APPLICATION OF MEMBRANE FILTRATION IN SYSTEM CLOSURE OF WHITE WATER SYSTEMS IN NEWSPRINT MILLS

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Contribution to posters: Devi Naicker-experimental work and preparation of poster. Supervisors-reviewed the poster and provided suggestions for improvements.

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Title of Presentation (Poster): The build-up of contaminants in white water due to system closure
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Contributions: Devi Naicker-experimental work and writing of the paper. Supervisors-reviewed the paper and provided suggestions for improvements.

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Abstract

The pulp and paper industry is considered to be one of the most water intensive industries in S.A. With increasing environmental regulations and awareness the industry is leaning towards system closure. By recycling water and using it back in the process, the industry can considerably reduce its consumption of fresh water as well as its production of waste water. One method that is gaining momentum for the purification of water is membrane filtration. Membrane filtration does not require any sophisticated heat-generating equipment as compared to conventional separation methods like evaporation making it a viable choice. It is, however, prone to fouling and requires long membrane cleaning cycles.

The first part of the study involved the simulation of system closure in the laboratory using a Rapid-Kothen sheet forming machine. This was conducted in order to determine the accumulation of the different contaminants as the white water is recycled. Results obtained indicate that the accumulation of contaminants with increasing number of cycles tends to exhibit a linear relationship. The burst index and brightness of the paper decreased as the level of closure increased.

The main aim of the project was to evaluate ultrafiltration as the core process for purification of white water in terms of productivity, retention, flux decline, fouling and cleanability of the membrane as well as to determine the optimum operating conditions that reduce fouling. Polymer membranes having different molecular weight cut offs (10, 50, 100 and 150 kDa) were tested. Overall it was established that the 100 kDa membrane exhibited the lowest degree of irreversible fouling, the best cleanability, the highest productivity and average permeate flux and the permeate obtained from this membrane met most of the water quality requirements for the reuse of water in the paper manufacturing process. The 100 kDa membrane was used in further studies. The optimum operating conditions that reduce fouling was determined using the Taguchi method. Three parameters were investigated at three levels i.e. temperature (20, 40 and 60°C), pressure (1,2 and 3 bar) and volume reduction factor (VRF) (0.63, 0.71 and 0.86). Results obtained indicated that low temperatures, pressures and VRF values reduced the fouling hence the optimum operating conditions were a temperature of 20°C, a pressure of 1 bar and a VRF of 0.63. The permeate quality obtained at the optimum conditions is in accordance with the water quality standards for the reuse of water in the process. Alum and $FeCl_3$ coagulation were used as pre-treatments to ultrafiltration to reduce the membrane fouling thereby increasing the membrane life. Results obtained indicate that twice as much $FeCl_3$ than alum is required to obtain a similar reduction in suspended solids and turbidity and a low sludge volume index (SVI). $FeCl_3$ is more expensive than Alum; requiring twice as much would considerably increase the cost of treatment. Hence alum was chosen as the coagulant to be used in further tests. It was found that the optimum dosage and pH were 288.8 mg/L and 7.68 respectively.

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CHAPTER 1 INTRODUCTION

1.1 Background and motivation

With our growing population, natural resources such as water are fast becoming scarce. Various countries including South Africa are experiencing water shortages and if not addressed the shortages could lead to drastic repercussions in the near future. Approximately two-thirds of the world's population will experience water shortages by the year 2025 (Kerr, 2012). In order to ensure sustainable development, measures to reduce the exploitation of the environment and natural resources need to be investigated and implemented.

South Africa is placed fifteenth among the major pulp producers in the world. The pulp and paper industry contributes 0.6% to the South African annual GDP and is a major job creator (PAMSA, 2012). However, the industry is one of the major consumers of water. Water is one of the key components involved in pulping, pulp processing and paper manufacturing (Macdonald, 2004). Processing alone requires approximately 85% of water resulting in the production of rather large volumes of waste water (Macdonald, 2004). The major portion of the effluent emanating from paper mills is white water, making it a viable choice for recycling. By recycling water and using it back in the process, the industry can considerably reduce its consumption of fresh water as well as its production of waste water. Increased operational costs for the paper machine as well as the effluent treatment plant are likely to occur if the large volumes of white water are not reused.

White water refers to paper mill water that has a cloudy appearance due to the presence of suspended and dissolved solids picked up when separated from the furnish on the paper machine (Bajpai, 2012). The term closure refers to the amount of white water that is recycled or the amount of fresh water consumed in the production process (Xu and Deng, 2004). The components of white water from newsprint mills can be classified into suspended solids and dissolved solids. Suspended solids consist of fibres, fines and inorganic particles such as clay fillers, wood extractives and polymers (Boeg et al., 1997). Dissolved solids consist of fatty and resin acids, hemicellulose and lignin derivatives (Boeg et al., 1997). Water loop closures in the mill process results in a build-up of dissolved solids in the white water systems and as the loop is gradually closed this build-up increases leading to various complications downstream (Xu and Deng, 2004). The build-up of these solids can result in deposition on equipment, fabrics and felts (Polverari et al., 2001). This leads to reduced runnability and productivity due to breaks and downtime required for wash-ups (Polverari et al., 2001). They also hinder the activity of retention aids, wet strength additives, cationic starch, sizing agents and cationic dyes (Polverari et al., 2001). Wet-web tensile strength and drying strength are compromised by the build-up of these solids (Polverari et al., 2001).

In order to overcome these various problems and to ensure successful system closure, strategic approach for white water treatment and reuse is required. Various white water treatment methods have been investigated for the closure of white water systems in newsprint mills such as biological treatment and evaporation (Gerbasi et al., 1993) and dissolved air flotation (Asano and Visvanathan, 1997). Dissolved air flotation is capable of recovering pulp and recycling water back into the process (Asano and Visvanathan, 1997). The main disadvantage with this method is that not all white waters are capable of producing a stable froth which is a requirement for the efficient operation of the flotation process (Haapala et al., 2010). When not used in conjunction with other treatments, the main problem experienced with biological treatment is poor dewatering and salt build-up (Hubbe, 2007).

Membrane filtration was chosen as the treatment method for waste water in this study since it does not require any sophisticated heat-generating equipment as compared to conventional separation methods like evaporation. Other advantages of membrane filtration include its capability of testing large samples, reduced preparation time of the sample when compared to other methods and ability for the removal of bacteria (Hubbe, 2007). Membrane filtration plants have a relatively high packing density thereby saving space on a mill (Scott, 1995). It is, however, prone to fouling and requires long membrane cleaning cycles (Hubbe, 2007). Different types of membrane filtration exist such as Nanofiltration (NF) and Ultrafiltration (UF). The membranes used in NF operate by diffusing liquids through their molecular structure (Gutman, 1987). UF differs in that rejection is based on size classification. The membranes involved in UF possess small openings or pores in the media (Gutman, 1987). NF membranes are highly effective in removing oil and rejecting divalent and multivalent ions (Gutman, 1987). These membranes are also capable of rejecting minute non-charged particles due to the fact that filtration occurs by diffusion (Gutman, 1987). In order to reduce colloidal fouling and polarization of the membrane due to concentration of rejected materials other membrane systems have been developed such as VSEP (vibratory shear enhanced process) (Gutman, 1987). This particular membrane system uses torsional vibration of the membrane surface resulting in high shearing energy at the surface and near pores (Gutman, 1987).

The membrane filtration study conducted utilised UF since NF requires higher operating pressures in order to force water through the smaller membrane pores (Hubbe, 2007). Another advantage of UF is its capability of removing higher mass polymeric material as well as colloidal byproducts of wood processing, these are the contaminants that adversely affect the efficiency of retention aids and wet-end additives (Hubbe, 2007). NF requires more energy than UF making it undesirable. Polymer membranes were used in the study since they are much cheaper than membranes constructed from other materials (Hubbe, 2007) . Unlike polymer membranes, membranes constructed from cellulose are prone to biodegradation and have to be operated within a narrow pH range (Hubbe, 2007).

This project involved the technical evaluation of membrane filtration for closure of white water systems in newsprint mills in order to reduce the consumption of fresh water. The study also investigated the concentrations of contaminants that accumulate in the white water as the loop is closed and the impact of using recycled water on paper quality. Although membrane filtration has been utilised over the years in the pulp and paper industry for waste water treatment, studies applicable to South African mills are limited hence this study aims to add to the existing knowledge of membrane filtration of waste water from South African mills.

The project as a whole has many positive implications for the pulp and paper industry. Since South Africa is a country that is experiencing water shortages, a better understanding of system closure and technologies to implement it in more mills across the country is vital in order to reduce fresh water consumption and the proposed project will enable the paper industry to do exactly that. From an economic point of view system closure will result in reduction in the costs incurred to treat waste streams. Coupled with global warming and the vast amounts of fresh water consumed on a daily basis by many industries including the paper industry, it is likely that access to fresh water will be threatened in the near future and projects like this will equip industries with the technology and knowledge necessary to move forward under such circumstances.

1.2 Problem statement

What is the quality of the recycled water produced by membrane filtration of white water? What is the accumulation trend of contaminants with increasing number of times the water is recycled? How does system closure affect paper properties?

1.3 Aims and objectives

The main aim of the project is to enable the reuse of white water in the mill after membrane filtration. The objectives of the project are to:

- Simulate system closure in the laboratory using a Rapid-Kothen sheet forming machine and determine the accumulation of the different contaminants.
- Evaluate coagulation as a pre-treatment to membrane filtration using the jar test apparatus.
- Evaluate ultrafiltration as the core process for purification of white water in terms of flux decline, retention, productivity and fouling and cleanability of the membrane using a stirred cell in order to determine an appropriate membrane to be used.
- Determine the optimum operating conditions for ultrafiltration that reduce membrane fouling and the quality of the water obtained.
- Determine the impact of the accumulation of contaminants on product quality by testing the paper properties at different levels of closure.

1.4 Approach

The Rapid-Kothen paper machine was used to simulate an industrial water circulation process. Other equipment required for this stage of the project included a hot plate and magnetic stirrer in order to agitate the pulp sample at the desired temperature before transfer to the paper machine. An operating consistency of 0.3% was used. The filtrate was collected in a beaker and used to dilute a fresh feed stock to the desired operating consistency before transfer to the paper machine. A sample was kept after each cycle for analysis.

Since fouling of the membrane is the main disadvantage associated with membrane filtration, coagulation was tested as a pretreatment to ultrafiltration. Alum and $FeCl_3$ were used as coagulants. Three different levels of coagulant dosage and sample pH were tested. The treatments were evaluated in terms of the ability of the treatment to reduce the suspended solids and the turbidity as well as produce a low sludge volume index (SVI). A central composite design was used and response surface methodology was applied in order to determine the optimum coagulant dosage and ph.

For the membrane filtration part of the project, a stirred cell was initially used to determine the appropriate membrane to achieve the highest retention of the contaminants. Three membranes having a MWCO of 10kDa, 50kDa, 100kDa and 150kDa were tested. Membranes were also evaluated in terms of cleanability, productivity, flux decline and fouling. Once a suitable membrane was chosen the stirred cell was then used to determine the optimum operating conditions. The Taguchi design of experiments was chosen. Three factors were investigated, namely temperature, pressure and feed flowrate, at three different levels in order to determine the optimum operating conditions that provide the lowest fouling of the membrane.

Hand sheets were manufactured at different levels of closure i.e. varying the amount of fresh water used in the manufacturing process in order to determine the effect of system closure on the burst and brightness of the hand sheets.

1.5 Thesis layout

The following is outlined in the thesis:

Chapter one introduces the project, provides a brief background and motivation for the project and discusses the aims and objectives of the project.

Chapter two starts off with a brief description on how newsprint is manufactured resulting in the production of large quantities of white water. It also touches on the different types of mechanical pulping. Since the effluent used in this study was obtained from a newsprint mill that uses and produces a large quantity of mechanical pulp, typical water consumption in mechanical pulping as well as sources and emissions from a mechanical pulp mill is outlined. The adverse effects of system

closure are then discussed highlighting the need for treatment prior to reuse. Ultrafiltration is the main focus of this study hence previous studies involving the application of ultrafiltration in the pulp and paper industry are discussed. The chapter also touches on the fundamentals of membrane technology and the performance characteristics associated with membrane filtration. Other technologies used in previous studies to implement system closure are also reviewed in order to gain an understanding of the pros and cons associated with these technologies and to choose a suitable pre-treatment method to ultrafiltration.

Chapter three presents the materials and methods involved in the study. It also touches on the chemical analysis conducted as well as the experimental design adopted in the pre-treatment and membrane filtration experiments.

Chapter four discusses the results and main findings from the combined coagulation pre-treatment and ultrafiltration studies as well as the simulation of system closure in the laboratory.

Chapter five states the conclusions drawn from the research conducted.

CHAPTER 2 LITERATURE REVIEW

2.1 Manufacture of newsprint paper

Newsprint paper is mainly manufactured from mechanical pulp or recovered paper. A small quantity of filler may also be used in the manufacturing process (Suhr et al., 2015). Certain mills use a combination of both mechanical pulp and recycled fibre in the ratio of 3:1 and the recycled fibre is made up of a mixture of 30% magazine and 70% newspaper (Smook, 2002). The addition of recycled fibre enhances smoothness & reduces porosity thus enabling improved printability (Smook, 2002).

2.1.1 Mechanical pulping

Mechanical energy is utilized in the mechanical pulping process in order to separate the fibres from each other into fibre bundles, fragments and single fibres (Bajpai, 2012). Various mechanical pulping processes exist such as stone groundwood (SGW), pressurised groundwood (PGW), thermomechanical pulping (TMP), refiner mechanical pulping, chemi-thermo mechanical pulping (CTMP) and refiner mechanical pulp (RMP).

SGW and PGW pulping involve pressing logs against a rotating grinder stone and water is concurrently added (Suhr et al., 2015). The stone is also referred to as the pulpstone. In this process the logs are placed in such a manner that they are parallel to the axis of the pulpstone enabling the removal of intact fibres (Smook, 2002). In order to press the logs against the pulpstone pressure is applied to the wood magazine of the grinder. Fibres are washed into the pit by showers which also serve the purpose of keeping the stone cool. The strength of the pulp produced as well as the drainage properties of the pulp is reliant on the surface characteristics of the pulpstone. The stone surface is generally rough, however, it starts to wear over time and requires sharpening. Sharp edged stones are undesirable (Biermann, 1996). PGW differs from that of SGW in that the grinder is pressurized with steam. The use of steam improves separation of fibres and reduces production of fines resulting in a brighter pulp with a higher freeness and tear strength (Biermann, 1996).

TMP utilizes heat as well as mechanical processes in production. Ground wood pulp is mainly used in newsprint mills since it aids in opacity and compressibility. However, they are weaker than TMP (Smook, 2002). Due to its strength TMP requires less reinforcing chemical pulp in the manufacture of newsprint and bleaching of mechanical pulp is not necessary for the production of newsprint (Bajpai, 2012). In the production of TMP the pulp is manufactured in refiners pressurized with steam. The process incorporates 2 refining stages. First stage refining utilizes high temperatures and pressures in order to achieve fibre separation whereas second stage refining is conducted at ambient temperature as a means to condition the fibres for the manufacture of paper (Biermann, 1996). The

pulp is washed between the two refining stages. The high temperatures in the first stage reduces the amount of fines produced (Biermann, 1996). TMP is much stronger than pulps produced by other mechanical methods. However, energy requirements for TMP production are much greater than that required for SGW pulp (Biermann, 1996). The yield of pulp obtained with this method is 91-95% (Biermann, 1996).

CTMP production is considered to be a modification of TMP production. In the CTMP process a chemical stage is introduced before the refining stage. In the chemical stage a small quantity of sodium hydroxide or sodium sulfite is used to pretreat the wood chips at a high pressure and temperature (Biermann, 1996). This chemical pre-treatment stage improves the bonding properties and brightness of the pulp as well as lowers the debris content. However, it tends to lower the scattering coefficient. Another advantage is that the cost of production of CTMP is lower than that of Kraft pulp. CTMP that is highly sulphonated is used for the production of tissue. One of the main disadvantages of the CTMP process is the production of effluent that is high in colour and BOD making it difficult to treat. Hence it is not used by many mills.

In RMP production chips are broken up at atmospheric pressure by utilizing rotating metal disks that have raised bars (Biermann, 1996). RMP produces fewer fines and is stronger than SGW. However, it is much darker in colour than SGW. The production of RMP incorporates two refining stages, an initial stage at a consistency of 20-30% in order to separate fibres and a second stage at 10-20% consistency that serves to improve fibre bonding. The RMP process has been replaced in many mills by the TMP process which is considered to be a modification of the RMP process.

The mechanical pulping processes mentioned all consume large quantities of water as illustrated in table 2-1 and these end up in effluent. Emissions from a CTMP mill are shown in Figure 2-1.

Table 2-1: Water consumption in mechanical pulping (Adapted from Suhr et al., 2015)

Pulping process	**m^3/ADt of pulp[1]**
GW	5-15[1]
TMP	4-15[1]
CTMP	15-50[1]
[1]The upper end of the range includes the water consumption of the paper mill for integrated production)	

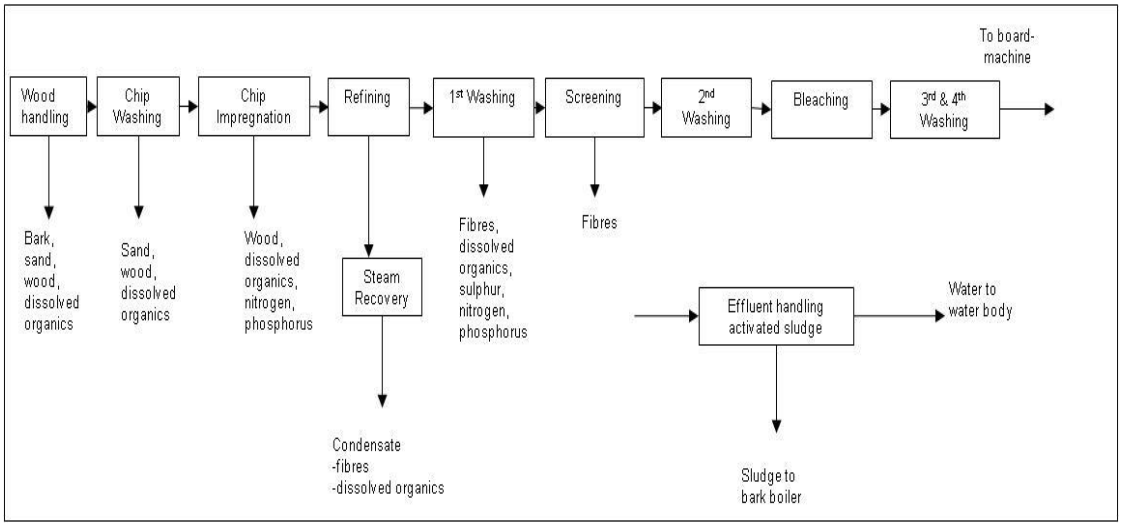

Figure 2-1: Emissions from a CTMP mill (Adapted from Suhr et al., 2015)

2.1.2 Production of paper

As described in section 2.1.1 the first stage of newsprint production is pulp formation. Stock preparation is the second stage in the paper making process. It serves the purpose of transforming raw stock into finished stock before it is sent to the paper machine (Bajpai, 2012). It is vital for the supply to the paper machine to be uniform in order to produce a high quality product and to ensure there are no breaks in operation. The stock preparation process involves various steps such as repulping, refining, addition of chemicals and blending after which the pulp is then transferred to the headbox of a paper machine (Smook, 2002). In repulping dry pulp fibres are converted into a water slurry with the aid of mechanical action. Refining is another mechanical operation that serves the purpose of developing the sheet forming properties of the pulp in accordance with the product manufactured. Chemicals are often added in order to improve the properties of the pulp thus obtaining a higher quality product. Different types of paper products require different stocks. Hence blending is required in order to combine various furnishes to obtain the desired stock. The main newsprint characteristics considered in the manufacturing process are runnability, printability and appearance (Smook, 2002).

Once the stock is ready the mixture is poured on to a travelling wire mesh in the machine, where water is drained through the mesh as the wire moves along the machine path (Bajpai, 2012). The fibres then align and interlace to form the sheet prior to moving to the pressing and drying section of the machine where more water is drained. Thereafter the paper proceeds onto a reel for winding at the end of the machine (Bajpai, 2012). White water refers to paper mill water that has a cloudy appearance due to the presence of suspended and dissolved solids picked up when separated from the furnish on the paper machine.

2.2 Chemistry of dissolved and colloidal substances (DCS) in white water

Dissolved and colloidal substances (DCS) are a combination of dissolved substances, polyelectrolytes and suspended substances that are less than 1 μm in dimension (Hubbe et al., 2012). DCS are liberated from the wood during the mechanical refining and grinding process and chemical Kraft cooking process. Once released they mix with the contaminants from recycled pulp, other chemicals and coating and bleaching additives (Zabihian et al., 2012). This leads to the formation of both organic and inorganic species. Various DCS's are found in white water such as lignin, starch, extractives, proteins, wood polymers, resin, dispersants, retention aids, defoamers, emulsifiers, fatty acids and alcohols, inorganic electrolytes and hemicelluloses (Boeg et al., 1997).

The colloidal systems in the white water from the paper machine can be either hydrophobic or hydrophilic. Wood pitch colloids are often liberated in mechanical pulping and consist of two layers, with the inner portion comprised of triglycerides and steryl esters and the outer layer comprised of fatty acids and resin acids. The size of the layers depends on their composition; the composition of the different colloids also influences their stability and deposition characteristics. Hydrophilic systems consist of lignans, lignin and dissolved hemicellulose and during peroxide bleaching the main hemicellulose group of o-acetyl-galactoglucomannans are deacetylated leading to increased acetic acid in the water (Zabihian et al., 2012). Due to the increased acetic acid deacetylated galactoglucomannans are adsorbed onto the fibres causing a reduction of the protective layer for steric stability of wood pitch colloids which eventually leads to hydrophobic colloidal material in the system that is unstable and undisturbed and prone to electrolyte-induced aggregation.

The pH of white water is generally between 7 and 8. An increases in pH result in the dissociation of resin and fatty acids from the colloid into solution while the inner portion of the hydrophobic colloid will not dissociate and remain neutral. However, increases in conductivity suppresses this dissociation (Zabihian et al., 2012). Reducing the pH can reverse the dissociation of the outer layer resulting in the resin and fatty acids returning to the colloidal state. However, in the presence of calcium ions dissolved resin and fatty acids form insoluble aggregates known as calcium soaps.

DCS in the white water may either deposit on equipment with time or deposit on the pulp fibre (Stebbing, 2002). They may also precipitate with multivalent metal ions resulting in the formation of insoluble soaps. Deposits on equipment can affect efficient running of the process and addition of electrolytes to the system can prevent the deposition of DCS on equipment. Anionic extractives such as resin acids, fatty acids, hemicellulose and lignin have the effect of increasing the cationic demand of the system and due to this the effectiveness of cationic polymers is reduced. A reduction in the effectiveness of retention aids occurs since lignin and hemicellulose components have the tendency

to react with the cationic polymers or pulp (Boeg et al., 1997).

The location of the white water in the paper machine plays a key role in the concentration of DCS in the white water. A study conducted by (Boeg et al., 1997) indicated that the concentration of DCS decreased in concentration as it proceeded from the headbox to the fourth press . They discovered that the concentration of DCS in the forming section is higher than the press section since the mat of pulp formed is course and less fines are retained leaving a greater amount to collect in the white water. The low DCS in the press section is a result of more DCS being retained in the sheet as it forms and the press felt serving as a filter to retain the DCS.

2.3 Problems associated with system closure

Although the closure of water systems in newsprint mills poses various advantages previous studies have reported numerous detrimental effects of system closure. A common problem associated with system closure is the build-up of contaminants in the system. These contaminants include fibres, fines, fillers, suspended solids and dissolved solids and the build-up of these substances in the closed water system can lead to various problems such as equipment corrosion, plugging, scaling and deposit formation (Baijpai, 2012). The product quality is also affected. These contaminants are often non-ionic and anionic dissolved and colloidal substances. Carbohydrates, wood extractives, hemicellulose, polysaccharides and lignin derivatives all constitute dissolved and colloidal substances (Polverari et al., 2001). Another problem reported by Baijpai (2012) is that of anionic trash which is a subcategory of DCS and results in the consumption of retention aids causing a reduction in the paper machine wire retention. The wood species and the pulping method employed affects both the nature and quantity of DCS found in white water.

DCS affects the production process in various ways. Microbial growth is a major concern in closed white water systems since organic compounds tend to accumulate in closed water systems and form a substrate on which microbial growth forms resulting in odour (Baijpai, 2012). The microbial growth forms a biofilm in the white water and fragments of this biofilm enter the headbox of the paper machine and are deposited on the wire together with the pulp feed. This results in the formation of holes in the paper due to the shrinking of the biofilm fragments in the drying section of the paper machine. Anaerobic microorganisms form volatile fatty acids in the white water increasing the need for retention aids (Baijpai, 2012). High temperatures are observed in closed white water systems due to the conservation of energy. As a result of the high temperature and the presence of high concentrations of anionic ions, corrosion of equipment occurs and over time this could lead to damage of the equipment thus adversely affecting the production process. Pitch is another concern that affects the production process, it is formed by fatty and resin acids together with hydrolyzed sizing agents and deposits on the press felt and adversely affects the operation (Baijpai, 2012).

System closure not only affects the production process but also affects the product quality. Wood resin is part of the DCS present in white water and affects paper properties more than other DCS constituents in the white water (Sithole and Allen, 2002). Papers produced from mechanical pulp such as newsprint are most affected since mechanical pulp contains more wood resin than Kraft pulp (Sithole and Allen, 2002). Wood resins are composed of fatty acids, resin acids, steryl esters and triglycerides. The wood resin tends to attach to the fibres and has the effect of disturbing fibre-fibre bonding which in turn affects the strength properties of the paper (Sithole and Allen, 2002). A study carried out by Tay (2001) confirms this phenomenon. The research found that fatty acids, resin acids and triglycerides have the effect of lowering water surface tension and reducing interfibre bonding (Tay, 2001). A build-up of these substances in the white water results in various adverse effects on the paper such as specks forming in the paper, impaired brightness and decreased wet-web and dry strengths (Stebbing, 2002).

Research carried out by Francis and Ouchi (2001) showed that DCS found in thermo mechanical pulp (TMP) white water tends to adversely affect the physical and optical properties of newsprint. They also reported that the effect of the DCS depends on the composition of the furnish used. Groundwood and semi chemical mechanical pulp (SCMP) newsprint furnish was found to be more sensitive to white water contaminants than that of the TMP. Increase in the contaminant levels and DCS resulted in a decrease in the breaking length, tensile strength, burst index and stretch of the newsprint. However, the porosity and bulk increased with an increase in the contaminant levels. These effects can be attributed to a decline in the interfibre bonding. The authors also reported that the brightness decreased with increased contaminant levels whereas the scattering coefficient increased due to a reduced bond area and absorption coefficients and opacity also tended to increase (Francis and Ouchi, 2001).

System closure also tends to affect the function of retention and drainage aid systems in newsprint mills (Polverari et al., 2004). Various water soluble polymers are used as retention and drainage aids in the manufacture of newsprint such as polyethylene oxide (PEO), charged and non-ionic polyacrylamides and polymers such as polyethyleneimine and polyamines which are highly charged and have a low molecular weight (Polverari et al., 2001). Polymers that are highly charged and have a low molecular weight are known as coagulants whereas those with a lower charge and high molecular weight are known as flocculants. A study by Polverari et al. (2001) investigated the performance of retention and drainage aid systems at different levels of system closure. They discovered that PEO retention and drainage aids performed fairly efficient when an enhancer was used at high degrees of system closure since the drainage rate and water retention value improved. However, the clay polymer system became inactive. It was also established that increased closure resulted in inefficient performance of cationic polymers such as cationic polyacrylamide (CPAM)

due to the build-up of dissolved and colloidal substances. A similar result was reported in a study carried out by Dunham et al. (2002) in which the effect of DCS on drainage properties of mechanical pulp suspensions was investigated. The authors concluded that the accumulation of DCS has a negative effect on CPAM-induced flocculation as well as drainage. Careful consideration needs to be given to the type of retention and drainage aids used in system closure.

