UF MEMBRANES OPERATED ON PAPER MACHINE WASTEWATER: FOULING TENDENCIES AND CHARACTERISATION

by

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Thesis

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DECLARATION

I the undersigned, hereby declare that the work contained in this thesis is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree.

SUMMARY

At the Mondi Kraft paper mill in Piet Retief, paper machine effluent is pre-treated by means of dissolved air flotation (DAF) and a microstrainer prior to ultrafiltration (UF). Despite the rigorous pre-treatment of the effluent, severe fouling of the UF membranes still persisted, resulting in a sharp decrease in operational flux. In an attempt to improve the flux performance of the UF membranes an investigation was launched into the possible causes of membrane fouling. The study yielded the following results:

Ultraviolet-visible (UV-Vis) spectrophotometric analyses of various effluent samples collected from different locations at the mill indicated the presence of aromatic compounds. Lignosulphonate appeared to be the main constituent in all the samples analysed.

UV-Vis spectrophotometry was also performed on fouling extracted from membranes in order to evaluate the different approaches attempted to reduce membrane fouling. Most of the UV-Vis spectra obtained did not show the absorbance maxima below 210 nm that were seen for the paper machine effluent, DAF product, lignosulphonate and microstrainer product. This indicated that the compounds with absorbance at lower wavelengths did not foul the membranes to the same extent as the aromatic substances with absorbance maxima between 230 and 400 nm.

The influence of pH on the absorption of the various effluent samples was also investigated. An increase in pH resulted in (1) a "shift" in the wavelength scans from a lower to a higher wavelength, suggesting ionisation (deprotonation) with a subsequent delocalization of electrons and (2) an increase in the turbidity.

The increase in turbidity which accompanied the increase in pH could be explained by complex formation between the carboxylate ions, phenolic groups and divalent metal ions present in the effluent. Inductively coupled plasma analyses of several effluent samples with pH values 7 and 13 indicated the presence of significant amounts of Ca^{2+} ions in the effluent. There was a significant decrease in the Ca^{2+} levels with an increase in pH, which supported the hypothesis that Ca^{2+} might contribute to complex formation. This resulted in a decrease in solubility and an increase in turbidity. The addition of a chelating agent (ethylenediaminetetra-acetic acid disodium salt) to an effluent solution at pH 13 redissolved the precipitate and considerably reduced the turbidity. The subsequent addition of $CaCl_2$

again induced precipitation and increased turbidity, confirming the role of Ca^{2+} in complex formation.

Gel permeation chromatographic analyses of microstrainer product at pH 13 showed the formation of high molecular mass organo-calcium complexes. The exact molecular mass of the complexes present in the microstrainer product could not be determined by electrospray mass spectrometry because of their poor ionisation ability.

Atomic force microscopy and scanning electron microscopy (SEM) showed distinct differences in the membrane surface texture before and after fouling. Furthermore, SEM images of the UF membranes exposed the limited ability of the 30 μm microstrainer, installed downstream from the DAF unit, to remove residual fibres from the DAF product.

Static fouling experiments performed on all the flocculants and coagulants used in the paper-making process at the mill showed that none of these substances fouled the UF membranes.

Cleaning of the UF membranes with Triton X100®, a non-ionic surfactant, caused a temporary increase in the operating flux to values higher than that of the initial flux.

Mechanical cleaning of the UF membrane surface with spongeballs proved to be one of the most effective and successful methods to prevent flux loss caused by fouling.

Pre-coating of the UF membranes with Pluronic® F108, another non-ionic surfactant, did not promote membrane productivity. Evaluation of various types of membranes indicated that hydrophilic or negatively charged membranes withstood membrane fouling more effectively than hydrophobic UF membranes under the same operating conditions.

OPSOMMING

By Mondi Kraft se papier meule in Piet Retief word afloopwater vanaf die papiermasjiene vir hergebruik met behulp van ultrafiltrasie (UF) behandel. Opgeloste lugflotasie (OLF) en mikrosiwwing word as voorbehandeling vir die UF membraanproses ingespan. Ondanks die intensiewe voorafbehandeling wat toegepas word, vind daar geweldige aanvuiling van die UF membrane plaas wat tot die vinnige verlaging in bedryfsfluks aanleiding gee. 'n Ondersoek na die moontlike oorsake van membraan-aanvuiling het die volgende bevindinge opgelewer:

Ultraviolet-sigbare (UV-Vis) spektroskopie van water monsters wat by die meule versamel is, het die teenwoordigheid van aromatiese komponente aangetoon, met lignosulfonaat die hoofkomponent in al die monsters wat ontleed is.

Ekstrakte afkomstig van aangevuilde membrane is ook met behulp van UV-Vis-spektroskopie geanaliseer om verskeie benaderings te evalueer om 'n afname in membraan-aanvuiling te bewerkstellig. Die oorgrootte meerderheid spektra het nie die absorpsie maksima onder 210 nm aangetoon wat teenwoordig was in monsters van die papier masjien afloopwater, OLF uitvloeisel, lignosulfonaat en mikrosif produkwater nie. Dit het aangedui dat die komponente wat by laer golflengte absorbeer nie die UF membrane in dieselfde mate aanvuil as daardie komponente wat by hoër golflengtes (tussen 230 en 400 nm) absorbeer nie.

Die invloed wat pH op die absorpsie van komponente teenwoordig in die onderskeie afloopwatermonsters het, is ook ondersoek. 'n Toename in pH het bygedra tot (1) 'n verskuiwing in die spektra vanaf 'n lae na 'n hoër golflengte vanweë ionisasie (deprotonering) met gevolglike delokalisasie van elektrone en (2) 'n toename in turbiditeit.

Die toename in turbiditeit wat verband hou met die toename in pH was verduidelik aan die hand van kompleksvorming tussen die karboksilaat ione, fenoliese groepe en divalente metaal ione in die afloopwater. Induktief gekoppelde plasma analise van verskeie water monsters by pH 7 en 13 het die teenwoordigheid van 'n groot hoeveelheid Ca^{2+} aangetoon. 'n Verlaging in die vlakke van opgeloste Ca^{2+} het met die toename in pH verband gehou. Dit het die moontlike verbintenis tussen Ca^{2+} en kompleksvorming ondersteun wat bygedra het tot die afname in oplosbaarheid en toename in turbiditeit. Die byvoeging van etileendiamientetra-asynsuur-dinatriumsout, 'n kelerings reagens by afloopwater (pH 13) het die presipitaat weer in oplossing gebring en die turbiditeit merkwaardig verlaag. Die

byvoeging van $CaCl_2$ het weer presipitasie geïnduseer, met 'n gevolglike toename in turbiditeit. Hiermee is Ca^{2+} se rol in kompleksvorming bevestig.

Gelpermeasie-chromatografiese analise van die mikrosif produk (pH 13) het die vorming van hoë molekulêre massa organo-kalsium komplekse bevestig. Dit was egter nie moontlik om met behulp van massaspektrometrie die korrekte molekulêre massa van die komplekse te bepaal nie vanweë hul onvermoë om te ioniseer.

Atomiese krag mikroskopie en skandeer elektron mikroskopie (SEM) het duidelik die voor en na verskil getoon wat aanvuiling op die membraantekstuur gehad het. 'n SEM foto van die aangevuilde UF membraan het die onvermoë van die mikrosif blootgelê om oorblywende vesels vanuit die OLF produkwater te verwyder.

Resultate bekom gedurende passiewe aanvuilingseksperimente het aangetoon dat al die in-proses flokkulante en koagulante wat gebruik word by die papier meule geen bydrae tot die aanvuiling van die UF membrane maak nie.

Skoonmaak van die UF membrane met Triton X100® bring 'n verhoging in bedryfsvloed teweeg, maar die verhoging, wat hoër as die oorspronklike vloed is, is kortstondig.

Meganiese skoonmaak van die buismembrane met behulp van sponsballe blyk die mees effektiewe skoonmaakmetode te wees.

Voorafbehandeling van die UF membrane met Pluronic® F108 het nie die membraanproduktiwiteit verhoog nie. Daar is ook bevind dat hidrofiliese of negatief gelaaide membrane groter weerstand bied teen aanvuiling in vergelyking met hidrofobiese UF membrane onder dieselfde bedryfstoestande.

Dedicated to my parents

Thank you for all the sacrifices you have made over the years.

You are appreciated.

"... Yet in all these things we are more than conquerors through Him who loved us..."

Romans 8:37

It is not the critic who counts; not the man who points out how the strong man stumbled or how the doer of deeds could have done them better. The credit belongs to the man who is actually in the arena, whose face is marred by dust and sweat and blood, who strives valiantly; who errs and comes short again and again; who knows the great enthusiasms, the great devotions, who spends himself in a worthy cause, who at best, knows in the end of the triumph of high achievement, and who, at worst, at least fails while daring greatly, so that his place shall never be with those timid souls who know neither victory or defeat.

Theodore Roosevelt

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ABBREVIATIONS

4CL	4-coumarate:coenzyme A ligase
AFM	atomic force microscopy
ATP	adenosine triphosphate
BSA	bovine serum albumin
C3H	coumarate 3-hydroxylase
C4H	cinnamate 4-hydroxylase
CAD	cinnamyl alcohol dehydrogenase
CCoA3H	coumaroyl-coenzyme A 3-hydroxylase
CCoAOMT	caffeoyl-coenzyme A *O*-methyltransferase
CCR	cinnamoyl-coenzyme A reductase
CIP	cleaning-in-place
COMT	caffeic acid *O*-methyltransferase
Da	dalton
DAF	dissolved air flotation
EDTA	ethylene diamine tetra-acetic disodium salt
ES-MS	electrospray mass spectrometry
F5H	ferulic acid 5-hydroxylase
FFA	free fatty acids
GLS	cinnamyl alcohol β-glucosidase
GPC	gel permeation chromatography
HPLC	high performance liquid chromatography
ICP	inductively coupled plasma
$L/m^2.h$	litres per square metre per hour
LiP	lignin peroxidase
MM_{av}	molecular mass averages
MMCO	molecular mass cut-off
MM_d	molecular mass distribution
MnP	manganese peroxidase
MS	mass spectrometer
NADH	nicotinamide adenine dinucleotide
NADPH	nicotinamide adenine dinucleotide phosphate

NSSC	neutral sulphite semichemical
NTU	nephelometric turbidity unit
OMT	*S*-adenosyl-L-methionine-dependent diphenol-*O*-methyltransferases
PA	palmitic acid
PAL	phenylalanine ammonia-lyase
PEO	poly(ethylene oxide)
PEP	phosphoenolpyruvate
PES	poly(ether sulphone)
PF	product flux
PO	peroxidase
PS	polysulphone
PWF	pure-water flux
RO	reverse osmosis
SA	stearic acid
SD	standard deviation
SEM	scanning electron microscopy
TAL	tyrosine ammonia-lyase
TIC	total-ion current
UF	ultrafiltration
UTG	UDP-glucose:cinnamyl alcohol glucotransferase
UV-Vis	ultraviolet-visible spectroscopy
WRC	Water Research Commission

GLOSSARY

Alum: A paper-making chemical used for precipitating rosin size onto pulp fibres to impart water-resistant properties to the paper. It is also called aluminium sulphate.

Black liquor: Spent cooking liquor from a Kraft or soda cook, containing dissolved organic wood materials and residual alkali compounds.

Boksliner: A coated paper used on the inside of boxes, which are used for food.

Broke: Paper trimmings or paper damaged from breaks on the paper machine and in finishing operations.

Consistency: Dry solids content (%) of pulp present in a pulp slurry.

Integrated mill: A mill that makes its own pulp from which it then produces paper.

Mondiliner: Unbleached packaging paper.

Noodle: Unbleached, softwood pulp produced at the Richards Bay paper mill by means of the Kraft method.

Stock: A mixture containing water, one or more grades of pulp, and various fillers and additives.

CHAPTER 1

INTRODUCTION

The pulp and paper industry is one of the largest freshwater consumers in the world. In Europe alone more than 8 million cubic metres of water is used daily by the pulp and paper industry [1]. In the United States between 44 000 and 83 000 litres of water is used to produce one ton of virgin paper [2]. In a water-scarce country such as South Africa (Pryor *et al.*, 1998), the consumption of such large volumes of water will have a negative impact on the environment in the long run and for this reason water consumption by these industries has to be minimised. Recycling of the process waters or effluents within the factory is one way to reduce the intake of fresh water. The effluent must, however, be purified before reuse in order to remove any contaminants that would interfere with the paper-making process. Membrane filtration is one option for effluent clarification (Nuortila-Jokinen *et al.*, 1998). In the pulp and paper industry ultrafiltration (UF) membranes, such as polysulphone (PS) and poly(ether sulphone) (PES) membranes, are routinely used because of their ability to withstand high temperatures (up to 75 °C), wide pH range (1 to 13) and their resistance to a variety of chemicals. It is also commonly used in the wine, diary, textile and automobile industries to separate various species (Cheryan, 1998).

At the Mondi Kraft paper mill in Piet Retief, effluent is treated by means of UF followed by ion exchange and reverse osmosis (RO). One of the limitations in applying UF, as with any other pressure-driven membrane filtration process, is fouling. Membrane fouling causes a reduction in product flux (PF). Consequently operational pressures must be increased to maintain flux at a reasonable level. This in turn translates to an increase in the operational costs. Membrane cleaning, furthermore, increases down time, electricity consumption, chemical usage and wastewater production (Boerlage *et al.*, 1998).

Prior to the inception of the UF plant, paper machine effluent was pumped into a series of 15 cascading dams (Figure 1.1). These dams were constructed with raised earth walls, and it was originally planned that the effluent would overflow from one dam to the next with a residence time of 7 days. The dams had a depth of 1.2 m that allowed for effective evaporation.

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[1] http://www.globaltechnoscan.com/4July-10July01/paper.htm
[2] http://www.ecopaperaction.org/problem.htm

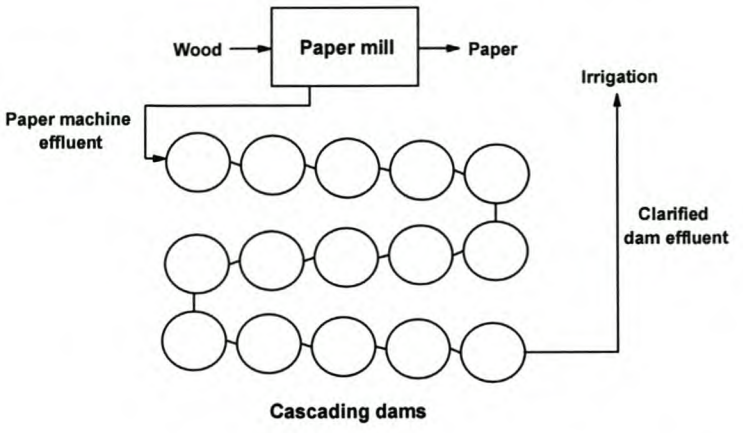

Figure 1.1: Simplified layout of the Mondi Kraft paper mill in Piet Retief. Paper machine effluent, emanating from the paper mill, was pumped into 15 cascading dams for evaporation and clarification, prior to irrigation.

With the implementation of the UF plant, paper machine effluent as well as effluent from the final cascading dam were evaluated as feed. It was found that the effluent from the final cascading dam (dam effluent) was the most suitable for UF treatment. The higher operating fluxes obtained with the dam effluent could be attributed to the long retention time in the dams and favourable anaerobic conditions. These conditions allowed for the partial biodegradation of the organic material and subsequent clarification of the dam effluent to very low levels of suspended solids.

After an initial period of normal operation, the performance of the tubular UF plant deteriorated. This deterioration was ascribed to the presence of reduced sulphur compounds in the dam effluent. It was concluded that sulphur reducing bacteria in the dams were responsible for the sulphur production. To overcome the "*sulphur problem*" the dam effluent was substituted with paper machine effluent fed directly from the factory to the UF plant. The low quality of the feed resulted in a rapid and total blockage of the membranes by fibres in the effluent. To overcome this problem a dissolved air flotation (DAF) clarifier was installed upstream of the UF process.

