wastewater treatment process.

4.4.1.2. Colour

Similar to the initial COD values, input colour values also varied greatly. There was a 10.4% reduction in colour after effluent was treated with coagulant and flocculant. Following DAF treatment and before biological treatment, the colour values were similar and showed minimal difference. Unlike COD, colour slightly increased after anaerobic treatment (4). Milestone et al. (2004) confirmed that when anaerobic conditions precede an aerobic system it initiates an increase in colour. This is because organic matters were being broken down, releasing dissolved carbon compounds, giving rise to more colour in the wastewater. Another explanation for the increase in colour is the production of sulphide under the presence of sulphate reducing bacteria (Paulo et al., 2015). These sulphide precipitate with metals, forming metal sulphide salts that are coloured. Sulphate reduction also creates hydrogen sulphide gas, which is known for its "rotten egg" smell. Hence, depending on the COD load, colour at stage (4) fluctuates accordingly. Despite that, the majority of colour was removed at the aerobic treatment stage (5) with little variation post the aerobic treatment process. At the last clarifying step, the results were on either side the green dotted line, illustrating colour removal did not always successfully achieve grade

A. Colour can cause unwanted aesthetic in receiving water bodies and might transfer onto the paper products if the wastewater is recycled.

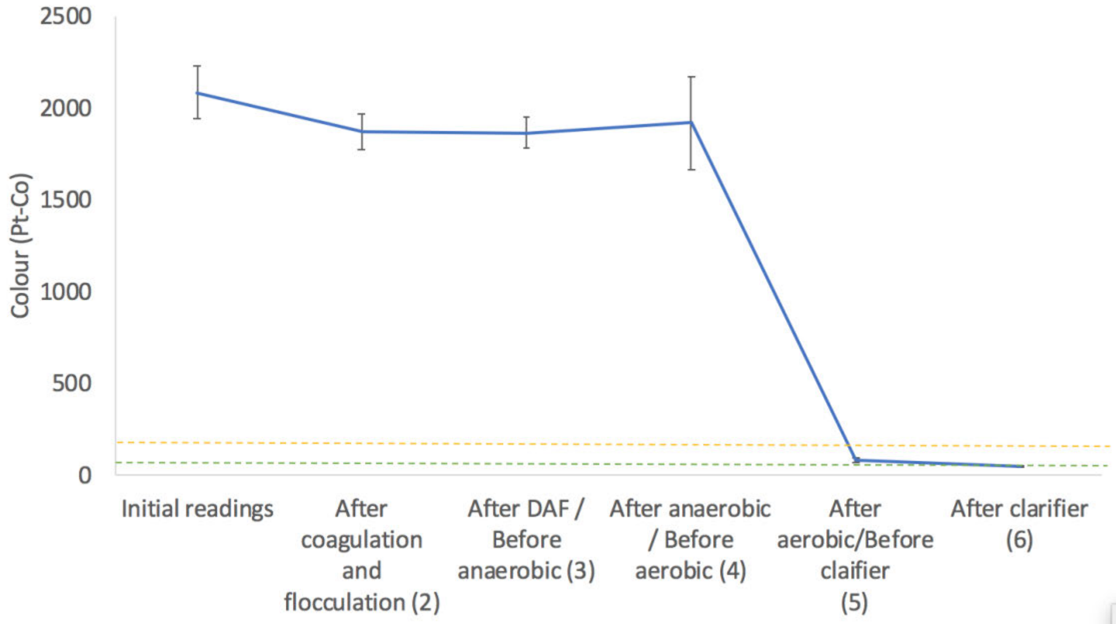

Figure 4.5. Colour values at each point of the wastewater treatment process

4.4.1.3. Total suspended solid (TSS)

The TSS feed concentration also fluctuated. TSS was significantly removed by DAF, while biological treatment on the other hand increased TSS. This is because biological treatment produces sludge, contributing to the elevation of TSS. If the initial TSS value is high, the sludge value for biological treatment will also be high. Aerobic treatment is known to produce more sludge than its counterpart anaerobic treatment, hence the rise in TSS was much bigger compared to that of anaerobic treatment. This explains the increase in TSS and decrease in COD (Figure 4.4) and colour (Figure 4.5). Organic matter remained after the anaerobic process were broken down and consumed by aerobic microbes to form sludge. Also, since the majority of TSS is attributable to organic matter, a low level of it indicates a low COD. Sludge is separated from the wastewater stream by a clarifier. The removal of TSS is fundamental due to TSS being problematic. Not only the accumulation of TSS causing clogging of equipment and piping, and it also promotes unwanted bacterial growth. TSS could also contribute to the deterioration of water quality, increasing the cost for effluent treatment.

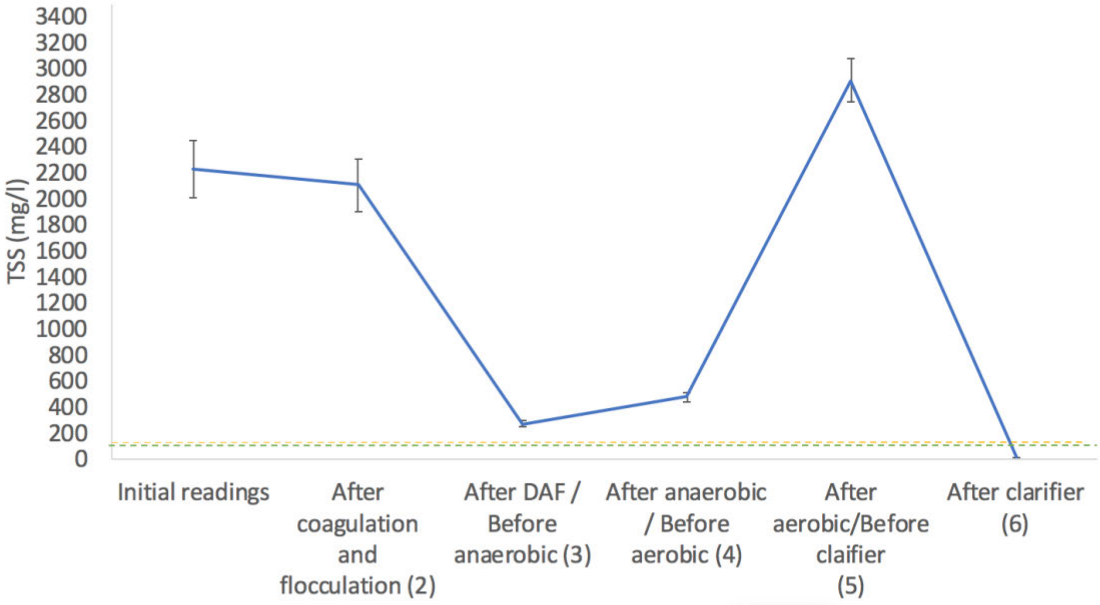

Figure 4.6. Total suspended solids values at each point of the wastewater treatment process.

4.4.1.4. Hardness

Hardness is not a normative indicator, but still important in water recovery as hard water could cause damage to equipment and the quality of the paper products if treated wastewater is recycled. High concentration of calcium and magnesium salts contribute to the hardness of water when water is reused. Calcium ions (Ca^{2+}) are more prevalent in recycling paper mill wastewater as abundant calcium carbonate can be found from filler and coating pigment in recycled materials (Kim et al., 2003). Thus, more than half of the dissolved inorganics is accountable to Ca^{2+}. Efficiency of polymer additives is reduced via competition between them and Ca^{2+}, as Ca^{2+} adsorbs on cellulose fibre surfaces. Moreover, scaling can occur due to the precipitation of calcium carbonate, which reduces the life of equipment, and increases the expense for un-clogging pipes.

Since the binding strength and sorption capacity of Ca^{2+} is in direct proportion to the pH level, Ca^{2+} can be reduced and scaling can be avoided by regulating the pH. As can be seen in Figure 4.7, the hardness of wastewater did not vary until it went through the anaerobic treatments, in which there was a drastic reduction in hardness. This is because the pH and hydraulic retention time (HRT) of the UASB reactor is favourable for calcium carbonate precipitation. These precipitates are subsequently discarded with sludge waste. Similarly, the same trend can be observed for the aerobic step, where constant aeration is involved that subsequently outgasses CO_2 and raises the pH level.

Similar trends can be observed for COD (Figure 4.4), colour (Figure 4.5), and $CaCO_3$ (Figure 4.7) throughout the whole wastewater treatment process. This is because the dyes used in the recycled paper mill are organic dyes, thus a similar removal trend with COD removal were observed. For COD and $CaCO_3$ removal trends, the similarity was because the biological treatment was efficient in removing organic matters, and the increase in the pH level in the anaerobic digester induced the precipitation of Ca^{2+}. $CaCO_3$ was then removed and discharged with anaerobic sludge.

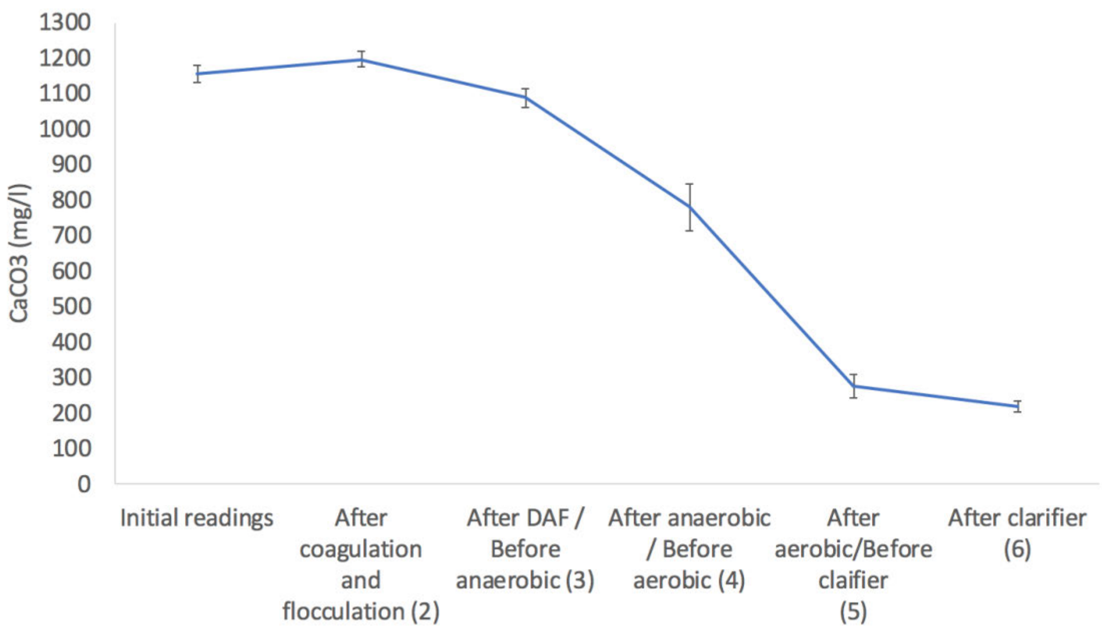

Figure 4.7. Hardness values at each point of the wastewater treatment process

4.4.1.5. pH

While the pH range observed in this study does not directly interfere with the final paper product quality, it effects some individual wastewater treatment processes. For example, as mentioned in section 3.4.1.1, pH influences calcium carbonate precipitation in the UASB process, aiding in the removal of said inorganic salts. In addition, microbes involved in the biological treatments are also pH sensitive (Kang, 2009). Bacterial behaviour can be greatly impacted when the pH is too low (<6.8) and high (8.2), or when there is a sudden increase or decrease in pH. Kang (2009) stated the optimal pH for aerobic bacteria is around 7-7.8, while for the anaerobic bacteria is 6.8-7.2. Lower or higher than the given pH ranges and the beneficial microbes might either die and give rise to harmful bacterial growth, or be inefficient in breaking down organic matter.

Moreover, the efficiency of added chemicals such as coagulant and flocculant rely on the pH level of water. Variations in pH value result in coagulation process suffering from less than optimum ions being formed in solution. Coagulation process cannot proceed at low pH, and coagulated particles are susceptible to redispersion at high pH. pH also affects the size of the coagulated particles, which in turn impacts the density of flocs formed by flocculants and their tendency and ability to settle. Since there are many coagulants and flocculants ready for commercial used, the optimum pH for them varies (Saritha et al., 2015). pH control, therefore, is specific to each application and depends on the water sample, coagulant and flocculation agents used, and targeted water quality. In this study, the coagulant used was PAC31, which can used in a wide range of pH from 6 to 9. The flocculant used was anionic PAM (PAM-), which has effective pH values between 5-14. From Figure 4.8, pH values were compatible for the coagulation and flocculation process, and the biological treatments.

Correspondingly to the trend for hardness seen in Figure 4.7, pH levels increased for the biological treatments. The anaerobic treatment involves a CO_2 stripping step, which encourages the precipitation of $CaCO_3$, which can easily be removed later along with sludge produced in this stage. Similarly, the aerobic treatment provides aeration that outgasses CO_2. Precipitated $CaCO_3$ in this treatment is once again removed with sludge waste. When there is less CO_2 present in the water, less carbonic acid is created, lowering the amount of hydrogen ions and bicarbonate ions, which increase the pH level when carbonic acid dissociates (Kim et al., 2003).

According to Figure 4.8, pH level changes slightly for all samples and tests. The decrease in pH after coagulation and flocculation was due to the acidic property of PAC. The pH in the anaerobic process was initially decreased with the production of volatile acids. However, as methane-forming bacteria consume volatile acids, alkalinity is produced and the pH of the digester increased and stabilised (Flanders, 2021).