Different contaminants tend to affect the paper properties differently (Stebbing, 2002). Lignin found in the white water is the main cause of reduced sheet strength and also has the effect of lowering sheet brightness due to redeposition on the pulp. System closure in recycled paper mills results in the accumulation of starch which, in the presence of the process water, tends to hydrolyse to form glucose. Due to the warm anoxic nature of the process water, glucose is converted to various volatile fatty acids such as lactic acid, butyric acid, propionic acid and acetic acid by the action of acidogenic bacteria, resulting in bad odours in the final product (Baijpai, 2012). Temperature and conductivity increase with increased closure and the pH also tends to fluctuate. This can affect the performance of wet end additives. Anions in the white water increase the demand for chemical additives and fibre swelling is decreased by cations altering sheet formation. Paper strength is drastically lowered by the accumulation of lignans, sterols and phenolic compounds in the white water as the system is closed (Stebbing, 2002).

All of these issues arising as a result of system closure need to be carefully monitored and controlled in order to successfully implement system closure in mills and to reduce the adverse effect on product quality.

2.4 System closure: water loop arrangement

The main objective in implementing water loops in paper mills is to obtain minimum consumption of fresh water (Suhr et al., 2015). White water from paper machines contain high quantities of fibre and can be used to dilute stock in the mixing chest ahead of the paper machine. This is referred to as the short circulation or the primary circuit. On the other hand it can be used in the stock preparation and this is known as the long circulation or secondary circuit. The main concept adopted in the reuse of process water is that white water should be allowed to flow counter current to the product flow. A portion of the white water is clarified in save all as illustrated in Figure 2-2. Various methods can be applied in the clarification of the white water such as filtration, flotation and sedimentation and the clarified water can be substituted for fresh water in various areas of the process such as showers used in the cleaning of machine clothing (Suhr et al., 2015). It is also possible to use the clarified water as seal vacuum pump water (LUCENSE SCpA, 2002). Any excess clarified process water is sent to a treatment plant.

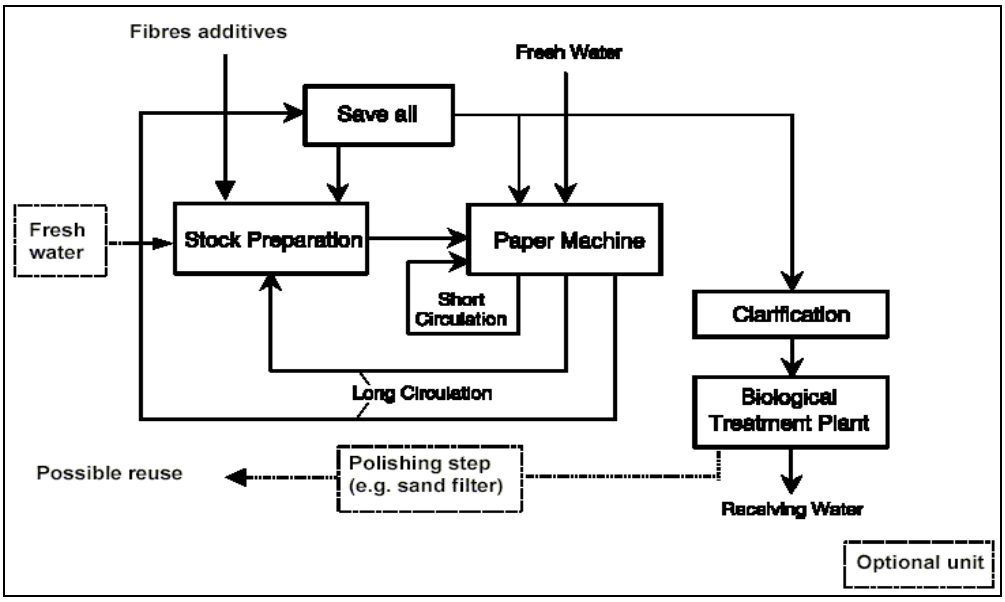

Figure 2-2: Scheme of water loop arrangement (Adapted from Suhr et al., 2015)

2.5 Technologies used in system closure in system closure

System closure is not only beneficial to the newsprint industry but also has the potential to positively impact on the entire pulp and paper industry. Various technologies and concepts for system closure have been investigated throughout the years such as membrane filtration, enzyme treatment, freeze crystallization, evaporation, flotation, coagulation and the application of the water source diagram. These technologies will be discussed in the paragraphs to follow.

The closed cycle configuration used depends on the type of mill and is usually made up of a combination of in-mill and ex-mill methods in order to achieve reduced discharge of effluent at minimum cost (Gerbasi et al., 1993). The main aspect that requires consideration in system closure is dissolved and suspended solids removal. The measures to remove dissolved solids or suspended solids from the water are often referred to as kidneys (Hubbe, 2007). The internal purification of white water can be rather expensive. However, it is beneficial in the fact that it is able to reduce costs in terms of purchasing and heating fresh water. The purified water can be used back in the process.

White water treatment and reuse to achieve system closure is unique and depends on each mill. Generally, the process begins (initial treatment) with fibre recovery using disc filters or thickeners. Dissolved air flotation clarifiers and gravity strainers are in the primary white water treatment stage, these aid in further removal of suspended solids (Gerbasi et al., 1993). Additional white water treatment may be required, depending on the end user water requirements. This may include fine separation systems such as membrane filtration technologies with a combination of biological treatments. Membrane filtration technologies such as micro filtration and ultrafiltration remove high molecular weight dissolved organic and inorganic solids. The purpose of the biological treatment is

to remove low molecular weight organic dissolved solids. Biological treatment of waste water often includes two stages, anaerobic treatment as the first stage followed by aerobic biological treatment (LUCENSE SCpA, 2002). An anaerobic treatment is carried out in different reactors such as an up flow anaerobic sludge blanket, fixed-bed reactor and fluidised-bed reactor. The dissolved organics that are not removed by anaerobic treatment are metabolised in an aeration basin.

2.5.1 Membrane filtration for system closure

2.5.1.1 Fundamentals of membrane filtration

A membrane operates on the action of a driving force in order to separate substances and is generally a thin semi-permeable material constructed from cellulose acetate or various polymers such as polyvinylidene flouride, polypropylene, polysulfone and polyethersulfone (Scott, 1995). Membrane processes usually have a permeate stream and a retentate/waste stream; substances that pass through the membrane accumulate in the permeate stream and those that are retained build-up in the retentate/waste stream. Figure 2-3 illustrates membrane filtration.

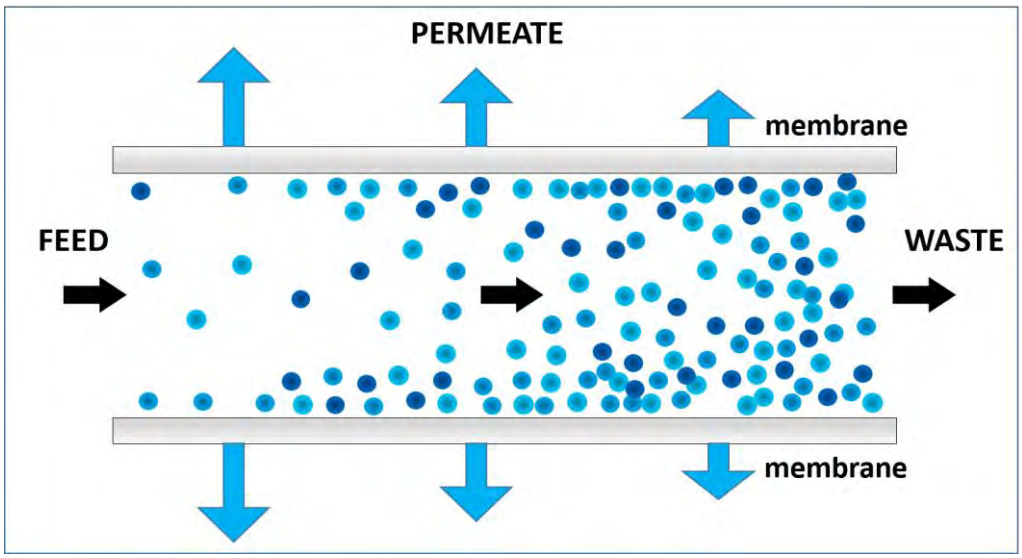

Figure 2-3: Illustration of membrane filtration (Adapted from Scott, 1995)

Membrane filtration is utilised in various industrial applications such as sterilization of drugs, purification of antibiotics, treatment of wastewater to remove impurities, removal of organics from water, recovery of methane from biogas and heamodialysis. It is less energy intensive as compared to other forms of separation and poses various other advantages such as the ability to test large sample volumes, limited preparation time as compared to other methods and is capable of allowing bacterial monitoring which is especially important in food and beverage manufacturing. However, membranes are prone to fouling (Seader and Henley, 2006).

Different types of membrane filtration exist such as ultrafiltration (UF), nanofiltration (NF), microfiltration (MF) and reverse osmosis (RO). UF and MF membranes work in a similar manner as that of a sieve and separation is mainly based on size of contaminants (Gutman, 1987). MF and UF are able to remove suspended and colloidal substances and RO and NF are generally used for the removal of dissolved substances. RO is capable of retaining all substances besides the solvent and is often referred to as a dewatering technique (Cheryan, 1986). This type of membrane filtration incurs high capital and operating costs. UF on the other hand can be used as a method to simultaneously purify, fractionate and concentrate macromolecules and requires fairly low operating pressures as compared to RO and NF since the osmotic pressures in UF are low. The low operating pressures required reduce operating and equipment cost making UF a desirable option. Another advantage of UF is that it does not require any sophisticated heat-generating equipment as compared to conventional separation methods like evaporation. Table 2-2 illustrates some parameters of the different types of membrane filtration (NDWC, 2005).

Table 2-2: Parameters for membrane filtration (Adapted from NDWC, 2005)

	Pore size (microns)	Molecular Weight cut-off (MWCO) (kDa)	Operating Pressure (kPa)
MF	0.03-10	> 1000	100-400
UF	0.002-0.1	10-100	200-700
NF	0.001	1-100	600-1000

2.5.1.2 Membrane Performance Characteristics

In membrane filtration the driving force required in order for separation to take place emanates from a pressure difference between the feed and permeate and the selectivity and permeate flux determines the performance of the membrane. Selectivity refers to the capability of a membrane to retain certain substances and is generally given by the rejection/retention obtained using equation 1 (Odhav, 2004).

$$R = \frac{C_f - C_p}{C_f} = 1 - \frac{C_p}{C_f} \quad \text{..... (1)}$$

Where:

C_f = Concentration of a component in the feed stream

C_p = Concentration of a component in the permeate

R ~ 0, component freely permeates

R ~ 1, Component is retained

The retention is based on the molecular weight cut-off of the membrane. The flux is defined as the permeate rate per unit area of membrane and is obtained by equation 2 (Bulsara et al., 2011).

$$J = \frac{V}{A_m\ t} \quad \text{..... (2)}$$

Where:

V = Volumetric flow (L)

A_m = Membrane area (m^2)

t = Time (hr)

The percent volume reduction or percent water removal is given by equation 3 (Cheryan, 1986).

$$Percent\ volume\ reduction = \frac{V_o\ - V_R}{V_o}\ x\ 100 \quad \text{..... (3)}$$

Where:

V_o = Initial feed volume

V_R = Retentate volume

V_o - V_R = V_p (Permeate volume)

Five main factors affect the flux of a membrane namely pressure, feed concentration, temperature and flow rate and turbulence. The effect of certain parameters on the membrane flux is depicted in Figure 2-4.

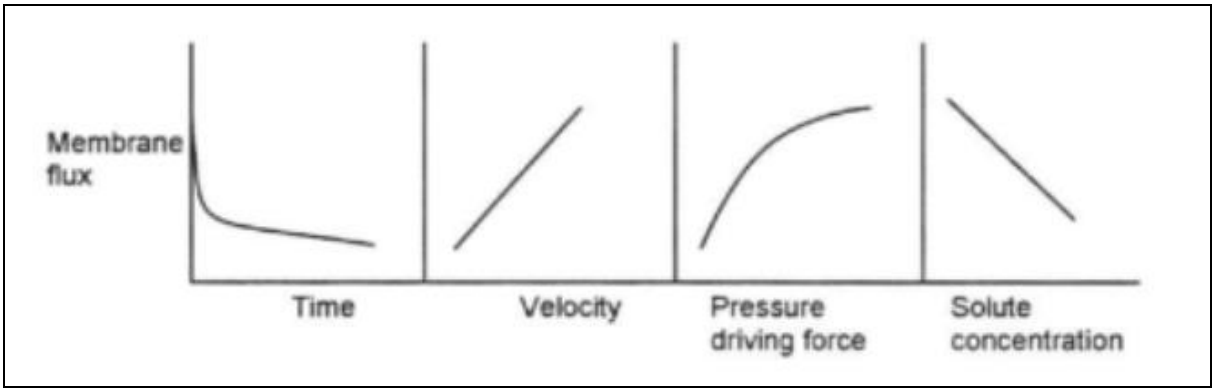

Figure 2-4: Effect of operating parameters on the membrane flux (Adapted from Odhav, 2004)

The flux is directly proportional to the applied pressure. However, this is true under certain conditions such as when the pressure is low, the feed velocity is high and the feed concentration is low (Cheryan, 1986). Concentration polarization effects are minute at these conditions and deviations from such conditions render the flux independent of pressure. Concentration polarization results when substances that are highly rejected by the membrane accumulate and tend to form a gelatinous layer on the membrane restricting the flow of permeate. Increased crossflow velocity

reduces fouling thus increasing the membrane flux. Cheryan (1986) states that the flux will decrease with increasing feed concentration and the viscosity, density and diffusivity will also be affected. Increased concentration of the feed results in a higher viscosity which in turn causes complications during pumping of the feed. Increase in temperature results in a reduction in the viscosity thus increasing the throughput and flux. However, in certain cases fouling occurs at higher temperatures as a result of precipitation of insoluble salts. Turbulence or agitation of the feed close to the membrane surface enables the control of concentration polarization by brushing away solute build-up thus increasing the flux.

2.5.1.3 Studies using ultrafiltration for treatment of white water

In an attempt to achieve a completely closed system, Gerbasi et al. (1993) investigated the application of biological treatment combined with membrane technology. Effluent from a 550 air-dried-tones/day TMP newsprint mill was treated and it was found that anaerobic technology reduced operating and capital costs involved in the biological treatment. The next stage of the process involved membrane treatment of the effluent, firstly, by ultrafiltration (UF) and then followed by reverse osmosis (RO). In the study it was assumed that the RO will enable water recoveries of 85% to 95% and the RO step served the purpose of removing inorganic constituents. It was also established that to achieve a fully closed system, evaporation and drying steps should follow the RO step. Since the distillate was already heated it could be directly used in the mill as process water and the ash could be sold to generate revenue.

The main advantage of membrane filtration is its durability and throughput (Hubbe, 2007). It is also cost effective and has the potential to save energy making it a viable method. Another study conducted by Elefsiniotis et al. (1997) investigated ultrafiltration and/or biological treatment to achieve system closure. A tangential flow ultrafiltration unit, consisting of two polyethersulfone membrane cassettes, with membranes having a molecular weight cut-off of 10 kDa and 100 kDa was used. A sequencing batch reactor was used for the biological treatment, the effect of membrane molecular weight cut-off and system operating temperature on the removal efficiencies of contaminants was also investigated.

When ultrafiltration was only used for the treatment of the white water, it was reported by Elefsiniotis et al. (1997) that the removal of resin and fatty acid was 69% and 55% for the 100 kDa and 10 kDa membranes, respectively and the removal of soluble COD, TDS and TOC were in the range of 10-37%. Removal efficiencies for the ultrafiltration treatment were affected by the membrane molecular weight cut-off which is the molecular weight that restricts 80% of the analytes from diffusing through the membrane but system operating temperature had no effect on the efficiencies when either or both of the methods were used. The use of biological treatment resulted in

a total and soluble COD and a TOC removal of over 70% and the removal of resin and fatty acids was over 90% for this particular treatment.

It was reported that when the white water was first biologically treated before ultrafiltration the highest overall removal efficiencies were observed and the removal of contaminants such as TDS, soluble COD, TOC, and resin and fatty acids were 48%, 95%, 93% and 100%, respectively (Elefsiniotis et al., 1997). Removal efficiencies were affected by the membrane molecular weight cut-off. Higher permeate fluxes were reported when biological treatment and ultrafiltration were used due to the reduction of fouling contaminants in the biological pre-treatment.

Tardif and Hall (1997) investigated the effectiveness of three alternatives for the treatment of newsprint white water. The treatment methods were ultrafiltration, sequencing batch reactor treatment (SBR) and biological pre-treatment followed by ultrafiltration (SBR and UF). The authors utilised a simulated white water made up of 1 L screw pressate from a TMP mill and 35 ml of 35% w/w evaporator concentrate from a BCTMP mill, diluted to a volume of 5 L in tap water. The nutrients used in the SBR experiments were aqueous solutions of trisodium phosphate and ammonium chloride. The SBR was operated at temperatures between 20-50° C. Ultrafiltration experiments were conducted in the same temperature range. A tangential flow unit was used in the study. It consisted of a polyethersulfone membrane cassette with one open channel. Experiments were conducted at a pressure of 137 kPa. The MWCO of each cassette was either 10 or 100 kDa.

The results obtained indicate that fatty acids were more effectively removed with UF than resin acids. UF achieved a fatty acid removal of 79 to 100%. The SBR treatment obtained a fatty and resin acid removal of 92 to 100% at temperatures of 20 to 40° C. They also found that poor resin acid removals were achieved at temperatures above 40° C. The removal of dissolved COD, TDS and DOC was moderate with UF. They reported that the use of a membrane with a smaller pore size significantly improved the removal of contaminants. However, temperature had little effect on the removal of contaminants. The combined SBR and UF treatment improved the removal of contaminants, indicating that biological treatment is an effective pre-treatment to ultrafiltration. The highest removal of TDS, dissolved COD and DOC was obtained with the combined SBR and UF treatment. The permeate flux for both the UF and combined UF and SBR treatment increased with an increase in temperature. The results also indicated that fluxes obtained for the combined UF and SBR treatment were much higher than those obtained for UF alone.

Another study conducted by Elliott and Mahmood (2007) investigated the ability of ultrafiltration, sand filtration, rotating biological contactors (RBC) and suspended carrier biofilm (SCB) reactors for the removal of contaminants from white water systems. For ultrafiltration tubular membranes were used with a half inch diameter and a molecular weight cut-off of 100 kDa, the sand filtration unit

consisted of a column with a height of 56 cm and a surface area of 180 cm^2 . A pilot rotating biological contactor was used in continuous-flow mode and consisted of 15 disks having a diameter of 31 cm with attached growth; the SCB used was also an attached growth process. However, in this process the biofilm attaches and grows on plastic carrier media and aeration serves the purpose of agitation and supplies dissolved oxygen.

In the study Elliott and Mahmood (2007) found that the RBC performed better than the SCB in terms of removing residual total suspended solids and the SBC produced significantly more sludge as compared to the RBC due to suspended growth in the reactor and restricted growth of biofilm on the carrier media. The RBC also resulted in higher removal of COD and BOD. It was also reported that ultrafiltration performed better than sand filtration since the sand filter continuously clogged and required frequent backwashing and the UF was able to remove all suspended solids. However, UF was inefficient in removing BOD as compared to the biological systems used. They also found that the biological systems were more effective than UF and sand filtration in removing dissolved organic contaminants.

Holmen paper mill, based in Madrid, is an excellent example of a mill which uses recovered fibre and recycled water. The mill is equipped with two paper machines, one producing 170000 t/yr of newsprint, magazine and light weight coated (LWC) paper and the other producing 300000 t/yr newsprint solely from recycled fibre (Bressler, 2010). Due to the shortage and the cost of fresh water in Madrid experienced in 2007, Holmen paper embarked on a project to recycle waste water and the mill opted to use ultrafiltration as the treatment method followed by reverse osmosis. The challenges experienced by the mill was cleaning of the membranes without interrupting operation and the electricity required to run both ultrafiltration and reverse osmosis. The treatment plant, situated 3km from the mill, was built in 2010. This treatment plant will have major positive implications for the mill and will enable the mill to be the first mill in Europe to utilise 100% recycled water as well as recycled fibre in their production process. The mill also incorporates other forms of good practice such as recycling sludge into building materials (Bressler, 2010).

2.5.1.4 Membrane bioreactor treatment for system closure

Membrane bioreactors (MBR) involve a combination of membrane filtration and biotechnology in order to achieve system closure (Ramaekers et al., 2001). Due to this combination, MBR's are able to remove dissolved substances such as COD, BOD_5 and calcium and solids (Simstich et al., 2012). The components of a membrane bioreactor include an aeration tank and a membrane filtration unit and the mill waste water is directed to the aeration tank. The presence of bacteria serves the purpose of converting the biodegradable organic matter as well as reduced nitrogen compounds. In the

second stage of the process the water from the aeration tank including biomass are sent to the membrane filtration unit for the separation of the sludge from the water. Thereafter the filtrate is drained off as effluent and the concentrate is then directed back to the aeration tank. Figure 2-5 illustrates a typical MBR setup.

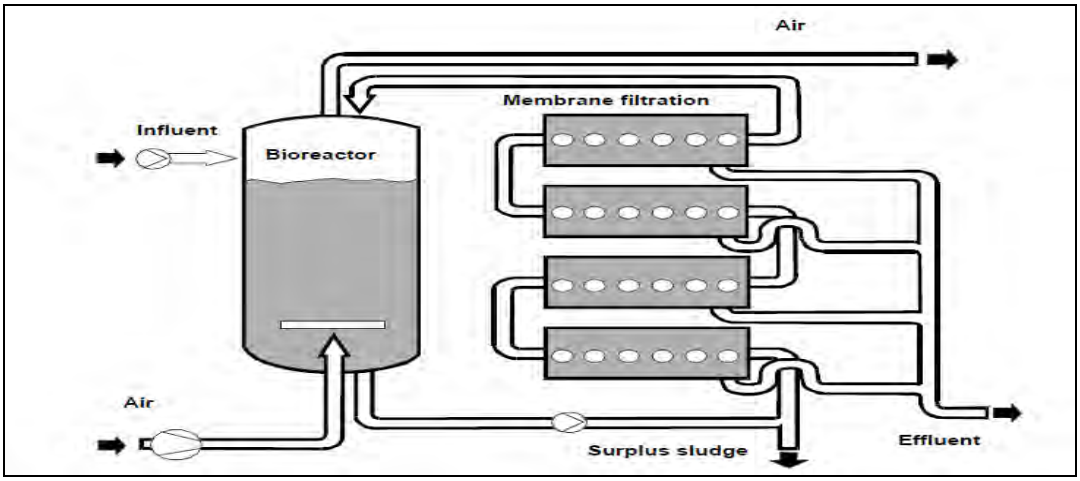

Figure 2-5: MBR process setup (Adapted from Ramaekers et al., 2001)

Tardif and Hall (1997) investigated the application of MBR treatment to system closure in newsprint mills and incorporated the use of aerobic membrane bioreactor treatment. The MBR set-up included a tubular ultrafiltration (UF) membrane unit, two sequencing batch reactors to supply the microorganisms used in the reactor and a perforated acrylic tube situated at the bottom of the reactor to supply aeration. The reactor was kept in a water bath with an immersion circulator to maintain a constant temperature of 40-55°C of the mixed liquor and the same membrane unit used in the MBR setup was used to perform only UF for system closure.

The results reported indicated that the MBR treatment could remove compounds contributing to COD more efficiently than that of ultrafiltration due to the bio-oxidation of the degradable organic substances in the MBR. UF was capable of removing colour with efficiencies in the range of 11-54% whereas MBR was not able to remove colour from the white water. However, MBR was more effective in the removal of TCOD, DCOD and DOC as compared to UF. Organic particles contribute significantly to colour problems. Fatty acids were effectively removed by the application of both processes. However, resin acids were more effectively removed by MBR due to the rapid sludge adsorption in MBR (Tardif and Hall, 1997). Pitch deposits did not occur in the MBR as compared to the UF. However, UF is much more easier to operate. The main advantages of MBR systems is the high quality of effluent produced and the reduced amount of sludge produced (Ramaekers et al., 2001). A major concern in MBR systems is the occurrence of microbiological growth in other parts of the mill water circuit due to the addition of nutrients for the biomass in the MBR as well as the

possibility that the efficiency of the biomass in the MBR can be affected by variations in temperature and pH.

In another study conducted by Sitabule (2004) a submerged membrane bioreactor (SMBR) was used for the treatment of final effluent from the Sappi Stanger mill. A SMBR pilot plant consisting of 10 flat sheet membranes with an effective pore size of 0.01 μm was used. The membranes were submerged into a 1.8m^3 stainless steel bio-reactor. The pilot plant also consisted of a coarse bubble aeration system which supplied a crossflow velocity of 0.5 m/s and two fine bubble diffusers in order to supply enough oxygen for efficient aerobic biodegradation of organics. Nitrogen and phosphorus in the form of urea and phosphoric acid were added to the feed wastewater to serve as nutrients for biological growth. The Results obtained show that the design flux of 19 l/m^2.hr was achievable with this pilot plant and a COD removal of 87% was obtained. The SMBR was able to produce a permeate with a COD of only 248mg/l. It was also reported that the concentration of the mixed liquor suspended solids in the reactor had no effect on the flux. However, higher organic loads increased the COD removal (Sitabule, 2004).

Thermophilic MBR treatment is also gaining popularity in the pulp and paper industry since increased system closure has the effect of increasing the temperature of process water within the mill (de Sousa et al., 2010). Due to the thermophilic conditions a considerable reduction in gas required for heating is achieved (Ramaekers et al., 2001).

2.5.2 Enzyme treatment for system closure

Substituting enzymes such as laccase for bacteria in white water treatment improves the control of the system as well as selectivity. However, it can increase the net biological oxygen demand of the system due to the biomass of the enzyme (Hubbe, 2007). The enzyme pectinase has the ability to reduce the cationic demand of white water from peroxide-bleached TMP mills. Hemicellulose derived macromolecules form strong bonds with cationic additives adversely affecting the performance of these additives and pectinase counteracts this effect by breaking up the hemicellulose macromolecules thus reducing their chain length and making them incapable of forming bonds with cationic additives. Lipases, esterases, cellulases as well as pectinases (hydrolytic enzymes) are capable of degrading pitch (Zhang et al., 2000). Drainage rates are increased when enzymes are used for treatment thus making enzyme treatment an attractive option and the addition of cellulases to the furnish tends to increase the dewatering rates. The increase in dewatering rates can be attributed to the dissolution of fine cellulosic material. However, adding cellulase to the furnish can lead to undesirable occurrences such as the partial degradation of long fibres (Hubbe, 2007).

A study conducted by Saddler et al. (1999) investigated the use of fungal enzyme treatment for the removal of DCS. They directed white water into a bioreactor in which fungi is grown and charged

the reactor with enzymes. It was reported that a majority of the DCS was degraded to less detrimental components. The concentration of lignans, triglycerides and steryl esters decreased by more than 90% after the treatment, however, resin and fatty acids were only reduced by 20-50%. In a study conducted by Zhang et al. (2000) the enzymes lipase, laccase, cellulase and mannanase were used for the treatment of white water from a TMP newsprint mill. In the study filtered and unfiltered white water were treated with the enzymes. The filtered white water was colloid-free whereas the unfiltered white water was not.

The results showed that the enzyme laccase enabled the degradation of the majority of extractives. However lipase, was only able to hydrolyze the ester-bonded extractives found in the original white water and monomeric sugars were released when cellulase and mannanase were used to treat the filtered white water. Cellulase was more effective in hydrolyzing the neutral carbohydrates than mannanase and the enzyme lipase had no effect on the dissolved constituents of the filtered white water.

Another study conducted by Stebbing (2002) investigated fungal enzyme treatment of white water from mechanical pulp and paper mills. It was found that fungal enzyme treatment had the effect of decreasing the average colloidal particle size thus improving paper surface properties and increasing the fibre surface charge, zeta potential of the particle and molecular weight of the phenolic compounds. Chemical-fibre bonding is increased when the fibre surface charge increases; this has the effect of reducing the quantity of additives needed and compounds become easier to remove when their zeta potential and molecular weight are increased since they become unstable (Stebbing, 2002). It was reported by Stebbing (2002) that fungal enzyme treatment reduced the total dissolved and colloidal substances (TDCS) in white water.