The product flux of UF membranes operating on feed from the DAF clarifier, however, turned out to be substantially lower than the flux obtained with dam effluent as feed. In addition, changes in the paper production process, the mill, and the pre-treatment regimes, implemented before DAF, altered the composition of the feed to the UF process. The sharp decrease in membrane flux necessitated characterisation of the UF effluent to identify the

cause of membrane fouling during UF.

The first step in the investigation entailed tracing the origin of the foulants present in the effluent. This required examination of the various processes applied at the different stages during paper production. In Chapter 2 the plant layout and a general description of the various processes are presented. During the pulping process, a certain percentage of the lignin present in wood is broken down into water soluble compounds which adds to the polluting characteristics of paper mill effluent. In Chapter 3 the biosynthesis and enzymatic biodegradation of lignin are discussed to clarify how this complex biopolymer might contribute to the fouling of the PES membranes during UF.

Other breakdown products of wood, such as cellulose and hemicellulose, also contribute to the high organic load in the UF feed and the subsequent fouling of the UF membranes. In an attempt to minimise the hydrophobic interactions between these foulants and the UF membranes it was decided to pre-coat the surface of UF membranes with various agents. Chapter 4 describes the modification of the PES membrane surface with the non-ionic surfactant, Pluronic® F108 and free fatty acids (FFAs) in an effort to enhance the anti-fouling characteristics of the membranes.

Various flocculants and coagulants are also added to the process water at the paper mill. These formulations are used on the paper machine and in the pre-treatment of paper machine effluent prior to DAF-clarification. PES membranes were statically fouled with the various flocculants and coagulants, to establish whether they participate in membrane fouling. These experiments are described in Chapter 5.

To develop the most efficient strategy against membrane fouling it is important to have as much physical and chemical data on the potential foulants in a given effluent. Several effluent samples, collected from various locations on the plant as well as foulants present on the PES membranes, were therefore characterised by ultraviolet-visible (UV-Vis) spectroscopy, inductively coupled plasma (ICP), gel permeation chromatography (GPC), and electrospray mass spectrometry (ES-MS). This work is described in Chapter 6. In Chapter 7, experiments to determine the surface characteristics of fouled and unfouled PES membranes, by atomic force microscopy (AFM) and scanning electron microscopy (SEM), are described. These modern imaging techniques yielded valuable information on the physical nature of the fouling process as well as the thickness of fouling layers. Chapter 8 describes various

membrane pre-treatment and cleaning procedures, characterisation of membrane extracts from flat-sheet test rig membranes and the evaluation of the performance of various membranes at the mill. Chapter 9 contains the general conclusions from all the experiments performed in the thesis.

CHAPTER 2

PLANT LAYOUT AND ORIGIN OF VARIOUS EFFLUENTS

The Mondi Kraft paper mill in Piet Retief, produces effluent with a potential enviromental impact. Currently this effluent is disposed by means of irrigation, but this practice has the potential to cause downstream pollution problems and will not be allowed in future. Alternative methods of effluent treatment therefore had to be found to reduce wastewater discharge as a step towards the implementation of mill effluent closure (Figure 2.1). A number of techniques are used to treat wastewaters originating from the pulp processing industry. These include aerobic and anaerobic treatments (Tirsch, 1990), lime and alum coagulation and precipitation, oxidation, adsorption onto ion-exchange resins and UF (Dorica *et al.*, 1986; Jönsson, 1987; Zaidi *et al.*, 1992).

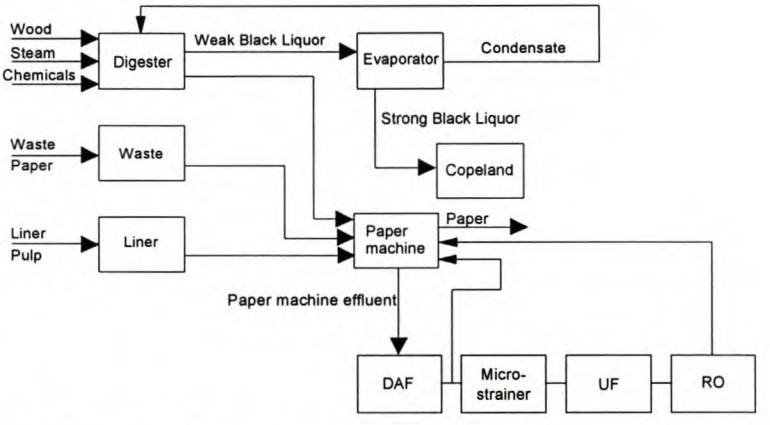

Figure 2.1. Flow diagram of the paper mill illustrating mill effluent closure (DAF: dissolved air flotation, RO: reverse osmosis).

Treatment of pulp and paper effluent by means of UF is an attractive method for treating these waters, as most of the polluting substances consist of high molecular mass compounds that are readily retained by UF (Jönsson, 1987; Zaidi *et al.*, 1992). Consideration of membrane technology for the treatment of effluent was therefore an attractive option at the paper mill and a UF plant consisting of 672 tubular modules with a total membrane surface area of 2 016 m^2, was commissioned in 1994. The design flux of the plant was 38 L/m^2h and the design feed 1 700 m^3 per day with a design recovery of 91%. Initial results reported on the UF plant performance were encouraging, but changes in production protocols to reduce water consumption and the use of different paper additives led to a significant decrease in the productivity of the UF plant. These fouling problems prompted the formation of a research

group comprising the Universities of Stellenbosch and Natal, the ML Sultan Technikon and senior engineers at the paper mill to address the fouling problem and increase the efficiency of the UF plant.

2.1 PROCESS DESCRIPTION AND ORIGIN OF EFFLUENT

The integrated pulp and paper mill can be divided into several sections that perform distinctly different functions. These different sections each produce effluent that, to a greater or lesser extent, is passed on to the DAF clarifier before UF.

2.1.1 Wood supply

Wood from pine (*Pinus sp.*) and gum trees (*Eucalyptus sp.*) is used in the production of paper. The former is obtained from sawmills in the surrounding area and occasionally chipped at the paper mill. Gum trees are supplied as whole logs and chipped on site, whereafter they are transported in a weak black liquor suspension to a chip pile. The pine and gum chips are separately screened, to control the chip size and remove dirt, bark and metal pieces. Thereafter, the pine and gum chips are mixed in the volumetric ratio 1:1 before transportation to the digester.

2.1.2 Digester

The wood chips are cooked in a continuous vapour phase digester at 175°C in a mixture of sodium sulphite (Na_2SO_3), sodium carbonate (Na_2CO_3) [10%] and anthraquinone as a catalyst. Only a portion of the lignin in the wood is converted to lignosulphonate. Under neutral sulphite pulping conditions the lignin is "softened" rather than dissolved to produce a high yield pulp (Helm, 1997) [3]. The yield target at the paper mill is 68%. During the cooking process various compounds, such as turpentine, pitch, soaps, wood resins, tannins, lignans, carbohydrates, fats and waxes (Helm, 1997), are extracted from the wood. The bottom half of the digester contains a high heat washing zone where heated wash water (usually evaporator condensate) flows counter current to the wood chips to wash the liquor out of the pulp. This liquor is extracted half way up the digester vessel as weak black liquor. The weak black liquor is evaporated and concentrated to 30% solids, whereafter it enters the Copeland scrubber for additional evaporation. The concentrated black liquor is "fired" (pyrolyzed) in the Copeland reactor where combustion of the organic compounds takes place

[3] http://www.chemistry.vt.edu/chem-dept/helm/3434WOOD/notes1/ultra.html

and the residual salts form a solid granular salt cake. The cake, consisting of sodium sulphate and sodium carbonate, is sold. The pulp exiting the digester is "refined" to break up any remaining chips to pulp. The water is extracted from the pulp and combined with the wash water stream entering the bottom of the digester. Thereafter, the pulp is pressed in a slurry press to a consistency of 40% and stored on noodle piles.

2.1.3 Waste plant

Waste paper, mainly cardboard boxes made from Kraft linerboard, is purchased and recycled at the paper mill. These boxes are repulped in water recovered from the paper machine. The pulp is screened, to remove any plastic and staples, and transferred to the paper machine at about 3% consistency. The waste paper contains glue, waxes, pitch, etc., that contribute a substantial amount to the chemical oxygen demand of the effluent.

2.1.4 Noodle/Baled pulp

Kraft pulp, obtained from the Mondi Kraft Richards Bay paper mill (at 30% mass noodle consistency), is repulped in water recovered from the paper machine and transferred to the paper machine (at about 3% consistency).

2.1.5 Paper machine stock preparation

A sheet of linerboard usually consists of two layers: the base or bottom liner and the top liner (Mimms *et al.*, 1993). The bottom liner consists of digester and waste plant pulp that are combined in a 1:1 ratio. Noodle pulp provides the top liner of "Boksliner grades", whereas, waste paper provides the top liner for "Mondiliner grades". The purpose of the top liner is to completely cover the bottom liner in order to form a good printing surface (Mimms *et al.*, 1993). The top liner usually comprises 20% of the total sheet weight. Broke, reject paper, from the paper machine is returned to the bottom liner and can supply up to 5% of the bottom liner.

2.1.6 Paper machine

Each liner stock is diluted to a final concentration of < 1% of the "original" concentration before it enters the headbox on the paper machine. The headbox sprays the pulp onto a forming wire, where the fibres form a mat and the water drains through the wire. The water collected below the forming wire is called backwater and is used in a multitude of dilutions as

well as for the repulping of waste paper in the waste paper plant. The top liner backwater is kept separate from the bottom liner backwater and is used to repulp noodle pulp and waste paper for the production of top liner. The top and bottom liners are joined as they leave the table and enter into a press section where pressure nips and felts are used to press water from the sheet. The sheet then passes through steam heated drying rollers to remove any remaining moisture.

2.1.7 Chemistry on the paper machine

Bentonite clay acts as a scavenger to collect fine particles of wood fibres, organics, trash, etc., when added to the stock entering the paper machine. Subsequently a slightly charged high molecular mass polymer is used as a flocculant to gather and remove the bentonite aggregates. Alum is added to assist with the collection of fines and trash as well as to retain "size", a water repelling agent which makes the paper water resistant. Dry strength resin is added to improve the bonding strength of the paper and dye is added to control the paper colour. Biocide is added to control biological growth and defoamer is used to reduce foaming. Felt cleaners are caustic based detergents used to keep felts clean.

2.1.8 Effluent emanating from the paper machine

The paper machine has many areas that require clean water. These include certain cooling showers, seals on the pumps, felt cleaning showers and for the make-up of polymers. The excess backwater from the paper machine is sent to the DAF clarifier, where the solids are removed by clarification, and returned to the paper machine as shower water. The DAF product (clarified paper machine effluent) also feeds the UF plant. Excess effluent which exceeds the offtake for the paper machine goes to the cascading dams and then to the effluent irrigation fields.

2.1.9 Membrane plant

Paper machine effluent is clarified by a DAF clarifier and polished by a 30 μm microstrainer before UF with PES membranes. The tubular membranes (12.7 mm internal diameter) are encased in modules of 19 parallel flow tubes per module (Figure 2.2). Modules are installed in banks and connected by 50 mm internal diameter stainless steel U-bends in series. The design inlet pressure and velocity are 600 kPa and 2.2 m/s respectively, and the design temperature is 40 °C. The system is operated in a feed and bleed mode at 92% recovery.

Figure 2.2. UF membrane plant in the Mondi Kraft paper mill at Piet Retief.

Wood contains many different chemical substances, which can be divided into four major groups: cellulose, hemicellulose, lignin and extractives. Generally when pulping, one aims to retain as much of the cellulose and hemicellulose as possible, while lignin and extractives are removed from the wood. The lignin and extractives are major ingredients of the paper machine effluent and will play an important role in the fouling of UF membranes used to treat this effluent. Characterisation of these lignin derived compounds is therefore very important to establish how they would interact with the UF membranes. For this reason the biosynthesis, biodegradation and chemical degradation of lignin is discussed in great detail in Chapter 3.

CHAPTER 3

LIGNIN: BIOSYNTHESIS, BIODEGRADATION AND CHEMICAL DEGRADATION DURING PULPING

"Among the natural compounds, lignin is next to cellulose the second most abundant substance in the biosphere" (Majcherczyk and Hütterman, 1997). It is found throughout the plant kingdom in all vascular plants where it acts as a structural component of supporting and conducting tissues. The woody stems of higher plants such as angiosperms, gymnosperms and monocotyledons contain 18-25%, 25-30% and 10-30% lignin on a dry mass basis, respectively (Crawford, 1981). Lignin is absent in Bryophyta (true mosses) and lower plant groups. The high percentage of lignin present in the wood is of particular interest in the pulp and paper industry as it influences the paper quality. During the treatment of wood for the manufacturing of paper, lignin is inevitably broken down into low molecular mass polymers. These lignin degradation products, rich in phenolic groups, are soluble in the process water and add to the polluting characteristics of paper mill effluent. The aim of this study was to get a better understanding of lignin as a possible foulant of the PES UF membranes during the UF of pulp and paper effluent.

3.1 LIGNIN STRUCTURE

Lignins are polymers consisting of three alcohol monomers or monolignols: *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Figure 3.1). Each one of these precursors can undergo various chemical reactions with other precursors during the formation of a lignin polymer. In addition to lignin these precursors, or monolignols, are also able to form bonds with other cell wall polymers cross-linking polysaccharides and proteins with lignin (Whetten *et al.*, 1998).

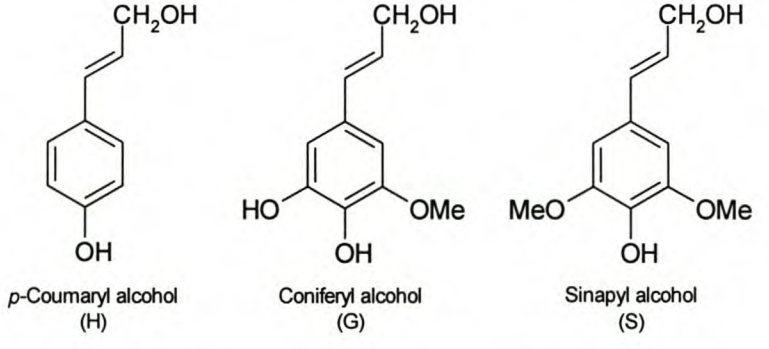

Figure 3.1: The three primary monomeric precursors of lignin.

Two major classes of lignin can be distinguished in higher plants, namely (*a*) gymnosperm lignins and (*b*) angiosperm lignins. Gymnosperm lignins primarily contain guaiacyl subunits (G-units), polymerised from coniferyl alcohol, and a small proportion of *p*-hydroxyphenyl units (H-units) polymerised from *p*-coumaryl alcohol. Angiosperm lignins contain syringyl units (S-units), polymerised from sinapyl alcohol, and G-units, with minor amounts of H-units. There are, however, exceptions to this basic classification found in both gymnosperms and angiosperms (Sarkanen and Ludwig, 1971).

3.2 BIOSYNTHESIS OF LIGNIN

Lignin biosynthesis requires the co-ordinated regulation of three major biosynthetic pathways, the shikimate, phenylpropanoid, and lignin branch pathways. The shikimate pathway (Figure 3.2) plays a key role in primary metabolism, providing building blocks for lignin synthesis as well as other plant products (Barber and Mitchell, 1997).

It entails the initial condensation of phosphoenolpyruvate (PEP) from the glycolytic pathway with erythrose-4-phosphate, an intermediate from the pentose-shunt pathway. Shikimate, formed after a series of reactions, is phosphorylated and combined to a second PEP molecule to yield prephenate via chorismate. Prephenate loses CO_2 to form phenylpyruvate or *p*-hydroxyphenylpyruvate which is subsequently transaminated to yield phenylalanine or tyrosine, respectively (Mathews *et al.*, 2000). These two aromatic amino acids then enter the phenylpropanoid pathway, which follows the shikimate pathway.

3.3 PHENYLPROPANOID PATHWAY

The phenylpropanoid pathway partakes in secondary metabolism in the plant and connects the shikimate pathway to the lignin branch pathway. The objective of this pathway is to produce hydroxycinnamic acids and hydroxycinnamoyl-CoA esters, varying in their degree of hydroxylation and methylation, which will serve as precursors for numerous phenolic compounds in the plant (Barber and Mitchell, 1997). The various enzymes responsible for these and other major catalytic reactions in the phenylpropanoid pathway are presented in Figure 3.3.