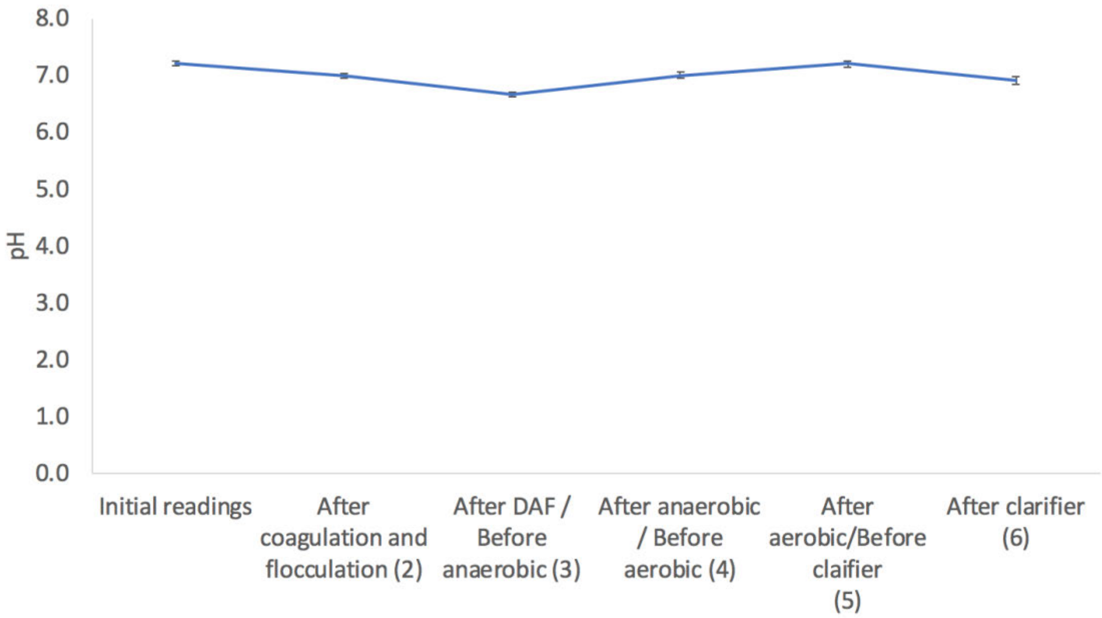

Figure 4.8. pH values at each point of the wastewater treatment process.

4.4.1.6. Temperature

According to Figure 4.9, temperature experienced no significant variation. No cooling towers were needed for the wastewater treatment plant as the temperatures were around 30-35°C in this location of Vietnam, and it corresponds to optimal anaerobic and aerobic organisms' performance (Samer, 2015). Lower or higher temperature would disrupt biomass growth and viability. If this were to occur, treated COD values would increase as biological treatments are now inefficient or don't have sufficient bacteria to break down organic matter at the same rate. Similar results were showed by Tejaswini et al. (2019). Since the targets for both grade A and B are 40°C, the treated wastewater temperature complied with discharge requirement throughout the whole treatment process.

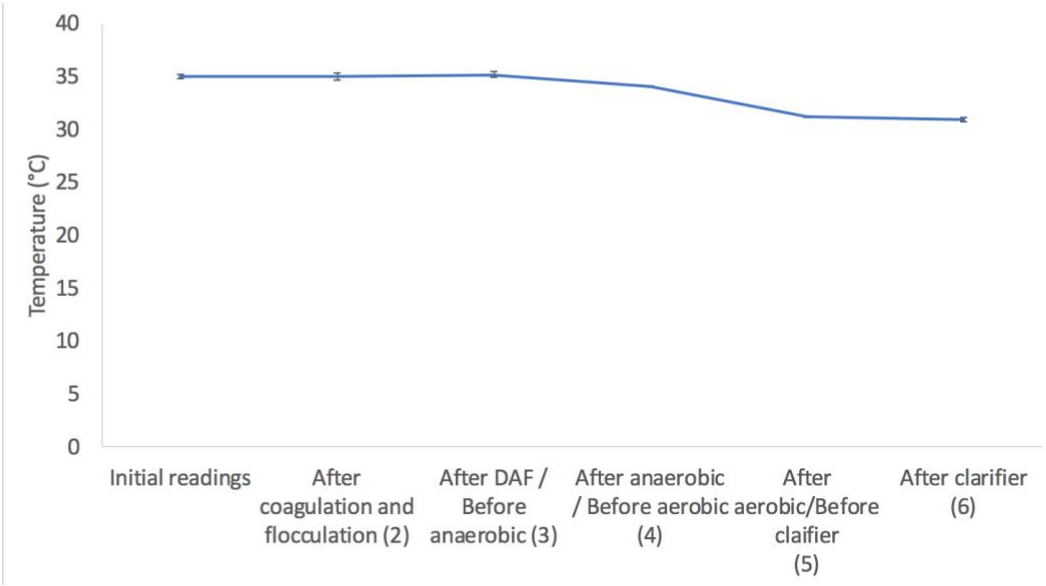

Figure 4.9. Temperature values at each point of the wastewater treatment process.

From a discharge perspective, temperature is a control parameter like pH. In wastewater treatment process, temperature is an important parameter. It effects the reaction kinetics and dissolved oxygen in aerobic process. For example, temperature can influence the reaction rate of molecules (Key, n.d.). The kinetic energy of the reactant molecules will be raised by the increase in temperature. Thus, a greater amount of the molecules will now have enough energy necessary for an effective collision. Therefore, reaction between chemicals will be accelerated under higher temperature. Tejaswini et al. (2019) mentioned an increase in temperature resulted in enhancement in SS removal as high temperature lowers the viscosity, hence increases the settling rate. This is important in determining the size of the retention unit as it one of the determinations for how long the water needs to be kept in the unit after coagulant and flocculant are added.

Relating to reaction kinetic and temperature, less dissolved oxygen is present in water when the water temperature is high as molecules are moving faster, thus allowing oxygen to escape from the water. The higher the liquid temperature, the lower the oxygen transfer rate would be. This is because high temperatures result in a lower gaseous (oxygen) solubility and lower solute viscosity due to higher kinetic energy, leading to a smaller driving force, and hence to a lower oxygen transfer rate (OTR). On the other hand, the diffusion rate of oxygen increases with increasing temperatures, while the liquid viscosity and surface tension decrease. These effects may offset the smaller driving force arising from the lower oxygen solubility. Oxygen is fundamental during the aerobic treatment process as the bacteria rely on the presence of oxygen to survive and perform degradation of organic matter. Thus, it is important to ensure the oxygen supplied should be the same as the amount or more as consumed by the bacteria.

4.4.2. Effluent quality for An Binh mill

A summary of the average data of An Binh wastewater system's performance collected over 14 days using daily samples and the average efficiency of each treatment steps, are provided in Table 4.4.

Table 4.4. Average values of An Binh's treated wastewater quality collected over 14 days using daily samples.

	Initial readings (1)	**After coagulation and flocculation (2)**	**After DAF (3)**	**After anaerobic (4)**	**After aerobic (5)**	**After clarifier (6)**	**Efficiency**
COD (mg/L)	3475	3563	3386	1247	93	24	99.31%
Colour (Pt-Co)	2088	1871	1868	1922	84	49	97.65%
TSS (mg/L)	2231	2106	275	479	2911	20	99.10%
Hardness ($CaCO_3$ mg/L)	1155	1197	1088	780	276	218	81.11%
pH	7.2	7	6.7	7	7.2	6.9	
Temp. (^oC)	35	35	35	34	31	31	

Variation of data is indicated by the error bars in figures showing the values for each treatment stage. Fluctuation in the data collected can be seen Section 4.4.1. All parameters achieved grade A, except for colour, which occasionally fell to grade B, thus colour poses a major concern for the mill. Since Khoi Nguyen aim to operate on less freshwater (6 m^3 freshwater/tonne product) compared to An Binh (10 m^3 freshwater/tonne product), contaminant inputs would be significantly higher per volume of water used and some parameters might not even achieve grade B, which is the target grade for Khoi Nguyen. Thus, tertiary or enhance treatment is required unless individual process can be improved to ensure all parameters meet the mill's discharge targets, especially colour. The new treatment must have a suitable colour removal efficiency and cost-efficient.

Assuming the treatment efficiencies are similar to that achieved by An Binh plant, for Khoi Nguyen plant, the COD and TSS of treated effluent would meet the desired discharge standards but the colour might exceed the value required for a grade B treated effluent. Predicted Khoi Nguyen effluent parameters are shown in Table 4.5. Predictions are made using the lowest and highest values obtained from the final wastewater treatment stage during the daily monitor of An Binh's wastewater treatment plant over the 14 days. These values were doubled as Khoi Nguyen mill has bigger production and produces twice the amount of wastewater a day compare to An Binh.

Table 4.5. Predictions for Khoi Nguyen effluent quality.

	Predicted values	**Target discharge standard (Grade B)**
COD (mg/L)	37 - 58	<135
TSS (mg/L)	23 - 61	<90
Colour (Pt-Co)	66 - 141	<135
pH	6.5-7	<5.5-9

Furthermore, based on the wastewater plant design for An Binh and the parameters given in Table 4.4, the treatments could be categorised into:

1) Primary treatment that includes coagulation and flocculation, and DAF that treats roughly 3%, 11% and 88% of COD, colour and TSS respectively.
2) First stage of secondary treatment with UASB that remove 63%, 8%, 79% of COD, colour and TSS respectively after the primary treatment.
3) Second stage of secondary treatment that involves the activated sludge treatment removes colour, COD and TSS by 98%, 99% and 99% respectively following anaerobic treatment.

In the case of high influent loads, Khoi Nguyen influent values were estimated to be 6,000 Pt-Co, 8,430 mg/L and 6,800 mg/L for colour, COD and TSS respectively, using An Binh's highest values for mentioned parameters obtained from the daily plant monitor over 14 days as a reference. Hence, the effluent colour, COD and TSS values would achieve values of 141 Pt-Co, 58 mg/L and 61 mg/L respectively. Based on this assumption, only colour in the final effluent is expected to fail to meet grade B standard when there is a high influent load. Moreover, as organic dyes will be used in Khoi Nguyen, the colour residues will contribute to COD in wastewater and based on COD analysis of colour solutions of 300- 350 Pt-Co, the input colour value of 300-350 Pt-Co and COD of 200-250 mg/L for samples were chosen, taking into accounts of fluctuation in production rate and variation in raw materials. Also, as Khoi Nguyen uses less water, contaminant concentration will be higher, especially if the removal rates for them is the same with An Binh, treated effluent would be high in colour and COD.

The primary treatment involving coagulation/flocculant, designed to remove suspended and colloidal solids achieved 88% TSS removal was found in this study. It is worth mentioning that the primary treatment's main focus is to reduce TSS for subsequence processes, and not as a stand-alone treatment. Hence, the chemical dosing rate and mixing tanks and operating conditions were optimised for TSS removal, not for COD and colour removal at this point of the process. In theory, coagulant and flocculants should have a high affinity to the aromaticity of dyes (Sperczyńska et al., 2014), therefore forming big flocs that are easy to settle or removed by DAF. However, results from this study revealed only 11% colour removal for the primary treatment. The low colour removal achieved in the plant was due to low dosage of coagulant and flocculant used to meet the treatment cost requirement. In An Binh, the costs for PAC and PAM make up more than 50% of the overall chemical cost for wastewater treatment.

Secondary treatment involves a UASB and an activated sludge process. UASB is important for its ability to handle a high organic load. UASB can remove up to 90% of COD depending on the type of wastewater and its contaminants (Setyani et al., 2020). For recycled paper wastewater, the COD removal efficiency of UASB can be expected to be 60%-70% (Bakraoui et al., 2020). This correlates to the efficiency obtained from this study where COD removal for UASB was 63%. The efficiency can be improved by optimising operational parameters such as the hydraulic loading capacity of the UASB. The hydraulic loading rate (HLR), which indicate the volume of wastewater being treated, influences the contact of bacteria with influent in the reactor. The higher the HLR, the shorter the hydraulic retention time as wastewater is encouraged to flow through the substrate particle (Farajzadehha et al., 2012). The HRT is the average period of wastewater entering the tank. Low HRT would decrease the efficiency in COD removal as wastewater contact time with sludge will be decreased, leading to less organic matter being consumed. However, despite breaking down more organic matter and producing more sludge and hence increased TSS, when the HRT is too high, efficiency also drops due to lower amount of mixing as the up flow liquid velocity is now reduced. The mixing in the reactor is caused by rising gas bubbles and the up-flow liquid velocity. Increase in expense is another reason why high HRT should be avoided, as for a given HLR the reactor size would need to be upgraded. Organic loading rate (OLR) influences the microbial biomass and the characteristics of the reactor itself. The higher the OLR, the higher the methane and biogas production, and COD removal (Musa et al., 2018). This is because there are more food or energy source available for the anaerobic bacteria. However, a very high OLR can result in a reduction in reactor performance due to disruption in the microbial biomass. Bakraoui et al. (2020) mentioned in their work that UASB can removed up to 90% total solid. TSS in this study was only able to achieve 79%. The difference could be due to most of the research conducted study UASB as a stand-alone treatment, rather than as a component of a larger process.

Aeration treatment is useful in treating biodegradable products. Ashrafi et al. (2015), reported aerobic treatment alone can achieve 70% COD removal. Alexandersson (2003) stated removal rate is expected to be up to 95% if coupled with anaerobic treatment. This finding is supported by the similar efficiency obtained through this study, in which the COD removal rate was 93% for aerobic treatment treating anaerobically treated wastewater. Colour removal efficiency of aerobic treatment can be improved with the addition of nutrients such as nitrogen and phosphorous. Sonkar et al. (2019) noted before the nutrients were supplemented, colour removal achieved was 61.5%. After the nutrient adjustment, efficiency increased to 73%. The result from this study, in which colour removal achieved 96% for aerobic treatment of anaerobically treated wastewater is higher than the data reported by Sonkar et al (2019) using aerobic process as a stand-alone treatment. One explanation could be due to the presence of lignin and its derivatives, and phenolic and chlorophenolic compounds generated from the bleaching stage for effluent sample used by Sonkar et al (2019), adding to the colour load.

4.4.3. Proposed water balance for Khoi Nguyen recycled paper mill

Figure 4.10 shows a simplified proposed water balance for Khoi Nguyen plant. The proposal was based on the following assumptions:

- Water loss by evaporation is 15.5% from the total supplied water, mainly in the drying process
- Make up water 20% for two 35t/h boilers
- Treated effluent meets requirement for reuse.