2.5.3 Freeze crystallization for system closure

Another closed cycle technology investigated by Gerbasi et al. (1993) is that of freeze crystallization, the principles of which is based on Brownian motion. When a crystalline solid is acquired from a solution it is referred to as crystallization (Lewis et al., 2010). Gradually decreasing the temperature of a solution results in the Brownian motion of water molecules reducing as a result the molecules move toward each other and they cluster resulting in ice crystals and the contaminants become concentrated. If the crystallization rate increases dramatically contaminants tend to get trapped within the crystal and in order to prevent such an occurrence temperature gradients and residence time need to be carefully controlled. The first stage of this process is effluent pre-treatment. The effluent has to be cooled before entering the crystallizers and this is achieved by using the melted water from the freeze crystallizers. Thereafter, the effluent is sent to the dissolved air flotation system in order to remove solids and then directed to the crystallization system (Gerbasi et al., 1993).

The crystallizer used in the study was able to process 1375m^3/d and could only handle an effluent with a total suspended solids level of 100-150 $mg.l^{-1}$ (Gerbasi et al., 1993). In this stage of the process the total dissolved solids is concentrated to 10-15%. However, it is important to note that the main problem associated with this method for system closure is that at concentrations of total dissolved solids exceeding 15%, resin and fatty acids tend to attach to the ice crystals. The crystals are dewatered and washed in a belt filter and then sent to a heat exchanger where they are melted to produce recycled water. Thereafter, the water is sent to a sand filter for removal of any solids (Gerbasi et al., 1993).

The final stage of the process involved liquor concentration which took place in a two-stage evaporator resulting in the solids being concentrated to 50%. The condensate was already heated and could be directly used back in the process. Since the amount of concentrated liquor emerging was not large it was proposed by Gerbasi et al. (1993) to burn the liquor in the hog fuel boilers or sell it to kraft mills where it can be used as a source of energy.

A study conducted by Long and Hsieh (1997) investigated the application of freeze crystallization for water treatment at the Louisiana-Pacific BCTMP mill in Chetwynd, British Columbia, Canada. It was reported that the concept worked well on a lab and pilot scale but proved unsuccessful when implemented at the actual mill due to problems encountered such as plugging of the crystallizer tubes as well as scaling of the tubes resulting in shutdowns (Long and Hsieh, 1997). In a review on the control of dissolved and colloidal substances in mills it was reported by Miao *et al*. (2013) that in order to effectively implement freeze crystallization for white water treatment it is vital to control the freezing speed. It was also reported that it is a rather difficult system to operate and start-up costs are extremely high.

2.5.4 Evaporation for system closure

Multi-effect evaporation is being more widely used in mechanical pulp and paper mills in order to implement system closure due to the fact that the method is energy efficient since many of the evaporation systems utilize waste heat streams as well as the latent heat of the effluent to operate the system (Suhr et al., 2015). Other evaporation configurations can also be used such as mechanical vapor recompression systems. However, the type of evaporation system used depends on the particular mill in question. A study conducted by Gerbasi et al. (1993) has indicated that mills with existing boilers that have little excess steam capacity are more likely to use mechanical vapor recompression and those in which low-cost steam is readily available lean towards the use of multi-effect evaporation. The concentrate produced by evaporation can be incinerated in a recovery boiler in order to achieve zero discharge of effluent and the condensate can be used back in the process to reduce the consumption of fresh water (Suhr et al., 2015).

The Meadow Lake CTMP mill in Canada uses evaporation, concentration and incineration to treat effluent emanating from the mill, in a process that begins with primary treatment involving clarifiers in order to remove dissolved solids which are dewatered prior to incineration. The next stage of the process involves mechanical vapour recompression. It was reported that the solids in this step increased from 2.5% to 35% . It is vital to ensure that the clean distillate is not contaminated and in order to achieve this, the distillate from the mechanical vapor recompression is internally separated into fractions (Suhr et al., 2015). At the mill a steam stripper is used to strip the organics from the fraction containing the highest amount of VOCs and is incinerated in a recovery boiler and since the distillate from the evaporation process is already at a reasonable temperature (65°c) it can be used directly back in the mill where needed.

The final step of the process at this particular mill involves increasing the dissolved solids in the concentrate from the mechanical vapor recompression evaporator to 70% in two concentrators and then incinerating it in a chemical recovery boiler. A number of other mills such as Louisiana-Pacific Canada Ltd. and Millar Western Pulp Ltd. have adopted evaporation techniques in order to reduce their production of waste (Stratton et al., 2004).
Evaporation requires much more energy as compared to other methods for system closure such as freeze crystallization making it less desirable. Evaporators are also prone to scale build-up.

2.5.5 Flotation for system closure

Many mills are equipped with flotation save-alls -these devices work by bubbling air through the water in order to lift the solids to the surface enabling them to be scraped off and returned to the paper machine since they contain some valuable fibre fines (Hubbe, 2007). Thickeners and disc filters may also be used for this purpose. Dissolved air flotation is popular for water clarification in paper mills since some of the solids are hydrophobic. Some applications of dissolved air flotation in the newsprint industry include the separation of ink droplets from water. The main disadvantage of dissolved air flotation is that due to its high removal rate of almost all solids, it tends to also remove valuable filler material and wood fines. Research conducted by Haapala et al. (2010) has reported that selective flotation is a better choice as opposed to dissolved air flotation since selective flotation possesses a higher selectivity for the removal of hydrophobic material, wood extractives, stickies and ink.

A study conducted by Miranda et al. (2009) investigated the treatment of mill process water by dissolved air flotation (DAF). The main focus was to test the chemical optimization of DAF using new chemicals. The effect of combining polyaluminium salts and cationic polyelectrolytes to be used in DAF was investigated. The results reported by Miranda et al. (2009) state that combining polyaluminium nitrate sulphate together with a polyamine was most effective in removing

contaminants. Waste water from newsprint and LWC paper mills was used in the study.

An earlier study conducted by Dionne et al. (2007) investigated the performance of a flotation column to clean whitewater emanating from the Bowater Gatineau mill in Canada. The mill produced newsprint manufactured from 50% TMP and 50% de-inked pulp (DIP). For this study a lab-scale flotation column with a height of 4.65 m and a diameter of 10.2 cm was used. The experimental set-up consisted of the pulp slurry being pumped into the column below the froth level and air was injected at the bottom of the column resulting in bubbles flowing counter current to the descending pulp slurry. The portion of the column below the feed point is known as the collection zone, in which hydrophobic particles are trapped by the air bubbles and carried to the froth zone and the region above the feed point is known as the froth zone which is forced to the top and removed as rejects. The cleaner water is collected at the bottom of the column. In the study wash water was introduced at the top of the column in order to decrease fibre entrainment and increase the selectivity of the flotation process.

Dionne et al. (2007) reported that column flotation was able to achieve 85% removal of extractives after six minutes and ink removal was enhanced with longer residence times of the white water in the flotation column. They also reported a flotation efficiency of 64% at a flotation time of six minutes and as the flotation time increased so too did the mean particle size of the rejects. From this they concluded that column flotation was able to remove the smallest and most hydrophobic contaminants (fines) thus improving the quality of the white water. It also had other advantages such as higher selectivity and fibre yield as compared to flotation cells, was relatively inexpensive, had low maintenance costs and took up less space (Dionne et al., 2007).

In a study conducted by Haapala et al. (2010) the selective flotation of white water was carried out in a lab-scale flotation cell. Three types of white water were used, namely white water from a board machine, a newsprint machine and a paper machine using mechanical virgin pulp made up of pressurized groundwood pulp and thermomechanical pulp. The experiments involved no adjustment of pH and no chemicals were used since most white waters contain calcium and surface active extractives enabling them to form froths without the addition of chemicals (Haapala et al., 2010). The study involved continuously removing the froth formed and analyzing the liquid phase for contaminants. The results reported by Haapala *et al*., 2010) stated that only the white water from the newsprint machine and that from the machine using mechanical virgin pulp were able to form froths and a removal of 10% total solids, 45% stickies, 27% ink and 20-50% wood extractives from the white water was achieved. The main short coming of the method is that not all white waters are capable of producing a stable froth which is a requirement for the flotation process.

A later study conducted by Haapala et al. (2012) investigated the ability of multiphase flotation to

purify and deaerate white water. In the study the white waters used were from two European mills with newsprint being their primary product. Two different types of white water were used, one obtained from a paper machine that uses a combination of 35% TMP and 65% deinked pulp (DIP) and the other from a machine that uses 100% DIP. The study involved investigating firstly channel flow flotation and secondary flotation separately and then investigating a combination of both with the aid of a modeling process. The reject from the channel flow flotation was used as the feed to the secondary flotation system. The channel flow flotation system comprised of a steam and water cooling casing within a storage tank, a collection system to accommodate the overflow as well as an air feed membrane system enclosed by a flow channel 1 m wide and 4 m long. The temperature of the feed was kept at 45° C, the channel flow loop was operated as a single-stage flotation system in continuous mode and the experiments were conducted in the presence and absence of channel flow aeration (Haapala et al., 2012).

The secondary flotation system consisted of a 65 L continuous flotation cell and was run at 45° C with a feed flow rate and air flow rate of 12 $L.min^{-1}$ and 20 $L.min^{-1}$, respectively. The rejects from the system were constantly sent to the mixed feed tank (Haapala et al., 2012). The results showed that aeration considerably improved froth build-up and the DIP water developed a greater amount of froth and a more stable froth as compared to the TMP/DIP water. Aeration also increased the removal efficiencies of contaminants in both white waters. A higher reject flow rate was used in the experiments conducted with DIP water. It was shown that the removal of stickies and wood extractives was better in the DIP water than the TMP/DIP water and the combination of the channel flow flotation and secondary flotation was able to remove 5%-10%, 10%-20% and 7% wood extractives, stickies and ink, respectively. It was also reported that secondary flotation was able to produce a more stable froth than channel flow flotation and the use of aeration in the channel flow flotation had the effect of increasing the relative solids losses in the Secondary flotation. However, the combined two-stage process significantly reduced contaminant concentrations and did not hinder the channel flow's deaerating function (Haapala et al., 2012).

From the investigations studied it can be noted that the main aspect to consider in order to obtain an efficient flotation process is the formation of a stable froth and adequate build-up of a froth.

2.5.6 Patex fine filtration system for system closure

The Patex fine filtration system operates by continuously circulating white water and retaining the fibres and colloidal material (Koepenick, 2011). This advanced system is capable of removing particles from 1-20 microns from white water containing approximately 2000 ppm solids (McGowan, 2002b). The system is applicable not only to newsprint mills but can also be successfully utilized in mills producing fine paper and recycled packaging board products. It does

not require chemical flocculants, precoats or sweetener stock, is capable of removing 90% contaminants in the size range of 1-20 microns and fines and high solids can be filtered in a single stage with this particular system. The consumption of fresh water in mills is reduced by approximately 30% with the use of the Petax fine filtration system (Koepenick, 2011).

The system consists of four to sixteen rotary filter disks, a pressurized vessel and a rotating hollow shaft. Figures 2-6 and 2-7 illustrates the internals of the filtration system; as can be seen the disks are mounted on the shaft which is housed in the pressurized vessel and a filter medium is situated on either side of the disks (McGowan, 2002b).

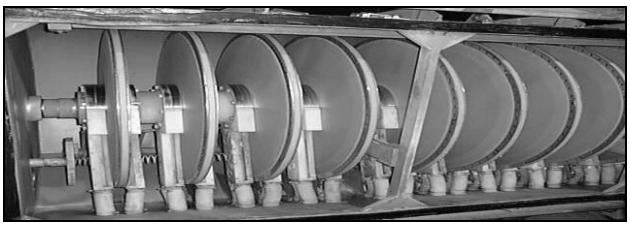

Figure 2-6: Internal Setup of Filtration System (Adapted from McGowan, 2002)

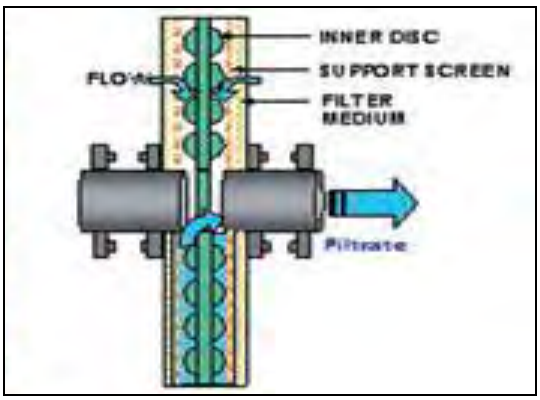

Figure 2-7: Components of the Disk (Adapted from McGowan, 2002)

Fluid is forced through the filter medium on the rotating, submerged disks by the low pressure in the vessel and the filtrate then enters the hollow shaft via the discs and exits the vessel at atmospheric pressure. It is capable of handling flows up to 4000 l/min. The exterior of the rotating disks trap the solids which are drawn out of the vessel and pumped to the couch pit. The discs are made up of three components namely the filter screen, support screen and the polypropylene support disc. The filter screens are situated on either side on the outer surface of the discs and serve the purpose of retaining solids during the filtration process (McGowan, 2002a). The support screen is placed behind the filter screen which provides strength and rigidity to the filter screen and both the filter screen and support discs are fabric layers. The polypropylene support disc is situated in the middle and these fabric layers are clamped on either side of it as illustrated in Figure 6 and the system is equipped with a three-stage continuous cleaning system in order to effectively remove the fines, fillers, fibres and

other material that are trapped on the outer surface of the filter as well as within the fabric. The first stage of the cleaning process involves filter cakes being doctored off and pumped into a header and exiting the system, the second stage involves clean filtrate being pumped back into the filter screen, this is known as backflushing and aids in removing particles trapped within the filter and the final cleaning stage utilizes a submerged, oscillating, high pressure shower for cleaning each disc (Koepenick, 2011; McGowan, 2002a). The filtrate leaving the system consists of 70-80% of the inlet flow to the system with the balance exiting as concentrated liquid containing fines, fillers, fibres and other particles (McGowan, 2002a).

McGowan (2002b) reported the application of the Patex fine filtration system at two newsprint mills. One of the newsprint mills utilized clear-leg saveall water with an average clarity level of 87 ppm. The mill used gravity strainers to reduce the white water solids and the quality of the water did not allow for efficient operation of the formers. However, trials on the Patex system indicated the potential to reduce the white water solids from 87 ppm to 2 ppm enabling efficient operation of showers in the forming section. The second newsprint mill used a pressure screen to reduce the white water solids from 212 to 148 ppm. However, results from trials on the Patex system indicate the potential to reduce the solids to 25 ppm. Other paper manufacturers such as Encore Tissue in Australia have opted to use the fine filtration system in their manufacturing process enabling showers to function properly and eliminating blockages (Koepenick, 2011).

This particular method for system closure has many advantages. Other methods pose various problems when it comes to the filtration of fines and small particles such as sand filters which experience severe plugging making them inefficient for fine filtration. Reverse osmosis filters, unlike the Patex system, are very expensive and often require the replacement of membranes (McGowan, 2002b). In the case of dissolved air flotation, further filtration methods are often required due to the clarified liquid from the flotation process containing both small and large particles and dissolved air flotation is also much more expensive than the Patex system due to the continual need for chemicals such as frothers, depressants, activators and collectors. The fine filtration system reduces the cost of waste water treatment and saves energy by reducing the amount of water required to be heated. It also reduces the plugging of nozzles limiting the disruptions in operation of the machine and the solids recovered can be reused in the stock preparation stage of the papermaking process (McGowan, 2002a).

2.5.7 Coagulation for system closure

In the coagulation process colloidal particles are destabilized with the aid of chemical reagents. The suspended particles are coated with the chemical reagent and coalesce to form larger flocs and settle

with time (Droste, 1997). The two main types of coagulants used are mineral coagulants such as iron salts and aluminium salts and organic coagulants such as polyamines, melamine-formaldehyde resins, polydadmac and dicyandiamide resins. Mineral coagulants are much cheaper than organic coagulants. The main advantages of coagulation are the short retention times and the low capital costs required (Stephenson and Duff, 1996). The efficiency of the process is governed by various factors such as the type of coagulant, the solution pH and the dosage of the coagulant used.

In a study conducted by Waghmare (2013), it was found that alum coagulation significantly reduced TSS, TDS and colour. Experiments were conducted at a contact duration of 4 hours and at room temperature on waste water from a paper mill producing board, Kraft paper and corrugated boxes.

Stephenson and Duff (1996) investigated the effectiveness of chemical coagulation for the treatment of mechanical pulping effluent. The coagulants used in this study were ferrous sulphate, ferric chloride, aluminium sulphate and aluminium chloride. Batch jar tests were conducted. Results obtained indicated that with regard to total carbon (TC) removal, ferric chloride was most successful and an increase in coagulant dosage resulted in an increase in contaminant removal. The results also showed that adjusting the pH from highly acidic to almost neutral levels improved the removal of TC, colour and turbidity. Coagulation with the aid of aluminium sulphate was not as sensitive to pH adjustment as compared to coagulation using iron salts. A removal of 88% TC and 90-98% colour and turbidity was achieved with both iron and aluminium salts as coagulants. Additionally precipitation reactions were highly influenced by pH.

In a study conducted by Verenich and Kallas (2001) coagulation was used as a post treatment for wet oxidation of waste water. Ferrous sulphate was used as a coagulant at dosages ranging from 0.29g Fe^{3+}/L to 0.98g Fe^{3+}/L. A high pressure batch reactor was used to conduct the wet oxidation experiments. They discovered that the coagulant functions well in a pH range of 5-6 with the optimum pH being 6. At the optimum pH and a coagulant dosage of 0.65g Fe^{3+}/L, they found that significantly larger flocs developed thus making the coagulation process more effective. The removal of contaminants increased with an increase in the dosage of the coagulant. At a dosage of 0.86g Fe^{3+}/L they obtained a colour removal and lignin reduction of 83% and 75% respectively.

As an attempt to achieve closed system, Chen and Horan (1998) investigated the use of chemical coagulation and solid separation in a tertiary treatment process. Furthermore, they applied electro dialysis reversal (EDR) and biological treatment after the tertiary treatment stage. The chemical coagulation and solids separation serves to reduce the organic contaminants by adding coagulation chemicals such as alum, whereas, the purpose of the EDR stage is for desalination. This pilot-scale study involved treating effluent from a newsprint mill (Shotton Paper Co. in the UK). The mill used a combination of thermo-mechanical pulp and recycled fibre.

Electro dialysis involves the use of ion-exchange membranes and operates by transferring electrolytes through the membrane by an electrical driving force resulting in a diluted solution and a concentrated stream, the membrane rejects the solutes (Chen and Horan, 1998). The electro dialysis reversal incorporates the same concept: however, a polarity reversal is implemented. The supernatant from the chemical coagulation stage is then pumped to the EDR stage which is operated in a semi-batch mode and the product stream is diverted back to the EDR feed tank if it does not meet the target conductivity of 500-600 $\mu S\ cm^{-1}$.

Chen and Horan (1998) reported that the TOC, COD and colour were reduced by 81%, 70% and 81%, respectively, and the EDR stage further reduced the residual organics by half resulting in an overall removal rate of 90%, 83% and 92% for TOC, COD and colour respectively. The residual TOC was reduced to the same level as that of the fresh water supply level and the EDR stage was able to achieve a COD and colour removal rate of over 20%. The chemical coagulation stage was able to reduce lignin and lignin derivatives by 78%. These constituents were further reduced by 30% in the EDR stage.

The main flaw of this process is the lack of a filtration stage resulting in low removal rates of suspended solids and turbidity (Chen and Horan, 1998). A significant reduction in conductivity (70%), TDS (80%), sulphate (70%) and calcium (76%) was achieved by the process and the removal of cations was substantially high with the level of cations being reduced to lower than that in the fresh water supply. This process was also capable of significantly reducing heavy trace metals, e.g. barium and sodium were reduced by 80% and sulphate was reduced by 76% in the EDR stage. The chloride level in the final product was half of that in the fresh water. The result also showed significant reduction in residual nutrients. However, the EDR stage was unable to remove silicates.

The membrane system of the process has several advantages such as the prevention of polarisation by disintegrating of polarisation films, ability to break up precipitated scale, the electrodes are automatically cleaned and continuous operation with no need for addition of chemicals (Chen and Horan, 1998). The main disadvantage of the process is the production of considerable amounts of chemical sludge due to agglomeration of colloidal materials with chemicals in the tertiary treatment stage.

A study carried out by Dorica and Elliott (1999) investigated alum coagulation as a form of tertiary treatment for biologically treated newsprint effluent emanating from both pilot and full- scale activated sludge plants. Other tertiary treatments investigated in the study were sand filtration and granular activated carbon (GAC) adsorption. In this study the full-scale biological treatment plant consisted of an equalization basin, an aeration basin and a secondary clarifier and the pilot plant set-up was similar except that an additional aeration basin was in place. The quality of effluent obtained

was compared to the water supplied by the river to the mill. A jar test apparatus was used for the alum coagulation experiments and involved addition of 1 litre of effluent in a beaker, after which alum was added and the sample was agitated for 1 minute at 160 rpm. The sand filter and the GAC filter were operated in the same manner, i.e., they were operated continuously for two bed volumes and thereafter samples were taken for analysis.

The results showed that biological treatment was able to reduce turbidity, iron, silica and aluminum to values less than those found in the river water supplied to the mill. However, the effluent still contained significant amounts of dissolved solids and required tertiary treatment. They found that tertiary treatment was able to reduce the BOD concentrations significantly (13 $mg.L^{-1}$ to 3-4 $mg.L^{-1}$) and in the full-scale system it was observed that alum coagulation and GAC adsorption exhibited the best removal of colour and COD. It was also reported that inefficient removal of TDS, sulphates and conductivity was exhibited by the tertiary treatments investigated and the TDS and sulphate concentrations were higher than those found in the river water supply.

Dorica and Elliott (1999) also found that in the full-scale system GAC adsorption was more efficient in reducing the concentration of residual COD. However, the effluent from all three tertiary treatments contained significantly higher concentrations of magnesium, hardness and calcium. They also found that the full-scale plant and pilot plant exhibited similar removal efficiencies for colour, turbidity and BOD and replacing 25% of the mill river water supply with tertiary effluent had no influence on the quality of the newsprint produced (Dorica and Elliott, 1999).

Orori et al. (2005) conducted an investigation to decolorize water emanating from a pulp and paper mill by combining electrochemical and coagulation methods. The mill involved in the study was the Pan African Paper mill in Kenya which is a major producer of newsprint, packaging and writing paper. In the study different treatment methods were investigated such as chemical coagulation with ferric chloride ($FeCl_3$), calcium oxide (CaO) or alum as coagulants, electrochemical coagulation and electrochemical coagulation combined with CaO, wood ash leachate or alum. The coagulation method required the determination of a suitable pH and dosage of the coagulant; to achieve this the authors used a standard jar test method and for the electrochemical methods, three iron electrodes were used that were separated 5mm from each other with the aid of a non-conducting material. The experimental set-up consisted of the electrodes being immersed in and suspended above a beaker of the wastewater with a magnetic stirrer and an electric current passing through the electrodes. In the combined electrochemical-coagulation methods the electrodes were rinsed with 8% sulphuric acid to prevent fouling.

The results showed over 90% colour reduction when chemical coagulation was used and of the three coagulants tested $FeCl_3$ exhibited the highest reduction in colour. They also showed that the

electrochemical method, with a combination of wood ash leachate, was the most effective in reducing colour as it was capable of reducing colour by 100%, COD by 80.66%, BOD by 81.25% and turbidity, TSS and TS by 92.14%, 94.90% and 97.26%, respectively. It was also reported that this method exhibited the lowest operational cost.

Another study conducted by Elliott and Mahmood (2007) also investigated the use of coagulation to treat whitewater. In the study a continuous flow system was adopted and polyaluminum chloride was utilized in order to clarify the whitewater since it is able to operate over wider pH ranges and, unlike alum, it does not leave high aluminum residues. It was reported by Elliott and Mahmood (2007) that coagulation was able to remove one third of the TOC and TSS was removed to values below the mean found in the fresh water.

A later study conducted by Ahmad et al. (2008) investigated the effectiveness of a combined coagulation-flocculation process for pulp and paper mill waste water treatment. Alum and polyaluminium chloride (PACL) were used as coagulants. The coagulants were first used alone and then combined with cationic polyacrylamide (C-PAM) and anionic polyacrylamide (A-PAM) for the treatment of the waste water. They found that with alum coagulation adjusting the pH close to neutral values improved the removal of TSS, COD and turbidity. The alum functions well in a pH range of 5 to 6.5 with the optimum pH being 6. At the optimum pH and alum dosage of 1000 mg/L they were able to obtain a 99.8% reduction in turbidity and a 91% reduction in COD as well as a 99.4% removal of TSS. They found that the optimum pH for PACL was the same as that of alum. However, the optimum dosage was half of that obtained for alum coagulation. PACL coagulation at the optimum conditions resulted in a 99.9% turbidity reduction, 91.3% COD reduction and a 99.5% removal of TSS. When using a combination of flocculants and coagulants they discovered that combining C-PAM with the coagulants was more effective than A-PAM alone. The best combination obtained was Alum and C-PAM: this combination resulted in a 99.7% reduction in turbidity, COD reduction of 95.6%, a low sludge volume index (SVI) of 38 mL/g, TSS removal of 99.5% and a significantly lower settling time.

2.5.8 Application of the water source diagram to system closure

The water source diagram was developed by Gomes et al. (2007) and the main principle behind the procedure is the synthesis of mass exchange networks. The main objective of the method is the minimization of water consumed in the process as well as the wastewater produced (Marques et al., 2008). This particular procedure takes into consideration water reuse, flow rate constraints, multiple water sources, regeneration and reuse, water losses along the process and regeneration and recycling.

The first step of the procedure involves dividing the process into concentration intervals; thereafter water is permitted to be used between these intervals. Each interval has a concentration limit and

these are taken as sources of water. The external water sources are the fresh water supply and regenerated water. The concentrations are represented in a grid in an orderly manner. The final step of the procedure involves calculation of the mass transferred in each interval of concentration in each operation and are indicated between parentheses on the actual diagram, e.g. (255 kg/d).

Once the water source diagram has been developed there are certain rules that need to be adhered to in order to achieve the objectives. In this procedure, external water sources are used when internal water sources are not available (Marques et al., 2008). In some instances, when an operation occurs in several intervals, the procedure addresses this situation by allowing the water flow of the operation to remain along the intervals until it comes to an end. In each interval of concentration the largest amount of mass must be transferred. This method is desirable due to the fact that the network structure and the minimum fresh water consumption target can be obtained simultaneously.

2.5.9 Integrated newsprint mills: system closure techniques

Certain integrated mills have adopted closed-loop recycling of vacuum pump seal water together with controlled blow-down in order to reduce the build-up of dissolved solids. Other methods to reduce the consumption of fresh water in such mills include reuse of seal water from high vacuum pumps to low vacuum pumps and in the paper machine water loop system (Houle et al., 1999). Limitations of this strategy is that the temperature of the seal water can affect the vacuum pump capacity.

To prevent this modern mills are integrated with cooling towers. Reduction in the flow of fresh water to pump sealing systems can result in considerable amounts of water being saved. Houle et al. (1999) have reported various techniques introduced by the Donohue mill in Amos, Quebec in order to reduce the consumption of water. The mill is an integrated one which produces newsprint from TMP and deinked pulp and the mill has introduced partial recycle of non-contaminated cooling water, partial recirculation of the effluent from the secondary treatment system and the re-use of a portion of the vacuum pumps discharge as sealing water for vacuum pumps in order to achieve system closure.

A pump was installed to increase the amount of non-contaminated water recycled to the fresh water tank (Houle et al., 1999). Recycling the water increases the temperature of the water in the fresh water tank enabling high temperatures to be maintained in the wastewater treatment system (LUCENSE SCpA, 2002). With this measure in place it was reported that fresh water consumption was reduced by 5500 m^3/d. Substitution of biologically treated water for fresh water to be used in paper machine showers can result in reduction in the cost associated with heating since the water is already heated. It is also possible to utilise clear or super clear white water from the save-alls in paper machine showers. However, plugging of nozzles is a major problem experienced in mills. In order to prevent plugging of the nozzles it is important to have strainers in place with an automatic purge

prior to sending the water to the showers (LUCENSE SCpA, 2002). An experiment carried out by the mill involved a portion of water from the secondary clarifier being sent to the sand filters and thereafter added to the fresh water tank. The sand filters in place at the mill serve the purpose of removing the suspended solids present in the water from the river. However, the main concern with this technique is the accumulation of viscous bio-solids from the effluent treatment. Due to this accumulation, backwashing of the filter was necessary. However, the experiment was abandoned due to these negative implications. In order for this technique to be a success the viscous suspended solids need to be firstly removed by implementing an extra filtration stage (Houle et al., 1999).