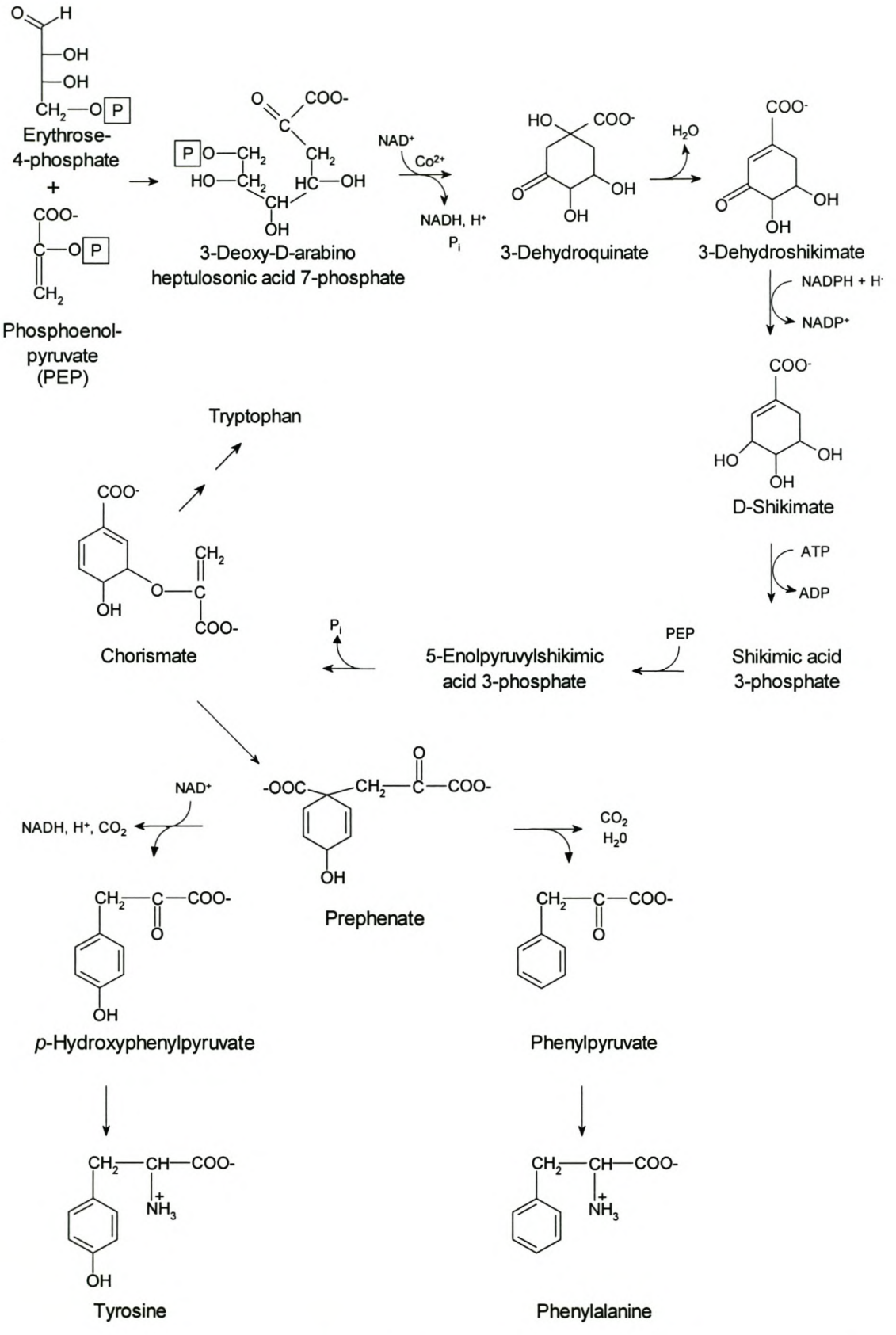

Figure 3.2: The shikimate pathway. ATP is used as an energy source and NADH or NADPH as a source of reducing power.

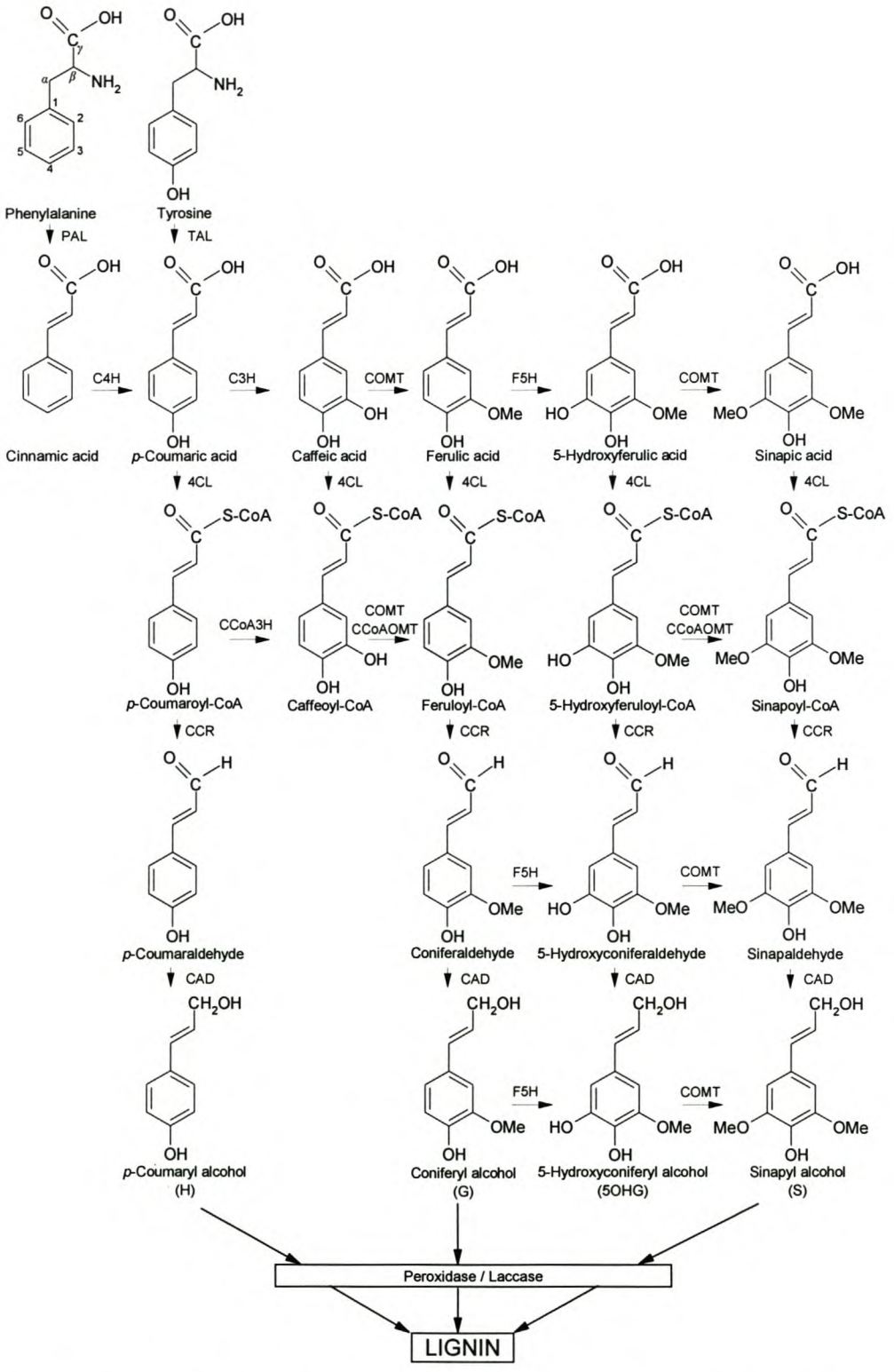

Figure 3.3: Monolignol biosynthesis pathway. CAD, cinnamyl alcohol dehydrogenase; C3H, coumarate 3-hydroxylase; C4H, cinnamate 4-hydroxylase; CCoA3H, coumaroyl-coenzyme A 3-hydroxylase; CCoAOMT, caffeoyl-coenzyme A *O*-methyltransferase; CCR, cinnamoyl-coenzyme A reductase; COMT, caffeic acid *O*-methyltransferase; F5H, ferulic acid 5-hydroxylase; 4CL, 4-coumarate:coenzyme A ligase; PAL, phenylalanine ammonia-lyase; TAL, tyrosine ammonia-lyase (Chen *et al.*, 2001).

A. Deamination Reactions

The first step in converting L-phenyalanine to lignin involves the removal of NH_3 in a reaction mediated by phenylpropanoid ammonia lyase (PAL). The latter enzyme is similar to the one found in grasses, called tyrosine ammonia lyase (TAL), that is responsible for catalysing the conversion of tyrosine to *p*-coumaric acid (Freudenberg and Neish, 1968).

1. Phenylpropanoid Ammonia Lyase

$$\text{L-Phenylalanine} \rightarrow \text{cinnamic acid} + NH_3$$

The first reaction in the phenylpropanoid pathway is catalysed by PAL and involves the deamination of L-phenylalanine to cinnamic acid (Higuchi, 1978). It is believed that PAL might play a key role in the regulation of lignin production because of its entry point in phenylpropanoid metabolism (Barber and Mitchell, 1997).

PAL activity has been detected in all green plants examined including Basidiomycetes (Freudenberg and Neish, 1968) and *Streptomyces* (Walker, 1975). It shows the highest activity in plant tissues associated with lignification and flavonoid biosynthesis (Baucher, 1998) and is almost undetectable in tissues not undergoing lignification (Walker, 1975). The enzyme exists as a tetramer with a molecular mass between 240 and 330 kDa, which can dissociate into subunits of 55 to 85 kDa (Whetton and Sederoff, 1992). A wide variety of external factors such as wounding, fungal elicitor treatment, fungal infection (Shields *et al.*, 1982; Bolwell *et al.*, 1985), light, UV exposure, ethylene, cold or freeze treatments have been found to induce PAL activity (Walker, 1975). Hydroxycinnamic acids and phenylalanine inhibited PAL activity (Baucher, 1998).

2. Tyrosine Ammonia Lyase

In grasses and cereal plants, L-tyrosine is directly converted to *p*-coumaric acid. This is contrary to the reaction catalysed by PAL whereby L-phenylalanine is first converted to cinnamic acid and then 4-hydroxylated to *p*-coumaric acid. The TAL catalysed reaction bypasses the 4-hydroxylation of cinnamic acid to yield *p*-coumaric acid directly (Whetten *et al.*, 1998). This conversion is, however, restricted to members of the grass family (Sarkanen and Ludwig., 1971). The combined effect of PAL and cinnamate 4-hydroxylase (C4H) on phenyalanine and the TAL activity on tyrosine both yield the same product, namely *p*-coumaric acid (Freudenberg and Neish, 1968).

B. Hydroxylation Reactions

Four enzymes, (C4H), coumarate 3-hydroxylase (C3H), ferulate 5-hydroxylase (F5H) and coumaroyl-CoA 3-hydroxylase (CCoA3H), mediate the hydroxylation reactions in the phenylpropanoid pathway. C4H catalyses the hydroxylation of cinnamic acid at its number 4-carbon to produce *p*-coumaric acid. Additional hydroxylation at the 3- and 5-carbons is mediated by C3H and F5H respectively, whereas CCoA3H catalyses the hydroxylation of the hydroxycinnamoyl-CoA esters (Barber and Mitchell, 1997).

1. Cinnamate 4-Hydroxylase

$$\text{Cinnamic acid} + O_2 + \text{NADPH} + H^+ \rightarrow p\text{-coumaric acid} + H_2O + NADP^+$$

The first hydroxylation reaction in the phenylpropanoid pathway is catalysed by C4H and involves the 4-hydroxylation of cinnamic acid to produce *p*-coumaric acid (Whetten *et al.*, 1998). C4H is a cytochrome P450-linked monooxygenase belonging to the CYP73 subfamily (Baucher *et al.*, 1998). It requires NADPH to split molecular oxygen, adding one oxygen atom to the aromatic ring and reducing the other to H_2O. C4H is linked to NADPH-cytochrome P450 reductase and participates in the transfer of electrons (Barber and Mitchell, 1997).

C4H exists as a glycosylated monomer with a molecular mass of 58 kDa. Glycosylation of C4H is not a prerequisite for enzyme activity (Teutsch *et al.*, 1993). Substrate specificity experiments have shown that C4H has a very high affinity for cinnamic acid and is unable to catalyse any other hydroxylation reaction in the phenylpropanoid pathway (Pierrel *et al.*, 1994). C4H activity can be induced by fungal elicitors, fungal infection, wounding and chemical inducers (Baucher *et al.*, 1998).

2. Coumarate 3-Hydroxylase

$$p\text{-Coumaric acid} + O_2 + \text{NADPH} + H^+ \rightarrow \text{Caffeic acid} + H_2O + NADP^+$$

C3H, a phenolase, is believed to be responsible for the hydroxylation of *p*-coumaric acid at the C3-position to form caffeic acid (Baucher *et al.*, 1998). Enzymes participating in this hydroxylation reaction *in vitro* have been purified, but their roles in monolignol biosynthesis *in vivo* have not yet been confirmed (Whetten *et al.*, 1998).

3. Coumaroyl-CoA 3-Hydroxylase

$$p\text{-Coumaroyl-CoA} + O_2 + \text{NADPH} + H^+ \rightarrow \text{Caffeoyl-CoA} + H_2O + NADP^+$$

In addition to the route converting *p*-coumaric acid to caffeic acid, an alternative route may exist whereby *p*-coumaric acid is converted to *p*-coumaroyl-CoA and subsequently hydroxylated by CCoA3H to yield caffeoyl-CoA (Whetten *et al.*, 1998). This implies that hydroxylation might occur at both the hydroxycinnamic acid and hydroxycinnamoyl-ester level (Barber and Mitchell, 1997).

4. Ferulate 5-Hydroxylase

$$\text{Ferulic acid} + O_2 + \text{NADPH} + H^+ \rightarrow \text{5-Hydroxyferulic acid} + H_2O + NADP^+$$

F5H catalyses the hydroxylation of ferulic acid at the 5-carbon position to form 5-hydroxyferulic acid. F5H is a cytochrome P450-linked monooxygenase belonging to the CYP84 subfamily and, like C4H, it also requires NADPH and O_2 (Grand, 1984).

The highest F5H activity has been observed in xylem and sklerenchyma, a tissue comprising of mainly S-units (Grand, 1984). An angiosperm mutant, with a dysfunctional F5H, produced a lignin that is deficient in syringyl residues (Chapple *et al.*, 1992). This observation supports the hypothesis that the lack of S-type lignin in gymnosperms may be due to the absence of F5H. Incorporation of the angiosperm gene that encodes for F5H into gymnosperms may alter the lignin content, promoting the formation of S-type lignin. This modification will result in the production of a lignin that is less dense, which would be favourable for chemical pulping (Baucher *et al.*, 1998).

C. Methylation Reactions

S-adenosyl-L-methionine-dependent diphenol-*O*-methyltransferases (OMT) are the enzymes that catalyse the methylation reactions in the phenylpropanoid pathway. Many OMTs are referred to as caffeate 3-*O*-methyltransferase (COMT), because of the extensive use of caffeic acid as substrate for OMT detection. Several of these COMTs also participate in the *O*-methylation of 5-hydroxyferulic acid to sinapic acid, and in some cases 5-hydroxyferulic acid is preferred as substrate. Caffeoyl-CoA 3-*O*-methyltransferase (CCoAOMT), a distinct form of OMT, might be responsible for the *O*-methylation of hydroxycinnamoyl-CoA esters (Barber and Mitchell, 1997).

1. *O*-Methyltransferase

$$\text{Caffeic acid} + \textit{S}\text{-adenosyl-L-methionine} \rightarrow \text{Ferulic acid} + \textit{S}\text{-adenosyl-L-homocysteine} \qquad (1)$$

5-Hydroxyferulic acid + *S*-adenosyl-L-methionine

→ Sinapic acid + *S*-adenosyl-L-homocysteine (2)

COMT catalyses the *O*-methylation of caffeic acid and 5-hydroxyferulic acid yielding ferulic acid and sinapic acid, respectively. In both reactions *S*-adenosyl-L-methionine is used as methyl donor which is subsequently converted to *S*-adenosyl-L-homocysteine (Baucher *et al.*, 1998).