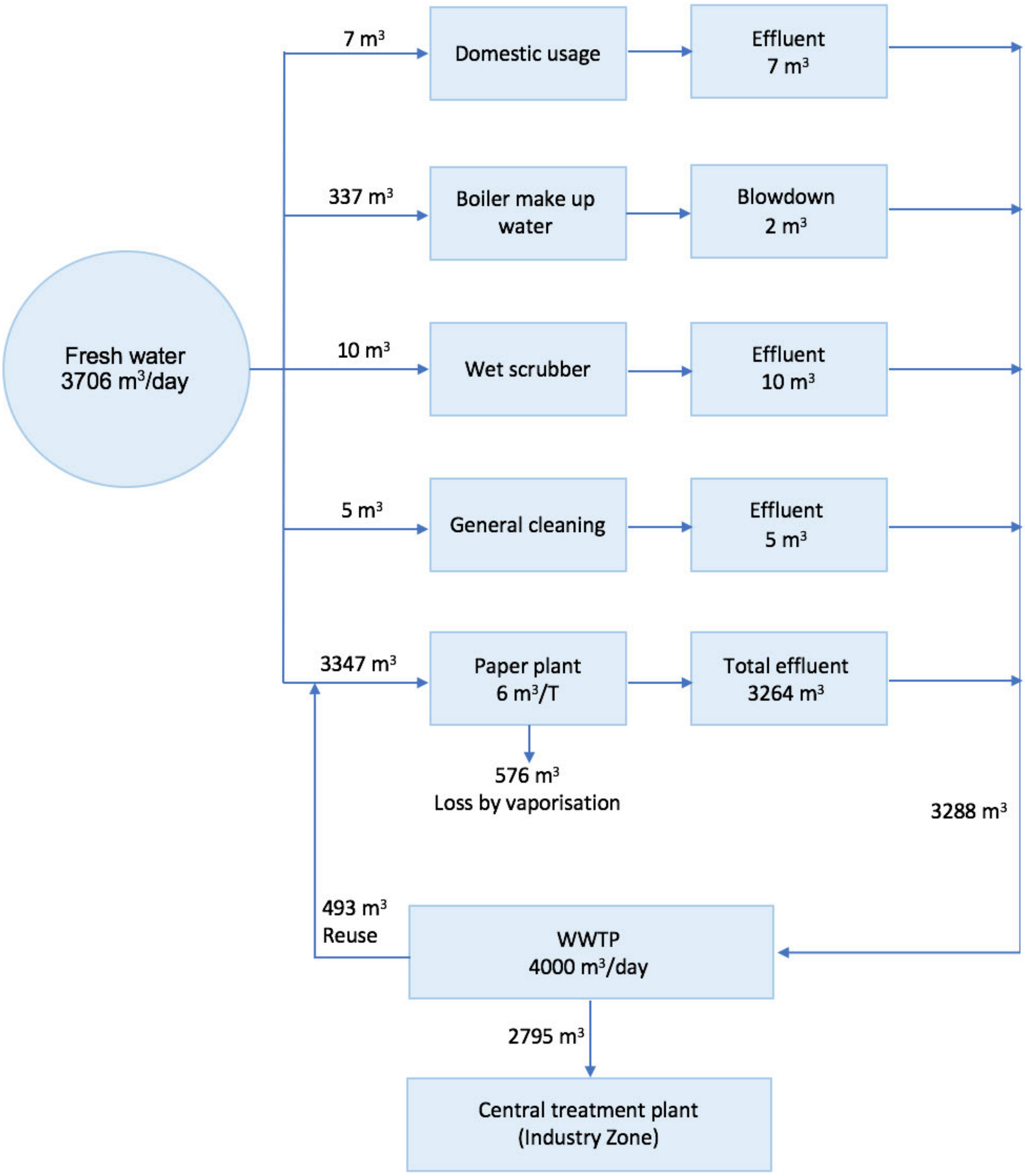

Figure 4.10. A proposed water balance for Khoi Nguyen using 6 m^3 fresh water/ T product, giving it a production capacity of roughly 180000 tonnes/year.

4.4.4. An Binh and Khoi Nguyen wastewater qualities

Figure 4.11 depicts the treated and untreated COD and colour values of An Binh and Khoi Nguyen mill. An Binh's treated effluent achieved grade A in both parameters while Khoi Nguyen's target is grade B.

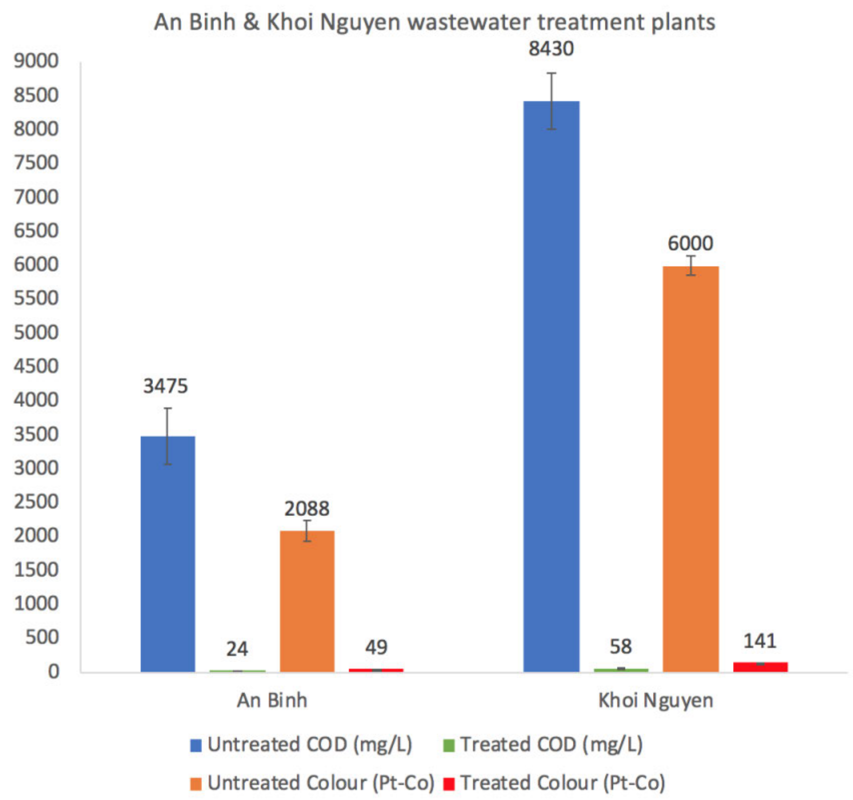

Figure 4.11. Khoi Nguyen wastewater quality targets compared to An Binh's.

Due to high fluctuations in production rates and variation in raw materials, a water consumption target of 6m^3/ton product, and reutilisation of treated wastewater, Khoi Nguyen untreated wastewater parameters were expected to be much higher than of An Binh. Thus, the COD and colour of treated effluent were predicted to be in the vicinity of 200-250 ppm and 300-350 Pt-Co respectively when production is at the highest rate, product's colour needs to be adjusted, and recovered materials contain the most contaminants such as dye, stickies and bacteria. Thus, tertiary treatment needs to be developed in order to meet requirement for a grade B effluent.

4.4.5. <u>Optimisation for colour removal</u>

Wastewaters from recycled paper plant are characterised by the presence of different colour loads. The colour intensity fluctuates depending on the functional and dosage of the colour and fixative used in the paper mill. Sources for colour arise at every stage of paper production. As the main material used as the fibre source is recovered paper, colour can come from the printed or dyed paper collected (Zhao et al., 2004). The second source is from the production stage where chemicals, fillers, starch and dyes are added to create a desirable appearance for the final paper products (Zhao et al., 2004). Some dyes characteristics (SANLIN Chemical, n.d.) can be found in Table 4.6.

Table 4.6. Dyes characteristics

Types	Characteristics
Direct or azo dye	• Synthetic • Strong direct dyeability and affinity to cellulose fibre • Low light fastness → colour fades easily with light exposure • Not very pigmented • Soluble in water • Good for dyeing paper and pulp
Basic or aniline dye	• Synthetic • Soluble in water → dissociate into a pigment cation and an acid anion in water • Pigmented • Poor light fastness • Good for dyeing mechanical pulp, chemical pulp and pulp with high lignin content
Acid dye	• Synthetic • Works well in acidic medium • Soluble in water • Low affinity to cellulose fibre → addition of aluminium ions or cationic fixing agent is needed • Good for acid sizing and surface application
Pigment	• Is a fine coloured powder that is insoluble but easily dispersed in any medium • Can be natural and synthetic • Low affinity to cellulose fibre • Strong light fastness • Pigmented • Good for coating paper

The following colours are used in Khoi Nguyen:

- Direct yellow from p-nitrotoluene sulphonic acid
- Direct Red from P-aminoazobenzene-4'-sulphuric acid
- Direct Blue from 4,4'-diaminostilbene-2,2'-disulphonic acid

Another source of colour at the wastewater treatment stage is from the biological treatment, especially anaerobic treatment has been known to produce colour (Milestone et al., 2004). Recycled paper mill wastewater contains high concentration of sulphurous compounds due to the use of aluminium sulphate for the retention of additives and in the sizing process. These compounds can change to malodorous and coloured substances under low-oxygen environment. During the anaerobic digestion process, sulphides interact with metal ions to create precipitation of metal sulphides. It depends on what metal is available, different metal sulphide is formed. For example, if iron is available, the ferrous iron (Fe^{2+}) would interact with the sulphide (S^{2-}) and precipitate as ferrous sulphide (FeS) (Kiilerich et al., 2017). Likewise, if aluminium or copper is available, the precipitation would be aluminium sulphide (Al_2S_3) or copper sulphide (CuS). These precipitations are often highly insoluble. The bonding between the transition metal and sulphides is highly covalent, giving metal sulphides the semiconductor properties.

An Binh and Khoi Nguyen are both recycled paper mills sharing the same raw materials, thus their effluent characteristics are expected to be very similar except that Khoi Nguyen aims for 40% lower in fresh water usage per ton product. In order to achieve the water consumption target, and according to the proposed water balance, Khoi Nguyen must reuse at least 15% of treated wastewater. To ensure the effluent meets the discharge standards, a tertiary treatment was proposed.

In this study, enhanced coagulation/flocculant and membrane filtration technology were investigated and the results are presented in the subsequent Chapters

CHAPTER 5. ENHANCED COAGULATION AND FLOCCULATION FOR COLOUR AND COD REMOVAL

Coagulation and flocculation are main processes used in primary wastewater treatment. As can be seen in Figure 4.6, Chapter 4, coagulation and flocculation processes are essential for primary wastewater treatment as colloidal particles are a significant part of the total suspended solid fraction. The main objective of this Chapter is to evaluate the effectiveness of this conventional technology as an enhanced method to achieve additional removal of COD and colour to ensure the discharge of a Grade B treated wastewater is met. Changes in colour and COD of treated wastewater after coagulation and flocculation processes were investigated while other parameters such as pH, temperature and influent turbidity were known. PAC31 and PAM(-) were used as coagulant and flocculant respectively. Existing data, including flow rate, the type and concentrations of coagulant and flocculant were also used to avoid complications in plant design and cost for implementation.

5.1. Effect of PAC/PAM ratio on colour removal

As PAM is usually used to aid in coagulation process, PAC volume was kept constant in order to determine the optimal amount of PAM needed. According to Figure 5.1, the best colour removal rate was achieved by the 1:1 PAC:PAM ratio, followed by 1:2 and then 1:0.5 ratio. Colour removal rates achieved 51%, 54% and 53% going from 350 Pt-Co to 171 Pt-Co, 161 Pt-Co, and 166 Pt-Co respectively. All ratios produced a desirable result, but at 1:1 ratio yielded the best removal rate, hence different volumes of PAC were investigated to distinguish the optimal ratio between the two chemicals, and the results are shown in Figure 5.2.

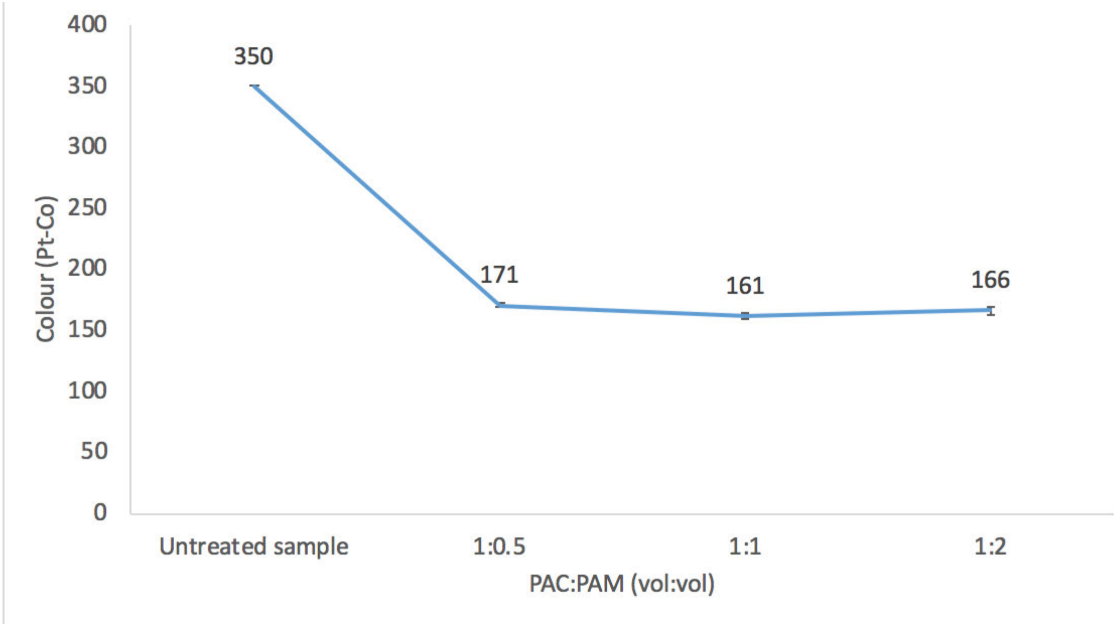

Figure 5.1. Colour removal efficiency of different PAC:PAM (vol:vol) ratios given a fixed amount of PAC and an increasing amount of PAM.

There is a high possibility of achieving a grade B effluent for colour in the feed as high as 350 Pt-Co units based on the results shown in Figure 5.2. The PAC:PAM ratios from 3:1 onwards achieved the target colour output, the treated colour values were below 150 Pt-Co (Grade B). The higher the PAC concentration, the higher the colour removal rate. However, starting from 6:1 ratio, the increase in colour removal rate was gradual, and at 9:1 and 10:1 ratio achieved a plateau. This was due to the colour contribution from excess PAC as more PAC was added.

Coagulation and a degree of aromaticity can be observed to have the linear relationship. Thus, large-molecular weight, hydrophobic, aromatic compounds are easier to be removed compared to low molecular non-ionic hydrophilic factions (Cui et al., 2020). The relationship between colour and atomicity compounds can be explained via how electromagnetic energy interacts with matter (UMass, n.d.). The structure of molecules that make up an organic compound dictates what and the portions of colour spectrums being absorbed. Organic compounds with few multiple bonds and functional groups are less likely to absorb visible light, thus appear as being white or colourless. On the other hand, molecules that have several multiple bonds that are conjugated can absorb visible light, thus appear as being coloured. This is because the more conjugated multiple bonds there are in a compound, the lower the light energy needed to excite the outer shell electrons in the system. Moreover, the excitement of these electrons is what makes colour visible to human eyes. When light is absorbed by a compound, the outer shell electrons in the ground state are now being pushed to a higher energy level, reflecting the unabsorbed portion of light. The colour perceived for an object is indeed the reflected portion of light. Furthermore, the closer the energy of the excited state to the ground state, the lower light energy is needed to excite the electrons. Plus, conjugated compounds, such as aromatic compounds, have lower energy difference between the two states, thus requiring lower light energy. In this study, since added azo dyes are large aromatic molecules (Cui et al., 2020), colour had a high removal rate.