The waste water treatment plant at the mill has a large hydraulic load and due to this, it was more attractive to implement measures that reduce water consumption as well as hydraulic load. By recycling water used to seal and cool vacuum pumps, a reduction in water consumption and hydraulic load can be achieved. The vacuum pump effluent is only moderately contaminated and thus does not require as intense treatment as mill white water (Houle et al., 1999).

Results from a study conducted at the Donohue mill indicated that when a portion of the vacuum pump effluent was used as seal water for all present vacuum pumps, the inlet water temperature often increases and if the temperature rise was too great, the degree of vacuum achieved by the pump could be affected. Houle et al. (1999) used a model developed by Ecole Polytechnique in 1997 to determine the thermal behaviour of the vacuum pump.

The results from their study indicate a temperature rise of the inlet water from 10°C to 27°C with no detrimental effect on pump performance and it was also established in the study that applying this measure results in the reduction of fresh water consumption by 47%. If the recycle rate of the pump sealing water was very high, the inlet water temperature to the pump would rise dramatically and cooling systems in the recycle line became necessary in order to ensure an adequate vacuum. A problem associated with this measure in the long term could be the plugging of the inlet orifices of the vacuum pump and a good preventative measure would be to install strainers (Houle et al., 1999). Clarified water is also used as sealing water in certain mills (LUCENSE SCpA, 2002).

In a study conducted by Shafiei et al. (2002) a method was developed to apply system closure to an integrated pulp and paper mill. The method involves characterizing white water networks in terms of water demands and sources and thereafter a genetic algorithm and linear programming is used to determine feasible white water network configurations based on process constraints as well as objective functions.

The separation of water loops and incorporation of counter-current flows are measures that apply well to integrated pulp and paper mills and mills using recycled paper (LUCENSE SCpA, 2002). The term separation implies that each section of the mill such as the pulping, the paper making and

bleaching department, if present, has its own water circuit and counter-current means that the white water from the paper machine will flow in the reverse direction to the preceding section usually to a section where a high quality of water is not necessary. Thickeners generally aid in the separation of water loops and the presence of an additional thickener to separate the stock preparation water and the paper machine water significantly reduces the organic contaminants in the paper machine water loop by a factor of 2-4. However, one of the cons associated with this measure is the high cost of thickeners (LUCENSE SCpA, 2002). It is also essential to separate the broke water system and the white water system since the quality of the white water system is fairly constant but the quality of the broke water system varies. If, allowed to mix considerable flow variations result in the white water system.

2.6 Summary of advantages and disadvantages of the treatment methods

Table 2-3 illustrates the advantages and disadvantages associated with various treatment methods used for system closure.

Table 2-3: Advantages and disadvantages of different treatment methods

Treatment Method	Advantage	Disadvantage
Coagulation	Short retention times and low capital costs required (Stephenson and Duff, 1996)	Residual cations tend to remain in the supernatant (Stephenson and Duff, 1996)
Enzyme Treatment	Improves the control of the system as well as selectivity. Drainage rates are increased (Hubbe, 2007)	Increases the BOD of the system
Membrane Filtration	Less energy intensive as compared to other methods, the ability to test large sample volumes, limited preparation time as compared to other methods and its capability of removing bacteria (Seader and Henley, 2006)	Membranes are prone to fouling which results in shut down of the operation in order to clean or replace membranes.
Flotation	High removal rate of almost all solids. Capable of recovering pulp and recycling water back into the process (Asano and Visvanathan, 1997).	Tends to also remove valuable filler material and wood fines. Not all white waters are capable of producing a stable froth which is a requirement for the efficient operation of the flotation process (Haapala et al., 2010).
Evaporation	Produces a superior quality condensate (Hubbe, 2007)	Can be energy intensive. Evaporators are prone to scale build-up over time
Freeze Crystallization	Produces a superior purity product; operating temperatures are relatively low; reduced corrosion effects on the materials of construction (Heist, 1981)	Plugging and scaling of crystallizer tubes leads to shutdowns required for cleaning (Long and Hsieh, 1997)
Biological Treatment	Highly efficient reduction of BOD (Hubbe, 2007).	Leads to salt build-up and inefficient dewatering (Hubbe, 2007)

As pointed out in the literature review system closure is associated with a build-up of contaminants in process streams which can have various negative implications on both the production process and

product quality. The literature review as provided insight into the various technologies that can be used to implement system closure, however, some are rather expensive and not viable. Membrane filtration was chosen for the treatment of newsprint mill white water since it does not require any sophisticated heat generating equipment. Membrane filtration is easily adapted to fit the needs of different mills in terms of the water quality required. The costs associated with installation is relatively low since membrane systems do not need to be housed in large buildings or on large pieces of land as compared to conventional systems (Scott, 1995). Membrane filtration is also capable of producing a high quality permeate and does not require excessive addition of chemicals.

CHAPTER 3 MATERIALS AND METHODS

The proposed project comprises of three main aspects namely, 1) simulation of system closure in the laboratory, investigating the concentrations of contaminants that accumulate in the white water as the loop is closed, determining the effect of system closure on product quality, 2) evaluating UF as the core process for purification of white water, and finally 3) determining the optimum operating conditions for UF that reduce fouling of the membrane.

3.1 Materials

The Mondi Merebank mill provided the pulp samples to be used in the study. Three samples pulp were collected from the mill namely thermo-mechanical pulp (TMP) from the TMP fibre line after the secondary refining process stage, recycled fibre pulp (RFP) from the recycled fibre line after the refiner and pulp samples from the headbox dilution water line in the paper machine system. The samples were stored in a refrigerator at 4±0.1 °C before use. White water was collected from the white water chest.

3.2 Methods

3.2.1 Simulation of system closure

System closure was simulated in the laboratory by using a Rapid-Kothen paper machine. In order to carry out the investigation the Rapid-Kothen paper machine had to be modified. Initially a bypass line was installed in place of the exit line of the machine. The line was then routed to an intermediate storage tank where the filtrate was collected. The inlet line for the suction pump was then re-routed to the storage tank to allow for the recycling process. However, this led to solids build-up in the line resulting in the pump being incapable of sucking all of the liquid out of the storage tank. To overcome this problem the suction line was removed and the filtrate was manually inserted into the machine.

The RFP and TMP samples were mixed in a ratio of 40:60. The consistencies of the samples were determined in duplicate in order to obtain a percentage error of less than 5%. The pulp from the headbox dilution line had a consistency of 0.6% and the combined RFP and TMP sample had a consistency of 3.7%. The pulp from the headbox dilution line was first diluted (2400ml pulp) with distilled water to the desired operating consistency of 0.3% and thereafter agitated for 20 min at 60°C - a similar agitation procedure was reported by Zhang et al. (2000). The pulp was then transferred to the Rapid-Kothen paper machine shown in Figure 3-1.

Figure 3-1: Rapid-Kothen paper machine

The filtrate was collected in a bucket and used to dilute a fresh pulp sample. The procedure was repeated for 20 cycles. No fresh water was added in each cycle resulting in a 100% level of closure. The filtrate after 20 cycles was then used to dilute the combined RFP and TMP samples (350ml pulp in 3967 ml) to the operating consistency. Again, no fresh water was added (100% level of closure). 3800ml of filtrate was collected after filtration using the Rapid-Kothen paper machine. The same volume of filtrate was collected from each sample indicating that the effect of the mat of fibres retained on the sieve of the Rapid-Kothen paper machine is equal in each sample - a similar observation was made by Miranda et al. (2009). A portion of the filtrate was retained in the mat of fibre formed and a sample was kept for analysis after each cycle. In order to achieve 100% closure and to prevent the addition of fresh water, the recycle process was conducted in a similar manner as that reported by Miranda et al. (2009). For each cycle multiple same batches of combined RFP and TMP pulp samples were mixed to the desired operating consistency, resulting in enough filtrate to dilute the pulp for the next cycle and a portion was retained for analysis. The number of same batches mixed reduces by one in each cycle due to the filtrate removed for analysis and that retained by the mat of fibres. The recirculation procedure was repeated 10 times. The experiments were conducted in duplicate. Figure 3-2 is a process flow diagram (PFD) of the simulated system closure process.

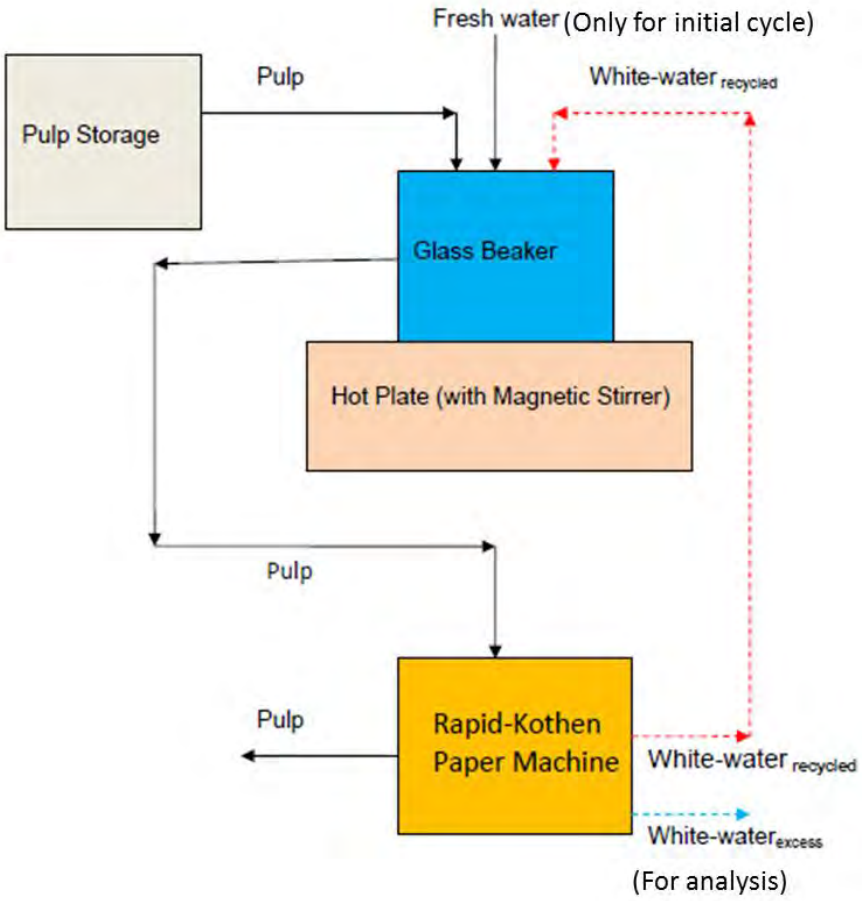

Figure 3-2: PFD of system closure

3.2.2 Hand sheet manufacture at different levels of closure

Hand-sheets were manufactured using a combination of the TAPPI test method T205 sp-95 and the ISO test method 5269-1:1998 (E) (TAPPI, 1994; ISO, 1998). Hand-sheets having an oven dry mass of 60g/m^2 were manufactured. Firstly 30g of oven dry equivalent pulp was weighed out using the following formula:

$$\text{Mass of pulp} = \frac{30\ g \times 100\%}{pulp\ consistency\ (\%)} \quad \ldots\ldots\ldots (5)$$

The pulp was then transferred to the disintegrator and disintegrated for 3 minutes. The disintegrated pulp was then transferred to the stock divider and made up to 10 litres .Air is bubbled through the pulp in order to enable agitation. 1 litre of pulp is then removed from the bottom of the stock divider via the tap and used to determine the freeness of the pulp according to the TAPPI test method T227 om-94 (TAPPI, 1994). A freeness tester was required in order to determine the freeness. The remaining pulp in the stock divider is made up to 13.5 litres. 1 litre of pulp is then removed from the stock divider and a test hand-sheet is made on the Rapid Kothen paper machine. The hand-sheet is

then removed from the machine and pressed at 600kPa for 5 minutes in a press. It is then removed from the press and dried in the dryer on the paper machine for 4 minutes. The hand-sheet is then further dried in the oven for 1 minute at 110°C. The weight of the hand-sheet was then determined. According to the method the weight of the test hand-sheet when using unbleached pulp should be between 1.79-1.98 g. If the weight of the hand-sheet is higher than 1.98 g, the pulp in the stock divider needs to be further diluted. The water that needs to be added is the difference between the total volume and the volume left in the stock divider. The total volume is calculated using equation 6:

$$Total\ volume\ (L) = \frac{Volume\ of\ water\ remaining\ in\ stock\ divider\ (L) \times ovendry\ mass\ of\ sheet\ (g)}{1.885} \quad \ldots (6)$$

The value 1.885 in equation 6 represents the average target mass i.e. average of 1.79 and 1.98 g. If the weight of the hand-sheet is lower than 1.79 g, water needs to be removed from the pulp in the stock divider. The air supply to the stock divider is closed and the pulp allowed to settle. The volume removed is calculated in the same manner as that which is removed. Thereafter a test hand-sheet is made again to check if the mass is within the limit. If the hand-sheet is within the limit, 10 1 litre batches of pulp are removed from the stock divider and 10 hand-sheets are made according to the method described above. Three different types of hand-sheets were manufactured. The first batch was made with 100% distilled water, in the second batch 50% distilled water and 50% white water was used and the third batch was manufactured with 100% white water. The three different types of hand-sheets were sent to Sappi Technology Centre to test the burst and brightness according to ISO test methods 2758, 2470-1 and 2470-2 (ISO, 2001; ISO, 1999). Analysis was conducted in triplicate.

3.2.3 Membrane filtration experiments: determination of suitable membrane

Laboratory scale ultrafiltration experiments were conducted in a dead end stirred cell. These experiments were conducted in order to determine the appropriate membrane to be used in further experiments. Four ultrafiltration membranes having molecular weight cut-off of 10 kDa, 50 kDa, 100 k Da and 150 kDa was studied. The membranes were manufactured from polyethersulfone (10 kDa), polyethersulfone (hydrophilic) (50 kDa and 150 kDa) and polysulfone (100 kDa). Experiments were carried out at a pressure of 1.5 bar, a temperature of 40°C and a stirring rate of 300 rpm.

Figure 3-3 illustrates the stirred cell apparatus: it consists of a heating coil and stirred cell, a magnetic stirrer, pump, water bath and air supply. The heating coil is wrapped around the stirred cell and hot water is pumped through it in order to maintain operating temperatures. The sample is manually inserted into the cell and the membrane sits at the bottom of the cell. The air supply is turned on and the pressure is adjusted via the regulator to the desired operating pressure. The

permeate exits via the tubing at the bottom of the cell and is collected in a measuring cylinder and kept for analysis. The time taken to collect 10 ml of permeate is recorded every 10 to 15min in order to produce the flux versus time curves. Flux versus time curves for the filtration of pure water were obtained before filtration of the white water sample and after cleaning the used membrane. These curves give an indication of the cleanability of the membrane. The extent of membrane fouling was determined by calculating the reduction in the pure water flux before and after filtration without cleaning the membrane as well as after cleaning the membrane in order to determine the irreversible fouling. Figure 3-4 is a process flow diagram (PFD) of the membrane filtration process. Experiments were conducted in duplicate.

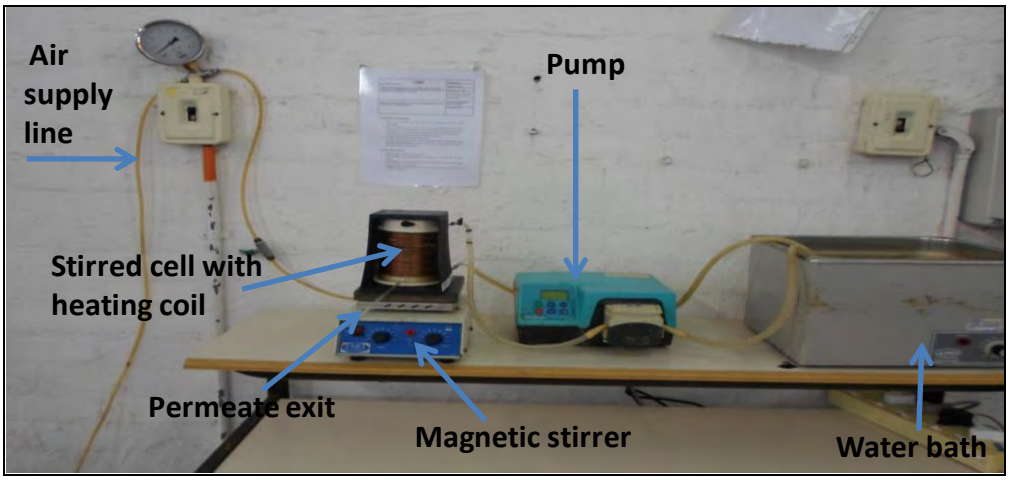

Figure 3-3: Stirred cell apparatus

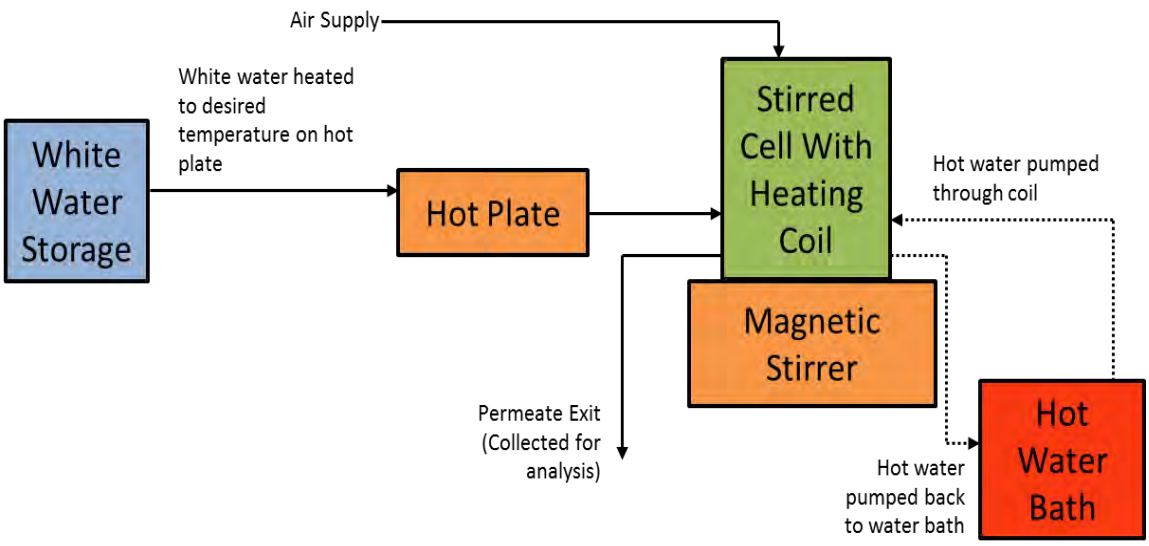

Figure 3-4: PFD of membrane filtration

3.2.4 Coagulation pre-treatment

Coagulation pre-treatment was conducted using a Jar test apparatus. The feed water had a high suspended solids concentration and turbidity which will plug the pores of the membrane and cause fouling, reducing the life span of the membrane. Coagulation pre-treatment was conducted to reduce the suspended solids concentration and turbidity thus reducing this effect. Alum and Ferric chloride were used as coagulants for the treatment of the white water samples. 500ml of white water was tested at three different levels of coagulant dosage (100, 300 and 500 mg/L) and pH (5, 7 and 9). The pH was first adjusted to the desired value by adding 1M NaOH or 1M H_2SO_4 to the solution. The chosen coagulant dosage was added to the white water sample and the solution was stirred with an overhead mixer at 250 rmp for 2min (flash mixing). Thereafter it was further mixed at 80 rpm for 15min.

The preceding mixing speeds were chosen since in the various studies in literature it was found that flash mixing was conducted between 200 and 300 rpm and slow mixing was below 100 rpm (Ahmed et al., 2008; Verenich and Kallas, 2001). It is also stated in literature that flash mixing speeds between 100 and 300 rpm adequately simulate the conditions on a plant (Freese et al., 2004). The flocs formed in the solution were allowed to settle for 1 hour. The supernatant was withdrawn using a syringe and turbidity and suspended solids of the supernatant were determined. The remaining sludge of the treated white water was used to measure the sludge volume index (SVI). The treatments were evaluated in terms of the ability of the treatment to reduce the suspended solids and the turbidity as well as produce a low sludge volume index (SVI). A central composite design was used and response surface methodology was applied in order to determine the optimum coagulant dosage and ph. Experiments were conducted in duplicate.

3.2.5 Membrane filtration experiments: determination of optimum operating conditions

Once a suitable membrane had been chosen the stirred cell was used to determine the optimum operating conditions. The design of experiments was carried out using the Taguchi method. This method incorporates fractional factorial experimental designs known as orthogonal arrays in order to minimise the number of trials conducted (Gonder et al., 2009). The type of orthogonal array chosen depends on the number of parameters and their levels as well as the total degrees of freedom (DOF) (Gonder et al., 2009). Three different levels of temperature (20, 40 and 60°C), pressure (1, 2 and 3 bar) and volume reduction factor (VRF) (0.63, 0.71 and 0.86) were investigated in order to determine the optimum operating conditions that provide the lowest fouling of the membrane (determined by flux reduction of the pure water flux). The VRF is the ratio of the permeate volume to the feed volume. Since this study has three parameters the DOF is six. The DOF of the array must be greater than or equal to the DOF of the parameters (Gonder et al., 2009). The Taguchi design L_9

(3^4) orthogonal array was chosen. This array applies to experiments involving four parameters with three levels. The DOF of this array is eight. Since it is greater than the DOF of the parameters in this study it can be applied in the design of experiments for this three parameter, three level study. The Taguchi method reduces the number of experiments required from 27 (3^3 for a full factorial design) to 9. The performance characteristic i.e. fouling were evaluated using the signal-to-noise (S/N) ratio. The S/N ratio enables the determination of the deviation of the performance characteristic from the desired value (Kumanan et al., 2007). It is also used to determine the optimum operating conditions. There are three different S/N ratios as listed below:

The smaller-the-better S/N ratio which minimises the performance characteristic (Wysk et al., 2000):

$$S/N = -10log\left[\frac{1}{n}\sum_{i=1}^{n} Y_i^2\right] \ldots\ldots\ldots (7)$$

The larger-the-better S/N ratio which maximizes the performance characteristic (Wysk et al., 2000):

$$S/N = -10log\left[\frac{1}{n}\sum_{i=1}^{n} \frac{1}{Y_i^2}\right] \ldots\ldots\ldots (8)$$

The nominal-the-better S/N ratio is used when a specific target value of the performance characteristic is desired (Wysk et al., 2000):

$$S/N = 10log\left[\frac{\overline{Y_i^2}}{S^2}\right] \ldots\ldots\ldots (9)$$

Where:

Y_i = value of the performance characteristic for the ith experiment

n = number of trials for the ith experiment

$\overline{Y_i}$ = average of the performance characteristic for the ith experiment

S= standard deviation

In order to optimize the fouling i.e. reduce the fouling, a lower flux reduction of the pure water (FR_{PWF}) is required, hence, the smaller-the-better S/N ratio is used to evaluate this performance characteristic. Once the optimum conditions are determined the predicted performance characteristic at these optimum conditions is determined using the following equation (Chaulia and Das, 2008):

$$S_{mp} = \overline{Y} + \left(\overline{A} - \overline{Y}\right) + \left(\overline{B} - \overline{Y}\right) + \left(\overline{C} - \overline{Y}\right) + \left(\overline{D} - \overline{Y}\right) \ldots\ldots\ldots (10)$$

Where:

$\overline{Y}$ = average of all readings for the performance characteristic

$\overline{A}, \overline{B}, \overline{C}, \overline{D}$ = average values of the performance characteristic at the optimum level of each parameter

The confidence interval is then calculated using the following equation (Chaulia and Das, 2008, Gonder et al., 2009):

$$CI = \sqrt{F(1, DOF_e) \times MS_e \times \left[\left(\frac{1}{n_{eff}}\right) + \left(\frac{1}{R}\right)\right]} \quad \ldots\ldots\ldots\ldots (11)$$

Where:

$F(1, DOF_e)$ = Value of the F ratio at the preferred confidence interval at a DOF of 1 and DOF of error

MS_e = mean of square of error (error variance)

n_{eff} = effective number of replications (total number of experiments divided by one plus the total degrees of freedom of the parameters i.e. excluding the error degree of freedom)

R = replications conducted for the confirmation experiment

Performance characteristics obtained in percentage had to first be converted to Ω (dB) using the following equation (Krishnaiah and Shahabudeen, 2012) in order to calculate the predicted performance characteristic and the confidence interval. The results obtained are then converted back to percentage using the same equation:

$$\Omega\,(dB) = 10log\left(\frac{P}{1-P}\right) \quad \ldots\ldots\ldots\ldots\ldots (12)$$

Where:

P= percentage of the performance characteristic

The predicted results are then verified by conducting a confirmation experiment at the optimum conditions. Anova analysis was also conducted in order to calculate the confidence interval using equation 11. At these optimum conditions that reduce fouling, hence improving the flux, the retention of contaminants is evaluated. Experiments were conducted in duplicate.

3.2.6 Chemical analysis of white water samples and permeate from UF

3.2.6.1 Total dissolved solids

The total dissolved solids were determined gravimetrically according to standard method APHA 2540 C (Eaton et al., 1995). 15 ml of sample was filtered through a 0.45 µm glass-fibre filter disk. The disk was washed with 3 successive 10 ml volumes of distilled water. The total filtrate was transferred to a pre-weighed crucible and evaporated to dryness in an oven. The evaporated sample was then dried in an oven at 180°C for 1hr. The crucible was then cooled in a desiccator and the weight recorded. The drying, cooling and weighing process was repeated until the weight change was less than 0.5 mg or 4%. Experiments were conducted in duplicates.

3.2.6.2 Total suspended solids

The total suspended solids were determined gravimetrically as described in the standard method APHA 2540 D (Eaton et al., 1995). The initial step involved washing a 0.45 µm glass-fibre filter with 3 successive 20 ml volumes of distilled water. The disk was then removed from the filtration apparatus, placed in a weighing dish and dried in an oven at 105°C for 1hr. It was then cooled in a desiccator and weighed. The drying, cooling and weighing was repeated until the weight change was less than 0.5 mg or 4%. The same filter paper was then used to filter 15 ml of sample and the filter paper was washed with 3 successive 10 ml volumes of distilled water. The disk was then removed from the filtration apparatus and transferred to the same dish previously used. The disk together with the dish was dried in the oven at 105°C for 1hr. The dish and filter was then cooled in a desiccator and the weight recorded. The drying, cooling and weighing process was repeated until the weight change was less than 0.5 mg or 4%. Experiments were conducted in duplicates.

3.2.6.3 Total solids

The total solids were determined gravimetrically according to the standard method APHA 2540 B (Eaton et al., 1995). The method involved drying a clean crucible in an oven at 105°C, cooling in a dessicator and recording the weight. 25 ml of sample was then transferred to the crucible and evaporated to dryness in an oven. The crucible was then dried in an oven at 105°C for 1hr. The sample was then cooled in a desiccator and the weight recorded. The drying, cooling and weighing process was repeated until the weight change was less than 0.5 mg or 4%. Experiments were conducted in duplicates.

3.2.6.4 Dissolved and colloidal solids

The content of dissolved and colloidal substances was measured using the method adapted from Jidong et al. (2011). The sample was centrifuged at 2000 rpm for 20 minutes in order to separate the suspended substances from the sample. After centrifugation the supernatant was collected and measuring the dry residue of the supernatant after evaporation in a rotary evaporator enabled the determination of the DCS content.

3.2.6.5 Ash content

The ash content measurement was adapted from Tappi standard methods (T 211 om-02) (TAPPI, 2002). 3-4 ml of the water sample was weighed and transferred to a crucible. The sample was then placed on a hot plate in order to evaporate the water as this would cause excess smoke in the furnace. The crucible was then placed in a furnace at 550°C overnight. Weighing the dry residue left behind enabled the determination of the ash present.

3.2.6.6 Extractives and lignin contents

The total amount of extractives in the samples was determined gravimetrically using liquid-liquid extraction. The method used was adapted from Orsa and Holmbolm (1994). The extraction solvent used was a mixture of toluene and ethanol in the ratio of 2:1. 50 ml of the sample was extracted twice with 100 ml of the extraction solvent. The amount of total extractives was determined by weighing the dry residue of the extraction solvent after evaporation in a rotary evaporator. UV absorbance at 280 nm with a spectrophotometer was carried out in order to determine the presence of lignin. 2ml of the water phase after liquid-liquid extraction was diluted with 3% sulphuric acid in a 20ml volumetric flask and then used to measure the UV absorbance at 280 nm. The UV280 of pure water was first performed and there after the samples. The absorbance of the sample at a wavelength of 280 nm was calculated by subtracting the absorbance of pure water at 280 nm from the sample absorbance at 280 nm.