The substrate specificity of COMT is very distinct amongst the various plant species. The COMT found in gymnosperms only *O*-methylates caffeic acid (1), whereas the angiosperm-type COMT preferentially catalyses the *O*-methylation of 5-hydroxyferulic acid (2) above caffeic acid (1). The bamboo-type COMT, found in monocotyledons, is able to *O*-methylate both substrates with equal efficiency. A correlation between the substrate specificities of the three COMT types and the degree of O-methylation of the lignin produced in the different plant groups has also been observed (Barber and Mitchell, 1997).

The introduction of an anti-sense tobacco gene into a tobacco plant, reduced the COMT enzyme level and altered the lignin composition without affecting the lignin quantity. The modified lignin (or lignin produced), had a reduced syringyl content (Zhong *et al.*, 1998) and contained a new monomer originating from 5-hydroxyferuloyl-CoA. This reduction in the syringyl content would aid the paper-making industry as this would decrease the *O*-methylation of lignin and reduce the amount of polluting mercaptans produced during processing (Barber and Mitchell, 1997).

2. Caffeoyl-CoA 3-*O*-Methyltransferase

Caffeoyl-CoA + *S*-adenosyl-L-methionine → Feruloyl-CoA + *S*-adenosyl-L-homocysteine

CCoAOMT catalyses the *O*-methylation of the hydroxycinnamoyl-CoA esters instead of the hydroxycinnamic acids. The conversion of caffeoyl-CoA into feruloyl-CoA is an example of such a reaction (Pakush *et al.*, 1991). It has also been suggested that CCoAOMT might catalyse the *O*-methylation of 5-hydroxyferuloyl-CoA to yield sinapoyl-CoA, a view supported by *in vitro* experiments whereby isolated CCoAOMT reacted with 5-hydroxyferuloyl-CoA (Ye and Varner, 1995). Lignin analysis of transgenic tobacco plants with a reduced CCoAOMT activity confirmed this result. These transgenic plants showed a reduction in the lignin content in association with a decrease in both guaiacyl lignin and syringyl lignin. This result confirms the ability of CCoAOMT to catalyse the methylation of

both caffeoyl-CoA and 5-hydroxyferuloyl-CoA. However, it has to be noted that the guaiacyl lignin was preferentially decreased over syringyl lignin, suggesting that CCoAOMT has a higher affinity for caffeoyl-CoA compared to 5-hydroxyferuloyl-CoA (Zhong *et al.*, 1998).

D. CoA-Esterification Reactions

Hydroxycinnamate-CoA ligases, also more commonly known as 4-coumarate-CoA ligase (4CL), catalyses the CoA-esterification reactions in the phenylpropanoid pathway (Barber & Mitchell, 1997). The hydroxycinnamoyl-CoA esters produced serve as key intermediates for the synthesis of various end products, including lignin (Baucher *et al.*, 1998).

1. 4-Coumarate-CoA Ligase

Hydroxycinnamic acid + CoA + ATP → Hydroxycinnamoyl-CoA + AMP + diphosphate

The formation of activated hydroxycinnamoyl-CoA esters from hydroxycinnamic acids is catalysed by 4CL and requires adenosine triphosphate, magnesium, and a thiol source for activity. These CoA thioesters are presumed intermediates in the biosynthesis of phenolic compounds such as lignin (Baucher *et al.*, 1998).

Ferulic acid and *p*-coumaric acid are readily converted by 4CL compared to sinapic acid, which has been shown to be a poor substrate for purified 4CL enzymes *in vitro* (Whetten *et al.*, 1998).

Numerous 4CLs were isolated from different plants such as spruce, poplar, loblolly pine and maize. The enzyme is a monomer with a molecular mass between 45 and 60 kDa (Barber & Mitchell, 1997). Isozymes of 4CL were also identified in certain plants with several of the isozymes exhibiting different substrate specificities (Becker-Andre *et al.*, 1991).

The substrate specificity of 4CL in gymnosperms and angiosperms were also found to be different. The 4CL in gymnosperms is unable to utilise sinapic acid, which concurs with the absence of syringyl units in gymnosperm lignin. The 4CLs in most of the angiosperms tested also displayed an inability to utilise sinapic acid even though they produce a guaiacyl-syringyl lignin (Barber and Mitchell, 1997). These findings suggest that sinapoyl-CoA might be produced via an alternative route, for example, the methylation of 5-hydroxyferuloyl-CoA by CCoAMT. It may also be that a yet undiscovered 4CL isozyme might be responsible for converting sinapic acid into sinapoyl-CoA (Baucher *et al.*, 1998).

3.4 LIGNIN BRANCH PATHWAY

The lignin branch pathway is considered to be the last of the three major pathways involved in the biosynthesis of lignin. This pathway is highly specific for lignification and directs metabolites stemming from the phenylpropanoid pathway towards monolignol production (Figure 3.3) (Barber and Mitchell, 1997).

A. Reductive Reactions

Two enzymes, cinnamoyl-CoA reductase (CCR) and cinnamyl alcohol dehydrogenase (CAD), catalyse the reactions of the lignin branch pathway (Barber & Mitchell, 1997). The CoA-thioesters, proceeding from the phenylpropanoid pathway, are reduced by CCR to yield the corresponding aldehydes. The aldehydes, in turn, are reduced by CAD to produce the three monolignols that will be incorporated into lignin (Whetten *et al.*, 1998).

1. Cinnamoyl-CoA Reductase

$$\text{Hydroxycinnamoyl-CoA} + \text{NADPH} + \text{H}^+ \rightarrow \text{Cinnamalaldehyde} + \text{CoA} + \text{NADP}^+$$

Hydroxycinnamoyl-CoA thioesters, emanating from the phenylpropanoid pathway, are reduced by CCR to their corresponding hydroxycinnamalaldehydes with the concomitant oxidation of NADPH (Luderitz and Grisebach, 1981). Characterisation of CCR identified the enzyme as a monomeric protein with a molecular mass between 36 and 40 kDa (Goffner *et al.*, 1994).

A partial correlation exists between the substrate specificity of CCR and the type of lignin produced by certain plant species. CCR in gymnosperms utilises feruloyl-CoA, but not sinapoyl-CoA, compared to the CCR found in most angiosperms which readily reduces both feruloyl-CoA and sinapoyl-CoA to their corresponding aldehydes in accordance with the guaiacyl-syringyl lignin found in angiosperms (Baucher *et al.*, 1998).

Transgenic plants with a reduced CCR activity showed a reduced lignin content (Whetten *et al.*, 1998), supporting the hypothesis that this enzymatic step might be a controlling point to regulate the flux towards the synthesis of lignin monomers (Lacombe *et al.*, 1997).

2. Cinnamyl Alcohol Dehydrogenase

$$\text{Cinnamalaldehyde} + \text{NADPH} + \text{H}^+ \rightarrow \text{Cinnamyl alcohol} + \text{NADP}^+$$

CAD is believed to catalyse the last enzymatic reaction in the lignin branch pathway. It

involves the reduction of cinnamalaldehydes to their corresponding cinnamyl alcohols or monolignols, which are incorporated into the lignin polymer (Chen *et al.*, 2001).

CAD belongs to the family of long-chain zinc-dependent alcoholdehydrogenases (Baucher *et al.*, 1998), that requires zinc as part of its enzyme structure and as a cofactor. Sequence analysis of CAD identified 22 highly conserved amino acid residues that include the structural zinc binding site and cofactor binding sites for $NADP^+(H)$ and zinc. An additional four amino acid residues, supposedly responsible for the substrate specificity of the enzyme, have also been identified. Three of the residues are present in all known CAD sequences but the fourth residue was found to differ between angiosperms and gymnosperms, supposedly responsible for determining the substrate specificity between the two species (Barber and Mitchell, 1997). Gymnosperm CAD preferably utilises coniferaldehyde above sinapalaldehyde as a substrate, which agrees with the guaiacyl-type lignin found in gymnosperms (Galliano, 1993) compared to angiosperm CAD that uses all three aldehydes as substrates (Baucher *et al.*, 1998).

Down-regulation of the CAD activity in transgenic tobacco plants, with the introduction of CAD anti-genes, altered the composition, structure and extractability of the lignin but not the lignin content (Halpin *et al.*, 1994). This can be attributed to the ability of these transgenic plants to compensate for the CAD deficiency by incorporating hydroxycinnamaldehydes, instead of the corresponding hydroxycinnamyl alcohols, into the lignin polymer through radical coupling (Kim *et al.*, 2000). The increased lignin extractability associated with these transgenic plants will favour the pulp and paper industry considering that less chemicals will be required to obtain an equivalent pulp quality with excellent paper-making properties such as high paper strength and brightness (Chen *et al.*, 2001).

3.5 TRANSPORT AND STORAGE OF MONOLIGNOLS

Very little is known about the transport and storage of monolignols. They are produced in the cytoplasm and are present as free monolignols or as monolignol glycosides (Barber and Mitchell, 1997). It is believed that monolignols are transported and stored in their glycosylated form (Matsui *et al.*, 2000). The monolignol glucosides also participate in the biosynthesis of other aromatic compounds such as lignans (Baucher *et al.*, 1998).

A. Glycosylation and Deglycosylation Reactions

UDP-glucose:cinnamyl alcohol glucotransferase (UTG), also referred to as coniferyl alcohol

glucotransferase, catalyses the glycosylation of monolignols to monolignol glycosides whereas cinnamyl alcohol β - glucosidase (GLS) deglycosylates the monolignol glycosides to yield monolignols (Barber and Mitchell, 1997).

1. Cinnamyl Alcohol Glucosyltransferase

UDP-glucose + cinnamyl alcohol → Cinnamyl 4-O-β glucoside + UDP

UTG catalyses the transfer of a glucose molecule from UDP-glucose to the phenolic hydroxyl of the various monolignols to yield monolignol glucosides (Whetten *et al.*, 1998). Glucosides derived from coniferyl alcohol, sinapyl alcohol and *p*-coumaryl alcohol are referred to as coniferin, syringin and *p*-hydroxycinnamyl alcohol glucoside respectively (Schubert, 1965).

The substrate specificity of the enzyme differs amongst the various plant species. In *Forsythia orata*, UTG readily utilises both coniferyl and sinapyl alcohol compared to spruce trees where coniferyl alcohol is the preferred substrate (Barber and Mitchell, 1997).

2. Cinnamyl Alcohol β-Glucosidase

Cinnamyl 4-O-β glucoside → Cinnamyl alcohol + glucose

Monolignol glucosides are hydrolysed by GLS, sometimes called coniferin β-glucosidase (Baucher *et al.*, 1998), liberating free monolignols which are dehydropolymerised to lignin (Barber and Mitchell, 1997). Numerous β-glucosidases are found in plants of which only several are linked to lignification. Induction of these β-glucosidases correspond with the induction of certain enzymes involved in phenylpropanoid metabolism, areas of active lignification (Hösel *et al.*, 1982) and peroxidase (PO) activity (Campbell and Ellis, 1992).

3.6 POLYMERISATION OF MONOLIGNOLS INTO LIGNIN

The final step in the biosynthesis of lignin involves the polymerisation of the cinnamyl alcohols to produce lignin (Figure 3.4). It is an oxidative process that entails the enzymatic dehydrogenation of the cinnamyl alcohols, forming free radicals that spontaneously and irreversibly polymerise to form structurally complex molecules, interconnected by various types of covalent linkages (Crawford, 1980).

A. Oxidative Reactions

The oxidative role of two distinct phenol oxidases, POs and laccases, in lignin polymerisation have long been studied (Schubert, 1965; Freudenberg and Neish, 1968). Both enzyme

systems displayed the ability to oxidise coniferyl alcohol, and subsequently other cinnamyl alcohols, generating free radical intermediates or phenoxy radicals that spontaneously polymerise into lignin (Sarkanen and Ludwig, 1971; Crawford, 1980). Higuchi (1958) proposed that PO may play a more important role than laccase in lignin biosynthesis, considering the widespread distribution of PO in higher plants (Schubert, 1965).

1. Peroxidase

$$2AH + H_2O_2 \rightarrow 2A^{\bullet} + 2H_2O$$

Classic POs are mainly N-glycosylated, heme-containing monomeric enzymes that are able to oxidise various compounds using H_2O_2 as an oxidising agent (Baucher *et al.*, 1998). It has been suggested that the production of H_2O_2 might be regulated by the hydroxycinnamyl alcohols, considering the involvement of the monolignols in the stimulation of the PO activity required for H_2O_2 production (Barber and Mitchell, 1997).

In addition to lignification, POs also participate in other activities, such as pathogen resistance, cross-linking of cell wall polysaccharides and structural proteins and phenol oxidation (Sarkanen and Ludwig, 1971).

Several PO isozymes appearing to participate in lignin synthesis have also been isolated (Baucher *et al.*, 1998). It is believed that some of the isozymes, differing in their specificity for monolignols, may even contribute in altering the lignin composition (Barber and Mitchell, 1997).

2. Laccases

$$4AH + O_2 \rightarrow 4A^{\bullet} + 2H_2O$$

Laccases mediate the oxidation of a large number of phenolic substrates [AH-hydrogen donor] to phenoxy radicals [$A^{\bullet}$ -dehydrogenated product] by using molecular oxygen as the electron acceptor. These enzymes are highly glycosylated, monomeric metalloproteins containing four copper ions with a molecular mass ranging between 52 and 110 kDa (Sarkanen and Ludwig, 1971; Baucher *et al.*, 1998).

Laccases are also associated with the oxidation of monolignols and the formation of dehydrogenative polymers. They preferably utilise coniferyl and sinapyl alcohol compared to *p*-coumaryl alcohol, which is poorly oxidised. It has been suggested that laccases might be involved during the early stages of lignification to polymerise coniferyl and sinapyl alcohols,

in the absence of toxic H_2O_2, and that the POs might participate at a later stage to polymerise the cross-linking of the monolignols and oligolignols (Sterjiades et al., 1993).

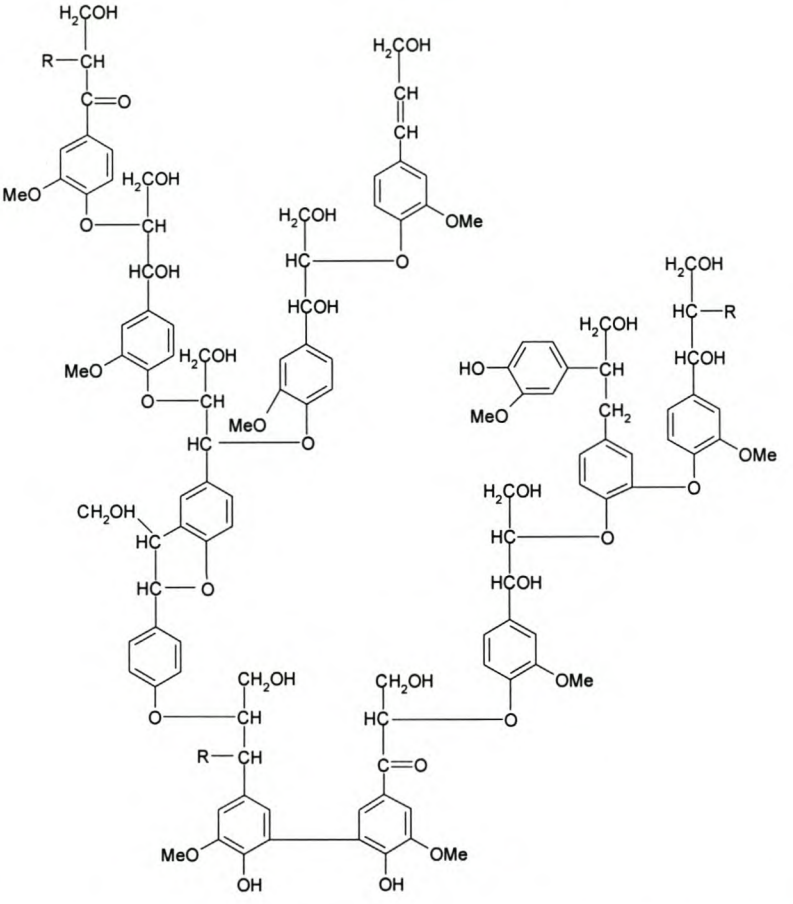

Figure 3.4: Shematic representation of coniferous lignin (Tien, 1987). R indicates that the chemical structure of the polymer extends beyond what is shown in the figure.