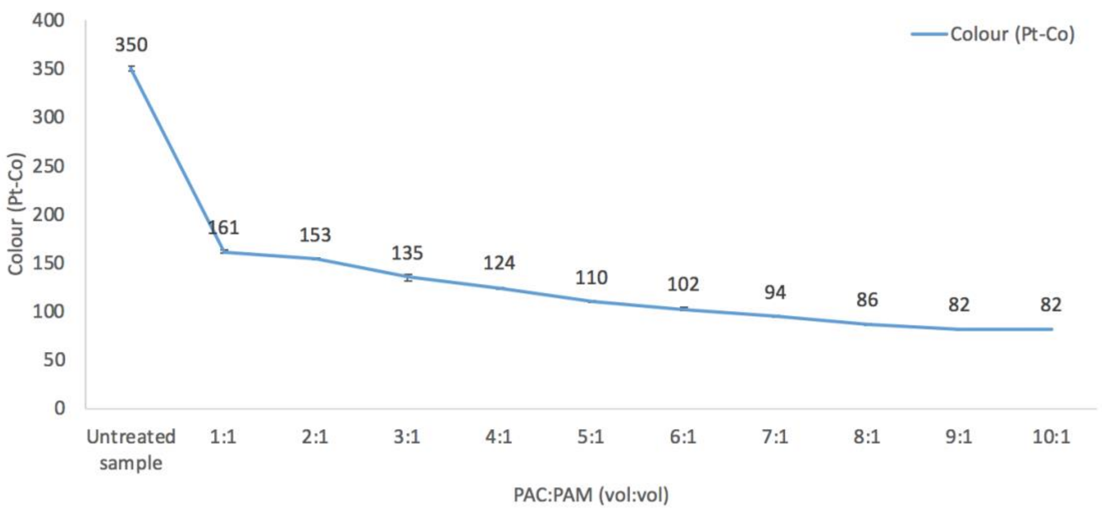

Figure 5.2. Colour removal efficiency of different PAC:PAM (vol:vol) ratios given a fixed amount of PAM and an increasing amount of PAC.

The addition of PAM caused an aggregative effect and overcame the repulsion between small particles, in this case would be coagulated particles created by PAC, to form larger aggregates, thus reducing more colour in wastewater by subsequent processes such as sedimentation or DAF. Ahmad et al. (2008) mentioned the coagulation efficiency of PAC can be improved with the addition of PAM. More specifically, Aguilar et al. (2005) proved that with the addition of anionic PAM, coagulation performance and flocs settling rate can be greatly increased. Consequently, the amount of coagulants needed can also be reduced. While PAC forms micro flocs via charge neutralization, initiating consolidation of small particles to bigger ones. These micro-flocs are hardly seen by naked eyes (Greenwood, 2020). With the addition of PAM and gentle mixing, these micro-flocs grow into flocs that can be visually observed. PAM acts as a long chain of polymer that encourages the entanglement or bridging of multiple tiny solid particles (Vajihinejad et al., 2018).

PAC could be more efficient when commercially used with actual wastewater circulating in the treatment plant as the wastewater would have a temperature of around 40°C or less (Suvilampi et al., 2001). Fitzpatrick et al., (2004) stated floc formation is slower at low temperatures for coagulant, but warmer temperature produces bigger flocs. However, the larger the flocs, the easier they break, suggesting weaker flocs. Therefore, under high temperature, flocs are easily and quickly formed, increasing the settling rate given there is no increasing shear force involved. In this wastewater treatment plant, no cooling tower was used as the temperature were kept at 30-35°C for optimal biological organisms' performance.

5.2. Effect of PAC/PAM ratio on COD removal

Figure 5.3 illustrates the effect of PAC:PAM ratios on COD removal. COD removal rates increased as PAC concentration was increased. At 5:1 PAC:PAM ratio, COD of treated wastewater started to reach the requirement for grade B, which is 135 mg/L (dotted line). The COD removal rate experienced minimal changes as the concentration of PAC was further increased.

For coagulation of wastewater, the optimal coagulant dosage is usually determined according to the coagulation performance of various coagulant dosages at a fixed initial pH value. In this study, the experiments were carried out at pH 7.2 as shown in Figure 4.8, which is the pH of An Binh and Khoi Nguyen mill, to avoid complication and cost associated with pH adjustment in the commercial plant.

At pH 7.2, the predominant coagulation mechanism was charge neutralisation and at higher PAC concentration, the colloidal particle surface may become destabilised and re-dispersed back, resulting in low removal efficiency for COD removal.

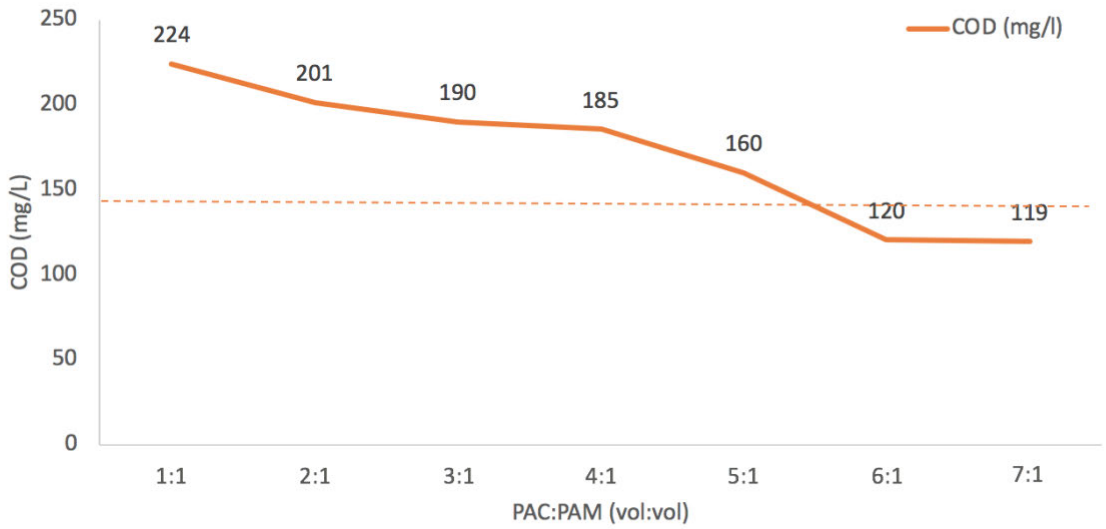

Figure 5.3. Enhanced coagulation and flocculation with different PAC:PAM (vol:vol) ratios for COD removal.

5.3. Toward the compliance of discharge requirement for colour

Based on Figures 5.2 and 5.3, at 3:1 ratio, while the colour removal rate reached 61%, COD removal was only able to achieve 17%. This is underwhelming compared to studies done by other researchers. For example, Irfan et al. (2017) revealed a reduction of 81% in COD can be achieved by using ferric chloride and PAC combination, and then cationic PAM to treat wastewater from a packaging paper mill. The main difference from this study is the addition of another coagulant. While this might increase the COD removal rate, colour reduction would not be effective as some coagulants, especially ferric chloride, contain colour. Another study by Ahmad et al. (2008) claimed the best coagulant and flocculant combination was alum and cationic PAM, which produced a 95.6% reduction in COD. When used alone, PAC performed better in removing COD than alum (Ahmad et al., 2008). This suggests cationic PAM contribute highly to the increase in COD removal. The trend continued even with an increase of PAC concentration, in which the COD removal rate remained substantially than the colour removal rate. This is because the effectiveness of removing organic matter in coagulation increases with the pollutants molecular weight (Sperczynska et al., 2014), indicating the majority of COD after biological treatments is low molecular weight (LMW) organic matter, potentially readily dissolved substances such as starch (as filler). LMW organic matters have also been reported to be less recalcitrant to biodegradation compared to the high molecular weight organic matters (Sperczynska et al., 2014). Thus, the higher the LMW organic matter content, the higher the biodegradability in the wastewater. Moreover, An Binh's wastewater sample was tested for BOD_5. The result revealed 224 mg/L of COD, the BOD value was 150 mg/L, demonstrating a BOD_5/COD of 0.7. The high load in LMW organic matters and high BOD_5/COD indicate An Binh wastewater is biodegradable and would be suitable for biological treatment. Subsequently, Sperczynska et al. (2014) stated in their work that the explanation for the low organic removal rate during coagulation process was due to the high dissolved organic carbon (DOC) load in the total organic carbon (TOC), which is true for recycled paper mill effluent.

Depending on colour and COD remaining in the treated wastewater, a control strategy method can be applied to obtain treated wastewater complying with local regulation. Colour and COD removal showed promising results, suggesting it is possible to meet the discharge standard (grade B) by coagulation and flocculation with suitable doses of PAC and PAM, and the identified doses appear to be in an economically viable range.

PAC:PAM ratio of 3:1 would be the most economical dose to treat colour when comparing the treatment price given in Table 5.1. When COD is also taken into consideration, 5:1 ratio would be a better option. If the ratio of 3:1 for PAC:PAM is used, the chemical expense would be $72,635/year to treat 4,000 m^3/day of wastewater provided the cost for PAC was $0.5/kg and for PAM was $4.5/kg at the time of the experiment. If 5:1 PAC:PAM is selected, it would cost $112,420/year.

Table 5.1. Chemical cost for various dose of PAC and PAM

PAC:PAM (vol:vol)	Cost for treating $1m^3$ of WW (AUD)	Cost for treating $4,000m^3$ of WW (AUD)
1:1	$0.023	$91
2:1	$0.036	$145
3:1	$0.050	$199
4:1	$0.063	$254
5:1	$0.077	$308
6:1	$0.091	$363

Moreover, it would not be cost-effective to use more than the determined PAC concentration, as an extra dose of PAC would cost $54/day, which is an extra $19,750/year for only a 3% increase in colour removal. Chemical costs for both PAC and PAM(-) have always been very affordable. However, with the implementation of a new treatment, other expenses such as capital investment, installation, maintenance and operating are also important and require further investigation. This study has provided information on commercial equipment sizing base on the retention times and flowrates generated from the experiments.

5.4. Conclusion

Enhanced coagulation and flocculation yielded very promising results, especially for colour removal. Ratio of coagulant PAC to flocculant PAM had significant effect on the treatment efficiency in terms of colour and COD removal. The treatment was able to achieve the target colour value of grade B even at low PAC:PAM ratio (3:1 PAC:PAM). On the other hand, a desirable COD value was only achieved at high PAC:PAM ratio (from 5:1 PAC:PAM). As colour is the main concern for both An Binh and Khoi Nguyen, 3:1 PAC:PAM ratio is deemed to be the most cost-effective option. If COD was also a concern, 5:1 PAC;PAM would then be the chosen ratio. A sludge disposal step would be required as agglomerated particles settled down.

CHAPTER 6. MEMBRANE FOR COLOUR AND COD REMOVAL

Membrane separation has been gaining attraction in the industry for its ability to removal both organic and inorganic compounds with small molecular weight, bacteria and virus, and even ions. Depending on the specific objectives of paper mills, membrane technology has been considered for potentially purifying process water for water recirculation, or to remove toxic contaminants and colour from the wastewater (Xu et al., 2018). Among the membranes, UF is considered one of the most outstanding options due to its water quality, low energy consumption, and small footprint (Xu et al., 2018). It is usually implemented when considering qualified discharges. One major disadvantage of membrane filtration is fouling. Beside the pore size, another factor that influences the fouling is the hydrophobicity or hydrophilicity of the membrane. Immersion of a hydrophobic surface in water, such as a membrane or a foulant particle with a low density of hydrogen bonding sites, disturbs the water's original dense network of hydrogen bonds, thus increasing the free energy at the enthalpic or entropic level. The surrounding water molecules will push the hydrophobic surface together spontaneously to lower the water-contacting interface area. This phenomenon is known as hydrophobic attraction (Xu et al., 2020). Xu et al. (2020) stated numerous studies have already confirmed that adsorptive fouling would be more severe on a membrane surface with a higher hydrophobicity, as high hydrophobicity encourages the hydrophobic adsorption. Treatment of pulp and paper effluent (PPE) by means of UF is an attractive method, as most of the polluting substances consist of high molecular mass compounds that are readily retained by UF. UF treatment of extraction stage (E-stage effluent) can result in 70–98% removal of colour and 55–87% removal of COD (Maartens et al., 2002). During E-stage, the chlorinated compounds and oxidised lignins produced from the degradation of wood component process are solubilised and dissolved into spent liquor, the effluent of E-stage (Nagarathnamma and Bajpai, 1999). For higher treated water qualities aiming at a complete water loop closure or zero-liquid-discharge system, membranes with smaller pore size such as NF and RO are preferred. Examples of membrane technology use in the P&P industry include NF membrane process for treatment of process water in Sappi Kirkniemi paper mill and UF membrane process for treatment of wastewater in Daio Paper mill in Khikoku (Manttari et al., 2010).

Since membrane filtration is also well known for its efficiency in removal of colour, it was an objective of this study to investigate its application for the treatment of secondary effluent from Khoi Nguyen. This section discusses colour and COD reduction of UF and NF membranes, and their fouling tendency for treating recycled paper mill wastewater. UF used in this study was made from hydrophobic PVDF while NF was made from hydrophilic PES.

6.1. Membrane screening for colour removal

Table 6.1 compares the colour removal efficiencies of membranes with different pore sizes. For quick screening experiments, synthetic feed was prepared by mixing de-ionised water and P-nitrotoluene-o-sulfonic acid and P-aminoazobenzene-4 ′ - sulfonic acid, the main chemicals in yellow and red dyes used in the paper industry to give a solution with colour of about 335 Pt-Co. These early screening tests only give information to direct subsequent experiments.

Table 6.1. Colour removal efficiencies of various pore sizes

	Feed water colour (Pt-Co)	Permeate (Pt-Co)	Efficiency (%)
Scinor UF (0.1 μm)	335	148	56
Memcor UF (0.04 μm)		99	70
Pentair NF (0.0013 μm)		64	81

Scinor UF was not very efficient for removing colour mainly due to its large pore size. Memcor UF and Pentair NF performed better by bringing the colour value to below the target colour standard for grade B (135 Pt-Co). Therefore, Memcor UF and Pentair NF were selected for subsequent studies. Memcor UF membrane used in this study was made from PVDF and Pentair NF used in this study was made from PES.

6.2. Colour and COD removal efficiency of NF and UF

The following experiments were conducted using a commercial recycled paper mill effluent and simulated biologically treated wastewater to evaluate the membranes ability to remove colour and COD. A summary of colour and COD removal rates of UF and NF membranes using untreated wastewater and simulated biologically treated wastewater are displayed in Table 6.2 and Table 6.3 respectively.