3.2.6.7 COD

The COD was measured using the ASTM D 1252-00 standard method (ASTM, 2000). Sealed digestion and spectrometry were used in the determination. The reagents required for this test were silver sulphate catalyst solution and potassium acid phthalate solution. 1.5ml of digestion solution was transferred to a glass tubes. 3.5ml of silver sulphate catalyst solution was then added to the tube, followed by 2.5ml of the sample. The sample was added down the side of the tube in order to ensure a layer is formed above the reagents. The tubes were then sealed and shaken vigorously to allow for the reagents and sample to mix. There after the tubes were placed in a heating block at 150°C for 2 hours. After the 2 hours have elapsed the tubes are removed from the heating block and allowed to cool. After 5 minutes the tubes are shaken and allowed to cool for a further 30min. Once cooled the absorbance is then measured at 600 nm. The COD of a blank of distilled water was determined in the same manner. The COD of the samples including the blank was determined using a calibration curve of COD vs absorbance. For the calibration curve 2.5, 5, 10, 20, 30 and 40 ml of potassium acid phthalate standard solution was diluted to 50 ml with distilled water. The absorbance of these samples was determined in the same manner as outlined in the procedure above.

3.2.6.8 Turbidity

The turbidity was measured using a HACH 2100P turbidity meter according to the standard method APHA 2130 (Eaton et al., 1995).

3.2.6.9 Conductivity

The conductivity was measured using the HANNA Instruments, EC215 Conductivity meter according to the standard method APHA 2510 (Eaton et al., 1995).

3.2.6.10 Colour

The colour measurement was adapted from the PAPTAC standard H.5 (PAPTAC, 2006). The measurement is expressed in terms of colour units (C.U). A spectrophotometer is used in the measurement. Experiments were carried out at 23 ± 5°C. Samples that were highly coloured were diluted with distilled water in order to reduce their colour to fit in the range of the method. The pH of the sample was then adjusted to 7.6 ± 0.1 using a pH meter and NaOH or HCL solution. The sample was then filtered through a glass microfibre filter. Absorbance measurements were then taken at a wavelength of 465 nm. The spectrophotometer was first adjusted to an absorbance of zero using distilled water thereafter the absorbance of two aliquots of the sample was measured. Six readings of the sample were taken (3 readings on each aliquot). Three absorbance readings were then taken on the platinum-cobalt standard solution. Samples that were lightly coloured required the platinum-cobalt standard solution to be diluted with distilled water (1 part 500 C.U. std solution added to 4 parts distilled water). The colour of the sample was then determined using the following equation (PAPTAC, 2006):

$$C.U. = \frac{(500 \times A_2 \times D)}{A_1} \quad \text{..... (13)}$$

Where:

A_1 = Absorbance of the 500 C.U. platinum-cobalt solution

A_2 = Absorbance of the sample

D = Dilution factor of the sample which is equivalent to the ratio of the total volume of the diluted sample and the volume of the original sample.

3.2.6.11 Chlorides

Chlorides in the samples were determined using the ASTM D 512-89 standard method (ASTM, 1989). 10 ml of sample was diluted to 50 ml with distilled water. The sample was then transferred to the magnetic stirrer and stirred at constant speed thereafter 5 drops of mixed indicator solution was added. If the solution changed blue-violet or red in colour after adding the indicator solution, HNO_3 (3+997) was added dropwise until the colour changed to yellow thereafter 1 ml excess HNO_3 was added. If the colour changed to yellow or orange after addition of the indicator solution, NaOH solution (10g/L) was added dropwise until the colour changed to blue-violet and the same procedure followed as described above. The sample was then titrated using 0.025N $Hg(NO_3)_2$ until the entire sample changed to blue-violet. The amount of $Hg(NO_3)_2$ was recorded in millilitres. A sample of distilled water and 50 ml of standard sodium chloride salutation was run through the same procedure. The following calculations were made in order to determine the chloride content:

Chloride in standard sodium chloride solution:

$$Cl^- = \frac{(A \times 1000)}{1.65} \quad \text{……. (14)}$$

Normality of $Hg(NO_3)_2$ solution:

$$N = \frac{([Cl^-] \times S)}{[(V_1 - V_2) \times 35453]} \quad \text{…….. (15)}$$

Chloride concentration in sample:

$$Chloride\ (\frac{mg}{L}) = \frac{[(V_1 - V_2) \times N \times 35453]}{S} \quad \text{…….. (16)}$$

Where:

V_1 = standard $Hg(NO_3)_2$ solution required for titration of sample (ml)

V_2 = standard $Hg(NO_3)_2$ solution required for titration of blank (ml)

N = Normality of the $Hg(NO_3)_2$ solution

S = Sample volume (ml)

A = Weight of dried sodium chloride

$[Cl^-]$ = Concentration of chloride (mg/L)

3.2.6.12 Sulphates

Sulphate concentration in the samples was determined using the ASTM D 0516-02 standard method (ASTM, 2002). The method involves the conversion of sulphate ions into a barium sulphate solution. The turbidity of the sample is then determined and the sulphate concentration obtained from a calibration curve obtained by determining the turbidity of standard sulphate solutions. 5 ml of sample was diluted to 100 ml with distilled water. The sample was placed on a magnetic stirrer and mixed at a constant rate while 20 ml of buffer solution was added. Thereafter 0.3 g of barium chloride was added and the sample was stirred for 60 seconds. The sample was then transferred to a turbidity cell and allowed to stand for 5 minutes before the turbidity was measured. The same procedure was applied to a sample blank except barium chloride was added to it. Standard sulphate solutions were prepared by diluting 0, 5, 10, 15, 20, 25, 30, 35 and 40 ml of standard solution to 100 ml with distilled water. The standard solutions and a sample blank of distilled water were run through the same procedure and a calibration curve of sulphate ion concentration versus turbidity was plotted.

3.2.6.13 Metals analysis (ICP and Flame photometry)

The concentration of aluminium (Al), magnesium (Mg), calcium (Ca), silica (Si) and iron (Fe) were determined by inductively-coupled plasma spectroscopy (ICP) and the concentrations of potassium

(K) and sodium (Na) were determined by flame photometry. Samples were prepared according to standard method APHA 3030 A, D-F (Eaton et al., 1995). 3 ml of concentrated nitric acid and glass beads were added to 50 ml of sample. The sample was then evaporated to less than 5 ml on a hot plate and thereafter cooled and 5 ml of concentrated nitric acid was added. A watch glass was used to cover the sample and the temperature of the hot plate was increased in order to create a reflux action. Heating and addition of concentrated nitric acid was continued until digestion was complete.

Complete digestion is indicated by a light coloured solution or if no change in appearance of the sample with further refluxing. The sample watch glass was then removed and the sample was evaporated to less than 5 ml and cooled. Thereafter 10 ml of (1+1) HCL (500 ml of concentrated HCL diluted to 1L with 500 ml of distilled water) and 15 ml of distilled water were added to the sample and the sample was heated for 15 minutes. The sample was then cooled and the walls of the flask were washed with distilled water prior to filtering with a 0.45 μm filter. The filtrate was then transferred to a 100 ml volumetric flask and the beaker in which the filtrate was collected was rinsed twice with 5 ml of distilled water and these washings were added to the 100 ml volumetric flask. The contents were diluted to the mark and mixed. An aliquot of this solution was used for ICP analysis and 1 ml of solution was diluted in a 10 ml volumetric flask in order to conduct flame photometry.

CHAPTER 4 RESULTS AND DISCUSSION

This chapter discusses the results and main findings of the combined coagulation pre-treatment and UF investigation carried out as well as the results obtained from simulating system closure in the CSIR lab (KwaZulu-Natal).

4.1 Accumulation of contaminants in system closure

4.1.1 Accumulation of solids and ash

The results illustrated in Figures 4-1 to 4-4 shows an increase in contaminants with increase in the number of times the water is recycled. The steady state for the accumulation of contaminants was not reached after 10 cycles. A similar observation was made in a study conducted by Vendries and Pfromm (1998) in which a dynamique sheet former was used to simulate system closure where a 100% level of closure was used and the water was recycled 15 times (Vendries and Pfromm, 1998). They found that after 15 recycle runs the accumulation of contaminants did not reach steady state. Xu and Deng (2004) also ustilised a dynamique sheet former to simulate system closure: they discovered that at higher levels of closure the accumulation of contaminants took longer to reach equilibrium.

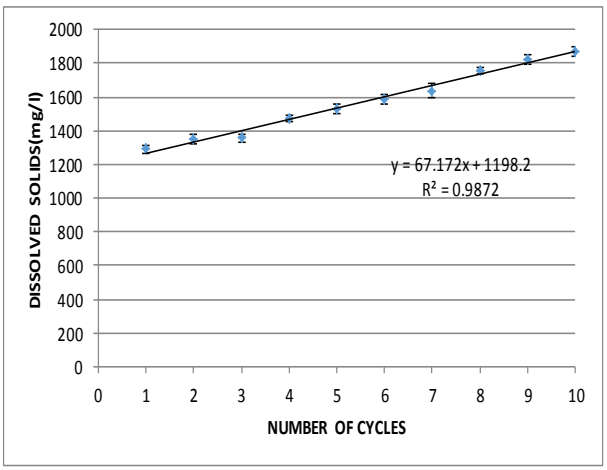

Figure 4-1: Accumulation of dissolved solids

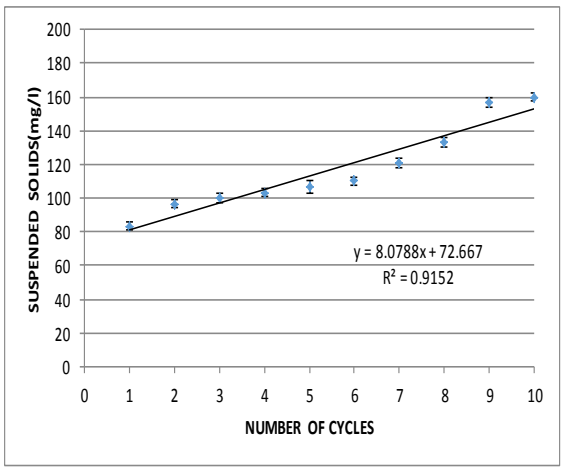

Figure 4-2: Accumulation of suspended solids

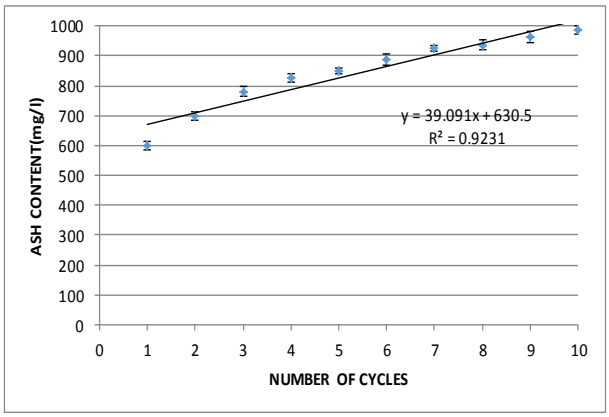

Figure 4-3: Accumulation of ash

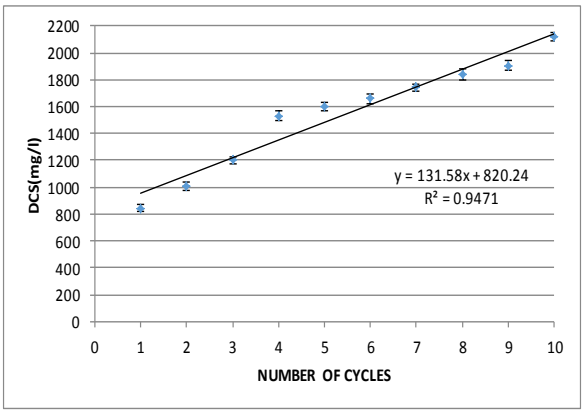

Figure 4-4: Accumulation of dissolved and colloidal solids

Figures 4-1 and 4-4 show that the dissolved solids and DCS increased by over 600 mg/l and 1000 mg/l after 10 cycles, respectively. The suspended solids shown in Figure 4-2 increased by nearly 100 mg/l after 10 cycles. A study by Jidong et al. (2011) yielded values of 670 mg/l and 3460 mg/l for DCS initially and after 10 cycles, respectively. The higher concentration of DCS obtained in their study can be attributed to the difference in raw materials used. In Jidong's study the raw materials were obtained from semi-chemical corrugated paper, waste paper board and waste boxboard paper-all systems that contain much more contaminants than newsprint mills. Figure 4-3 illustrates the build-up of ash as the number of times the water was recycled increased. The ash content increased from 600 mg/l to nearly a 1000 mg/l after 10 cycles. Ash build-up in the process water can lead to both operation and product quality problems. The build-up of ash in the water and the recirculation of this water can lead to refiner plate wear over time (Walraven, 1977). Increased ash content in the water results in elevated sheet ash which in turn causes the deterioration of sheet properties (Jones, 1993). Thermomechanical pulp (TMP) usually contains less ash than recycled fibre pulp (RFP) due to the deinking process used to produce RFP.

The accumulation factor (AF) and release factor (RF) were calculated for each contaminant present in the water. These factors were introduced by Alexander and Dobbins (1977). The AF gives an indication of how fast the contaminant concentration increases as the water is recycled (Alexander and Dobbins, 1977). The accumulation factor was calculated using equation 17 (Miranda et al., 2009):

$$(AF)_i = \frac{[(C_n)i-(C_0)i]}{[(C_1)i-(C_0)i]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (17)$$

$(AF)_i$ = accumulation factor of contaminant i in a closed system in which the recycling cycles is n

$(C_n)_i$ = concentration of contaminant i in cycle n

$(C_1)_i$ = concentration of contaminant i in cycle 1

$(C_0)_i$ = concentration of contaminant i in fresh water

The release factor is the ratio between the discharge of a contaminant in the first cycle and the discharge of the same contaminant during the final cycle as illustrated in the equation 18 (Miranda et al., 2009):

$$(RF)_i = \frac{(C_1)i}{(C_n)i} \quad \text{..... (18)}$$

Alexander and Dobbins (1977) also introduced the concept of substantive and non-substantive contaminants. Substantive contaminants were defined as those that had a high affinity for the fibres and fillers whereas those that had no attraction to the fibres and fillers were regarded as non-substantive species. As the number of times the water is recycled increases substantive contaminants will leave with the fibres and non-substantive contaminants will accumulate in the system. The contaminants with the highest accumulation factors are referred to as non-substantive contaminants whereas those with the lowest values are referred to as substantive contaminants (Jidong et al., 2011). Higher RF values imply that the effect of the contamination of the process water on the discharge of contaminants is higher (Miranda et al., 2009).

The accumulation and release factors obtained for dissolved solids (DS), suspended solids (SS), DCS and ash are illustrated in table 4-1. The table also shows values found in literature.

Table 4-1: AF and RF literature and experimental values

Contaminant	**Accumulation Factor**		**Release Factor**	
	Experimental	**Literature**	**Experimental**	**Literature**
Dissolved Solids (DS)	5.83	5.15 and 5.1	0.69	1.5
Suspended Solids (SS)	6.75	-	0.52	-
DCS	6.74	6.98	0.39	6.79
Ash	8.88	-	0.61	-

From the results obtained it can be seen that ash is a non-substantive species and accumulates faster than DS, SS and DCS. In studies conducted by Jidong et al. (2011) and Miranda et al. (2009) a similar accumulation factor was obtained for DS. The AF values obtained for SS and DCS are quite similar and the AF for DCS closely resembles that obtained by Jidong et al. (2011). DS appears to be a substantive contaminant as compared to SS, DCS and ash. The release factor for DS obtained by Miranda et al. (2009) was twice as high as that obtained in this study. DCS appears to have the lowest RF value as compared to DS, SS and ash. RF values close to 1 imply that the releases of the contaminant in the first cycle and in the final cycle are quite similar (Miranda et al., 2009). Values

greater than 1 indicate that the first cycle exhibits a greater release of the contaminant as compared to the final cycle. The higher RF values obtained for DS and ash imply that the effect of the contamination of the process water on the discharge of these contaminants is higher than that of DCS and SS.

The accumulation of DCS is detrimental to both the production process as well as the paper quality. A problem reported by Baijpai (2012) is that of anionic trash which is a sub-category of DCS and results in the consumption of retention aids causing a reduction in the paper machine wire retention. The wood species and the pulping method employed affects both the nature and quantity of DCS found in white water (Polverari et al., 2001). DCS affects the production process in various ways such as depositing on equipment resulting in inefficient running of the process. Microbial growth is a major concern in closed white water systems since organic compounds tend to accumulate in closed water systems and form a substrate on which microbial growth forms resulting in odour problems (Baijpai, 2012).

The build-up of these solids (dissolved, suspended and colloidal) can lead to deposition on equipment, corrosion of equipment and various adverse effects on the final paper produced such as specks forming on the paper, impaired brightness and decreased strength (Baijpai, 2012). According to water quality specifications, suspended solids should be between 10-15 mg/l if the water is to be reused for felt and wire cleaning in the paper machine area (Majcen Le Marechal et al., 2010). In order to reuse the water for water ring vacuum pumps the dissolved solids should not exceed 1000 mg/l (Majcen Le Marechal et al., 2010). As can be seen in the results the concentrations of these contaminants in the sample water are above these limits. Thus the water would not be suitable for reuse in newsprint mills.

4.1.2 Accumulation of total extractives (lipophilic) and lignin

Figure 4-5 illustrates the increase in the amount of wood extractives as the number of times the water is reused increases. The wood extractives increased from below 50 mg/l initially to over 200 mg/l after 10 cycles. The wood extractives have an AF of 5.38 and a low RF of 0.19. The wood extractives have a lower tendency to accumulate than DS, SS, DCS and ash as indicated by the lower AF value obtained. The low RF value implies that the release of the contaminant in the 10th cycle is much greater than the release of the contaminants in the first cycle. Lipophilic wood extractives make up approximately 1-5% of the wood; although this value may seem minute the adverse effects they cause in paper production are quite significant. Wood extractives are composed of fatty acids, resin acids, steryl esters and triglycerides (Stebbing, 2002). The wood resin tends to attach to fibres and has the effect of disturbing fibre-fibre bonding which in turn affects the strength properties of the paper (Sithole and Allen, 2002). In studies conducted by Francis and Ouchi, (2001) it was found

that the accumulation of these detrimental substances affected the properties of the newsprint. They found that decrease in inter fibre bonding led to reduced wet-web tensile strength and dry strength properties were also reduced as a result of reduction in bond strength and bonded area. It was also reported that fatty acids due their elevated surface activity are harmful to the strength properties of paper. The coefficient of friction (COF) of paper surfaces is also affected by the presence of wood extractives in process waters (Sithole and Allen, 2002). It has been reported that triglycerides have the effect of elevating the COF (Inoue et al., 1990).

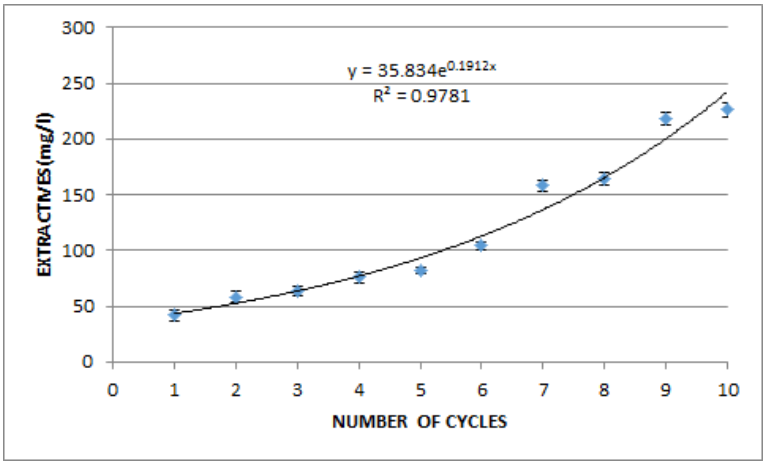

Figure 4-5: Accumulation of wood extractives

From Figure 4-6 it can be seen that the ultraviolet absorption of the sample at 280 nm increased from 0.2 initially to over 0.5 after 10 cycles. UV_{280} is used to measure the content of lignin hence an increase in the UV_{280} of the sample indicates an increase in the lignin present in the sample. 17-33% of the dry weight of wood is made up of lignin which is an aromatic polymer (Roberts, 1996). Lignin contains phenolic hydroxyl components and ionization of these components tend to produce a stable absorption peak at a wavelength of 280 nm- hence this peak is indicative of the presence of lignin in the sample (Jidong et al., 2011). The AF of the UV_{280} (10.87) was much higher than the AF values obtained for the solids, ash and extractives. A study conducted by Jidong et al. (2011) also observed higher AF values for the UV_{280} as compared to those obtained for the solids. The RF value (0.38) obtained for UV_{280} is higher than that obtained for the wood extractives. This implies that the release of lignin in the 10th cycle decreases to a greater extent than the release of wood extractives. Lignin has the effect of lowering sheet brightness due to redeposition on the pulp (Stebbing, 2002). The presence of lignin also results in paper becoming brittle and the yellowing and discoloration of paper is caused by the photooxidation of lignin (Roberts, 1996).

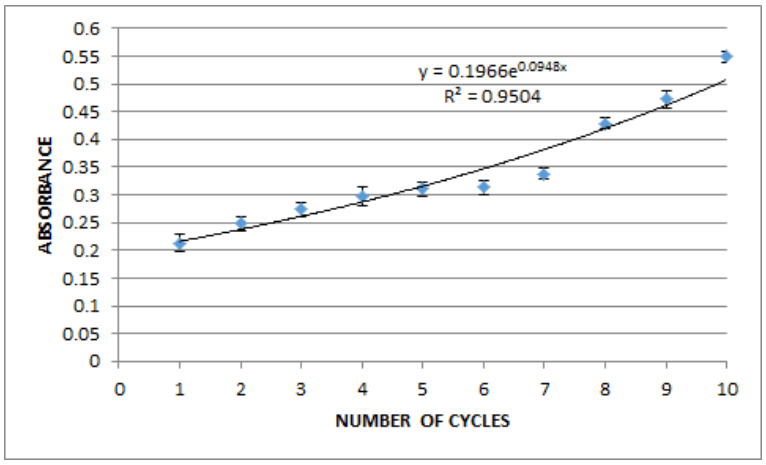

Figure 4-6: Accumulation trend of UV_{280}

4.1.3 Accumulation of inorganic ions

The build-up of inorganic ions in the white water can lead to various problems in the production of pulp and paper. It can result in deposition on equipment such as washing machines and nozzles as well as filter lines (Jidong et al., 2011). The build-up of certain inorganic ions such as chlorides and sulphates results in corrosion and scale formation. The build-up of Al leads to scaling and it is capable of forming a precipitate with sulphates which results in impaired paper quality (Jidong et al., 2011). It has also been reported that increased concentrations of Mg leads to corrosion of equipment and the build-up of Cl can lead to the formation of AOX and also corrosion of equipment (Jidong et al., 2011). Ca is another major contributor to scale formation. The efficient operations of steam boilers are often affected by the formation of a calcium sulphate scale in the boiler (Tappi and Chamberlin, 1957). Figure 4-7 illustrates the build-up of inorganic ions in the white water as the number of times the water is recycled increased.

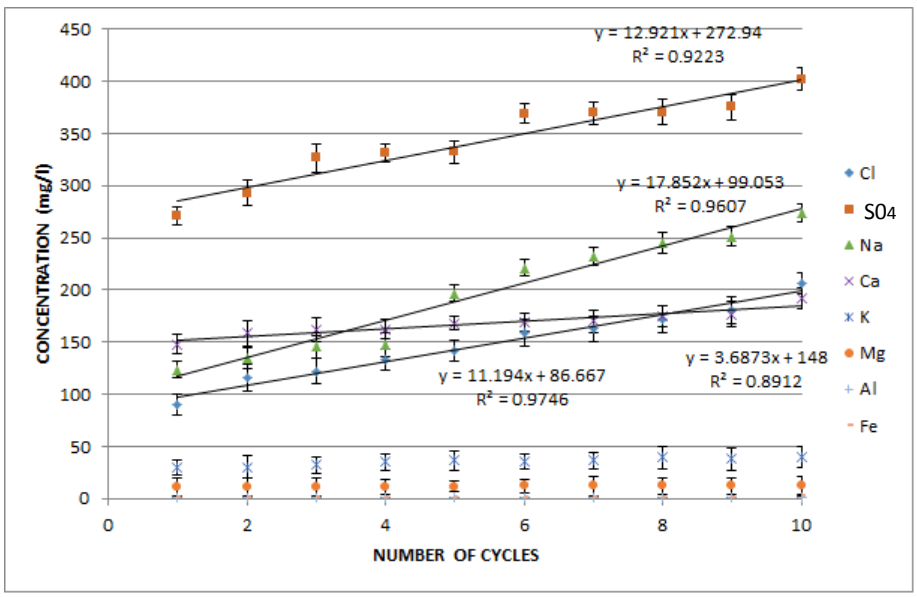

Figure 4-7: Build-up of inorganic ions

The AF values obtained for Al, Ca and Mg were 0.36, 0.13 and 0.02 respectively. The increasing rate of Al is higher than that of Ca and Mg despite the accumulated concentration being low as shown by the higher accumulation factor obtained for Al. A similar result was obtained by Jidong et al. (2011). The increasing rate of Cl is faster than those of Al, Ca and Mg. A similar result with regard to Mg was obtained by Miranda et al. (2009). The AF obtained for Cl was 7.75. According to TAPPI specifications for the chemical composition of process water, the chloride content should not exceed 75 mg/l (Tappi and Chamberlin, 1957). As can be seen in the results the chloride concentration is well above this limit after 10 cycles. The AF values obtained for SO_4, K, Na and Fe were 9.23, 5.13, 6.22 and 0.04, respectively. From the AF values obtained it can be seen that SO_4 has a greater accumulation tendency than the other inorganic ions as indicated by the higher AF obtained. Na has a higher accumulation tendency than K and Mg, and Fe accumulates rather slowly as indicated by the lowest AF values obtained for these ions.

The RF values obtained for all of the inorganic ions are less than 1; this implies that the release of the contaminant in the 1st cycle is lower than the release of the contaminant in the 10th cycle. Mg had the highest RF value (0.88) followed by Ca (0.77), K (0.75) and SO_4 (0.67): this implies that the effect of the contamination of the process water on the discharge of these ions is greater than that of the other ions present. However, the RF of Mg is relatively close to 1 indicating that the release of the ion in the 1st cycle (low contamination) is similar to the release of the ion in the 10th cycle (high contamination). The ion with the lowest RF value was Fe (0.26) followed by Na (0.45), Cl (0.44) and Al (0.59). This indicates that the release of these ions is much greater in the 10th cycle as compared to the 1st cycle. The low RF value obtained for Fe can be attributed to the relatively low value of Fe in cycle 1.

4.1.4 Variation of other parameters with increasing number of recirculation cycles

Turbidity measurements illustrated in Figure 4-8 indicate that the turbidity increased by nearly 100 NTU after 10 cycles. The AF and RF obtained for turbidity was 7.03 and 0.64, respectively. Turbidity is due to the presence of finely divided particles such as clay, microorganisms and silt. Thus an increase in the turbidity is an indication of an increase of these constituents (Tappi and Chamberlin, 1957). The brightness and colour of white papers as well as tinted papers are affected by turbidity (Tappi and Chamberlin, 1957). If the turbidity of the water is high it is not suitable as a substitute for boiler feed water since it may result in scale formation and cause foaming thus limiting the reuse of the water.