3.7 BIODEGRADATION OF LIGNIN

"The only organisms known to extensively degrade lignin are fungi" (Reid, 1995). These lignin degrading fungi can be categorised into 3 groups based on the component utilised and characteristics of the decayed wood. These categories include the white-rot fungi, brown-rot fungi and soft-rot fungi [4].

Lignin-degrading Fungi

White-rot fungi are the only organisms in nature that are able to extensively degrade lignin (Cullen, 1997). Several thousand white-rot fungi exist of which the majority are Basidiomycotina, in addition to a few Ascomycotina that can cause white rot. White-rot

[4] http://www.minnesotascience.org/rot.htm

fungi, belonging to the subdivision Basidiomycotina, decay both hard and softwoods, whereas Ascomycotina presumably degrade only hardwood. In addition to lignin, white-rot fungi can also utilise hemicellulose and cellulose as substrates. White-rot fungi can delignify wood in a selective or non-selective manner. Selective delignification involves the removal of lignin without any marked loss of cellulose, whereas during non-selective delignification all the major cell wall components are removed (Tuomela *et al.*, 2000).

Brown-rot fungi, in contrast to white-rot fungi, extensively degrade cellulose and hemicellulose in wood while leaving the lignin as a crumbly brown residue. The lignin in brown-rotted wood has been demethylated, partially oxidised and depolymerised, but not completely degraded (Reid, 1995). Brown-rot fungi preferably colonise softwoods and account for approximately 6% of all wood-rotting Basidiomycotina (Tuomela *et al.*, 2000).

Soft-rot fungi are Ascomycotina or Deuteromycotina that degrade both hardwood and softwood, with hardwood being degraded to a greater extent. These fungi degrade all the wood components, but at a degradation rate which is minimal compared to that of white-rot or brown-rot fungi (Tuomela *et al.*, 2000).

Lignin degrading enzymes

In nature, white-rot fungi are responsible for producing a suite of enzymes involved in the initial depolymerising transformations of lignin. The more important enzymes are lignin peroxidase (LiP), manganese peroxidase (MnP) and laccases (Nutsubidze, 1998).

Lignin peroxidase

LiP is a heme peroxidase with a low pH optimum (< pH 3) and high redox potential. These enzymes react with a wide variety of lignin model compounds and show very little substrate specificity (Reid, 1995). LiP catalyses a variety of oxidations which are all H_2O_2 dependent. These include cleavage of the C_α-C_β bonds of the propyl side chains of lignin and lignin models, depolymerisation of methylated lignin *in vitro*, hydroxylation of benzylic methylene groups, oxidation of benzyl alcohols to the corresponding aldehydes and ketones, phenol oxidation as well as aromatic ring cleavage of non-phenolic lignin model compounds (Cullen, 1997). The oxidative action of LiP on lignin is enhanced by veratryl alcohol which acts as a one electron transfer mediator (Garcia *et al.*, 1987; Leonowicz *et al.*, 1999) and protector against inactivation (Higuchi, 1993).

Manganese peroxidase

MnP is a heme peroxidase that is widely distributed among lignin-degrading fungi (Cullen, 1997). Like LiP, MnP is synthesised and secreted by the white-rot fungus *Phanerochaete chrysosporium* in response to nutrient (carbon, nitrogen or sulphur) starvation (Cai and Tien, 1993). The key function of MnP is to oxidise Mn^{2+} to Mn^{3+} in the presence of H_2O_2 (Cullen, 1997). Mn^{3+} forms a complex with organic acids, for example oxalate and malonate, and diffuses away from the enzyme to oxidise other materials such as lignin. Because the Mn peroxidase-Mn system has a lower redox potential than LiP, it does not oxidise non-phenolic compounds. It can, however, oxidise phenolic substrates to form phenoxy radicals that can react further by demethylation, alkyl-phenyl cleavage, C_α-C_β cleavage or C_α oxidation (Reid, 1995).

Laccases

Laccases are produced by most white-rot fungi with the exception of *Phanerochaete chrysosporium* (Reid, 1995). They are copper-containing enzymes which reduce molecular oxygen to water and oxidise phenolic compounds. However, in the presence of certain mediators, laccases can also oxidise non-phenolic compounds. This finding has generated considerable interest as a possible approach to the enzymatic bleaching of kraft pulps (Cullen, 1997).

Economic consequences of lignin biodegradation

The use of selectively lignin-degrading fungi reduces the energy input required for mechanical pulping and also enhances the bonding ability of the fibres to yield stronger paper. Biological delignification of wood can also facilitate the chemical sulphite and kraft pulping processes. These fungi can, furthermore, aid in the degradation of various pollutants in wastewaters and soils, increase digestibility of lignocellulosics, and possibly aid in the bioconvertion of lignins to yield higher-value products (Reid, 1995).

3.8 CHEMICAL DEGRADATION OF LIGNIN

Besides lignin, wood is also composed of cellulose, hemicellulose and extractives (such as resins, fats and pectins) of which cellulose is the primary source for the production of pulp and paper. Depending on the pulping process, some or most of the lignin can be removed without sacrificing fibre strength, thereby freeing the fibres and removing impurities that may

cause discoloration and possible future disintegration of the paper [5]. At the integrated pulp and paper mill in Piet Retief neutral sulphite pulping is used instead of the Kraft method. This process involves the use of Na_2SO_3 and Na_2CO_3 as reagents in conjunction with anthraquinone, a redox catalyst responsible for accelerating delignification (Tay *et al.*, 1984). Normally hardwood (*Eucalyptus sp.*) and softwood (*Pinus sp.*) are pulped separately, but during this process these species are pulped together. Under neutral sulphite conditions, the reactivity of the sulphurous acid solution is reduced, to limit sulphonation reactions to the β-O-4 ethers with free hydroxyls only. The main reactions occurring at these positions are α-sulphonation and β-ether cleavage [3].

Neutral sulphite pulping produces a high yield pulp (more than 75%) that is only partially delignified because of the slight sulphonation and partial β-ether cleavage of the lignin (Figure 3.5). During lignin sulphonation three major reactions usually proceed simultaneously: sulphonation, hydrolysis and condensation. Other minor reactions with lignin include oxidation, reduction, rearrangement, dehydration, thiosulphation and sulphidation. Hydrolysis and condensation can also occur between lignin and associated wood components (Sarkanen and Ludwig, 1971).

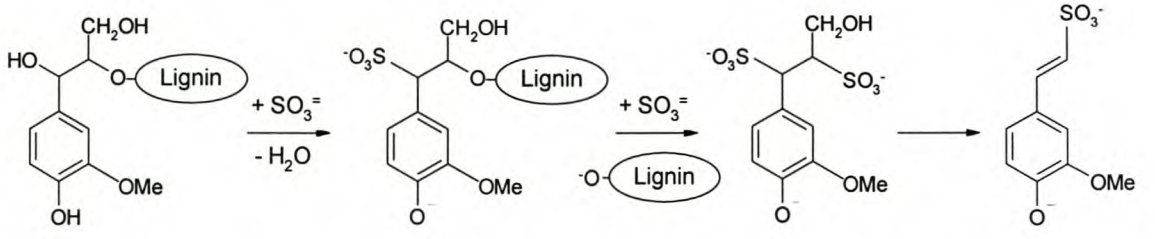

Figure 3.5: Reactions of lignin during neutral sulphite pulping conditions. Redrawn from [3].

The lignin contained in the pulp is somewhat "softened" and when processed under higher temperatures it produces a thick molasses that spreads amongst the fibres. When made into a sheet and cooled down, lignin hardens producing a stiff sheet that can be used for making card boards [3].

The digestion step is usually followed by mechanical breakdown using discs so that the total pulping operation is called the neutral sulphite semichemical (NSSC) process [6].

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[5] (http://www.wws.princeton.edu/cgi-bin/byteserv.prl/~ota/disk1/1989/8931/893104.PDF.)

[6] (http://www.farmland.com/agoperat/feed/ingredients/spe_872.as)

Research done by Suckling (1989) on a 3-carbon β-ether lignin model compound, guaiacylglycerol-β-guaiacyl ether, in the presence of sulphite liquor and anthraquinone, indicated the formation of small amounts of α-sulphonates (isomers), 2-carbon α-sulphonates, disulphonates, major amounts of coniferyl sulphonates and 1,3-disulphonates as well as a small amount of 2-carbon apocynol sulphonate as reaction products (Suckling, 1989).

Lignosulphonates can act as possible foulants of the PES UF membranes because of their amphipathic character. The sulphone groups on these molecules are able to chelate metal ions and form macro molecular complexes that will increase the fouling potential of these molecules. These polymers are, however, difficult to characterise and part of this study involves the identification and partial characterisation of these compounds to ultimately facilitate the design and implementation of membrane cleaning methods. The methods used to identify and characterise these compounds included UV-Vis spectrophotometry, ICP, GPC and ES-MS. This section of the work is discussed in Chapter 6.

CHAPTER 4

STATIC FOULING AND NON-COVALENT MODIFICATION OF PES FLAT-SHEET MEMBRANES

Various compounds, for example some of the NSSC breakdown products, glue, waxes, pitch and some of the additives added to the different effluent streams, might participate in the fouling of the UF membranes. The properties of these compounds as well as that of the membrane material influence the solute/membrane interactions and, consequently, the degree of adsorption and fouling (Mulder, 1995). Modification of the membrane surface can help to reduce fouling and thereby enhance flux through the membrane (Nyström, 1992). Coating of the membranes with various surfactants (Chen *et al.*, 1992; Kim *et al.*, 1998; Maartens, 1998; Allie, 1999; Swart *et al.*, 1999), enzymes (Chen *et al.*, 1992) and exposure to high energy (Nyström *et al.*, 1991; Stevens *et al.*, 1998) are but a few examples of how membranes can be modified to influence solute/membrane interactions.

For this study PES membranes were modified by statically adsorbing Pluronic® F108, a non-ionic surfactant, and charged FFAs onto the membrane surface. Pluronic® F108, a tri-block copolymer, consists of one hydrophobic poly(propylene oxide) anchor group, located in the middle of the molecule, and two hydrophilic poly(ethylene oxide) groups situated at both ends of the molecule. The hydrophobic section of the molecule attaches itself to the hydrophobic membrane surface and orientates the hydrophilic end-groups of the molecule towards the aqueous phase. The idea was that the hydrophilic end-groups of the surfactant would serve as a steric hindrance, to prevent the hydrophobic interactions between compounds in the effluent and the hydrophobic PES membrane surface. By pre-coating the PES membrane surface with charged FFA it was hoped that the adsorbed charge from the ionised function would change the surface characteristics of the membrane, rendering it more hydrophilic and promoting electrostatic repulsion between like-charged residues, thereby reducing membrane fouling.

The pre-coated membranes were statically fouled with various effluent samples and model foulants to (1) evaluate the change in the pure-water flux (PWF) before and after fouling and (2) establish whether pre-coating with Pluronic® F108 and charged FFA could reduce long-term membrane fouling.

The decision to use static fouling to model dynamic fouling was based on results obtained by Maartens *et al.* (1996) which showed that similar results could be obtained for static and dynamic fouling experiments.

UV-Vis analyses were also conducted on the extracts of coated FFA PES membranes fouled with microstrainer product. This was done to establish whether a difference could be observed between the absorption spectra of uncoated PES membranes and PES membranes coated with FFA before protein fouling.

EXPERIMENTAL

A. Static fouling

Uncoated and Pluronic® F108 pre-coated PES membranes were statically fouled with DAF product, provided by the paper mill. Flat-sheet PES membranes were cast on a 30 cm wide polyester backing to a thickness of 200 μm. The casting solution was provided by Weir Envig (Pty) Ltd. and the casting apparatus was supplied by the Institute of Polymer Science, University of Stellenbosch. The PES membrane strips were placed in beakers with 600 mL DAF product for 48 h at room temperature. After incubation the membranes were rinsed thoroughly with distilled water and cut into 4 evenly sized pieces for PWF determination.

The effect of membrane pre-coating on membrane fouling

The hydrophobic character of foulants in the paper mill effluent prompted an investigation into the possibility of non-covalent coating of the PES membranes with a hydrophilic agent to reduce hydrophobic adsorption (Swart *et al.*, 1999). Pluronic® F108 was used as the hydrophilic agent in the coating trials. The PES membranes were placed in a 0.5% m/v aqueous Pluronic® F108 solution for 24 h, whereafter it was rinsed with distilled water. Each pre-coated membrane strip was then placed in 600 mL DAF product for 48 h, and rinsed with distilled water before PWF determination.

Pure water flux determination

The PWF determinations were performed on a 3-cell flat-sheet test rig. The test was conducted at an operating pressure of 200 kPa, constant flow rate of 500 L/h and a temperature 20 ± 0.2 °C. The temperature was controlled with a heat exchanger. The permeate flow through the membranes was measured using a 10 mL volumetric flask and stopwatch. All experiments were performed under the same operating conditions unless

otherwise stated.

B. Membrane surface modification by FFA

Preparation of the protein samples (model foulants)

Bovine serum albumin (BSA) and lysozyme (supplied by Roche, South Africa) were used as model foulants. The pI values of BSA and lysozyme are 4.8 and 10.45 respectively. BSA (0.1% m/v) and 0.1% m/v lysozyme solutions were prepared and the pH corrected to 7.4, thereby inducing a negative charge on BSA and a positive charge on lysozyme.

Preparation of the free fatty acid solutions

Palmitic acid (PA) and stearic acid (SA) (BDH Chemicals Ltd., Poole, England) were used as PES coating materials. Twelve 5x5 cm PES flat-sheet membrane square sections (25 cm^2) were placed in each of the following 4 solutions: 0.0025% m/v PA (2 L, 0.015% m/v NaOH), 0.002% m/v SA (2 L, 0.005% m/v NaOH), 0.015% m/v NaOH (2 L) and 0.005% m/v NaOH (2 L) for 24 h, and rinsed with RO water. The FFA were dissolved in NaOH solutions to ensure stabilisation of the molecules in an aqueous medium. The NaOH-containing FFA solutions had pH values greater than 10.5, which would cause deprotonation of the carboxylic terminal groups (pKa 4.5). The 0.005 and 0.015% m/v NaOH solutions served as controls for the PA and SA solutions respectively. After being placed in one of the above-mentioned solutions, each group of 12 pre-coated membranes was subdivided into 4 subsets of 3 membranes each and placed in the following 4 solutions for 48 h: deionised water (blank), microstrainer product (pH 10), 0.1% BSA (pH 7.4) and 0.1% lysozyme (pH 7.4).

The experiment was repeated with positively charged BSA (pH 3) (below pKa value of acids) and negatively charged lysozyme (pH 12).

Quantitative determination of the proteins adsorbed onto membranes

The following reagents were used to quantify the proteins that adsorbed onto the membranes:

Solution A : 0.2 g sodium tartrate and 10 g Na_2CO_3 dissolved in 55 mL 1M NaOH and diluted to a final volume of 100 mL with distilled water;

Solution B : 2 g sodium tartrate and 1 g $CuSO_4 \cdot 5H_2O$ dissolved in 90 mL of distilled water and 10 mL 1M NaOH;

Solution C : 1 volume Folin-Ciocalteu reagent (Merck Dramstad, Germany) diluted with 2

volumes distilled water. (This solution should always be freshly prepared.); and

Solution D : 5% sodium dodecyl sulphate (SDS) from Merck Dramstad, Germany, dissolved in 0.5 M NaOH.