Table 6.2. Colour removal rate of UF and NF membranes using untreated wastewater and simulated biologically treated wastewater.

	Feed colour (Pt-Co)	UF permeate (Pt-Co)	UF removal rate (%)	NF permeate (Pt-Co)	NF removal rate (%)
Untreated wastewater	1343	46	97	16	99
Simulated biologically treated wastewater	328	44	87	12	96

Table 6.3. COD removal rate of UF and NF membranes using untreated wastewater and simulated biologically treated wastewater.

	Feed COD (mg/L)	UF permeate (mg/L)	UF removal rate (%)	NF permeate (mg/L)	NF removal rate (%)
Untreated wastewater	8800	7216	18	5300	40
Simulated biologically treated wastewater	230	184	20	131	43

Figure 6.1 depicts COD and colour removal efficiency of NF and UF using untreated recycled paper mill. The dotted orange line indicates the minimum colour value (150 Pt-Co) and the blue dotted line marks the minimum COD value (135 mg/L) for discharge standard of grade B, which is the target for Khoi Nguyen mill. This is the same for Figure 6.2. In this experiment, these membranes were used as a stand-alone treatment. Despite the difference in COD removal efficiency, both UF and NF were extremely efficient for colour removal, with NF (99%) performing slightly better than UF (97%). NF performed significantly better than UF for COD removal, achieving 40% COD removal as compared to only 18% for UF. With colour outputs of 16 Pt-Co for NF and 46 Pt-Co for UF, both membranes satisfied the discharge requirement of a grade A in terms of colour removal. On the other hand, COD concentrations of the permeates for both membranes could not even meet the discharge target for grade B. Evidently, it is not recommended to use UF or NF as a stand-alone treatment without pre or post-treatment to aid in reducing the COD load.

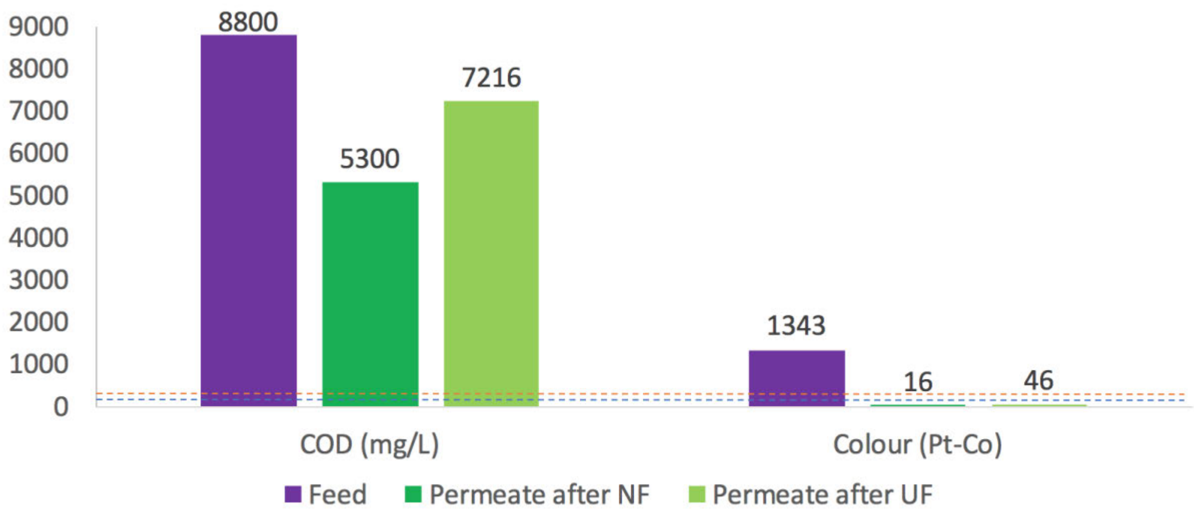

Figure 6.1. Colour and COD removal efficiency using untreated recycled paper mill wastewater

COD and colour removal efficiency was further studied using simulated biologically treated wastewater, which was prepared by diluting the Australian commercial paper mill effluent with deionised water, as seen in Figure 6.2. In this experiment the COD and colour were adjusted to 230 mg/L and 320 Pt-Co respectively, which represent typical treated effluent after secondary treatment.

Similar to the trend obtained through the membrane experiment using untreated recycled paper mill wastewater, both COD and colour removal rates of NF were higher than of UF. NF's COD removal rate was 43% while colour removal was 96% compared to UF's COD and colour removal rates of 20% and 87% respectively. The higher rejection rates for NF were achieved by the immensely smaller pore size compared to UF, allowing for the retention of more and smaller sized particles (Mora et al., 2019). The rejection rate increased with a decrease in pore size. Treatment of inorganic materials is relatively straightforward, whereas treatment of organic pollutants can be extremely complex and challenging due to the diverse nature of wastewaters.

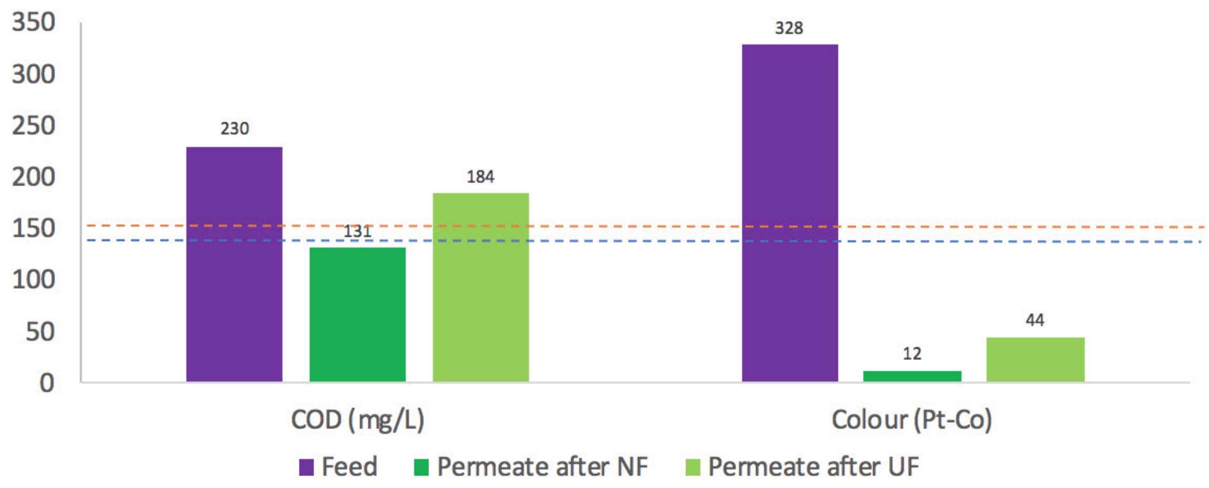

Figure 6.2. Colour and COD removal efficiency using simulated biologically treated wastewater.

COD removal rate obtained by UF in this experiment was lower than of Simonic and Vnucec (2011)'s work. COD was lowered by 50% by using UF membrane to treat untreated paper mill effluent. The drastic difference in the results could be dictated by the UF membrane's material. Simonic and Vnucec (2011)'s membrane was ceramic with an active layer made of Al_2O_3 and ZrO_2. The membrane used in this thesis was PVDF. The material for the active layer was undisclosed by the manufacturer. Hence, the special active layer could be the key to a higher COD removal rate. Ceramic membranes are also known to be more resilience and less prone to fouling.

Findings by Gonder et al. (2011) presented a COD removal rate up to 91% using NF membrane. This was done by operating the membrane under the optimal conditions of pH 10, temperature at 25 °C, transmembrane pressure at 12 bar. NF should be able to remove organic carbon owing to its small pore size. The operating conditions are very different from this study's, which could be the reason why COD removal rate for NF used was only 40%. Plus, As Gonder et al. (2011) mentioned, the mentioned operating conditions can greatly affect the performance of membranes.

Based on Table 6.2, colour removal was higher when untreated wastewater was used as feed water (99% for NF and 97% for UF) compared to simulated biologically treated wastewater (96% for NF and 87% for UF). This is simply because the colour input was higher for untreated wastewater, but the removal efficiencies were similar for both feed sources. This phenomenon occurred due to the size exclusion mechanism for contaminant rejection being directly related to the pore size of the membranes. Since the simulated biologically treated wastewater was made by diluting the untreated wastewater, the composition of both waters was similar with one just being more diluted. Hence, the colour levels after membrane treatment represent the rejection limits by membrane pore sizes, and the results simply indicate the same compounds were retained on the feed side of the membranes for both wastewaters, producing similar removal efficiencies. For NF, colours of filtrates were 16 Pt-Co and 12 Pt-Co for untreated wastewater and simulated biologically treated wastewater respectively. For UF, colours of the filtrates were 46 Pt-Co and 44 Pt-Co. In both cases, colour outputs satisfied the target value for grade B for both UF and NF filtration using untreated wastewater and simulated biologically treated wastewater. Furthermore, the colour outputs also satisfied the requirement for a grade A discharge in term of colour when compared against the standards given in Table 4.3. These results suggest that both UF and NF are very efficient in removing colour for a wide range of colour input.

Overall, NF is more effective than UF in treating paper mill wastewater. As mentioned earlier, NF and UF membranes cannot be used as a stand-alone treatment processes for paper mill's wastewaters. For the simulated biological treated wastewater, NF can attain the COD requirement for grade B treated effluent.

6.3. Membrane fouling in UF and NF

A major impediment to the improved performance of membrane separation processes is membrane fouling. Flux decline (constant pressure operation mode) or transmembrane pressure increase (constant flux operation mode) caused by the irreversible adsorption of foulants is a major obstacle to the economic implementation of membrane technology for the treatment and recycling of pulp & paper wastewater. Fouling has detrimental effects on the membrane performance, as it can cause higher filtration resistance, lower separation efficiency, increased membrane cleaning frequency/cost and a significantly reduced lifespan.

The NF experiments in this study were performed in crossflow filtration mode under a constant pressure. Membrane fouling was indicated by the decline of flux with time. Figure 6.3 shows a big flux drop (53%) at the start of filtration. The dashed lines mark the recovery rate. This is mainly because the initial membrane compaction at high pressure. Compaction of the membrane played an important role in the initial flux drop as a new membrane was used for this experiment. As the NF membrane require a high pressure, which in this study was around 300 kPa to acquire the desired initial flux, it compacted the membrane itself. This is in agreement with study by Volkov that once the membrane is compacted at the operating pressure, performance will become steadier (Volkov, 2014). As the feed is being continuously pushed through under high pressure, some contaminants, especially those of large molecular size, were stuck in the pores, hence reducing the flux. This further explains why once filtration reach 3% water recovery as shown in the Figure 6.3, the flux started to stabilise until the 23% recovery rate, and then steadily decreased to the end of the filtration (63% water recovery) where 80% reduction in flux had been achieved.

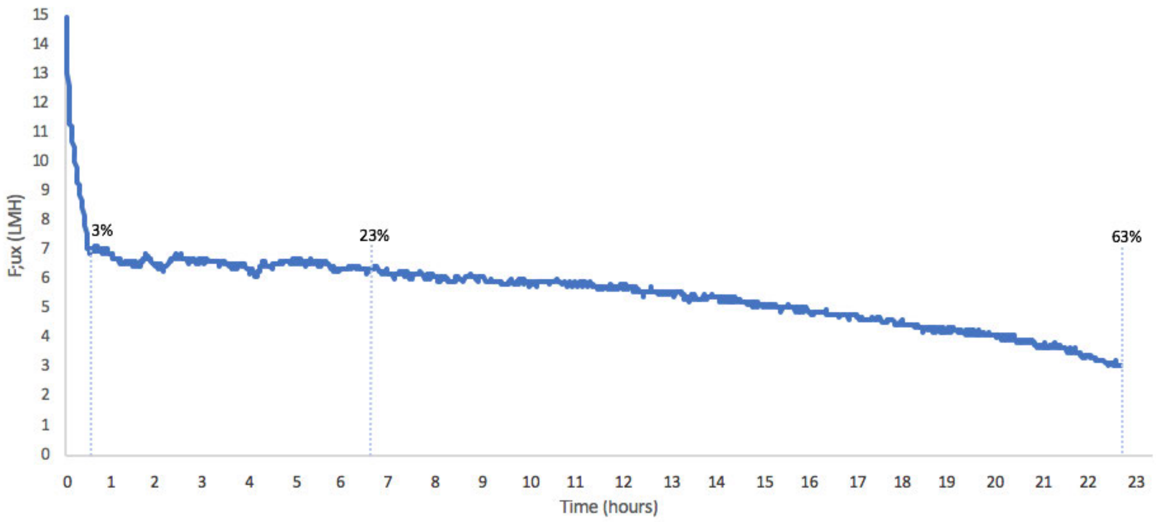

Figure 6.3. NF fouling trend when flux experienced an 80% reduction.

The UF experiments in this study were conducted in the dead-end mode, in which fouling was observed as an increase in operating pressure under a constant flux. Membrane fouling was obvious at around 80 kPa as seen in Figure 6.4, and appeared significant from 5-7% recovery rates.

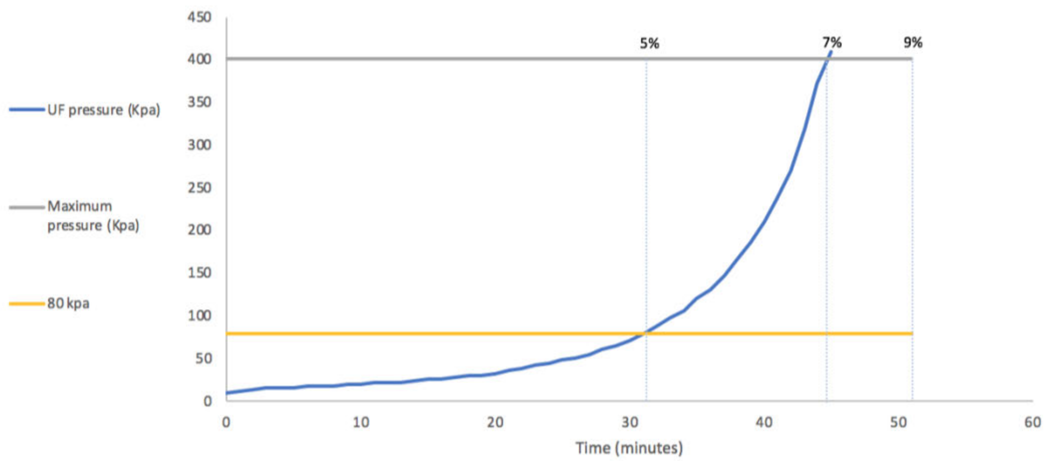

Figure 6.4. UF fouling trend when pressure reached the critical threshold.