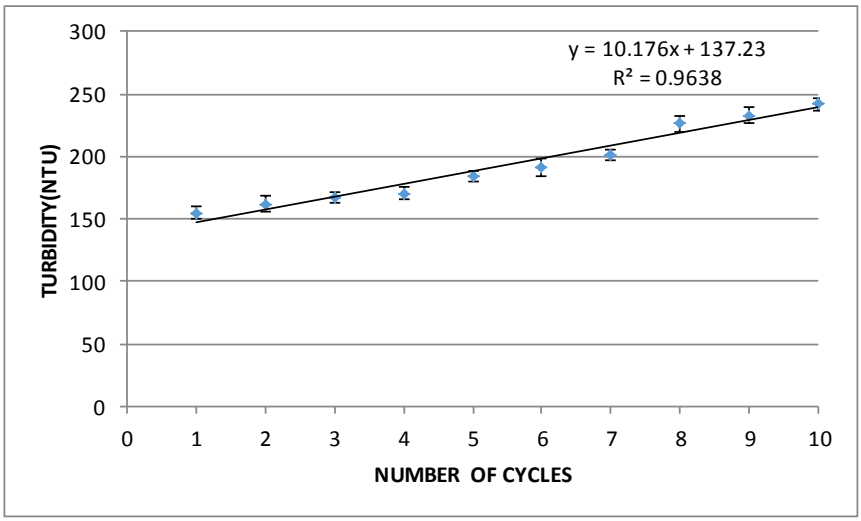

Figure 4-8: Increase in turbidity

From Figure 4-9 it can be seen that the electrical conductivity increased by 40 mS/m after 10 cycles. An AF of 4.63 and a RF of 0.84 was obtained for electrical conductivity. A similar AF value (4.4) was reported by Miranda et al. (2009). The AF value obtained for turbidity is much greater than that obtained for electrical conductivity. This indicates that turbidity has a greater accumulation tendency than conductivity. The electrical conductivity of water is an indication of the quantity of total dissolved salts or the total quantity of dissolved ions present in the water (Baijpai, 2012). It provides an indication of the quality of water. A low conductivity indicates cleaner/ more pure water. Higher conductivity increases the potential for corrosion. If the water is to be used for water ring vacuum pumps the electrical conductivity should be less than 200 mS/m (Majcen Le Marechal et al., 2010).

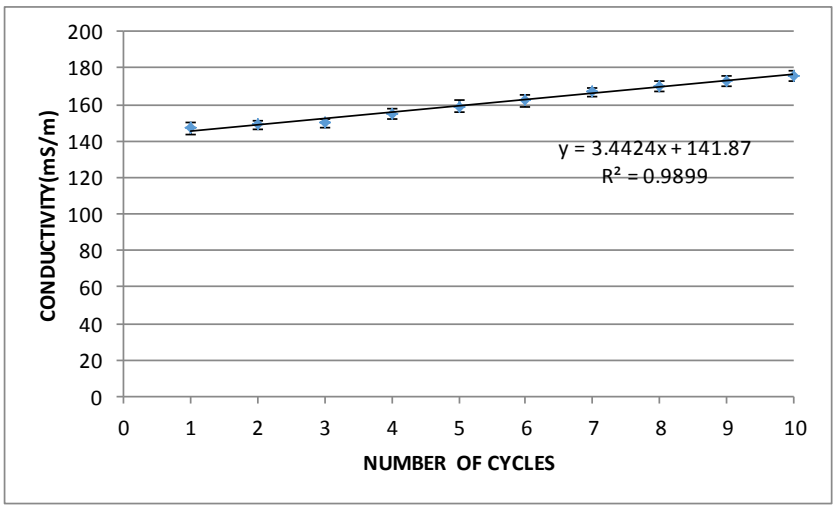

Figure 4-9: Increase in electrical conductivity

Figure 4-10 illustrates the increase in the COD concentration as the number of times the water is recycled increases. The COD increased by over 600 mg/l after 10 cycles. An AF of 12 and a RF of 0.57 was calculated for COD. The AF value obtained for COD is almost three times the value

obtained for conductivity. This indicates that organic contaminants depicted as COD have a greater tendency to accumulate than inorganic contaminants measured in the form of conductivity. A similar result was obtained by Miranda et al. (2009). The higher RF obtained for conductivity implies that the degree of the contamination of the water has a greater effect on inorganics as compared to organics measured as COD.

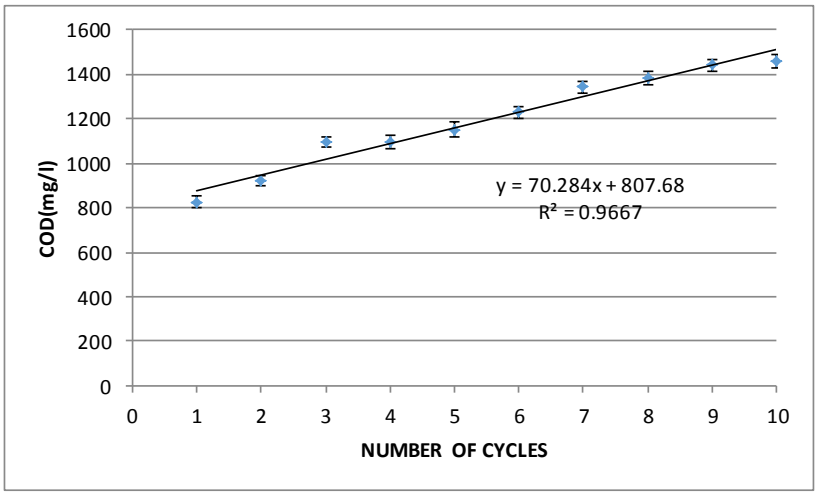

Figure 4-10: Increase in COD

4.1.5 Effect of system closure on paper properties

The effect of system closure on the brightness and burst strength of paper was investigated by preparation of hand-sheets at 0, 50 and 100% closure. Three hand-sheets of each type were tested. Brightness is a very important factor when it comes to the sale or market value of paper (Smook, 2002). It is an indication of the quality of paper. The higher the brightness the more desirable the paper product is. Brightness is described as the reflectance percentage of blue light at a wavelength of 457 nm. The burst strength is defined as the amount of pressure the paper (kPa) can withstand prior to rupturing and is reported as burst index, i.e., the ratio of the burst strength (kPa) to grammage (g/m^2) (Smook, 2002). The effect of system closure on brightness is illustrated in Figures 4-11. A decrease in the brightness can be observed as the percentage of fresh water is reduced. A similar trend was observed by Zhang et al. (2000).

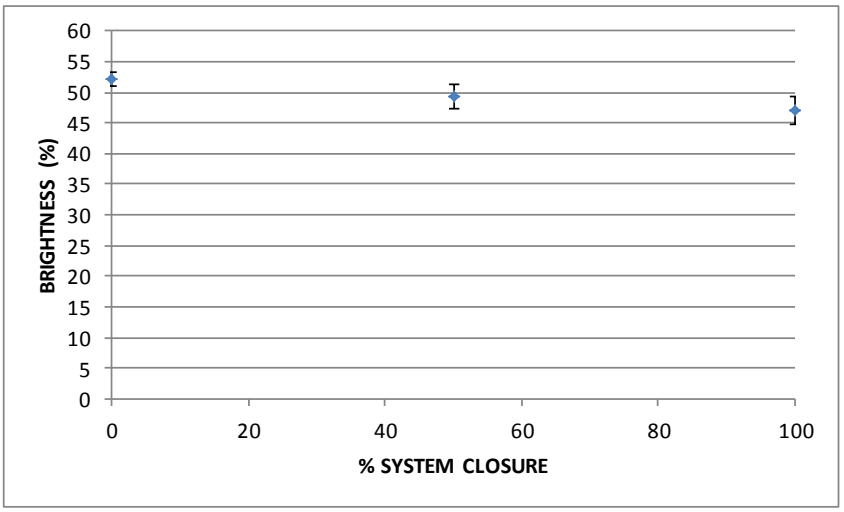

Figure 4-11: Effect of system closure on brightness

In Figure 4-12 it can be seen that the burst index decreased as the percentage of closure increased i.e. as the amount of white water used instead of fresh water increased. A similar observation was made by Francis and Ouchi (2001).

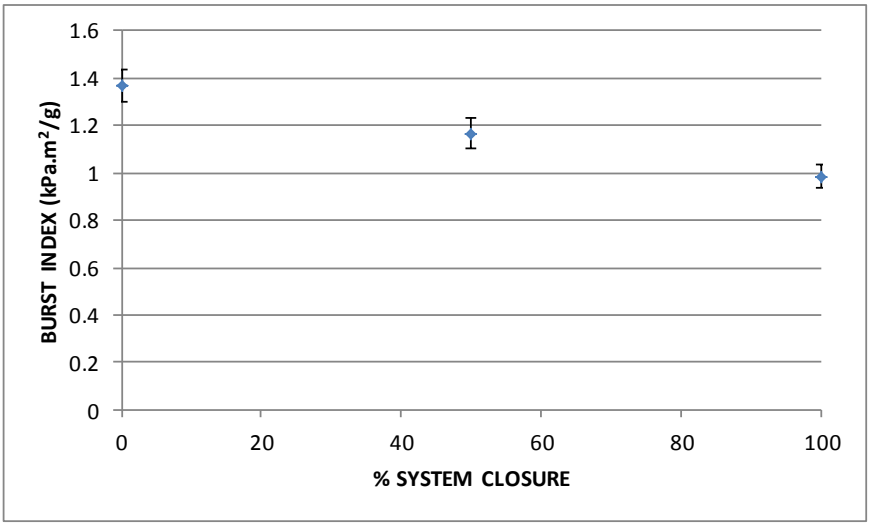

Figure 4-12: Effect of system closure on burst index

The decrease in these physical properties can be attributed to the decrease in the amount of fresh water used as the system is closed thus resulting in an increase in the contaminant levels.

The preceding results indicate that increase in system closure, although a desirable thing, is detrimental to the paper production process. Hence this can be achieved only by prior cleaning of the whitewater.

The next section discusses results of water purification by membrane filtration.

4.2 Determination of the appropriate membrane for ultrafiltration of white water

4.2.1 Flux versus Time

Figure 4-13 illustrates the flux versus time curves obtained during ultrafiltration of white water. All membranes studied achieved a fairly stable flux in less than 1 hour. It was observed that the flux decline was greatest in the 150 kDa membrane. The flux decreased from an initial value of 410 L/m^2.hr to approximately 43 L/m^2.hr. The flux decline was lowest in the 10 kDa membrane. The flux decreased from 134 L/m^2.hr to 54 L/m^2.hr in the 50 kDa membrane and from 300 L/m^2.hr to 59 L/m^2.hr in the 100 kDa membrane. The flux decline can be attributed to membrane surface fouling. It was found that the 100 kDa membrane exhibited the highest average permeate flux (59 L/m^2.hr). The 10 kDa membrane exhibited the lowest average flux (34 L/m^2.hr) followed by the 150 kDa (43 L/m^2.hr) and the 50 kDa (54 L/m^2.hr). The average permeate flux is an important factor that affects equipment costs and energy consumption (Scott, 1995). Membranes with a high average permeate flux are required hence the 100 kDa membrane is a desirable choice (Scott, 1995).

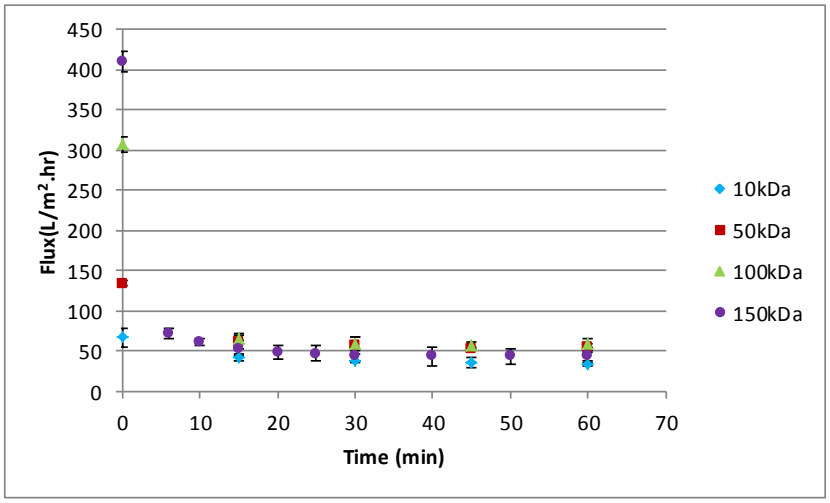

Figure 4-13: Flux versus time (UF of white water)

4.2.2 Cleanability and fouling

In order to determine the cleanability of the membrane the pure water flux was determined before filtration of the white water sample and after filtration and cleaning of the used membrane with distilled water. Figures 4-14 to 4-17 illustrates the flux reduction of each membrane. The degree of fouling of the different membranes was determined by calculating the flux reduction of the pure water flux (FR_{PWF}) before cleaning the membrane. The FR_{PWF} after cleaning the membrane is a measure of the irreversible fouling. The FR_{PWF} was calculated using the following equation (Manttari et al., 2004):

$$FR_{PWF}(\%) = \frac{PWF_b - PWF_a}{PWF_b} \times 100 \quad \ldots\ldots\ldots\ldots (19)$$

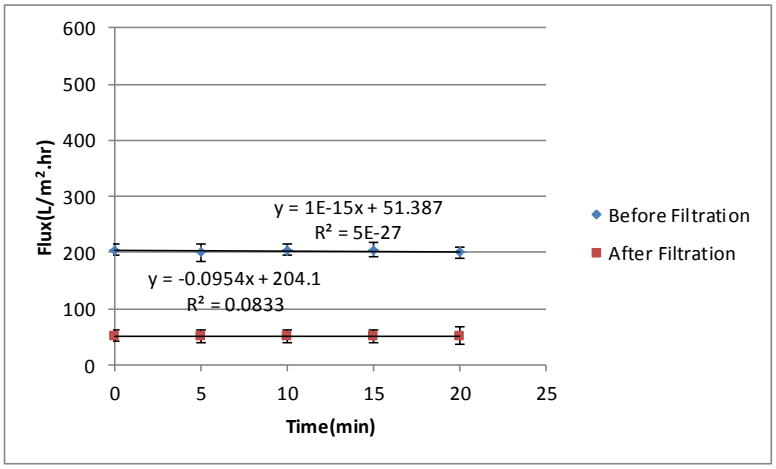

Figure 4-14: Flux versus time 10 kDa (Pure water)

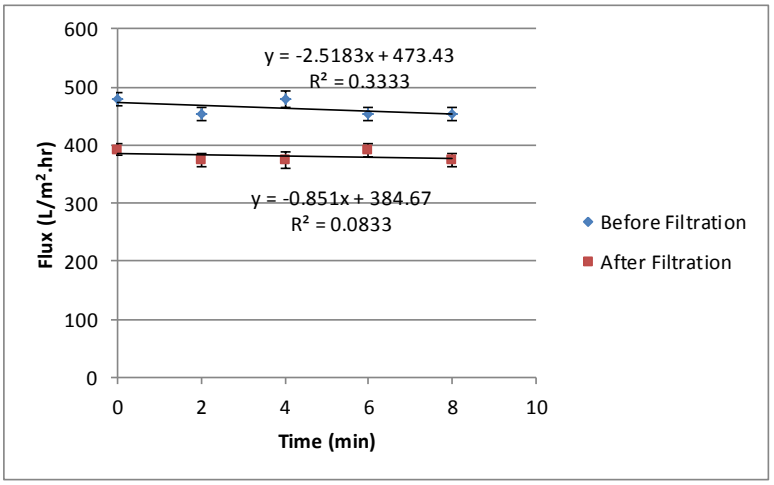

Figure 4-15: Flux versus time 50 kDa (Pure water)

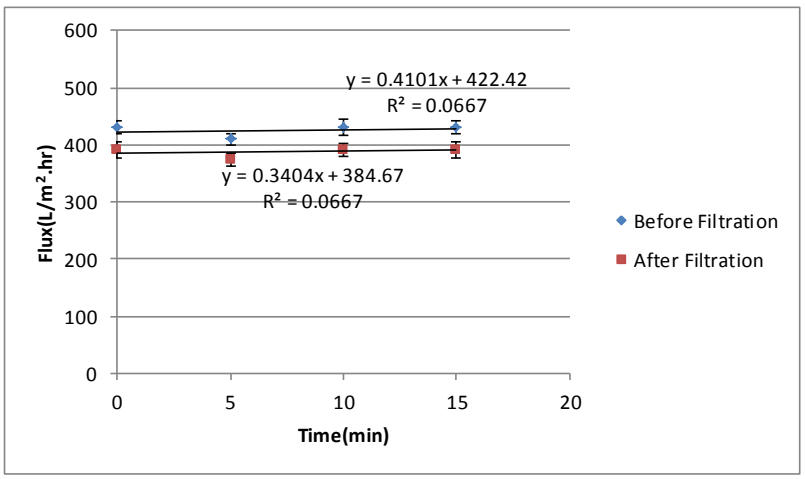

Figure 4-16: Flux versus time 100 kDa (Pure water)

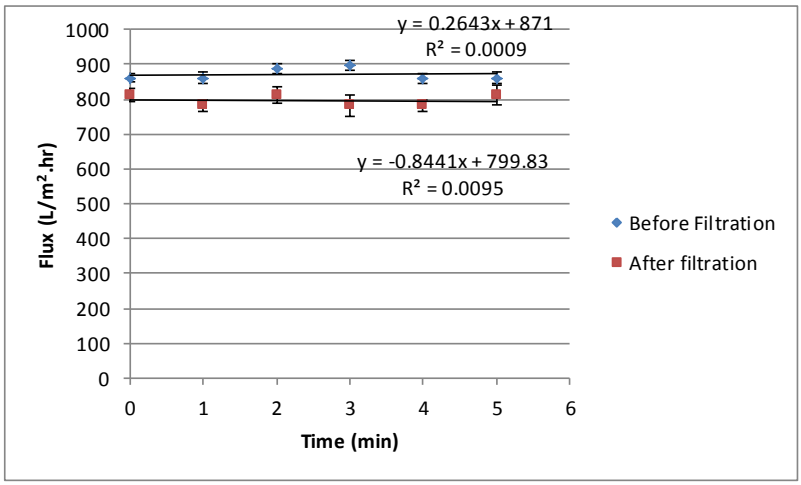

Figure 4-17: Flux versus time 150 kDa (Pure water)

From Figures 4-14 to 4-17 it can be seen that the 10 kDa membrane exhibited the worst cleanability since the difference in fluxes obtained before and after filtration and cleaning of the membrane is relatively large (approximately 150 L/m^2.hr) as compared to the other membranes. Results indicated that the membrane with the best cleanability was the 100 kDa membrane with a difference in flux of only 39 L/m^2.hr before and after filtration and cleaning. The 150 kDa membrane also exhibited a fairly reasonable cleanability with a difference in flux of only 49 L/m^2.hr. It was observed that the membranes with the larger molecular weight cut-offs exhibited a better cleanability.

Table 4-2 illustrates the degree of fouling as well as the irreversible fouling of the different membranes.

Table 4-2: Flux reduction of the pure water flux

Membrane	**FR_{PWF}(%) (Before cleaning)**	**FR_{PWF}(%) (After cleaning)**
10 kDa	88	82
50 kDa	81	57
100 kDa	53	13
150 kDa	51	39

The reduction of the pure water flux was highest with the 10 kDa membrane which suggests that the degree of fouling was highest with this membrane. The degree of fouling was lowest with the 150 kDa membrane followed by the 100 kDa membrane indicated by the low FR_{PWF} values obtained. It was observed that the hydrophilic membranes (50 kDa, 100 kDa and 150 kDa) fouled less than the hydrophobic membranes (10 kDa). Paper mill effluent generally contains hydrophobic compounds in the form of extractives and lignans that absorb on to the membrane resulting in fouling (Manttari et al., 2004). In a study by Manttari et al. (2004) it was found that hydrophilic membranes had a low contact angle against water and fouling of the membrane was much lower than those with a higher contact angle. The FR_{PWF} after cleaning the membrane indicates the degree of irreversible fouling

and was highest with the 10 kDa membrane, this was expected since the 10 kDa membrane exhibited the worst cleanability. The 100 kDa membrane had the lowest irreversible fouling making it a desirable choice for further studies. Fouling is a factor that impacts running costs, because if a membrane has extensive irreversible fouling it would have to be replaced thus increasing operational costs.

4.2.3 Retention and productivity of the different membranes

Tables 4-3 and 4-4 shows the retention achieved by the different membranes and the concentration of contaminants in the permeate from different membranes respectively.

Table 4-3: Retentions achieved by the different membranes

	RETENTION(%)			
	MEMBRANE MWCO			
CONTAMINANT	**10 kDa**	**50 kDa**	**100 kDa**	**150 kDa**
Total solids	49.92	43.57	40.88	38.60
Dissolved solids	28.78	13.82	7.12	5.78
Suspended solids	99.20	98.39	97.58	93.56
Dissolved and colloidal solids	36.19	32.84	15.06	9.62
Wood extractives	52.27	43.18	25.00	18.18
Lignin	65.26	56.42	43.46	33.03
Ash	18.25	12.98	9.32	7.54
Chloride	21.26	16.34	6.48	1.58
Sulphate	14.55	7.17	5.26	4.62
COD	73.91	69.97	67.02	63.28
Sodium	72.17	67.85	60.93	43.63
Potassium	32.14	32.14	29.80	23.70
Aluminium	33.33	28.07	21.05	15.79
Calcium	38.32	36.67	34.48	10.10
Iron	54.29	30.00	15.71	5.71
Magnesium	34.76	29.96	28.91	23.07
Silica	68.54	54.39	46.20	33.63

Table 4-4: Concentration of permeate from different membranes

	Feed Concentration	Permeate Concentration			
		MEMBRANE MWCO			
Contaminant		**10 kDa**	**50 kDa**	**100 kDa**	**150 kDa**
Total solids(mg/l)	2456.00	1230.00	1386.00	1452.00	1508.00
Dissolved solids(mg/l)	1493.00	1063.33	1286.67	1386.67	1406.67
Suspended solids(mg/l)	827.00	6.60	13.30	20.00	53.30
Dissolved and colloidal solids(mg/l)	1707.00	1089.29	1146.43	1450.00	1542.86
Wood extractives(mg/l)	88.00	42.00	50.00	66.00	72.00
Lignin(mg/l)	54.00	18.76	23.53	30.53	36.16
Ash(mg/l)	676.00	552.64	588.28	613.02	625.00
Chloride(mg/l)	80.70	63.54	67.51	75.47	79.43
Sulphate(mg/l)	393.00	335.82	364.83	372.32	374.86
Conductivity(mS/m)	131.00	124.00	129.00	131.00	131.00
Turbidity(NTU)	885.00	1.15	1.61	7.19	2.05
COD	1950.00	508.80	585.60	643.20	715.95
Sodium(mg/l)	185.00	51.48	59.48	72.28	104.28
Potassium(mg/l)	35.40	24.02	24.02	24.85	27.01
Aluminium(mg/l)	0.06	0.04	0.04	0.05	0.05
Calcium(mg/l)	96.00	59.21	60.80	62.90	86.30
Iron(mg/l)	0.07	0.03	0.05	0.06	0.066
Magnesium(mg/l)	9.58	6.25	6.71	6.81	7.37
Silica(mg/l)	17.10	5.38	7.80	9.20	11.35

Results obtained indicate that the 10 kDa membrane exhibits the best retention of contaminants (see Table 4-3), however, this membrane had the worst cleanability and the highest degree of fouling making it an undesirable choice. The 150 kDa membrane had the lowest retention. The retentions of the 50 kDa membrane and the 100 kDa membrane for certain contaminants such as suspended solids, total solids and COD are quite similar. Contaminant removal was affected by the MWCO of the membrane. The COD removal with the 50 kDa and 100 kDa membranes were over 65%. Similar results were obtained by Tardif and Hall (1994) in a study utilizing UF to treat recirculated white water. The reduction in turbidity was approximately 99% in all four membranes. The retention of dissolved solids was over 20% with the 10 kDa membrane but less than 15% for the 50, 100 and 150 kDa membranes similar results were observed for the 10 kDa membrane and the 100 kDa membrane in a study conducted by Elefsiniotis et. al (1997). In order to determine the appropriate membrane to be used in further studies, the concentration of contaminants in the permeate obtained from the

different membranes were compared to general water quality standards for the reuse of water in the pulp and paper manufacturing process. If the water is to be used for water ring vacuum pumps the electrical conductivity should be less than 200 mS/m (Majcen Le Marechal et al., 2010). The water from all the membranes meets this requirement. In order to reuse the water as process water the chloride content must be 75 mg/l or less. Only the 150 kDa membrane does not meet this requirement. The turbidity of the permeate obtained from all four membranes is less than 20 NTU indicating that it is appropriate to be used as process water. According to water quality specifications the concentration of magnesium and silica should be less than 12 mg/l and 100 mg/l respectively if the water is to be reused as process water - the permeates from all 4 membranes met this requirement (Majcen Le Marechal et al., 2010).

Table 4-5 indicates the productivity achieved with each membrane. The 100k Da membrane exhibited the highest productivity and the 10k Da membrane exhibited the lowest productivity.

Table 4-5: Productivity of the different membranes

Membrane	Permeate collected in 1hr (ml)
10 kDa	170
50 kDa	265
100 kDa	290
150 kDa	252

From the results is can be seen that the permeate obtained from the 150 kDa membrane does not meet most of the requirements for the reuse of water in the pulp and paper manufacturing process - hence it was not used in further studies. The 10 kDa membrane exhibited the highest degree of fouling as well as irreversible fouling; the worst cleanability, the lowest productivity and average permeate flux making it undesirable for further studies. Overall, it was established that the 100 kDa membrane depicted the lowest degree of irreversible fouling and a relatively low degree of fouling, the best cleanability, the highest productivity and average permeate flux and the permeate obtained from this membrane meets most of the water quality requirements for the reuse of water in the paper manufacturing process. The 100 kDa membrane was chosen as the most appropriate membrane to be used in further studies.

4.3 Coagulation as a method of pre-treatment

4.3.1 Experimental design

Two variables were investigated namely coagulant dosage and pH at three different levels as illustrated in table 4-6.

Table 4-6: Factors and levels investigated

Factor	Levels		
	-1	0	1
Coagulant Dosage (mg/L) (A)	100	300	500
pH (B)	5	7	9

The central composite face-centred design (CCFD) shown in table 4-6 together with response surface methodology was used to optimise the two variables investigated. Table 4-7 illustrates the coded levels as well as the actual levels used. The first 9 experiments are arranged in a factorial design and the last four replicate the central point.

Table 4-7: CCFD For the experiments carried out

Experiment number	Coded Levels		Actual Levels	
	Coagulant Dosage	pH	Coagulant Dosage (mg/L)	pH
1	-1	-1	100	5
2	1	-1	500	5
3	-1	1	100	9
4	1	1	500	9
5	-1	0	100	7
6	1	0	500	7
7	0	-1	300	5
8	0	1	300	9
9	0	0	300	7
10	0	0	300	7
11	0	0	300	7
12	0	0	300	7
13	0	0	300	7

The CCFD was applied to two different coagulants i.e. aluminium sulphate (alum) and ferric chloride ($FeCl_3$). The results obtained for each response are illustrated in table 4-8. The regression method was used to fit the response variables in table 4-8 to a quadratic equation model. A Matlab code was written to plot the response surface plots. Refer to Appendix A for the Matlab code.