Each of the 5x5 cm PES membrane square sections, fouled respectively in the BSA or lysozyme protein solutions, was rinsed in RO water and placed into a stripping solution consisting of solution D (5 mL) and distilled water (2.5 mL). The membranes with the stripping solution were placed in a shaking incubator for 2.5 h. 500 μL of 2M NaOH and 900 μL of solution A were added to 750 μL of the stripping solution and the mixture was vortexed and left at room temperature for 30 min. 100 μL of solution B was added to the mixture, vortexed and left at room temperature for 20 min. Two 1.5 mL aliquots of solution C were added to the mixture, which was vortexed after each addition, and left at room temperature. After 30 min the absorbance was determined at 620 nm on a Titertek® Multiskan plate reader. The various pre-coated membranes which had been placed in the analytical grade water were treated in the same manner as the fouled membranes and used as blanks. The amount of protein extracted from the PES membranes was interpolated from a standard curve.

UV-Vis spectrophotometric analyses of FFA coated PES membranes fouled with microstrainer product

FFA coated and uncoated PES membranes fouled with microstrainer product, pH 4.5 and 10, respectively, were incubated in an ammonia solution (7 mL, 0.1% Triton X100®, 1.5% NH_4OH) for 2 h at 40 °C, whereafter the extracts were diluted with analytical grade water and analysed by UV-Vis spectrophotometry. The absorbance of the diluted extracts was measured between 190 and 400 nm. The various FFA coated membranes placed in the deionised water were treated in the same manner as the fouled membranes and used as controls.

4.1 RESULTS AND DISCUSSION

A. Static fouling

The values presented in Figure 4.1 are the arithmetic mean and the standard deviation (SD) for three determinations. The results displayed show a 21% reduction in flux after static fouling of the uncoated PES membranes with DAF product. The reduction in PWF was

attributed to the adsorption of the organic compounds present in the effluent to the surface of the hydrophobic PES membranes. Pre-coating the unmodified PES membranes with the hydrophilising agent, Pluronic® F108 reduced the original PWF by 64%. A permeate flux of 39%, that is 61% less than the original PWF, was obtained with the Pluronic® F108 coated membranes fouled with DAF product. Pluronic® F108 coated membranes fouled with DAF product yielded a slightly higher PWF than that obtained for unused Pluronic® F108 coated membranes. From these results it could be deduced that pre-treatment of the PES membranes with Pluronic® F108 had no apparent advantage for fouling prevention and productivity enhancement.

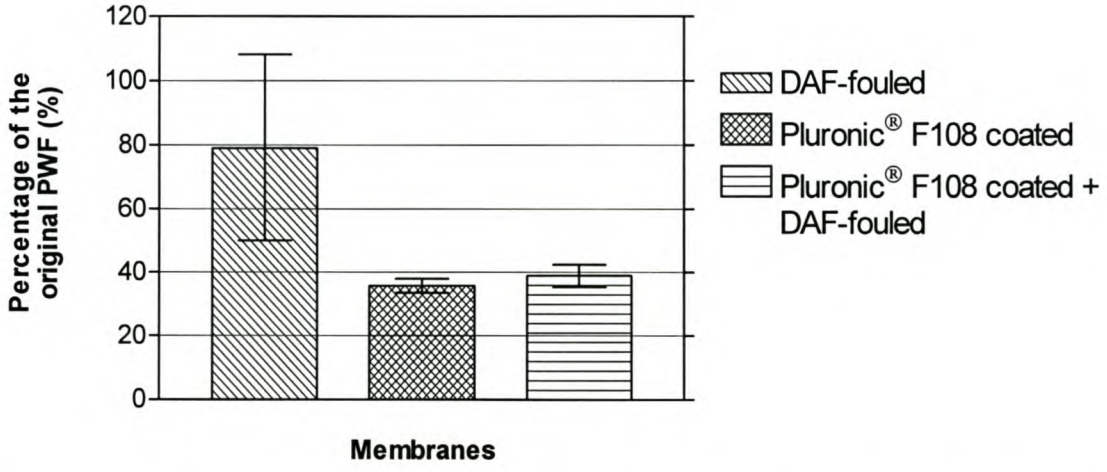


Figure 4.1: Changes in the PWF values, obtained with uncoated and Pluronic® F108 pre-coated membranes, fouled in DAF product. The values presented are the arithmetic mean for three determinations ± SD represented by the error bars.

B. Membrane surface modification by FFA

Figure 4.2 represents the standard curves obtained for the proteins BSA and lysozyme. The values obtained for the coating experiments (interpolated from the standard curves) are shown in Table 4.1 and are expressed as bar graphs in Figures 4.3 to 4.6.

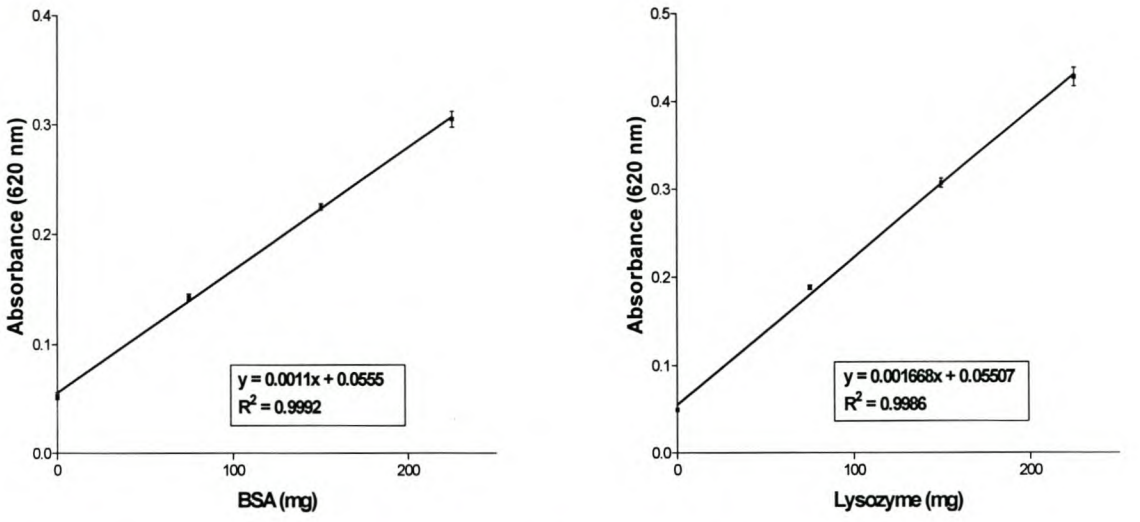


Figure 4.2: Standard curves obtained for BSA (left) and lysozyme (right).

Table 4.1. Protein recovered from uncoated and FFA coated PES membranes.

	Uncoated (mg ± SD)	**Palmitic acid (0.015% NaOH) (mg ± SD)**	**Uncoated (mg ± SD)**	**Stearic acid (0.005% NaOH) (mg ± SD)**
BSA (-)	22 ± 1.5 mg	19.1 ± 2.7 mg	22.9 ± 3.2 mg	22 ± 1.5 mg
BSA (+)	16.7 ± 0.8 mg	27.7 ± 2.2 mg	18.2 ± 2.8 mg	28.9 ± 2.3 mg
Lysozyme (+)	31.7 ± 3.2 mg	46.7 ± 1.9 mg	24.1 ± 0.6 mg	37.7 ± 5.2 mg
Lysozyme (-)	46.9 ± 2.7 mg	48.5 ± 4.4 mg	44.1 ± 4.9 mg	48.7 ± 5.6 mg
(-) negatively charged (pH 7.4 for BSA and 12.0 for lysozyme)				
(+) positively charged (pH 3 for BSA and 7.4 for lysozyme)				

PES membranes fouled with negatively charged BSA yielded 22 ± 1.5 mg protein whereas PES membranes pre-coated with negatively charged PA and subsequently fouled with negatively charged BSA, yielded 19.1 ± 2.7 mg protein (Figure 4.3 and Table 4.1). The uncoated and SA coated PES membranes, fouled with negatively charged BSA, yielded 22.9 ± 3.2 mg BSA and 22.1 ± 1.5 mg BSA, respectively (Figure 4.3 and Table 4.1). No significant decrease in BSA adsorption was observed after pre-coating PES membranes with FFA. It is well known, however, that serum albumin binds FFA *in vivo*, and therefore the results were not totally unexpected.

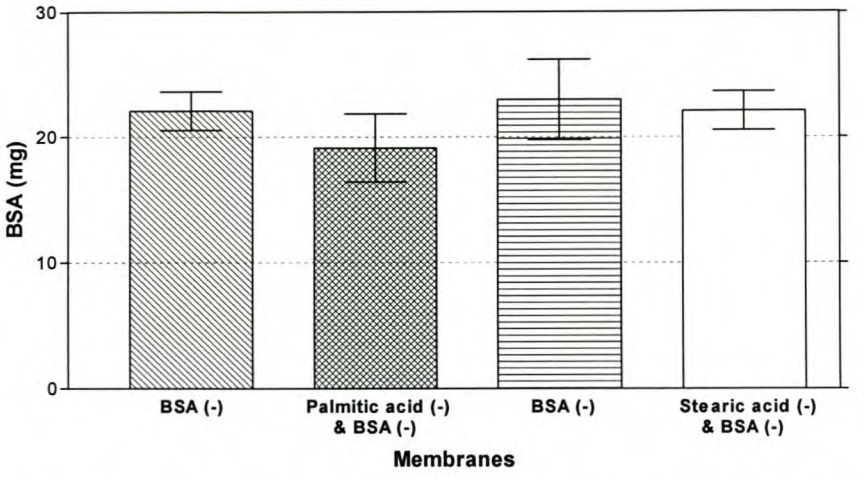


Figure 4.3: Effect of FFA coated PES membranes on the adsorption of negatively charged BSA. The values presented are the arithmetic mean for three determinations ± SD represented by the error bars.

Fouling of the PA and SA coated PES membranes with positively charged BSA (pH 3) showed an increase in protein adsorption (Figure 4.4 and Table 4.1). The amounts of protein recovered were 16.7 ± 0.8 mg and 27.7 ± 2.2 mg for the uncoated and the PA coated PES membranes respectively, compared to the 18.2 ± 2.8 mg and 28.9 ± 2.3 mg protein obtained for the uncoated and SA coated PES membranes. At pH 3 the BSA molecules were denatured and the carboxylic groups of the FFA protonated. The positively charged, denatured BSA molecule lost its tertiary structure, exposing its hydrophobic interior which interacted with the aliphatic chain of the FFA and the PES membrane via hydrophobic interactions.

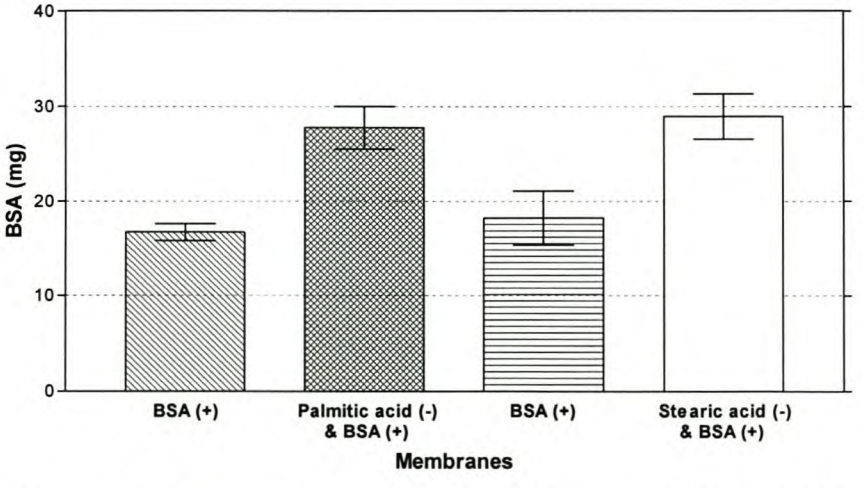


Figure 4.4: Influence of PES membranes coated with negatively charged PA and SA on the adsorption of positively charged BSA. The values presented are the arithmetic mean for three determinations ± SD represented by the error bars.

An increase in protein adsorption was observed for the FFA coated PES membranes fouled with positively charged lysozyme. The amounts of protein recovered from the uncoated and PA coated PES membranes were 31.7 ± 3.2 mg and 46.7 ± 1.9 mg, respectively, compared to the 24.1 ± 0.6 mg and 37.7 ± 5.2 mg protein recovered for the uncoated and SA coated PES membranes (Figure 4.5 and Table 4.1). The increase in protein adsorption can be attributed to the electrostatic attraction between the negatively charged FFA coated PES membranes and positively charged lysozyme molecules.

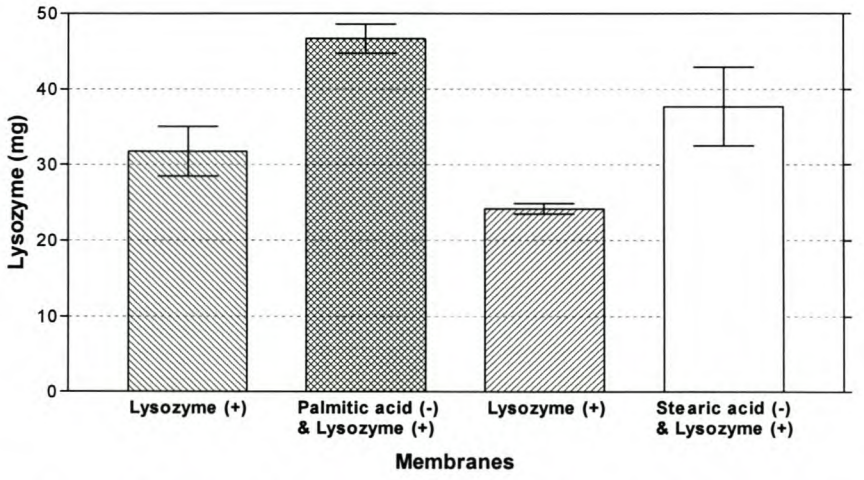


Figure 4.5: Influence of coating PES membranes with FFA on the adsorption of positively charged lysozyme. The values presented are the arithmetic mean for three determinations ± SD represented by the error bars.

Uncoated and pre-coated PES membranes fouled with negatively charged lysozyme showed no significant difference in protein adsorption. This result was counter intuitive. The amount of protein recovered from the uncoated and negatively charged PA coated PES membranes was 46.9 ± 2.7 mg and 48.5 ± 4.4 mg, respectively (Figure 4.6 and Table 4.1). Similar values were obtained for uncoated (44.1 ± 4.9 mg) and negatively charged SA coated (48.7 ± 5.6 mg) PES membranes.

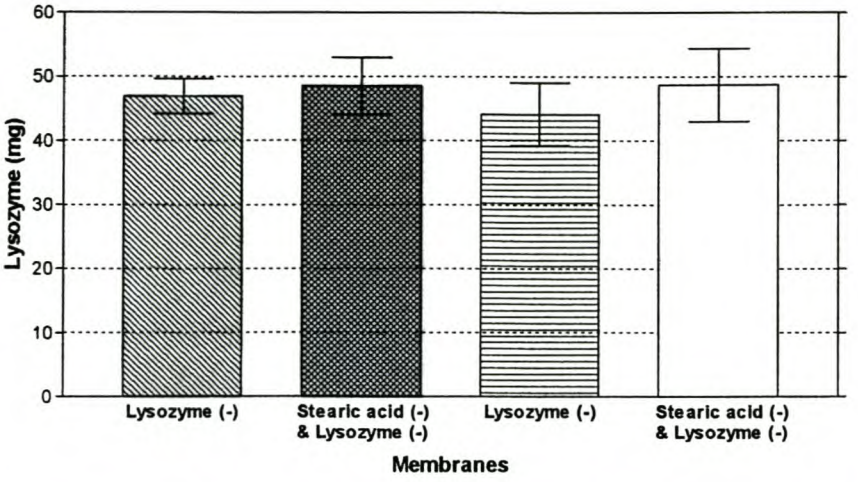


Figure 4.6: Influence of FFA coated PES membranes on the adsorption of negatively charged lysozyme. The values presented are the arithmetic mean for three determinations ± SD represented by the error bars.

UV-Vis spectrophotometric analyses of FFA coated PES membranes fouled with microstrainer product

Wavelength scans performed on the extracts collected from PES membranes (1) fouled with microstrainer product and (2) pre-treated with FFA and subsequently fouled with microstrainer product, gave identical results (Figure 4.7). This implies that that there was no electrostatic repulsion between the foulants in the effluent and the negatively charged FFA pre-adsorbed onto the PES membrane. The hydrophobic compounds in the effluent adsorbed onto the PES membrane irrespective of the residual surface charge.