The main reason for a difference in fouling behaviour in the NF and UF experiments was due to the filtration modes used. Cross-flow filtration is designed to reduce fouling as solute accumulation is reduced on the membrane surface through the sweeping effect of the tangential flowing of the water (Nagy, 2019). Contrastingly, dead-end filtration is notorious for fouling caused by high concentration polarisation due to its perpendicular fluid flow to the membrane surface (Nagy, 2019). A filtration cake is formed when the retained particles are accumulated on the membrane surface. This layer makes it more difficult for more particles to pass through the membrane pores, hence decreasing membrane's permeability. As particles continue to accumulate, thicker cake layer is formed, and it requires higher operating pressures for a desired flux compromising the filtration process efficacy. Thus, although the dead-end mode is simple in design, it may cause some problems in operation. While UF can be operated in both dead-end and crossflow, UF filtration in this study was carried out in dead-end mode due to its recent commercial use in the paper industry (Chen et al., 2015). Currently, UF membranes have only been used to filter pre-treated paper mill effluent, aiding the discharge compliance to local standards, which is also an objective for this study. NF, on the other hand, was used in crossflow mode as the concentration polarisation would be detrimental for NF small pore sizes. Thus, crossflow is the only preferred mode for NF (Van der Bruggen, 2018).

Some organic pollutants can adsorb on the membrane surface and cause membrane fouling, while others can chemically degrade the membrane or element materials. There is strong need for a robust membrane that can tolerate higher chemical concentrations or be cleaned with more aggressive cleaning agents. Thus, while pore size is a factor, feed composition can also influence the fouling mechanism and fouling can either be partial, total, or internal pore blocking or cake formation (Mora et al., 2019). Membrane fouling can be divided into three types: hydraulically reversible, chemically reversible and irreversible fouling. Hydraulically reversible fouling can be removed physically by introducing turbulence at the proximity of a membrane surface or through backwashing of membranes. On the other hand, chemically reversible fouling can only be removed by chemical cleaning methods, while irreversible fouling is permanent. Partial fouling indicates that hydraulic fouling and chemical fouling can be reversed either through backwashing or chemical cleaning. The severity of the fouling depends on the type of fouling, in which internal pore-blocking suggests the foulant particles are comparable or smaller than the membrane pore size, and cake formation specifies the deposition of larger particles on the membrane surface. As result of fouling, the membrane efficiency and lifespan suffered associated with the increased cleaning cost, which posed an obstacle to the economic viability of membrane technology for wastewater treatment. Fouling control and prevention are, therefore, very important considerations.

6.4. Fouling control

6.4.1. Fouling control with chemical cleaning: alkaline and acid washing

Chemical cleaning is a common fouling control technique to remove the chemically reversible fouling. Typically, chemical cleaning is performed when fouling cannot be physically removed. Chemical cleaning of the membrane will remove foulants from the membrane surface and restore the membrane performance. Choosing the right cleaning chemicals and respective concentration depends on the nature and intensity of fouling, and their chemical compatibility with the membrane and the wetted materials in the membrane unit. In this study, alkaline and acid chemical cleaning were evaluated for both UF and NF membranes. Figure 6.5 shows permeability decreased after every wash for both NF and UF membranes. This trend suggests irreversible fouling occurred to the membranes, thus preventing permeability to be fully restored. When membranes were washed with both cleaning agents, permeability recovery was substantially better and there was reduced irreversible fouling.

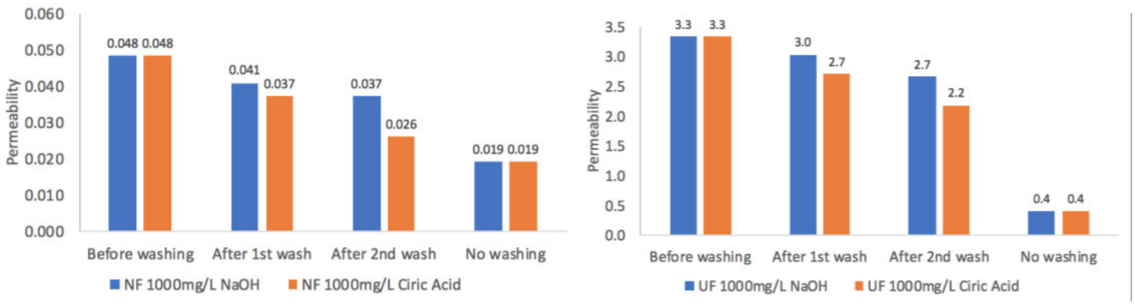

Figure 6.5. Permeability of NF (left) and UF (right) being cleaned with 1000 mg/L of NaOH and 1000 mg/L of citric acid separately.

Moreover, alkali cleaning (1,000 mg/L NaOH solution) yielded a lower reduction in permeability after each washing cycle compared to acid cleaning (1,000 mg/L citric acid solution) for both membrane types. This indicates the occurrence of organic fouling during the treatment, since organic fouling can be effectively controlled by alkaline solutions rather than acid solutions (Tragardh, 1989). This also concurs with work by Zhang et al. (2019), where they explained alkaline washing works by performing hydrolysis and solubilisation to remove the organic foulants from the membrane. The alkaline solution's hydroxide ions aid in the dissolution of the fouled layer by disrupting chemical links between the membrane and the foulants. Furthermore, the alkali also saponify organic foulants, resulting in water-soluble micelles. NaOH was primarily used as a bulking agent and protein solubiliser during the cleaning process. By raising the pH of the water, the carboxyl groups and phenolic compounds are deprotonated, increasing the solubility and negative charge of the organic foulants. Thus, creating repulsion with the membrane and initiating foulant separation from the membrane.

Upon comparing alkaline and acid wash, both NaOH and citric acid showed no effect on colour removal for NF, indicating there was no changes in the pore size of NF membrane. A similar result was observed by Malczewska and Zak (2019) as they identified that NaOH could reduce some fouling and had minimal effect on PES membranes. Also, no fouling with respect to colour removal for NF occurred as the experiments performed in this section were within the region where fouling was not evident as shown in Figure 6.3. NF membranes started to show signs of fouling at around 40% recovery rate. However, the experiments were concluded at 30% recovery rate before fouling could happen, and colour removal remained the same. It is evident that NF's ability to treat colour is very significant and reliable. UF, on the other hand, experienced an increased in permeate colour when citric acid was used. The decay in colour rejection could be caused by the degradation or ageing of the UF membrane as suggested by Gan et al. (2021), who did a study on different cleaning agents and their effects on the ageing of PVDF UF membranes. A similar phenomenon could have occurred in this study with UF membrane affected by citric acid, causing damage to the membrane, thus creating small openings for contaminants to get into the permeate stream. Therefore, despite the fouling that caused the decrease in permeability, more coloured contaminants are now getting through the pores due to the membrane being damaged.

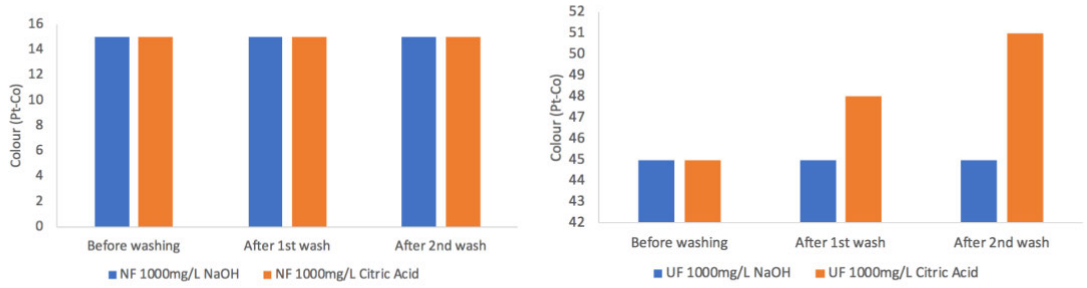

Figure 6.6. Colour removal of NF (left) and UF (right) being cleaned with 1000 mg/L NaOH and citric acid (Feed colour = 1343 Pt-Co)

After washing, permeability decreased for UF (Fig.6.5) correlating to an increase in COD rejection which resulted in decreases in COD in the permeate as shown in Figure 6.7. This is because as more foulants continued to build up on the membrane surface, this increasing cake layer acted as a physical interceptor to other contaminants, easily retaining them in the reject stream as the pores become smaller. One the other hand, both permeability and COD rejection decreased for NF when citric acid was used. This could be caused by the swelling of pores after washing, letting some contaminants in pores being pushed out into permeate. Huang et al. (2021a) explained that while chemical cleaning can aid in removing foulants, it could also cause adverse effects to the membrane. They claimed membrane pore swelling could be induced by chemical cleaning, and small foulants could get trapped inside the enlarged pores when the pores return to their original size, leading to irreversible fouling. The shrinkage of pores after they swell could be induced by water filtration at neutral pH. After water filtration, pores are assumed to revert back to their regular size, but this did not seem to be the case for this study. This might be due to the different water filtration duration used between the studies. In the study of Huang et al. (2021a), the filtration period was 30 minutes, in comparison with 10 minutes in this study which might not be enough time for all pores to gain back their original size, leaving some pores to remain bigger than their original size. Therefore, the overall permeability still decreased due to some foulants being entrapped in enclosed pores, and colour and COD removal still decrease due to some pores not able to revert back to their original size, allowing more contaminants to pass through.

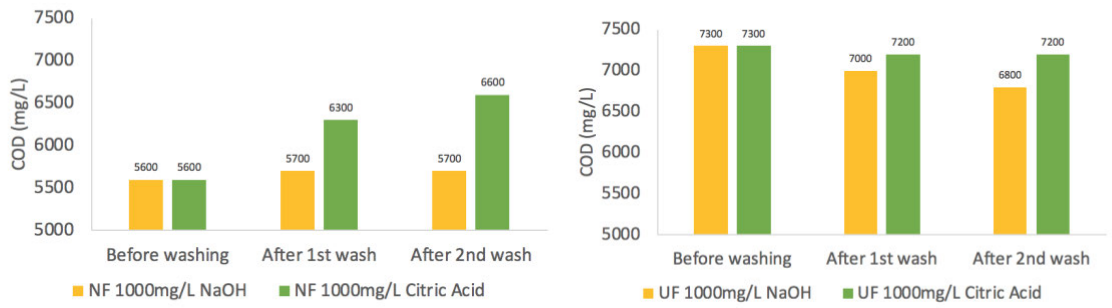

Figure 6.7. COD rejection of NF (left) and UF (right) after cleaned with 1,000 mg/L NaOH and citric acid (Feed COD = 8,800 mg/L).

<u>6.4.2. Fouling control with physical cleaning via backwashing</u>

Backwashing refers to the reversal of flow through a membrane system in comparison to the normal flow direction required for permeate production, and is one of the fouling mitigation methods to remove hydraulically reversible fouling. The purpose of backwashing is to remove or loosen foulants from the membrane surface and within the membrane pores to control membrane fouling. It can be very effective in dislodging and flushing contaminants stuck in the pores of a membrane and is achieved by flow reversal of permeate into the feed side. Backwashing is utilized with low pressure membrane systems like MF and UF, while high pressure membrane systems like NF and RO do not employ backwashing to control fouling. Backwashing effectiveness on UF membrane was investigated in this study.

With the flux kept constant at 15 LMH, fouling was highlighted through the changes in the initial pressure. Permeate was used to backwash the membrane for 3 minutes each cycle. In Figure 6.8, the orange line shows that when the membrane was not backwashed between each filtration cycle, fouling became very severe, resulting in a half running time compared to the first filtration. The fouling trend can be seen as the blue dashed line, indicating the occurrence of irreversible fouling. The starting pressure for the second filtration cycle drastically increased up to 5.4 times the pressure for the former cycle. When feed water was pre-treated with UF, the increase in pressure for the second cycled was only 1.5 more than the first cycle, suggesting foulants were removed from the membranes, resulting in less fouling. This type of fouling is referred to as reversible hydraulic fouling. However, there was a slight increase in the initial pressure after every wash, indicating the occurrence of irreversible hydraulic fouling when backwashing was applied between the filtration cycles. Reversible hydraulic fouling caused by biopolymers and humic-like substances can be controlled by backwashing, while irreversible hydraulic fouling caused by low-molecular organics of building blocks and neutral can only be removed with chemical cleaning (Huang et al., 2021b). Therefore, more frequent backwash combined with chemical cleaning or pre-treatment of feed water could improve backwashing efficiency, reducing both reversible and irreversible fouling, as well as prolonging membrane performance.

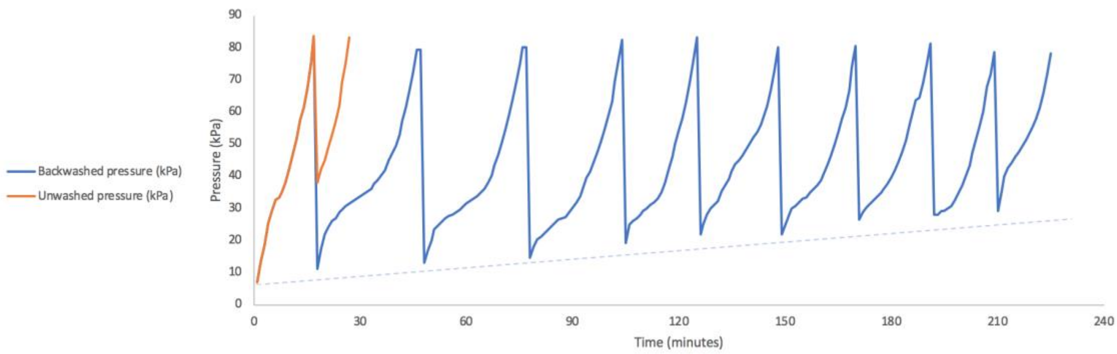

Figure 6.8. The effect of backwashing on UF membrane.

6.5. Fouling prevention: pre-treatment of feed with coagulant

As fouling is inevitable with membrane filtration, along with fouling control, prevention to delay fouling in order to prolonging the life of the membrane also needs to be taken into consideration. Thus, pre-treating feedwater is an important step. Amongst all of the pre-treatments, pre-coagulation has been one of the most successful approaches (Huang et al., 2009). This section discusses the effect of pre-treating feedwater with a coagulant on membrane fouling.