Table 4-8: Response Results

Experiment number	Turbidity Reduction (%)		TSS Reduction (%)		SVI (ml/g)	
	Alum	Ferric Chloride ($FeCl_3$)	Alum	Ferric Chloride ($FeCl_3$)	Alum	Ferric Chloride ($FeCl_3$)
1	70.40	62.74	83.68	81.06	148.31	108.51
2	85.14	74.83	90.53	88.71	141.42	91.64
3	93.32	79.24	89.52	83.07	69.32	74.96
4	89.27	94.80	87.51	92.14	105.70	94.22
5	73.79	89.21	78.23	87.71	85.01	102.14
6	93.24	90.74	91.13	95.16	114.61	92.02
7	76.07	81.58	89.32	88.71	131.76	110.44
8	96.59	82.03	92.74	79.85	123.50	102.12
9	88.05	82.71	90.33	81.46	99.55	104.49
10	96.88	94.53	95.16	91.94	89.04	103.57
11	97.01	94.41	96.78	94.36	92.41	96.31
12	97.03	94.44	95.97	91.13	90.03	99.50
13	96.00	94.89	93.55	93.55	89.31	94.94

4.3.2 Optimization of response variables

The response variables were expressed as a function of pH of the sample and dosage of the coagulant. Analysis of variance (ANOVA) was conducted to determine the quality of the model fitted to the response variables. The statistical significance of the model was determined using the Fisher F-test. The regression model for turbidity reduction using alum and ferric chloride respectively are as follows:

Alum: $-30.460 + 0.209X_1 + 21.443X_2 - 0.00017X_1^2 - 0.997X_2^2 - 0.012X_1X_2$ …….. (20)

$FeCl_3$: $-75.90 + 0.055X_1 + 41.634X_2 - 7.58e^{-5}\ X_1^2 - 2.801X_2^2 - 0.002X_1X_2$ …….. (21)

The F statistic i.e. ratio of the mean square as a result of regression to the mean square as a result of real error (Montgomery, 2001) , obtained for the model using alum as the coagulant was 5.95 and the critical F value at a significance level of 0.05 was 3.97 i.e. $F_{0.05,\,5,7}$ (Montgomery, 2001). Since the F statistic is greater than the critical F value it can be concluded that the model is significant. The R^2 value i.e. the correlation coefficient, obtained was 0.81 which is relatively close to 1 indicating that the model is a good fit for the turbidity and adequately describes the data. A P value of 0.018 was obtained which is smaller than the significance level of 0.05 indicating that the model fits the data fairly well and not all the coefficients in the model are zero. The model obtained using $FeCl_3$ as the coagulant had a F statistic of 4.61 and the critical F was the same as that obtained for the model when alum was used. The model is significant since the F statistic is greater than the critical F value. The R^2 value obtained for this model was 0.77 which is fairly close to 1 signifying that the model is a good fit for the data. When a linear model was fitted to this data a R^2 value of 0.32 was obtained, this

is quite low indicating that the linear model does not adequately describe the data. The P value obtained for this model was 0.035 since it is smaller than the significance level it implies that the model fits the data relatively well.

The regression models fitted to the data for TSS reduction using alum and ferric chloride respectively are as follows:

Alum: $56.394 + 0.152X_1 + 2.925X_2 – 0.00016X_1^2 – 0.053X_2^2 – 0.006X_1X_2$ …….. (22)

$FeCl_3$: $21.369 – 0.008X_1 + 19.455X_2 + 3.6e^{-5}\ X_1^2 – 1.429X_2^2 + 0.0009X_1X_2$ …….. (23)

Equation 22 illustrates the model obtained for TSS reduction when alum was used as the coagulant. The F statistic value obtained for this model was 4.12 which is greater than the critical $F_{0.05,5,7}$ hence it can be concluded that the model is significant. The R^2 value obtained for this model was 0.7 which is fairly close to one implying that the model adequately describes the data. When a linear model and a model with no interaction were fitted to the data the R^2 values obtained were 0.19 and 0.64 respectively. These values are relatively lower than one implying that the models are not a good fit for the data. The P value obtained for equation 22 was 0.045 and is lower than the significance level indicating that the data fits the model relatively well. Equation 23 represents the model for TSS reduction when $FeCl_3$ is used as the coagulant. The F statistic of 4.8 is higher than the critical $F_{0.05,5,7}$ indicating that the model is significant. The R^2 value of 0.55 obtained is not very close to 1, however, it was the highest R^2 value obtained as compared to when the data was fitted to a linear model (R^2=0.29) and a model with no interaction term (R^2=0.41). The P value of 0.031 is lower than the significance level implying that the data fits the model.

The regression model for SVI using alum and ferric chloride respectively are as follows:

Alum: $527.171 – 0.117X_1 – 110.397X_2 – 3.8e^{-5}\ X_1^2 + 6.574X_2^2 + 0.027X_1X_2$ …….. (24)

$FeCl_3$: $168.529 – 0.043X_1 – 13.824X_2 – 0.0002X_1^2 + 0.270X_2^2 + 0.023X_1X_2$ …….. (25)

Equation 24 illustrates the model for SVI when alum was used as the coagulant. The F statistic obtained for this model was 6.62 which is much higher than the critical $F_{0.05,5,7}$ implying that the model is significant. The R^2 value obtained was 0.83 which is quite close to 1 indicating that the model adequately describes the data. The P value of 0.013 is fairly lower than the significance level indicating that the model is a good fit for the data. Equation 25 represents the model for SVI when $FeCl_3$ was used as the coagulant. It can be concluded that this model is significant since the F statistic of 5.03 is higher than the critical $F_{0.05,5,7}$. The R^2 value of 0.78, which is fairly close to 1, indicates that the model describes the data fairly well. The P value of 0.028 obtained is much lower than the significance level implying that the model is a good fit for the data.

In a study conducted by Ahmed et al. (2008) alum was used as the coagulant to treat pulp and paper mill effluent. In their study polynomial models were also obtained for TSS reduction and SVI.

4.3.3 Alum coagulation: Response surface plots

Figures 4-18, 4-19 and 4-20 illustrate the response surface plots and corresponding contour plots for the reduction of the 3 parameters i.e. suspended solids, SVI and Turbidity investigated in the coagulation experiments. From Figure 4-18 it can be seen that the suspended solids reduction increases as the pH is adjusted to near neutral and alkaline values. It also indicates that the reduction tends to increase with an increase in coagulant dosage and pH. It reaches a maximum level and their after starts to decrease; a similar result was obtained in a study by Ahmad et al (2008). The optimum pH range for TSS reduction is between 6.5 and 9 and the optimum dosage range appears to be between 250 and 350 mg/l.

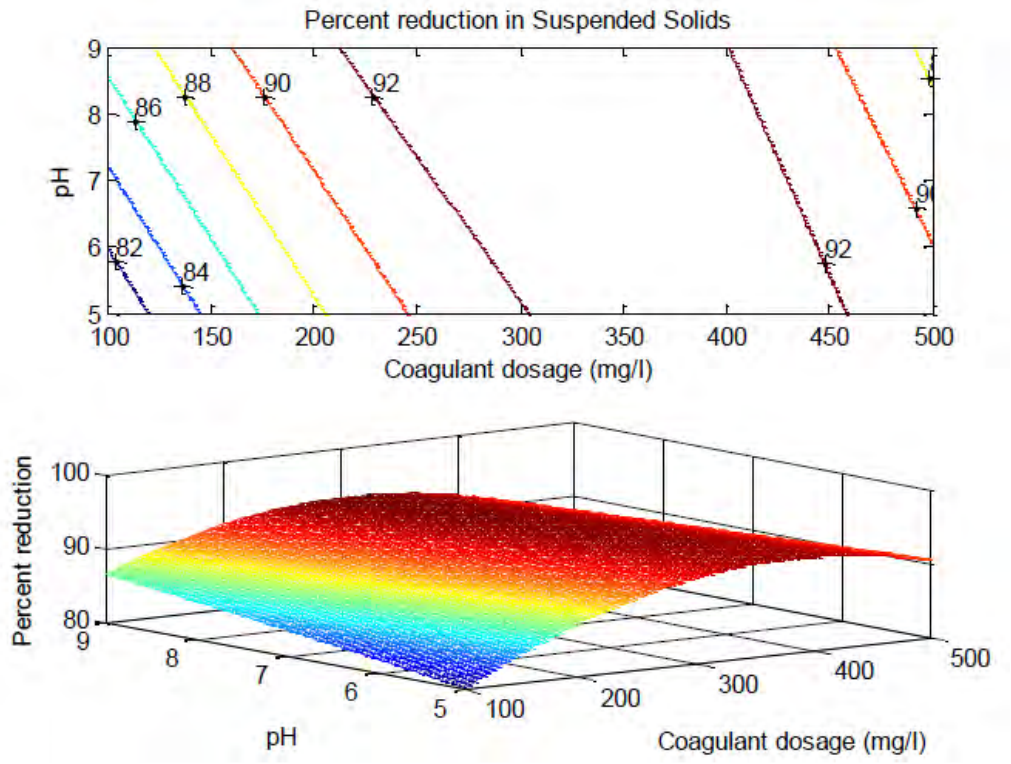

Figure 4-18: Response surface plot and 2D contour plot (suspended solids)

From Figure 4-19 it can be seen that the SVI slightly increases with coagulant dosage; however, the effect of pH on the SVI is much more significant. The SVI appears to increase as the pH approaches the neutral and acidic range. A low SVI is desirable and from Figure 4-19 it can be seen that a pH range between 7 and 9 provides a low SVI.

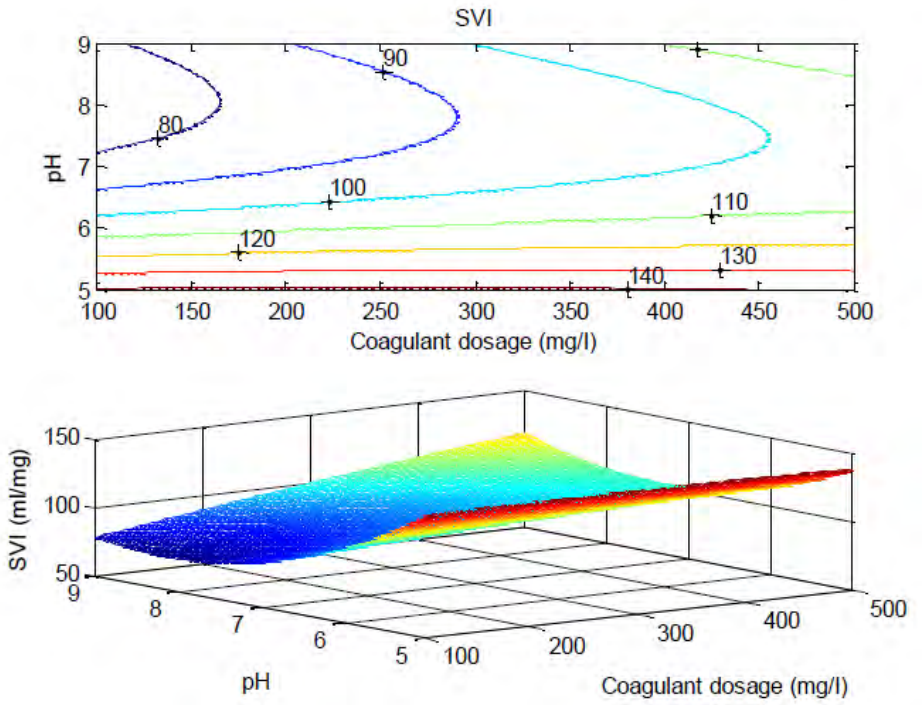

Figure 4-19: Response surface plot and 2D contour plot (SVI)

Figure 4-20 illustrates the surface response for turbidity. The reduction in turbidity increases as the pH increases from acidic to neutral and alkaline values. It is also observed that the turbidity reduction increases with an increase in coagulant dosage and pH until it reaches a maximum and there after gradually decreases. The optimum pH range for reduction in turbidity is between 7 and 9 and the optimum dosage range is between 250 and 350 mg/l. Ahmed et al (2008) found that pH values close to neutral produced a high reduction of turbidity.

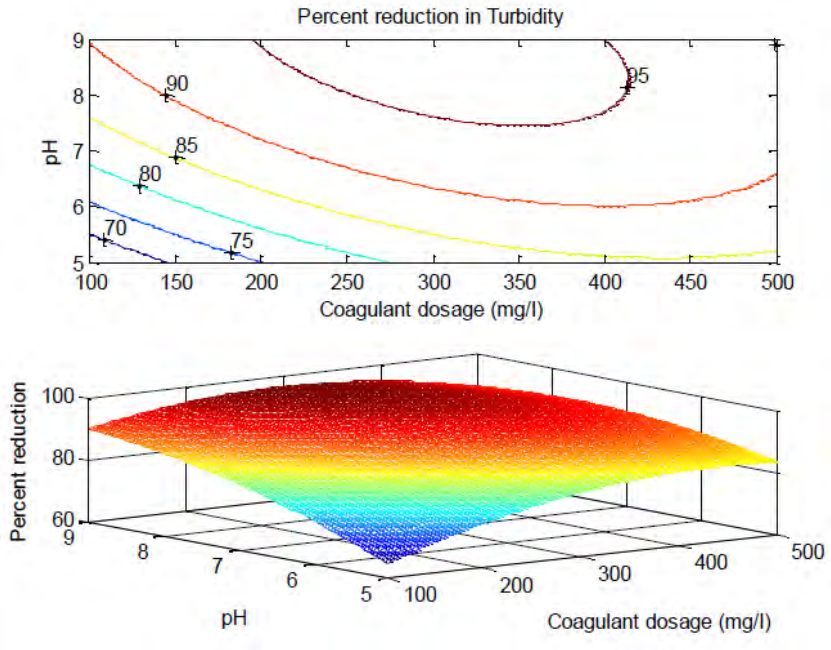

Figure 4-20: Response surface plot and 2D contour plot (Turbidity)

4.3.3.1 Overall optimum conditions: Alum

In order to obtain the overall optimum conditions the contours of the three response surfaces were plotted in an overlay plot illustrated in Figure 4-21. A low SVI and a high suspended solids and turbidity reduction is desirable. The shaded region depicted in Figure 30 is the optimum region which meets these requirements. According to the overlay plot the optimum dosage and pH was 288.8 mg/l and 7.68 respectively. These optimum conditions provide a 95% and 90% reduction in turbidity and suspended solids respectively and a SVI of 90 mL/g.

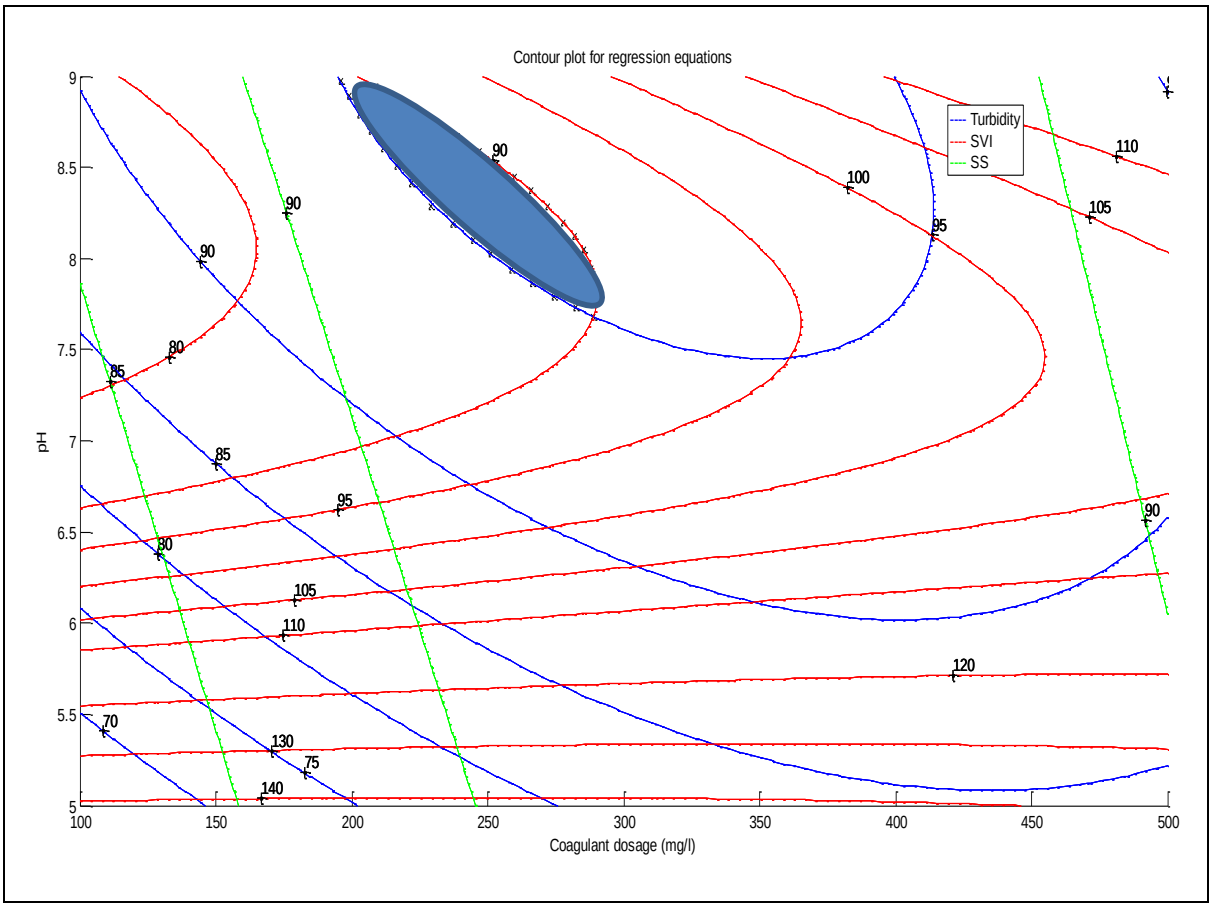

Figure 4-21: Overlay plot optimal region (Alum)

4.3.4 $FeCl_3$ Response surface plots

Figures 4-22, 4-23 and 4-24 depict the response surface plots and corresponding contour plot for the reduction of suspended solids, turbidity and SVI when FeCl3 is used as the coagulant. From Figure 4-22 it can be seen that the reduction in suspended solids increases as the pH increases from acidic to near neutral and alkaline values, the reduction increases until it reaches a maximum level at an optimum pH and there after decreases. A similar trend was observed when Alum was used as the coagulant. It was also observed that the reduction in suspended solids increases with an increase in coagulant dosage. From the Figure it can be seen that the optimum pH range for suspended solids reduction is between 6.5 and 8, the optimum coagulant dosage range is between 500 and 600 mg/l.

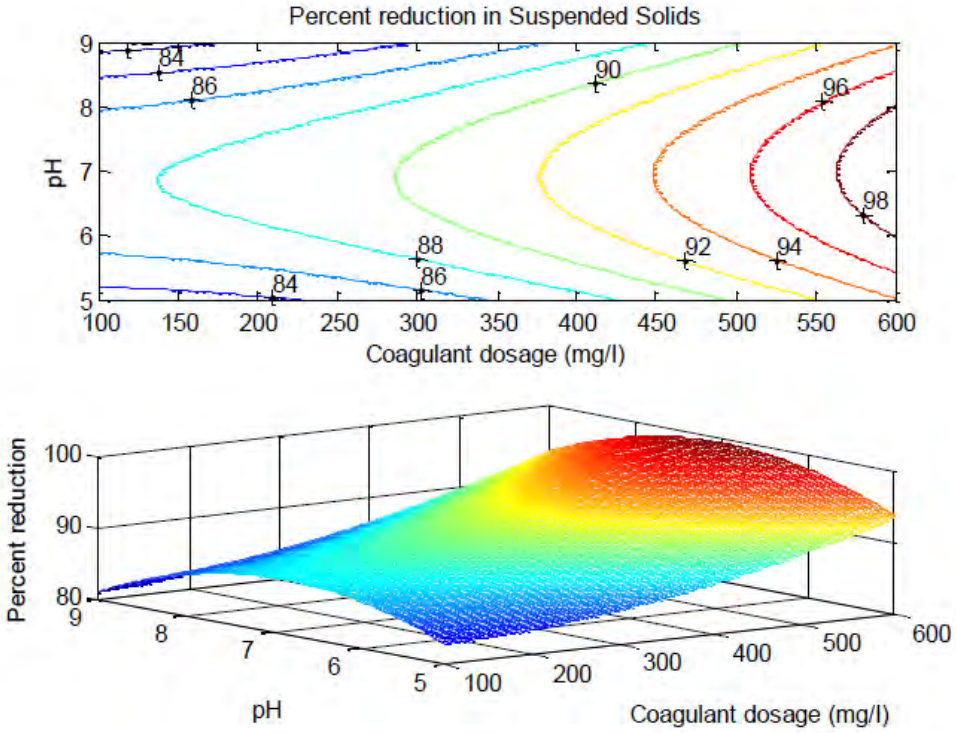

Figure 4-22: Response surface plot and 2D contour plot (suspended solids)

From Figure 4-23 it can be seen that the SVI increases as the pH approaches more neutral and acidic values. The SVI also tends to gradually decrease as the coagulant dosage increases this is opposite to what was observed when Alum was used as the coagulant. Since a low SVI is desirable the optimum pH range appears to be between 7 and 8 and the optimum dosage is 500 to 600 mg/l.

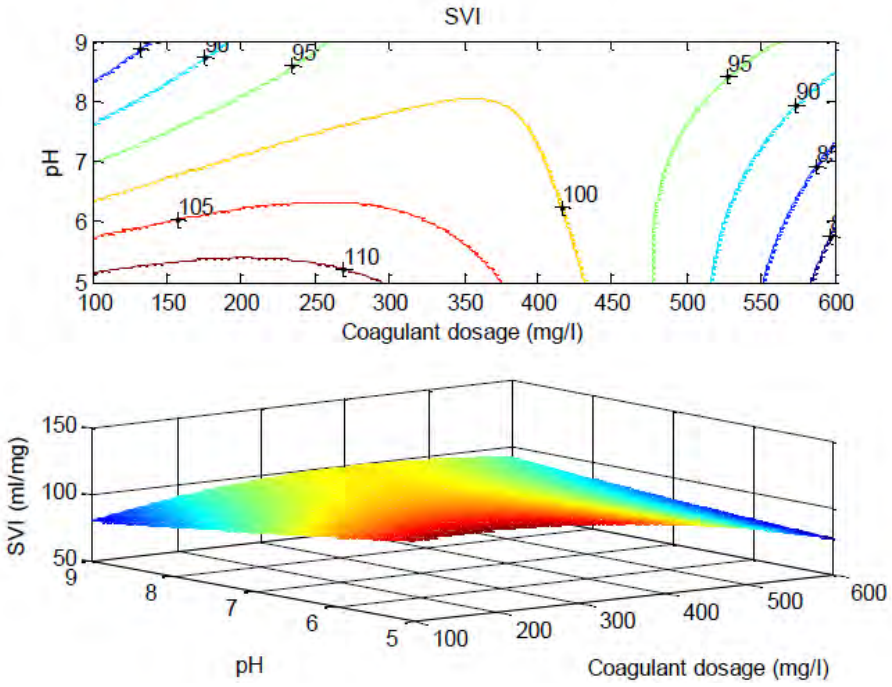

Figure 4-23: Response surface plot and 2D contour plot (SVI)

Figure 4-24 illustrates the surface response for turbidity. It is observed in Figure 4-24 that the turbidity reduction increases as the pH increases from acidic to more neutral and alkaline values. It is also noticed that the turbidity reduction increases with pH and coagulant dosage until it reaches a maximum value and there after decreases. A similar result was obtained when alum was used as the coagulant. The optimum pH range for the reduction in turbidity is between 7and 8 and the optimum dosage is between 400 and 550 mg/l.

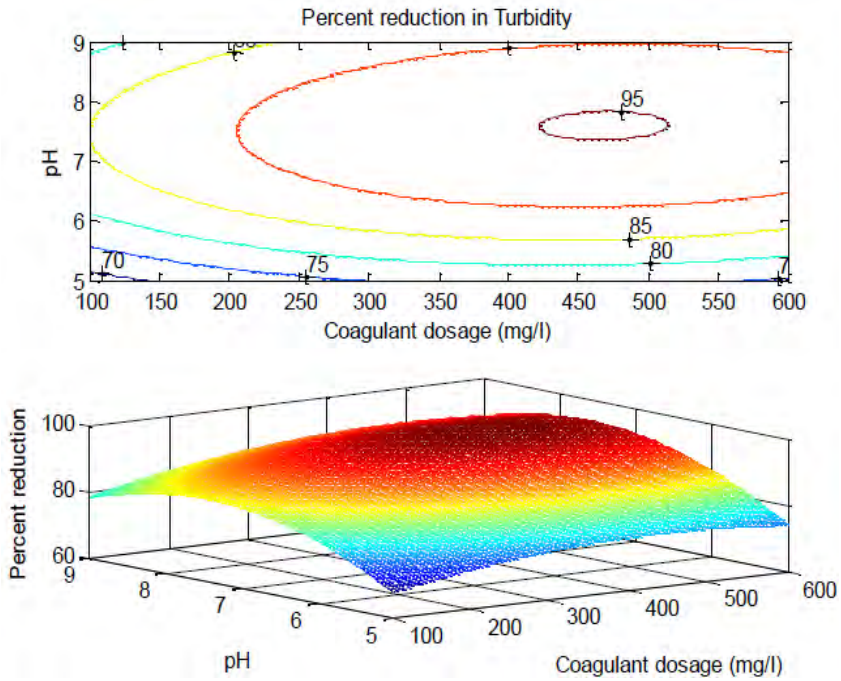

Figure 4-24: Response surface plot and 2D contour plot (Turbidity)

4.3.4.1 Overall optimum conditions: $FeCl_3$

The overlay plot depicting the contours of the three responses are illustrated in Figure 4-25 and used to determine overall optimum conditions. As mentioned previously a low SVI and a high reduction in suspended solids and turbidity is desirable. The shaded region in Figure 4-25 represents the optimum region. According to the overlay plot the optimum dosage and pH that meet the required criteria was 500.6 mg/l and 7.61 respectively. These optimum conditions provide a 95% reduction in suspended solids and turbidity and a SVI of 95 mL/g.

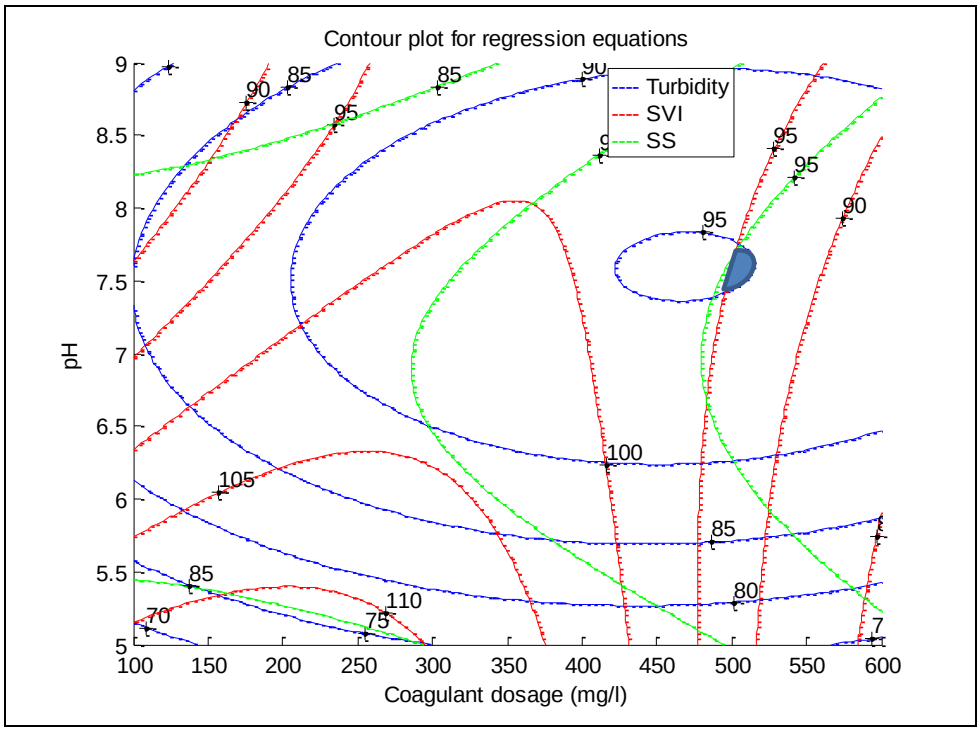

Figure 4-25: Overlay plot optimal region ($FeCl_3$)

From the results obtained it can be seen that neutral pH values provide the best results when Alum or $FeCl_3$ is used as the coagulant. Both coagulants provide the same reduction in turbidity. The suspended solids reduction is slightly higher when using $FeCl_3$ as the coagulant, however, twice as much $FeCl_3$ coagulant than Alum is required for only a minimal increase in reduction. A higher SVI is obtained when $FeCl_3$ is used as the coagulant as compared to when Alum is used. Since a low SVI is desirable and much less Alum coagulant is required than $FeCl_3$ to obtain similar reductions, Alum was chosen as the most suitable coagulant to be used in the pre-treatment to ultrafiltration. A confirmation experiment was conducted using Alum at the optimum conditions (dosage: 288.8 mg/l and pH=7.68). The confirmation experiment at the optimum conditions yielded a 93% and 89% reduction in turbidity and suspended solids respectively and a SVI of 92 mL/g. These values are similar to those predicted using the models (turbidity reduction: 95%, SS reduction: 90%, SVI: 90 mL/g).