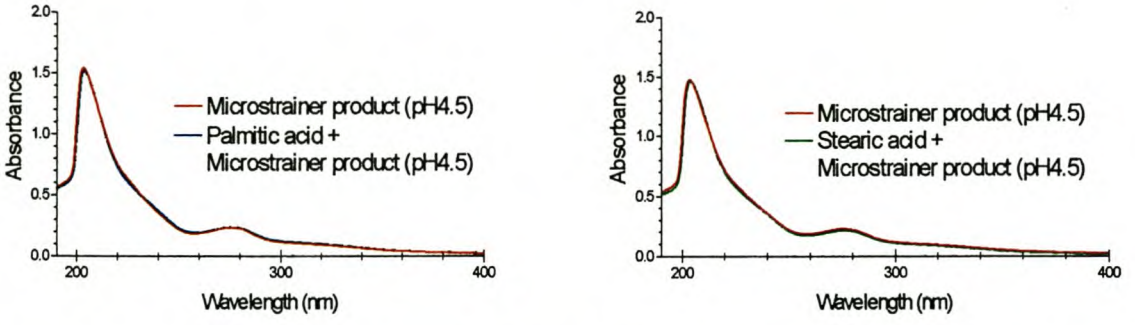


Figure 4.7: Absorption spectra of uncoated and coated FFA membranes fouled with microstrainer product (pH4.5)

Similar results were obtained at an elevated pH of 10 (Figure 4.8).

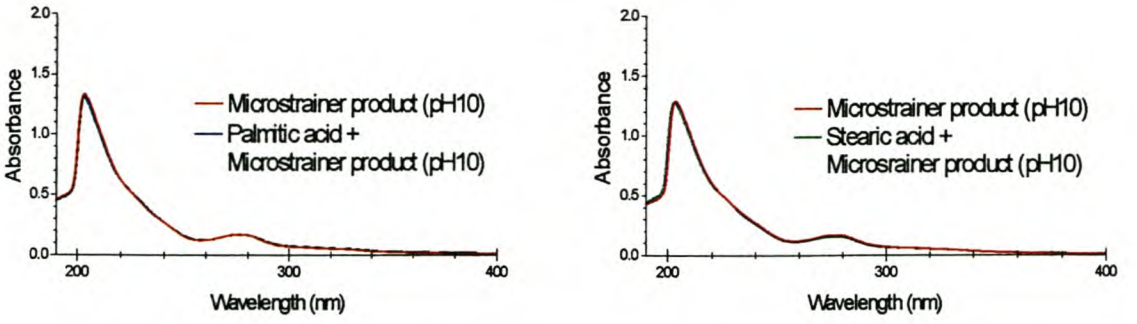


Figure 4.8: Wavelength scans of FFA coated and uncoated PES membranes fouled with microstrainer product (pH 10).

4.2 CONCLUSIONS

The following conclusions were reached from experiments performed on uncoated and Pluronic® F108 pre-coated membranes, fouled in DAF product.

- The reduction in PWF through the uncoated DAF fouled membranes was attributed to the adsorption of the organic compounds, present in the effluent, to the hydrophobic membrane surface of the PES membranes. (This result corresponded with the results obtained at the paper mill.)
- Coating of native PES membranes with Pluronic® F108 reduced the PWF through the membranes considerably.
- The PWF of Pluronic®-coated membranes fouled with DAF was slightly higher than the unfouled Pluronic®-coated membranes.
- Coating membranes with Pluronic® F108, however, had no apparent advantage for fouling prevention and productivity enhancement.

The results obtained for PES membranes pre-coated with FFA can be summarised as follows:

- An increase in protein adsorption was observed between uncoated and negatively charged FFA coated PES membranes fouled with positively charged BSA and lysozyme, respectively. The increase in the amount of BSA can be attributed to hydrophobic interactions between the proteins and hydrophobic PES membrane and aliphatic FFA chains. The increase in lysozyme adsorption can be attributed to the electrostatic attraction between the FFA and the protein (Wilbert *et al.*, 1998). This result confirms

successful modification of the PES membrane surface.

- There was no significant difference in the amount of protein recovered from uncoated and negatively charged FFA coated PES membranes, fouled with negatively charged BSA. This was because the attractive hydrophobic force exceeded the electrostatic repulsion between the BSA and PES membrane. An increase in protein adsorption was also observed when the negatively charged FFA coated PES membranes were fouled with negatively charged lysozyme. This increase in protein adsorption can be attributed to the attractive hydrophobic interactions between lysozyme and the aliphatic tail of the FFA, that exceeded the electrostatic repulsion between the membrane and the protein (Mänttäri *et al.*, 2000).
- There was no difference between the absorbance spectra for uncoated and FFA coated PES membranes fouled with microstrainer product at pH 4.5 and 10, suggesting that the increase in the hydrophilicity of PES membranes coated with FFA was ineffective in reducing adsorption between the hydrophobic compounds present in the effluent and the membrane surface.

Flocculants and coagulants, used extensively in the pre-treatment of the paper machine effluent, can also act as foulants of the UF membranes and therefore their influence will be discussed in the Chapter 5.

CHAPTER 5

FOULING POTENTIAL OF COAGULANTS AND FLOCCULANTS USED IN THE PRE-TREATMENT OF PAPER MACHINE EFFLUENT PRIOR TO DAF

The coagulation and flocculation pre-treatment processes, prior to DAF, have been shown to facilitate the removal of particles e.g. suspended solids, organic matter and heavy metals from the effluent (Klute *et al.*, 1995; Ødegaard, 1995). In order for these processes to function optimally the correct coagulants and flocculants should be used (Bunker *et al.*, 1995). At the paper mill, Bubond® 123 (resin) and Bubond® 127 (polyethylene oxide (PEO)) (both provided by Buckman Laboratories International, Hammarsdale, RSA) are currently being used as coagulants and flocculants, respectively, in the pre-treatment of the DAF feed. The resin adsorbs onto the fibres and organic material in the effluent and creates an anchoring place for PEO, the flocculant. PEO associates with the resin through hydrogen bonds that are formed between the hydroxyl groups of the phenolic rings in the resin and the oxygen sites of PEO. The relative size of the PEO molecule (2 to 10 MDa) allows for the collection of organics, fibres and resin to form a floc large enough for clarification.

The aim of the work presented in this chapter was to establish whether the flocculants and coagulants used at the paper mill contributed towards the fouling of the UF membranes. PWF determinations performed on the UF membranes, statically fouled with the above mentioned coagulants and flocculants, were used as a measure to indicate the degree of membrane fouling. Bentonite clay was previously used as a coagulant.

5.1 EXPERIMENTAL

PWF determinations were performed on PES membranes fouled with various flocculants and coagulants.

Pure-water flux determination

The PWF determinations were performed on a 3-cell test rig that could be fitted with flat sheet membranes. The test rig was operated at an operational pressure of 200 kPa, a linear velocity of 1 m/s and 20 °C. The temperature was controlled with a heat exchanger. The permeate flow through the membranes was measured using a 10 mL volumetric flask and stopwatch. All experiments were performed under the same operating conditions, unless

otherwise stated.

Experiment 1

A bentonite suspension with a concentration of 50 g/L was diluted 10-, 50- and 100-fold, respectively. Unused PES UF membranes were placed in the various bentonite suspensions for 48 h at room temperature. The membranes were then thoroughly rinsed in RO water and the PWF was determined.

At the time of this experiment bentonite was evaluated as a coagulant on the DAF clarifier at the paper mill. The use of bentonite has subsequently been suspended.

Results and Discussion - experiment 1

The results presented in Figure 5.1 indicated that static fouling of the PES membranes with bentonite had no significant effect on the permeate flow through the membranes. Bentonite clay was, therefore, not a possible foulant of the UF membranes at paper mill.

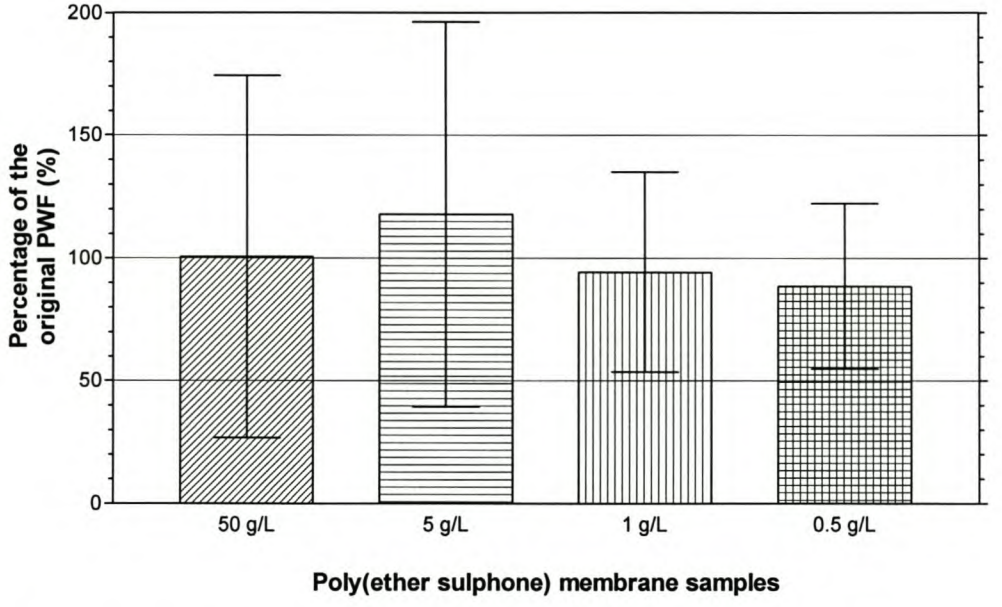


Figure 5.1: The PWF values obtained for PES membranes fouled in bentonite suspensions, varying in their respective concentrations. The values presented are the arithmetic mean for three determinations ± SD represented by the error bars.

Experiment 2

PES membranes were statically fouled in Bufloc® 5031 (quaternary ammonium) (provided by Buckman Laboratories International, Hammarsdale, RSA) suspensions at different concentrations. The essence of the investigation was to establish whether the coagulant

facilitates membrane fouling. The membranes were fouled for 48 h at room temperature, rinsed in RO water, before the PWF was determined.

Results and Discussion - Experiment 2

The results displayed in Figure 5.2 showed a 7, 19 and 11% decrease in the mean PWF of membranes fouled in the Bufloc® 5031 suspensions, with concentrations 15, 0.3 and 0.15 mg/L, respectively. Although a 4% increase in permeate flux was obtained for the membranes fouled in the 1.5 mg/L Bufloc® 5031 suspension, this increase is not statistically significant (analyses done by one way Anova-nonparametric using the GraphPad Prism version 3.0 program).

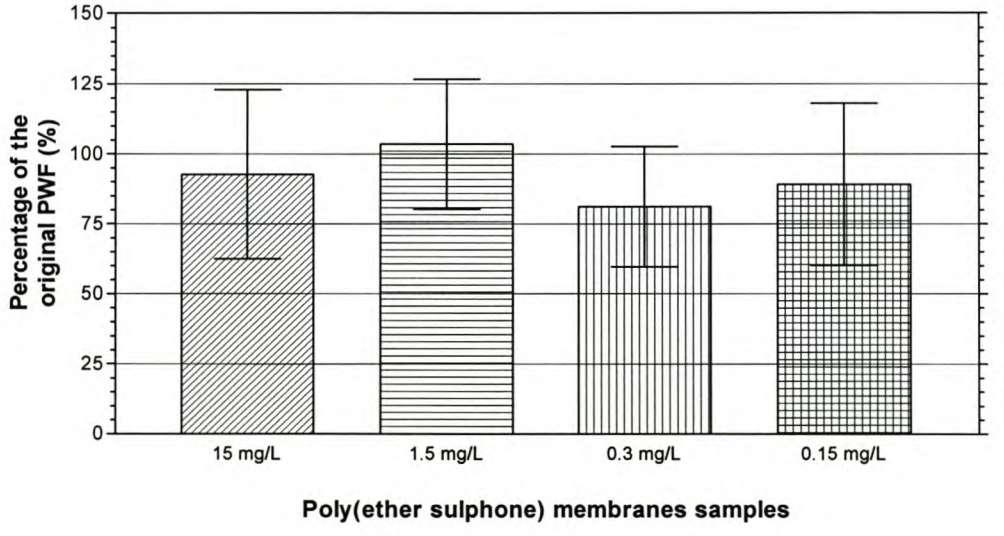


Figure 5.2: PWF values obtained for PES membranes fouled in 15, 1.5, 0.3 and 0.15 mg/L Bufloc® 5031 suspensions. The values presented are the arithmetic mean for three determinations ± SD represented by the error bars.

Experiment 3

Bubond® 123 (resin), a coagulant, is currently being used in the pre-treatment of the DAF feed at the paper mill. Bubond® 123 is added to the effluent at a concentration of 3 mg/L. A dilution series of 3, 0.06 and 0.03 mg/L was prepared and the PES membranes placed in the Bubond® 123 suspensions for 48 h at room temperature (ca 20 °C), rinsed with RO water and the PWF determined.

Results and Discussion - Experiment 3

Permeate fluxes with an 11% and 5% increase above the original PWF were obtained for PES membranes fouled in a 3 mg/L and 0.6 mg/L Bubond® 123 suspension, respectively (Figure 5.3). The PES membranes fouled in the 0.03 mg/L Bubond® 123 suspension showed an average 22% decrease in the permeate flux compared to the original PWF obtained for the unfouled membranes.

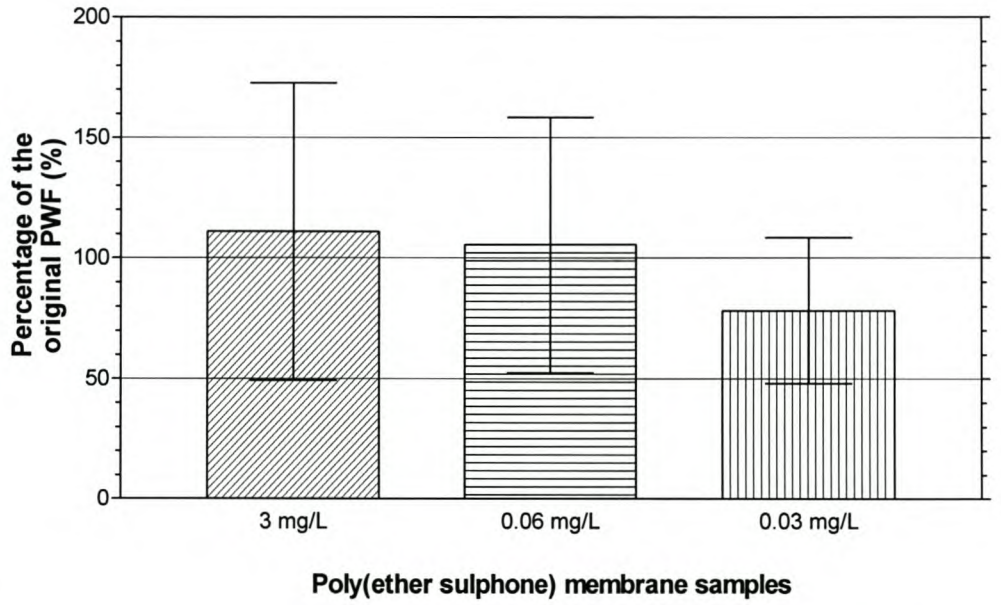


Figure 5.3: PWF values obtained for PES membranes fouled in various Bubond® 123 suspensions, differing in their respective concentrations. The values presented are the arithmetic mean for three determinations ± SD represented by the error bars.

Experiment 4

Bubond® 127 (PEO) is currently used as a flocculant prior to the DAF clarifier. A 1.5% m/v Bubond® 127 solution is prepared and added to the effluent at 1 mg/L. A Bubond® 127 stock solution with a concentration of 1.5% m/v was prepared and diluted to a final concentration of 1, 0.02 and 0.01 mg/L, respectively. PES membranes were placed in the various Bubond® 127 solutions for 48 h at room temperature (ca 20 °C), whereafter, the membranes were rinsed with RO water and the PWF determined.