According to Figure 6.9, there was a 28.5% reduction in the fouling rate when wastewater was pre-treated with 20 µl of “Fast Floc”. An extra 2% recovery rate was achieved before UF reached the critical pressure of 400 kPa. This was because less pressure was required for the maintenance of permeate flux due to the reduction of fouling compared to when the feed sample was not pre-treated prior to filtration. Since “Fast Floc” is poly-aluminium chloride, similar result were obtained by Huang et al. (2018) that polyaluminium chloride performed well in reducing membrane fouling. PAC ability to reduce membrane fouling comes from its ability to remove not only colloids and particles, but also natural organic matter. It happens to be that feed water used was recycled paper mill wastewater, which is known to be rich of all those mentioned contaminants. Therefore, after the coagulation process, pre-treated feed water would contain less colloidal and small materials that could easily clog the membrane pores. The so-called hybrid coagulation-ultrafiltration process has been investigated by many researchers previously (Bergamasco et al., 2011; Barbot et al., 2008; Malkoske et al., 2020). The consensus from all the studies was that coagulation before filtration reduces fouling by lowering cake formation, reducing pore obstruction, and improving backwash efficiency. While cake formation and backwash efficiency require further testings to gain a more definite conclusion, it is apparent that pore obstruction was reduced in this study, and was confirmed by the extra time gained for the membrane to reach the critical pressure. If the pores were obstructed, the time to reach critical pressure would decrease due to higher operating pressures being required for the membrane module as a result of smaller pores. While organic or polymer coagulants can be adsorbed on to the membrane, contributing to more fouling, it is worth mentioning that flocs created by polymer coagulants are larger than those created by inorganic coagulant, allowing for better filtration performance in terms of hydraulic resistance (Barbot et al., 2008).

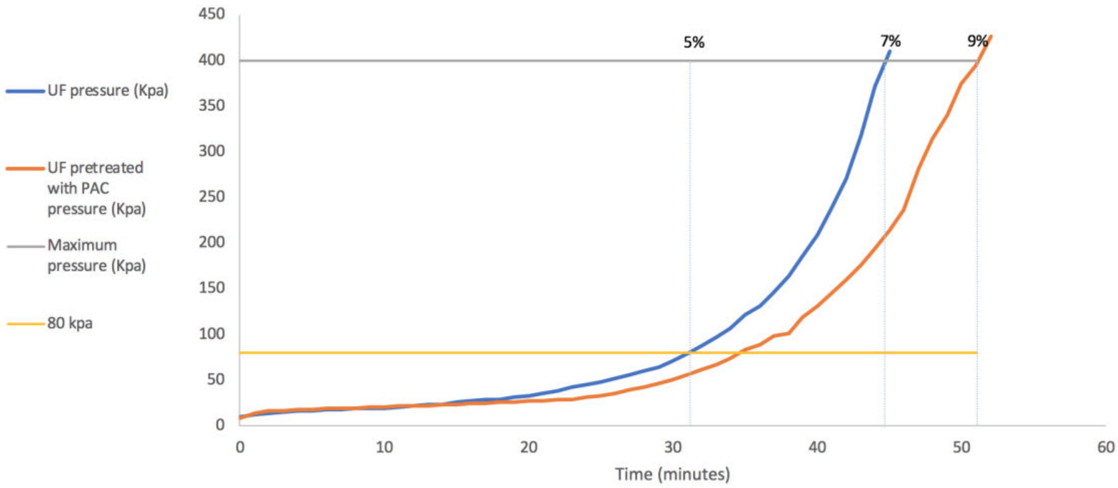

Figure 6.9. Fouling trend of UF compared to pre-treated UF

When wastewater was pre-treated with PAC, COD removal rate by UF was higher than that for untreated wastewater as seen in Figure 6.10. The blue dashed line indicates target level for COD while the orange dashed line shows the colour target. The COD removal rate was comparable to that of NF filtration. A similar result was observed by Malkoske et al (2020) using UF and MF for the removal of suspended materials in drinking water. Without pretreatment, results showed that UF removes more organics than MF due to the smaller pore size, but when a coagulant was used, performance was similar for both membranes. Malkoske et al (2020) explained that the pretreatment aided in reducing the COD load of feedwater. Therefore, the increase in COD removal rate observed by this study can be attributed to the decrease in the COD load prior to membrane filtration through the pre-treatment. Colour removal rate did not variate much, achieving only 9% higher than when the wastewater was not pre-treated. This is because UF pore size remain the same for both treated and untreated wastewater, resulting a similar colour-carrying contaminants rejection.

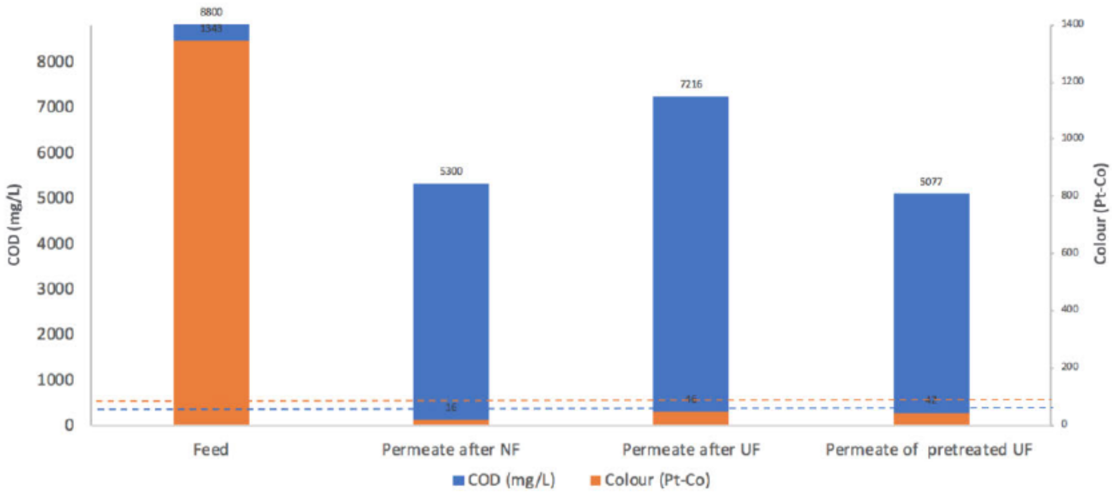

Figure 6.10. Colour and COD rejection rates of NF and UF compared to pre-treated UF for untreated effluent.

Figure 6.11 compares the permeability of UF membrane pretreated with coagulant and UF without pretreatment. The length of constant permeability operation for pre-treated UF was longer than of when UF feed was not treated with coagulant. This is because the duration of filtration was different for both as explained previously in this section. Moreover, permeability was higher for pretreated UF as coagulation helped in removing colloidal and suspended solids, effectively reducing the accumulation of contaminants on the membrane surface (Bokhary et al., 2018). However, as filtration continues, more and more contaminants accumulate on the membrane surface, blocking the pores, thus reducing permeability. Therefore, this phenomenon was observed for both pre-treated and untreated UF membranes.

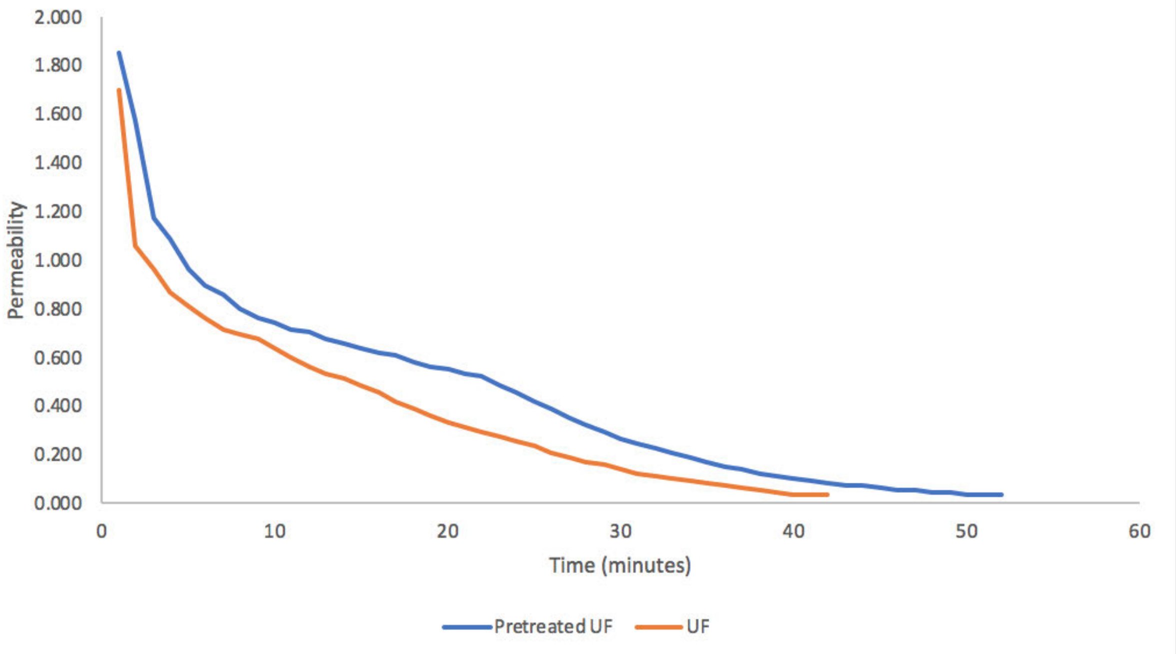

Figure 6.11. Permeability of UF membrane without pretreatment and UF membrane pretreated with coagulant.

6.6. Colour and foulant identification

6.6.1 Colour identification

HPLC was used for identifying the presence of colour. In the recycled paper industry, yellow, red and blue dyes are commonly used to adjust the colour of the paper products. Of all the colours, yellow is the most used. A typical ratio is 10/1/0.03 for yellow, red and blue respectively, and this ratio varies depending on the raw material. Red and blue dyes are sometime not in the combination. As mentioned earlier, due to Australia’s border protection regulations, effluent samples from Vietnam are not allowed into Australia due to it containing potential foreign bacteria that could endanger the country’s wildlife and flora.

Thus, membrane related experiments were conducted in Australia on samples of effluent obtained from a similar commercial recycled paper mill. Therefore, feedwater and its subsequent permeate used for HPLC testing was of untreated wastewater from a recycled paper mill in Australia.

Figure 6.12 shows the presence of diethanolamine in the feedwater. Diethanolamine is a stabiliser commonly used with p-nitrotoluene sulphonic acid in the making of yellow dye. This indicated the presence of yellow dye in the feedwater. On the other hand, as P-aminoazobenzene-4’-sulphuric acid is the main component for red dye, and triethanolamine is used as a stabiliser for this colour, and no peaks that correlate to these materials are shown in Figure 6.12. The absence of such peaks indicates there was no red dye used at the time this sample was collected or the concentration for this dye is much lower than the detection limit of the HPLC.

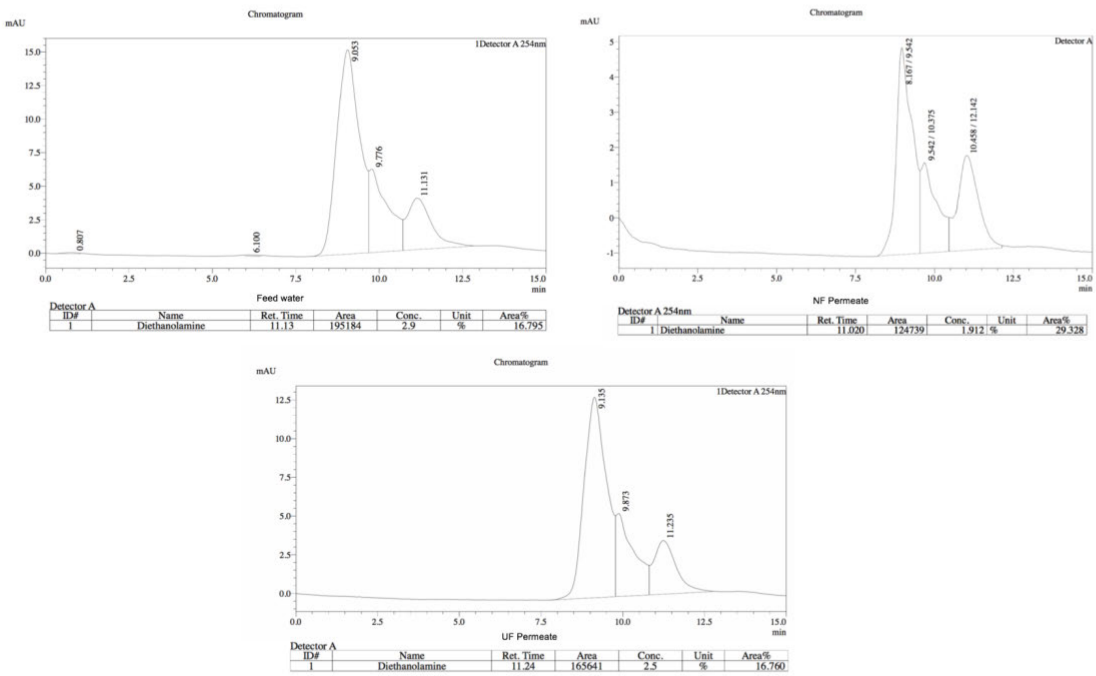

Figure 6.12. HPLC graph of feedwater, NF permeate and UF permeate.

Similar to HPLC result for feed water, peaks detected were only Diethanolamine, indicating the presence of colour yellow in the permeates. The concentrations detected for both permeates were lower compared to the feedwater. This means there was less yellow dye detected in the permeate after feedwater was filtrated with UF and NF, suggesting a degree of removal of the colour yellow. Dye removing capability of UF and NF has been noted by Abedi and Nekouei (2011). They revealed that all kinds of dye can be removed using UF and NF with careful consideration for minimising membrane fouling.