4.4 Ultrafiltration: determination of optimum conditions

The experimental design was based on the Taguchi method. Three factors at three different levels each were varied. The Taguchi method is capable of incorporating fractional factorial experimental design known as orthogonal arrays in order to minimise the number of experiments required to carry out the investigation. Tables 4-9 and 4-10 illustrate the factors at the different levels as well as the orthogonal design respectively. Since fouling is a major problem in most membrane processes, it was chosen as the performance characteristic to be optimised. In total 9 experiments were conducted in order to determine the optimum conditions that provide the lowest fouling of the membrane. The fouling is determined by calculating the flux reduction of the pure water flux after cleaning the membrane (FR_{PWF}) using equation 19. Once the optimum conditions that reduce fouling were determined a confirmation experiment was conducted to determine the retention of the contaminants at these optimum conditions that reduce fouling.

Table 4-9: Factors investigated

Parameters	**Levels**		
	1	**2**	**3**
A=Temperature (°C)	60	40	20
B=Pressure (bar)	3	2	1
C= Volume reduction factor (ratio of permeate to initial feed)	0.86	0.71	0.63

Table 4-10: Orthogonal design

Experiment	**A**	**B**	**C**
1	1	1	1
2	1	2	2
3	1	3	3
4	2	1	2
5	2	2	3
6	2	3	1
7	3	1	3
8	3	2	1
9	3	3	2

Figure 4-26 illustrates the flux versus time curves obtained during ultrafiltration of the pre-treated white water at the different operating conditions depicted in tables 4-8 and 4-9. It can be seen that a relatively stable flux was achieved within an hour. Experiment 1 (P=3 bar, T= 60°C, VRF= 0.86) exhibited the highest flux decline. The flux decreased from an initial value of 453 L/m^2.hr to approximately 43 L/m^2.hr. The flux decline was lowest in experiment 6 (P=1 bar, T= 40°C, VRF=0.86). The flux drops from an initial value of 139 L/m^2.hr to approximately 41 L/m^2.hr. The observed flux declines were due to membrane surface fouling. The experiments carried out at the highest pressure appear to start at a very high flux, however, they drop dramatically within an hour. The observations made from the flux versus time curves are not enough to determine conclusively the optimum conditions that will reduce fouling of the membrane hence the percentage fouling and S/N ratios were determined.

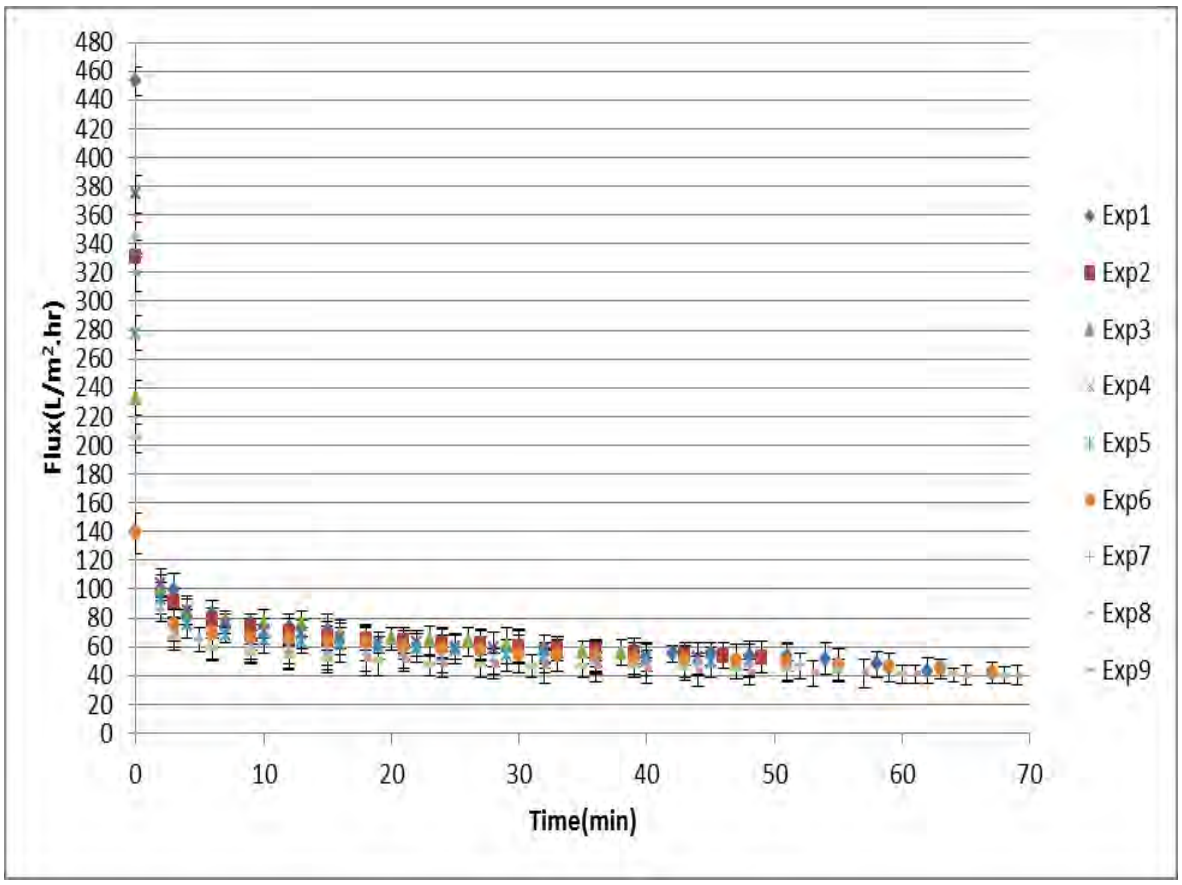

Figure 4-26: Flux versus time at different operating conditions

The signal-to-noise (S/N) ratio was used in order to evaluate the performance characteristic. Optimizing the fouling requires a lower flux reduction of the pure water (FR_{PWF}) hence a smaller-the-better S/N ratio (equation 7) is used to evaluate the fouling. Table 4-10 illustrates the percentage fouling represented by the FR_{PWF} and the corresponding S/N ratio for each experiment. From the FR_{PWF} values it was observed that experiment 1 exhibits the highest degree of fouling whereas

experiment 7 exhibits the lowest degree of fouling. In order to determine the optimum conditions the average S/N ratio obtained for each factor at the different levels were calculated. For example the average S/N ratio for temperature at level 1 can be obtained by averaging the ratios that were obtained for all experiments that were conducted at a temperature at level 1 i.e. experiments 1-3 according to table 4-11. Table 4-12 depicts the average S/N ratios calculated for each factor at each level.

Table 4-11: Flux reduction and S/N ratios for experiments conducted at different

Experiment	FR_{PWF}(% Fouling)	S/N Ratio
1	22.222	-26.936
2	18.182	-25.193
3	9.677	-19.715
4	12.500	-21.938
5	10.000	-20.000
6	15.152	-23.609
7	6.667	-16.478
8	10.000	-20.000
9	9.677	-19.715

Table 4-12: Average S/N ratios for each factor at different levels

	Average S/N ratio at each level		
Level	Factor A	Factor B	Factor C
1	-23.948	-21.784	-23.515
2	-21.849	-21.731	-22.282
3	-18.731	-21.013	-18.731
Range	5.217	0.771	4.783

Figures 4-27 to 4-29 illustrate the effect of the factors on the average S/N ratio. The average S/N ratio at each level for each factor was plotted in these figures. From Figures 4-28 and 4-29 it is observed that the gradient of the lines between the levels are different indicating that the effect of the levels on the fouling is different (Gonder et al., 2010). Fouling decreases to a greater extent when the VRF and pressure changes from level 2 (VRF=0.71, P= 2 bar) to level 3 (VRF=0.63, P=1 bar) than when it changes from level 1 (VRF=0.86, P=3 bar) to level 2 (VRF=0.71, P= 2 bar). Figure 4-27 indicates that the gradient of the lines between the different levels of temperature are fairly similar.

Figure 4-27 illustrates that the S/N ratio increases as the temperature decreases. The highest S/N ratio was observed at the lowest temperature (Level 3), hence, the lowest degree of fouling occurs at this temperature. A similar result was obtained by Gonder et al. (2010). Higher temperatures result in higher permeate fluxes as can be seen in Figure 4-26 where experiment 1 had the highest flux. This can be attributed to a decrease in the solvent viscosity as the temperature increases which in turn causes the membrane solvent diffusion coefficient to increase (Gonder et al., 2009). Even though

higher temperatures results in higher fluxes they reduce the lifespan of the membrane due to fouling. The increased fouling at higher temperatures is due to the expansion of the structure of the membrane which in turn enables solutes to enter the enlarged membrane pores and surface thereby clogging them (Gonder et al., 2010).

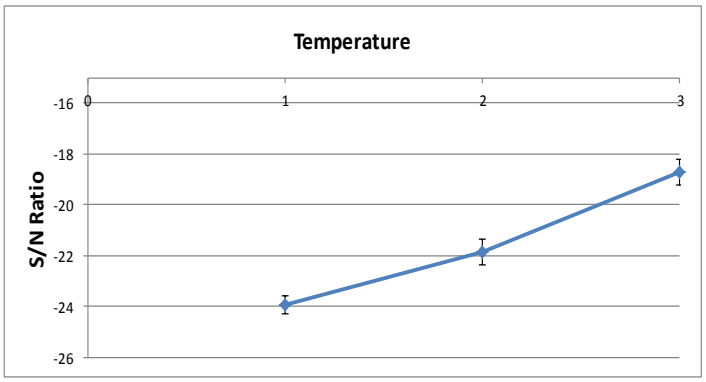

Figure 4-27: Effect of temperature on average S/N ratio

From Figure 4-28 it can be seen that the S/N ratio increases as the pressure decreases. The highest S/N ratio was observed at level 3 (1 bar) indicating that the lowest degree of fouling occurs at this lowest pressure. The highest degree of fouling occurs at the highest pressure (3 bar, level 1). Higher pressures cause concentration polarisation to take place on the membrane surface forming a gelatinous layer at the surface which in turn causes a rise in the osmotic pressure and a decrease in the driving force which results in a higher flux reduction, hence, a higher degree of fouling (Gonder et al., 2010).

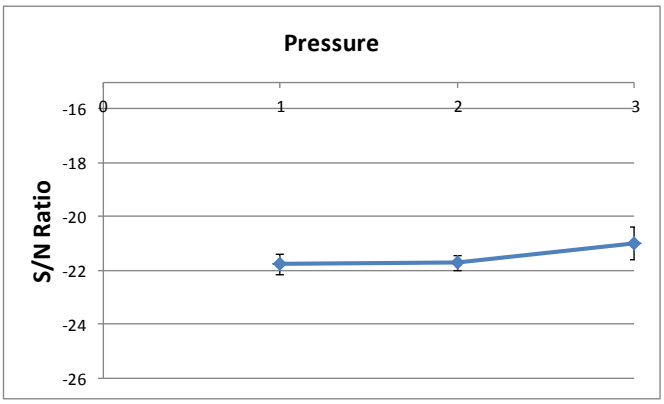

Figure 4-28: Effect of pressure on average S/N ratio

Figure 4-29 illustrates that the S/N ratio increases as the VRF decreases implying that the fouling decreases at lower VRF values. The lowest degree of fouling occurs at the highest S/N ratio at level 3 (VRF= 0.63). The increase in fouling as the VRF increases can be attributed to concentration polarisation occurring on the membrane surface. The concentration of contaminants in the concentrate increases as the VRF increases resulting in a higher concentration of contaminants at the surface of the membrane which, in turn clog the pores of the membrane (Ragona and Hall, 1998).

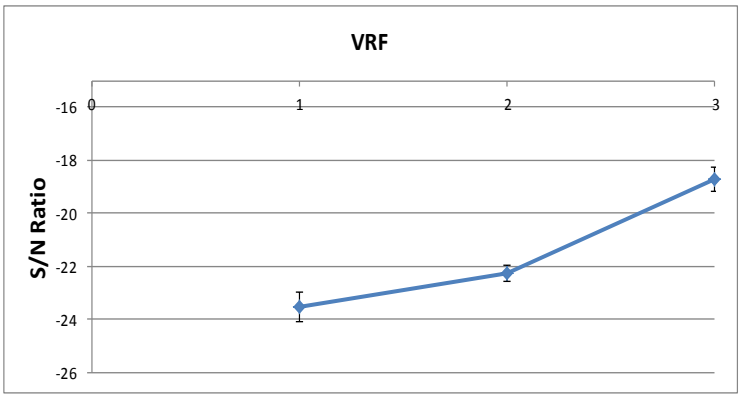

Figure 4-29: Effect of VRF on average S/N ratio

The optimum conditions that reduce fouling occur at the factor levels that produce the highest S/N ratios. From Figures 4-27 to 4-29 it can be seen that the highest S/N ratios occur at level 3 for each factor. The optimum conditions are a temperature of 20°C, a pressure of 1 bar and a VRF of 0.63. The last row of table 4-11 illustrates the range of each parameter which is the difference between the highest and the lowest S/N ratio for that parameter. The range gives an indication of the effect of each parameter on the process, the higher the range the greater is the effect of that parameter (Makrahy et al., 2013). From table 4-11 it can be seen that temperature has the greatest effect on fouling followed by VRF and pressure. The low effect of pressure can be due to the lower range of pressures investigated due to equipment limitations.

4.4.1 Confirmation experiment

Once the optimum conditions were established the predicted percentage fouling (performance characteristic) and 95% confidence interval (CI) was determined using equations 10 and 11 respectively in section 3.2.5. In order to use equations 10 and 11 the percentage fouling in table 4-10 had to be converted to decibel values using equation 12. Table 4-13 illustrates the corresponding decibel values. Once the decibel values were determined Anova had to be conducted in order to determine the CI using equation 11. Anova results required for the evaluation of equation 11 is shown in table 4-14. Also required in the evaluation of the CI was the F value from statistic tables at the significance level of 0.05, degrees of freedom of 1 and the error (DOF_e), hence, $F_{(0.05,1,2)}$ is 18.51 (Montgomery, 2001). The predicted fouling and CI value obtained in decibels were then converted back to percentage using equation 12.

Table 4-13: Corresponding decibel values for percentage fouling

Experiment	Ω (dB)
1	-5.441
2	-6.532
3	-9.700
4	-8.451
5	-9.542
6	-7.482
7	-11.461
8	-9.542
9	-9.700

Table 4-14: Anova results in decibels

Parameter	SS	DOF	MS
A	13.706	2	6.853
B	0.446	2	0.223
C	12.117	2	6.058
Error	1.623	2	0.812
Total	27.892	8	

The predicted percentage fouling and 95% confidence interval was 5.77% and 1.83%-16.75% respectively. The confirmation experiment was conducted at the optimum conditions i.e. P= 1 bar, T= 20°C and VRF=0.63. The percentage fouling for the confirmation experiment was determined using equation 19. The observed fouling for the confirmation experiment was 5.88%. As can be seen the predicted value and the observed value are fairly similar. The observed fouling is within the 95% confidence interval thus the predictions and the results obtained are valid. The reduction of contaminants was then determined in the permeate obtained from the confirmation experiment since the lowest degree of fouling is obtained at these conditions.

Table 4-15 illustrates the feed composition, the composition after coagulation pre-treatment and the composition of the permeate after ultrafiltration at the optimum conditions as well as the overall percent reduction. Coagulation pre-treatment enhanced the percent reduction of the contaminants. Coagulation pre-treatment reduced suspended solids to 93 mg/l which enabled UF to further reduce it to 13 mg/l resulting in an overall reduction of 98%. The concentrations of sulphates and aluminium, and the conductivity initially increase after coagulation pre-treatment due to the addition of aluminium sulphate, however, they are moderately reduced after UF. The optimum conditions not only reduce the fouling on the membrane but it also produces a permeate that meets the general water quality standards for the reuse of water in the pulp and paper manufacturing process. As mentioned previously in order for the water to be used for water ring vacuum pumps the conductivity

and concentration of dissolved solids should be less than 200 mS/m and 1000 mg/l respectively (Majcen Le Marechal et al., 2010). If the water is to be used as process water the chloride content should not exceed 75 mg/l (Tappi and Chamberlin, 1957). In order to use the water for felt and wire cleaning in the paper machine the suspended solids content should be between 10-15 mg/l (Majcen Le Marechal et al., 2010). If the water is to be substituted for process water the turbidity, magnesium and silica should not exceed 20 NTU, 12 mg/l and 100 mg/l respectively (Majcen Le Marechal et al., 2010). As illustrated in table 4-15 the permeate obtained meet these requirements for the reuse of the water.

Table 4-15: Quality of pre-treated water and permeate after UF

CONTAMINANT	Feed	Quality of white water after coagulation pre-treatment	Permeate quality	Overall percent reduction
Total solids(mg/l)	2456.000	1708.000	1368.000	44.300
Dissolved solids(mg/l)	1493.000	1300.000	987.000	33.891
Suspended solids(mg/l)	827.000	93.333	13.333	98.388
Dissolved and colloidal solids(mg/l)	1707.000	1675.000	1042.857	38.907
Wood extractives(mg/l)	88.000	68.000	52.000	40.909
Lignin(mg/l)	54.000	40.561	16.867	68.765
Ash(mg/l)	676.000	600.000	575.000	14.941
Chloride(mg/l)	80.700	74.500	55.000	31.846
Sulphate(mg/l)	393.000	574.400	355	9.669
Conductivity(mS/m)	131.000	170.000	128.000	2.290
Turbidity(NTU)	885.000	62.000	0.670	99.924
COD	1950.000	884.925	455.662	76.633
Sodium(mg/l)	185.000	145.000	70.000	62.162
Potassium(mg/l)	35.400	21.820	19.280	45.537
Aluminium(mg/l)	0.057	0.790	0.040	29.825
Calcium(mg/l)	96.000	94.000	59.900	37.604
Iron(mg/l)	0.070	0.040	0.037	47.143
Magnesium(mg/l)	9.580	8.600	4.500	53.027
Silica(mg/l)	17.100	10.990	6.900	59.649
Colour (Pt/Co)	1669.233	79.053	51.182	96.934

CHAPTER 5 **CONCLUSIONS**

The research conducted illustrates the advantages of system closure as well as the effect of system closure on the process by simulating system closure in the laboratory. It also highlights the need for treatment of the white water prior to it being introduced back into the process. Ultrafiltration was identified as an appropriate technology to achieve system closure.

In the simulation of system closure the results obtained indicate that the concentration of contaminants increased significantly with the increasing number of times the water was recycled. This indicates that using the Rapid-Kothen paper machine is a suitable method for the simulation of system closure in the laboratory and can be used to predict the effects of water loop closures on the actual process. The method would also be a facile technique to study the effect of additives on system closure. The accumulation of contaminants with increasing number of cycles tends to exhibit a linear relationship except for total extractives and UV_{280}. Paper properties were also adversely affected by an increase in the percentage of system closure i.e. as the percentage of white water used increases instead of fresh water. The burst index and brightness of the paper decreased as the level of closure increased, reinforcing the need for treatment of the water before it can be used back in the process.

Various membranes were investigated in order to determine the most appropriate membrane to be used in UF of the white water. It was found that hydrophilic membranes had the tendency to foul less than hydrophobic membranes. Retention of contaminants was affected by the MWCO of the membranes. The 10k Da membrane exhibited the best retention; however, it had the highest degree of fouling. The 100k Da membrane was the best choice since it exhibited the lowest percentage of irreversible fouling, the best cleanability and the permeate quality from this membrane is in accordance with the water quality requirements for the reuse of water in the process.

The turbidity of the feed water was relatively high as well as the suspended solids concentration. Waters having such characteristics tend to plug the pores of membranes hence increasing the fouling and reducing the life span of a membrane. Coagulation pre-treatment was applied to the white water in order to minimize this phenomenon. It was established that twice as much ferric chloride was required than alum to achieve a similar reduction in suspended solids and turbidity and a low SVI. The optimum dosage and pH was 288.8 mg/l and 7.68 respectively. It was found that reduction in suspended solids and turbidity tends to increase as the pH is increased to near neutral and alkaline values.

The Taguchi method was used to determine the optimum operating conditions that reduce the fouling of the membrane. Higher temperatures resulted in increased fouling of the membrane due to the expansion of the structure of the membrane which results in plugging of the pores of the

membrane. It was established that lower pressures are desirable since higher pressures resulted in increased fouling due to concentration polarisation taking place on the membrane surface. Fouling decreased at a lower VRF value which is also attributed to concentration polarisation on the membrane surface. It was found that the optimum conditions that reduce fouling was a temperature of 20°, a pressure of 1 bar and a VRF of 0.63. These optimum conditions reduced the suspended solids, turbidity and colour by 98%, 99% and 96% respectively. It also produced a permeate that meets the water quality standards for the reuse of water.

Ultrafiltration techniques can be ideal for water purification and system closure. The ultimate technology to be used will be determined by each mill taking into consideration the purity required and costs associated with equipment installation.

Since the stirred cell is a laboratory scale piece of equipment the results should be corroborated with a large scale set-up.

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APPENDIX A: MATLAB CODE

Alum Coagulation

```
% Contour and curve plot for Alum

% x1 = Coagulant dosage (mg/l)
% x1(lower limit) = 100
% x1(upper limit) = 500

% x2 = pH
% x2(lower limit) = 5
% x2(upper limit) = 9

% Grid for coagulant dosage and pH
[x1,x2] = meshgrid((linspace(100,500)),(linspace(5,9)));

% Regression equations for Turbidity, SVI, SS and COD
Turb = -30.450 + 0.209*x1 + 21.443*x2 - 0.00017*x1.^2 -0.997*x2.^2 -
0.012*x1.*x2;
SVI = 527.171 - 0.117*x1 - 110.397*x2 - 3.8*10^-5*x1.^2 + 6.574*x2.^2 +
0.027*x1.*x2;
SS = 56.394 + 0.152*x1 + 2.925*x2 - 0.00016*x1.^2 - 0.053*x2.^2 -
0.006*x1.*x2;
COD = 87.482 - 0.094*x1 -2.442*x2 + 0.012*x1.*x2;

%Plot multiple subplots showing the contour and curve plot for each of
the
%regression equations

%Figure 1 is subplot for Turbidity
figure(1)
subplot(2,1,1), [cs_Turb] = contour(x1,x2,Turb);
xlabel('Coagulant                    dosage                    (mg/l)'),
ylabel('pH'),clabel(cs_Turb),title('Percent reduction in Turbidity')
subplot(2,1,2), mesh(x1,x2,Turb)
xlabel('Coagulant  dosage  (mg/l)'),  ylabel('pH'),  zlabel('Percent
reduction')

%Figure 2 is subplot for SVI
figure(2)
subplot(2,1,1),[cs_SVI] = contour(x1,x2,SVI);
xlabel('Coagulant  dosage  (mg/l)'),  ylabel('pH'),  clabel(cs_SVI),
title('SVI')
subplot(2,1,2), mesh(x1,x2,SVI)
xlabel('Coagulant dosage (mg/l)'), ylabel('pH'), zlabel('SVI (ml/mg)')

%Figure 3 is subplot for SS
figure(3)
subplot(2,1,1), [cs_SS] = contour(x1,x2,SS);
xlabel('Coagulant  dosage  (mg/l)'),  ylabel('pH'),  clabel(cs_SS),
title('Percent reduction in Suspended Solids')
subplot(2,1,2), mesh(x1,x2,SS)
xlabel('Coagulant  dosage  (mg/l)'),  ylabel('pH'),  zlabel('Percent
reduction')

% Plot in a new window the contour plots of the different regression
% equations on the same plot
figure(5)
hold on
[c_Turb]=contour(x1,x2,Turb, [50,55,60,65,70,75,80,85,90,95,100], 'b');
```

```
clabel(c_Turb); str(1) = {'{\color{blue}----} Turbidity'};
[c_SVI]=contour(x1,x2,SVI, [60,70,80,90,95,100,105,110,120,130,140,150],
'r'); clabel(c_SVI); str(2) = {'{\color{red}----} SVI'};
[c_SS]=contour(x1,x2,SS,[50,55,60,65,70,75,80,85,90,95,100],      'g');
clabel(c_SS); str(3) = {'{\color{green}----} SS'};
title('Contour plot for regression equations')
xlabel('Coagulant dosage (mg/l)'), ylabel('pH')
text(420,8.65,str,'BackgroundColor',[1 1 1],'EdgeColor',[0 0 0])

%Get values of 'good' area and print table with N possible points
N = input('Number of points in "good" area (between 1 and 20):');
x1 = zeros(N,1);
y1 = zeros(N,1);
```

$FeCl_3$ Coagulation

```
% Contour and curve plot for FeCl3

% x1 = Coagulant dosage (mg/l)
% x1(lower limit) = 100
% x1(upper limit) = 600

% x2 = pH
% x2(lower limit) = 5
% x2(upper limit) = 9

% Grid for coagulant dosage and pH
[x1,x2] = meshgrid((linspace(100,600)),(linspace(5,9)));

% Regression equations for Turbidity, SVI, SS and COD
Turb = -75.90 + 0.055*x1 + 41.634*x2 -7.5*10^-5*x1.^2 - 2.801*x2.^2 +
0.002*x1.*x2;
SVI = 168.529 -0.043*x1 -13.824*x2 - 0.0002*x1.^2 + 0.270*x2.^2 +
0.023*x1.*x2;
SS = 21.369 - 0.008*x1 + 19.455*x2 + 3.6*10^-5*x1.^2 -1.429*x2.^2 +
0.0009*x1.*x2;

% Plot multiple subplots showing the contour and curve plot for each of
the
% regression equations

%Figure 1 is subplot for Turbidity
figure(1)
subplot(2,1,1), [cs_Turb] = contour(x1,x2,Turb);
xlabel('Coagulant                    dosage                    (mg/l)'),
ylabel('pH'),clabel(cs_Turb),title('Percent reduction in Turbidity')
subplot(2,1,2), mesh(x1,x2,Turb)
xlabel('Coagulant  dosage  (mg/l)'),  ylabel('pH'),  zlabel('Percent
reduction')

%Figure 2 is subplot for SVI
figure(2)
subplot(2,1,1),[cs_SVI] = contour(x1,x2,SVI);
xlabel('Coagulant  dosage  (mg/l)'),  ylabel('pH'),  clabel(cs_SVI),
title('SVI')
subplot(2,1,2), mesh(x1,x2,SVI)
xlabel('Coagulant dosage (mg/l)'), ylabel('pH'), zlabel('SVI (ml/mg)')

%Figure 3 is subplot for SS
figure(3)
subplot(2,1,1), [cs_SS] = contour(x1,x2,SS);
```

```
xlabel('Coagulant dosage (mg/l)'), ylabel('pH'), clabel(cs_SS),
title('Percent reduction in Suspended Solids')
subplot(2,1,2), mesh(x1,x2,SS)
xlabel('Coagulant dosage (mg/l)'), ylabel('pH'), zlabel('Percent
reduction')

% Plot in a new window the contour plots of the different regression
% equations on the same plot
figure(5)
hold on
[c_Turb]=contour(x1,x2,Turb, [50,55,60,65,70,75,80,85,90,95,100], 'b');
clabel(c_Turb); str(1) = {'{\color{blue}----} Turbidity'};
[c_SVI]=contour(x1,x2,SVI, [60,70,80,90,95,100,105,110,120,130,140,150],
'r'); clabel(c_SVI); str(2) = {'{\color{red}----} SVI'};
[c_SS]=contour(x1,x2,SS,[50,55,60,65,70,75,80,85,90,95,100],      'g');
clabel(c_SS); str(3) = {'{\color{green}----} SS'};
title('Contour plot for regression equations')
xlabel('Coagulant dosage (mg/l)'), ylabel('pH')
text(420,8.65,str,'BackgroundColor',[1 1 1],'EdgeColor',[0 0 0])

%Get values of 'good' area and print table with N possible points
N = input('Number of points in "good" area (between 1 and 20):');
x1 = zeros(N,1);
y1 = zeros(N,1);
```

APPENDIX B: LIST OF STANDARD METHODS USED

- Preparation of hand-sheets - TAPPI T205-sp-95 and ISO 5269-1:1998 (E)
- Freeness of pulp - TAPPI T227 om-94
- Testing of hand-sheets - ISO 2758, ISO 2470-1 and ISO 2470-2
- Determination of total dissolved solids - APHA 2540 C
- Determination of total suspended solids - APHA 2540 D
- Determination of total solids - APHA 2540 B
- Determination of ash content - TAPPI T211 om-02
- Determination of COD - ASTM D 1252-00
- Determination of turbidity - APHA 2130
- Determination of conductivity - APHA 2510
- Determination of colour - PAPTAC Standard H.5
- Determination of chlorides - ASTM D 512-89
- Determination of sulphates - ASTM D 0516-02
- Preparation of samples for metals analysis - APHA 3030 A,D-F