6.6.2. Foulant identification on membrane surface by FTIR

6.6.2.1. Fouling identification on UF membrane surface

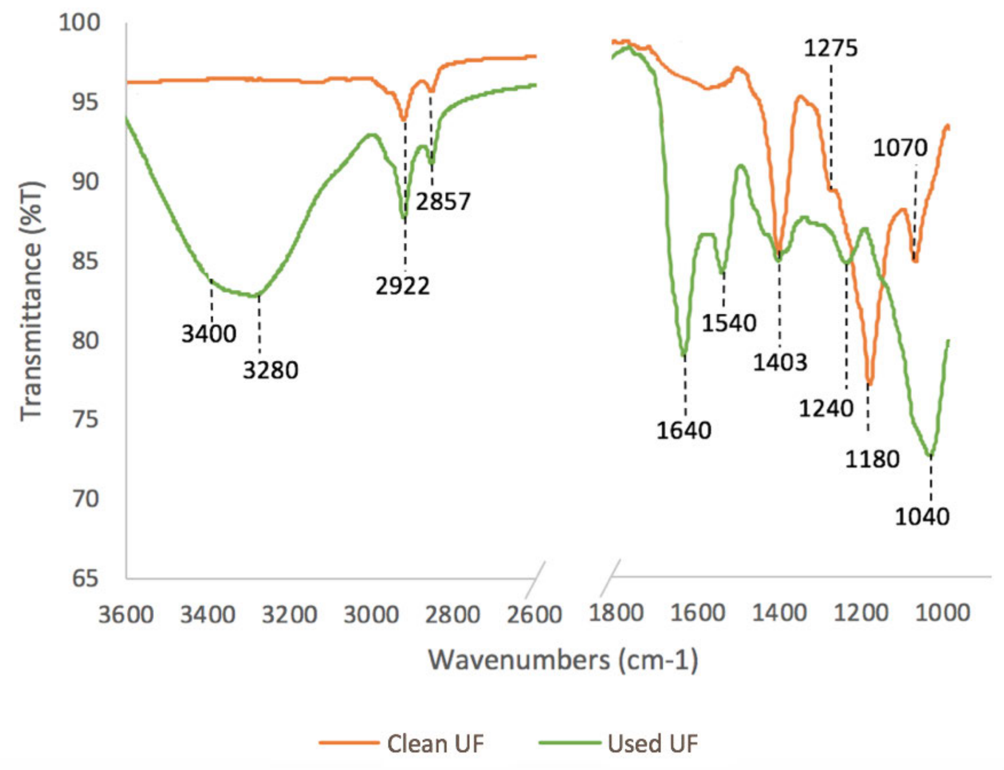

Figure 6.13. FTIR spectra of clean and used UF membrane.

Figure 6.13 shows FTIR spectra of clean UF membrane (orange) and used UF membrane (green). The following bands are present for clean UF membrane. Two distinct peaks at 2924 cm^{-1} and 2857 cm^{-1} are assigned to the CH_2 asymmetric and symmetric vibration of PVDF (Bai et al., 2012). The peak at 1403 cm^{-1} can be attributed to CH_2 wagging vibration (Bai et al., 2021) and the β-phase of PVDF (Rabuni, 2014). A C-F out-of-plane deformation was characterised by the presence of 1275 cm^{-1} peak (Amouamouha and Gholikandi, 2017). The peak 1180 cm^{-1} can be attributed to the C-C band and C-F stretching of the PVDF. Another C-C band can be observed at 1070 cm^{-1}.

The 1180 and 1070 cm^{-1} bands are also the characteristic bands of PVDF containing α-phase (Rabuni, 2014).

Besides from all the bands seen in the clean membrane, the FTIR spectrum for fouled UF membrane showed the appearance of two new bands 3400 and 1640 cm^{-1} that were assigned to the O-H stretching and bending of water remaining after filtration experiments. The peak exhibited at 3400 cm^{-1}, indicating the presence of polysaccharides on the membrane surface (Thuvander et al., 2018). The broadness of the peak at 3000–3400 cm^{-1} suggests the presence of polysaccharides, since they contain significant numbers of –CH and –OH groups also manifest as peak intensification at 1080 cm^{-1} and 2967 cm^{-1} (Thuvander et al, 2018). The appearance of the C-O stretching modes was seen at 1240 cm^{-1} (Mukherjee and Gowen, 2015). The distinct peak at 3280 cm^{-1} indicates the presence of amino group in protein foulant residues. The presence of protein foulant was also evidenced by the presence of a new band at 1540 cm^{-1}, which is assigned to amide II or perhaps indicated the presence =CH in aromatic rings of the yellow dye residues on the surface of the fouled membrane. The 1040 cm^{-1} peak is assigned to the C-O stretching band associated with carbohydrate or polysaccharides (Rahman et al., 2018). Since the PVDF membrane was used in this experiment, the presence of amino group, amide group, and carbohydrate indicate the accumulation of protein and starch compounds from paper mill wastewater on the surface of used UF. A summary of peak assignment for clean and used UF membrane FTIR spectra can be found in Table 6.4.

Table 6.4. Peak assignment of FTIR spectra for virgin and fouled UF membranes

Peaks	Assignment
3400	O-H stretching of water
3280	N-H stretching
2922	CH_2 asymmetric stretching
2857	CH_2 symmetric stretching
1680	C=O stretching
1640	O-H stretching of water
1540	Amide II, =CH (aromatic rings)
1403	CH_2 wagging vibration
1275	C-F out of place deformation
1240	C-O stretching
1180	C-C and C-F stretching
1070	C-C stretching
1040	C-O stretching

6.6.2.2. Foulant identification on NF membrane surface

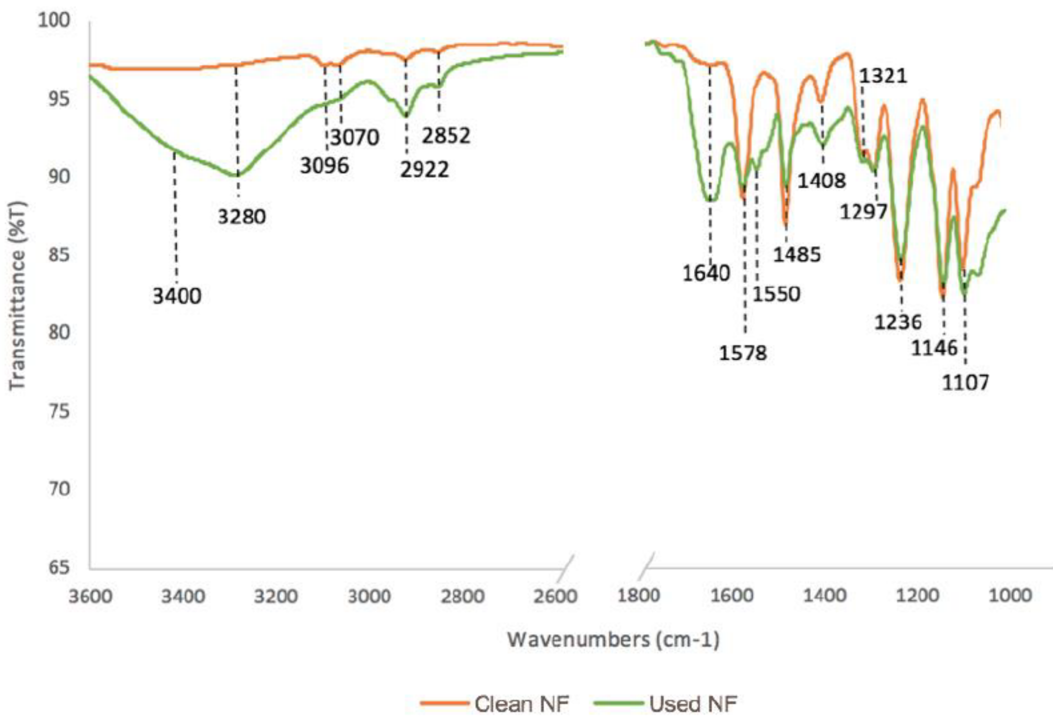

Figure 6.14. FTIR spectra of virgin and fouled NF membrane.

Figure 6.14 shows FTIR spectra of clean PES NF membrane (orange) and of used PES NF membrane (green). A complete peak assignment for NF membranes can be found in Table 6.5. Peak at 3400 cm $^{-1}$ and two peaks aromatic C-H stretching modes at 3096 cm^{-1} and 3070 cm^{-1} were identified, indicating the presence of polysaccharides on the membrane surface (Thuvander et al., 2018). The aromatic C=C stretching modes of aryl rings are assigned to the 1578, 1485 and 1408 cm^{-1}. The S=O asymmetric stretching in -SO_2- is assigned to the peaks 1321 and 1297 cm^{-1} while the 1146 cm^{-1} peak is the symmetric stretching mode. Another characteristic of PES membrane can be seen by the presence of the 1236 cm^{-1} peak, which is attributed to the asymmetric stretching of Ar-O-Ar ethers. Angione et al (2015) concurred the finding these spectra as these were reported in their work which involves ATR-FTIR spectra of PES membrane. The peaks 2922 and 2852 cm^{-1} are assigned to the CH_2 asymmetric and symmetric aliphatic stretching in PES, respectively (Belfer et al., 2000). A C-O stretching band is evident at the 1107 cm^{-1} peak (Zhao et al., 2017). As these spectra are characteristics of a typical PES membrane, both the clean and used NF membranes exhibit them.

For used NF membrane, the broad peak at 3400 and 1640 cm^{-1} present for used NF membrane can be assigned to the O-H stretching and bending of residue water in the membrane (Angione et al., 2015). A N-H stretching band at 3280 cm^{-1} represent either hydroxy or amino groups (Rahman et al., 2018). Amide groups are distinct at 1550 cm^{-1} peak. The presence of amino and amide groups for both NF and UF used membranes, but absent for their clean counterparts, suggests formation of new or more proteins, hence organic matter, on the surface of the fouled membranes.

Table 6.5. Peak assignment of FTIR spectra for virgin and fouled NF membranes

Peaks	Assignment
3400	O-H stretching
3280	N-H stretching
3096	C-H stretching
3070	C-H stretching
2922	CH_2 asymmetric stretching
2852	CH_2 symmetric stretching
1640	O-H stretching
1578	C=C stretching
1550	Amide II, =CH (Aromatic rings)
1485	C=C stretching
1408	C=C stretching
1321	S=O stretching
1297	S=O asymmetric stretching
1236	Ar-O-Ar ether asymmetric stretching
1146	S=O symmetric stretching
1107	C-O stretching

6.7. Toward the compliance of discharge requirement for colour

Both UF and NF membrane modules obtained a significantly high colour removal rate. They both produced similar results for feed with high and low colour and COD loads, demonstrating high reliability. Depending on the required active area to treat a specified amount of wastewater, the membrane type of interest can be expensive due to small pore-sized membranes having a small hydraulic diameter, requiring more or longer fibres and a more powerful pressure pump. Thus, the smaller the pore, the more pressure is required, which leads to high energy consumption. Maintenance cost could also be a concern as regular cleaning and washing are required to reduce fouling. According to Glueckstern and Priel (2003) the treatment cost for UF is $0.27/m^3 - $0.67/m^3 for desalination of seawater, costing $1,080 - $2,680 to treat

4,000m^3 of seawater a day. The treatment cost for NF is roughly \$1.29/m^3 - \$7.76/m^3 (Samhaber and Nguyen, 2014), indicating \$5,160 - \$31,040 would be needed to treat 4,000m^3 of wastewater a day. Needless to say, almost every application is unique, based on the industry and their wastewater (Kallioinen, 2015). Therefore, since colour is the main concern for Khoi Nguyen paper mill, a UF membrane system would be highly recommended over NF. Moreover, with a proper pre-treatment, UF could produce similar COD rejection rate to NF, making it efficient in removing both colour and COD.

6.8. Conclusion

Both UF and NF demonstrated high and reliable Colour removal with NF performing better than UF for COD removal for treating both untreated recycled paper mill wastewater and simulated biologically treated wastewater. When simulated biologically treated wastewater was used, NF was able to satisfy the target value for grade B discharge in terms of both colour and COD removal. Due to NF operational conditions being cross-flow, the NF module had an advantage in fouling resistance in this study. Depending on the severity of fouling, it can be controlled with chemical cleaning or physical cleaning through backwashing, or a combination of both. Despite membrane technology being more affordable nowadays, retrofitting a new membrane system into an existing wastewater treatment plant is still difficult. While space requirement would not be a problem, the high initial investment cost combined with the operating, maintenance, and pre-treatment of wastewater costs might pose as a challenge, especially for small paper mills.

CHAPTER 7: OUTCOMES AND RECOMMENDATIONS

7.1. Outcomes

The objectives of the dissertation have been largely achieved. Key outcomes of this study are:

- The water circuit of the commercial mill used as a case study for this research was analysed and a water balance to enable a reduction of fresh water consumption from $10m^3$ to $6m^3$/tonne product was proposed.
- Pulp and paper wastewaters were found to vary significantly in characteristics and different contaminant loads depending on raw material used and the quality of the products. The quality of the wastewater in terms of contaminant loads including COD, BOD, colour and total suspended solids (TSS) after various individual treatment process was determined to be high, but this is the norm for a recycling paper mill. Out of all, colour was the only parameter of concern as it sporadically achieved the target grade for effluent discharge. Various characterisation methods were used to support the qualitative and quantitative analyses of contaminants.
- Methods for wastewater treatments such as enhanced coagulation and flocculation and membrane technologies for tertiary treatment that enable water recycling in a commercial paper plant were considered. The interactive effects of the experimental factors such as the initial contaminant inputs, process conditions, chemical dosages as process parameters for process optimisation were investigated. Most of the experimental inputs were applied in relation to commercial process parameters to support the implementation.
- A suitable technology was identified in terms of contaminant removal performance to meet the discharge standard and enable reuse of wastewater. A preliminary cost analysis was also provided.

Overall, both enhanced coagulation and flocculation, and membrane filtration demonstrated favourable results. Only a low dose of coagulant and flocculant were needed to obtain colour value that satisfies the discharge standard.

Similarly, both UF and NF were successful in removing colour from the wastewater to a desirable level. Thus, both were able to achieve a high colour removal rate and satisfy the discharge standard targeted by the paper mill. On the other hand, COD removal was a challenge for enhanced coagulation and flocculation, and UF. A high dose of coagulant and flocculant were required to reduce the COD value to the target level. Furthermore, pre-treatment of feed with a coagulant was a prerequisite for UF to produce permeate of quality. Out of all techniques, only NF had the capability to remove both colour and COD to the desired levels.

For membrane filtration, fouling is a major predicament as it greatly affects the efficiency and lifespan of the membrane. Thus, fouling preventions such as regular or periodic membrane cleaning and pre-treatment of feedwater need to be considered.

The results obtain from both the enhanced coagulation and flocculation, and membrane filtration suggest the colour concern for Khoi Nguyen mill can be addressed successfully. Additionally, since Khoi Nguyen mill’s main concern is only colour, enhanced coagulation and flocculation is recommended over membrane filtration. The obvious reason would be due to the more affordable chemical cost.

7.2. Future work recommendations

Despite the promising results obtained from this research, additional studies are recommended to advance this work to the point where a fully optimised process can be established and a commercial scale facility can be demonstrated. The following subjects need to be further studied:

For coagulation/flocculant process:

- Further cost analyses need to be performed to accurately assess the viability of the implementation.
- The effect of retention time for coagulation and flocculation to support commercial equipment sizing.

For membrane filtration, a study on ceramic membrane is highly recommended given its advantages in physical strength, easy to clean by backwashing and possibly higher resistance to organic fouling.

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