Results and Discussion - Experiment 4

The results displayed in Figure 5.4 indicated an increase in flux of 30% and 1% above the

original flux for PES membranes fouled in a 1 mg/L and 0.02 mg/L (1.5%) Bubond® 127 solution, respectively, compared to the 1% decrease in the original flux obtained for the membranes fouled in the 0.01 mg/L (1.5%) Bubond® 127 solution. As is the case in the previous tests, statistical analyses of the results showed no significant difference in the flux for the different Bubond® 127 concentrations. It was concluded that Bubond® 127 does not contribute to the fouling problem.

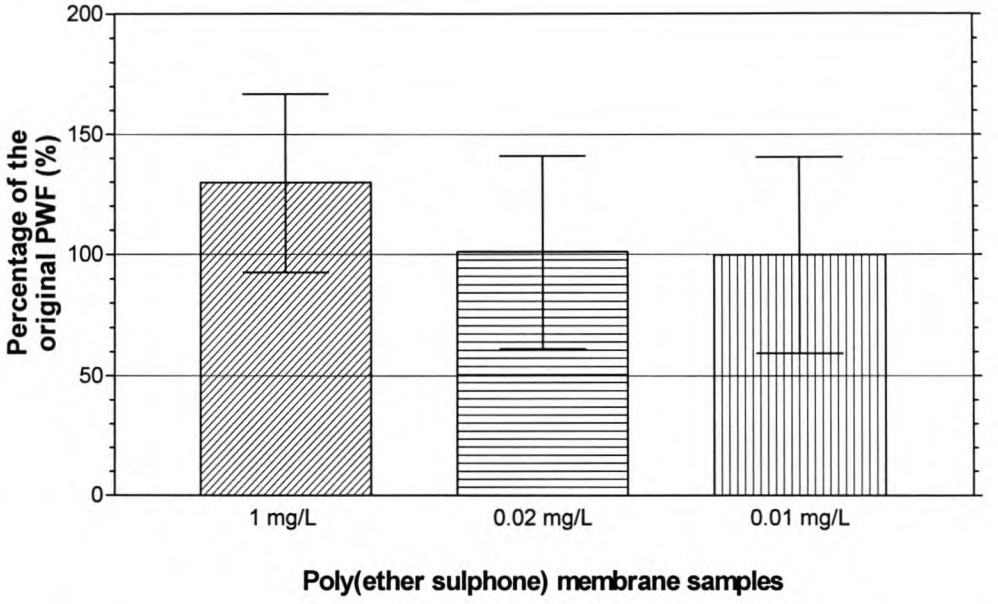


Figure 5.4: PWF values for PES membranes fouled in a solution containing 1, 0.02 and 0.01 mg/L of a 1.5% m/v PEO stock solution. The values presented are the arithmetic mean for three determinations ± SD represented by the error bars.

5.2 CONCLUSIONS TO FLOCCULANT AND COAGULANT EVALUATION

- The static fouling experiments carried out on the flocculants and coagulants in this study showed that none of the agents adsorbed onto the membranes irreversibly.
- The results also showed that flocculants and coagulants used to assist clarification of the effluent in the DAF clarifier, did not act as fouling agents of the UF membranes tested.

The work described in this chapter clearly excludes the involvement of the coagulants and flocculants in the foulanting process of UF membranes used for the clarification of paper machine effluent. These findings showed that the breakdown products of lignin and other wood related compounds were the most likely membrane foulants. The identification and partial characterisation of these compounds are subsequently discussed in Chapter 6.

CHAPTER 6

CHARACTERISATION OF VARIOUS EFFLUENT SAMPLES

During the NSSC process various by-products are synthesised, as discussed in Chapter 3, which can act as foulants of the UF membranes. The high phenolic content and sulphonated aromatic rings of these compounds give them their high fouling potential. The aromatic content of these compounds allowed for their characterisation by means of UV-Vis spectrophotometry. The ionizable groups of these compounds could be expected to affect their UV-Vis characteristics and therefore the influence of pH on these compounds was also investigated by means of UV-Vis analyses.

6.1 UV-VIS SPECTROPHOTOMETRY

UV-Vis spectrophotometry is a versatile analytical technique that is applied in all areas of modern biochemistry and biotechnology. The technique is sensitive, non-destructive, fast and easy to use. UV-Vis spectrophotometry has three main areas of application with regard to the analysis of biochemical samples:

- The concentration of a sample in solution can be determined by measuring its absorbance at a single wavelength and calculating the concentration of the sample directly by means of the molar absorption coefficient, if it is known, or the concentration can be extrapolated from a standard curve.
- Changes in the concentration of reagents or products in a chemical reaction can be determined by measuring the change in absorbance with time, either at a fixed wavelength or by repetitively scanning over a given wavelength range.
- Unknown compounds can be characterised on the basis of their spectral characteristics over a wide wavelength range (Müller and Schweizer, 1996).

The essence of this investigation was to characterise compounds in the effluent samples and to correlate it with the foulants on the UF membranes. Different effluent samples were collected from various locations at the paper mill and analysed. The effect of pH changes on the different effluent samples was also studied by UV-Vis spectrophotometry.

6.2 UV-VIS ANALYSES OF EFFLUENTS GENERATED IN THE PAPER MILL

As shown in Figure 6.1, the paper mill generates effluent at various stages during the

production process which contribute to the effluent stream that is finally passed on to the DAF clarifier and ultimately, the UF plant. In an attempt to identify possible foulants, UV-Vis analyses of the major effluent contributors in the paper mill were carried out.

6.2.1 Experimental

All the UV-Vis measurements were performed on a Varian Cary 100 UV-visible spectrophotometer. Analytical grade water was used as a blank for all analyses. The samples analysed were black liquor, evaporation condensate, Mondi Kraft Richards Bay pulp, waste paper effluent and paper machine effluent. The origin of these effluents is shown in Figure 6.1. The pH of the various effluent samples was adjusted to pH 7. The effluent samples were diluted, when necessary, and the absorbance measured between 190 and 400 nm.

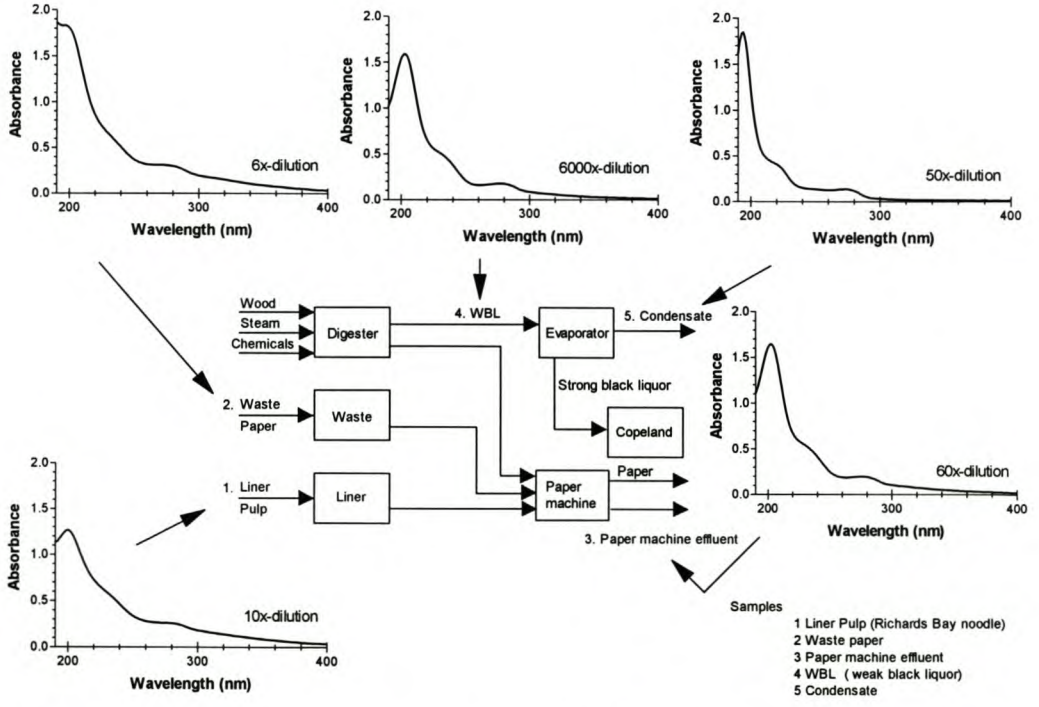


Figure 6.1: Schematic representation of the origin of different effluent streams generated in the paper mill and their respective UV-spectra.

6.2.2 Results and Discussion

The absorption maxima at 230 and 280 nm in UV-Vis spectra of all the effluents analysed indicate the presence of aromatic substances (Figures 6.1 and 6.2). As the paper mill produces a high yield pulp for the production of linerboard, it is safe to assume that the

different effluent samples contain a high concentration of aromatic lignin breakdown products, responsible for the common features in the UV-Vis spectra. As is shown in the overlayed spectra in Figure 6.2, black liquor and paper machine effluent have identical UV-Vis characteristics, indicating similarity in composition.

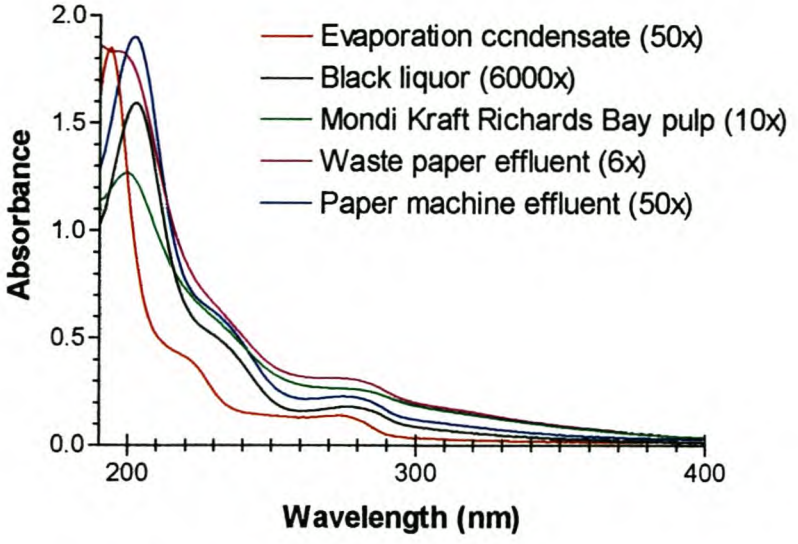


Figure 6.2: Overlay of absorption spectra of diluted effluent samples collected from various locations at the paper mill.

In addition to the absorption maxima at 230 and 280 nm, these effluents exhibit a strong peak at 203 nm. Mondi Kraft Richards Bay pulp and waste paper effluent have strong absorbance maxima in the range 198 to 200 nm while evaporation condensate has a strong and sharp absorbance maximum at 194 nm. Absorbance maxima below 210 nm normally indicate the presence of unconjugated double bonds in a polymer. Figure 6.3 shows the influence of the DAF clarifier and microstrainer on the UV-Vis properties of the effluent. Although the absorbance maxima decreased, the spectra indicate that the DAF clarifier and the microstrainer did not change the composition of the effluent significantly as the spectra are identical in shape. It is not possible to deduce the exact structure of any given substance from the UV-Vis properties alone, but the similarities between spectra of the paper machine effluent and black liquor indicated that the major constituents in these two effluents could be similar. In the digester, wood is cooked at 175 °C in a mixture of sodium sulphite and sodium carbonate to partially solubilize the lignin as lignosulphonate (Helm, 1997) [7]. As lignosulphonate is a major component of the solubilized lignin derived effluent, it was decided to record an absorption spectrum of commercially obtained sodium lignosulphonate.

[7] http://www.chemistry.vt.edu/chem-dept/helm/3434WOOD/notes1/ultra.html

This spectrum is shown in Figure 6.4. The absorption spectra displayed in Figure 6.3 correlate well with the absorption spectrum obtained for pure lignosulphonate. From these results it can be deduced that the paper machine effluent, DAF product and microstrainer product contain substantial amounts of lignosulphonate.

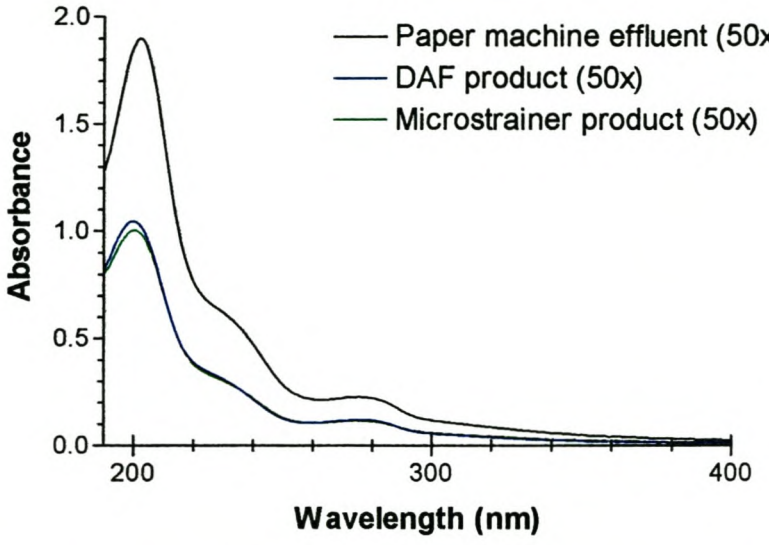


Figure 6.3: Spectral analyses of paper machine effluent, DAF and microstrainer product before and after purification of the paper machine effluent on the DAF clarifier.

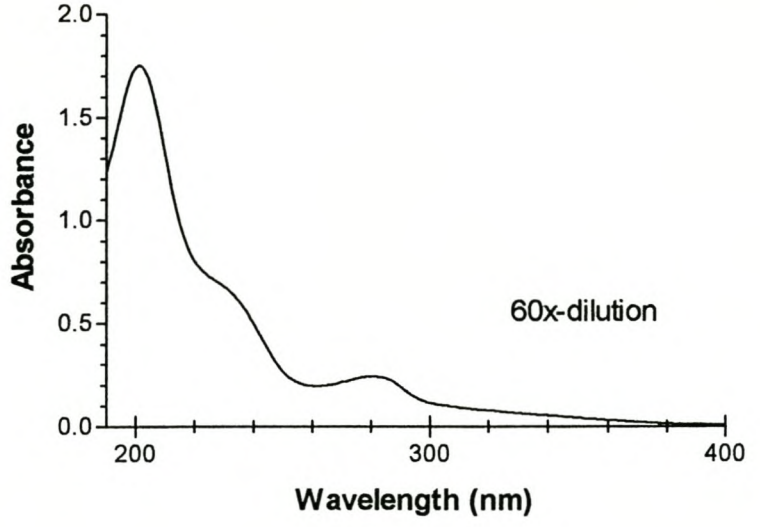


Figure 6.4: Wavelength scan of a diluted 0.1% m/v commercial lignosulphonate solution at pH 7.

6.2.3 Influence of pH on the spectroscopic properties of various effluents

The UF plant at the paper mill is presently operating at a relatively low pH value of between pH 4.5 and 4.8. Under these conditions severe fouling of the PES membranes was experienced. Similar results were obtained with humic substances, the breakdown products of lignin, carbohydrates and protein, at low pH (Nyström *et al.*, 1996; Jucker and Clark, 1994). Clark and Lucas reported that the adsorption of humic substances onto hydrophobic membranes increased significantly with a decrease in the pH value from 6 to 4 (Clark and Lucas, 1998). Jucker and Clark showed that an acidic pH value decreased the solubility and hydrophilicity of humic substances, thereby favouring adsorption onto the hydrophobic UF membranes (Jucker and Clark, 1994).

During the trial runs at the paper mill a decrease in membrane fouling was observed for PES membranes operating at an alkaline pH. This prompted an investigation into the influence of pH on the character of the effluent.

6.2.4 Experimental

A series of paper machine effluent, DAF and microstrainer product samples was prepared and the pH of these samples was adjusted in a range from 2 to 13. The effluent samples were subsequently diluted and analysed by UV-Vis spectrophotometry at 190 and 400 nm as previously described.

6.2.5 Results

An absorption maximum in the region 240 to 260 nm, was observed with an increase in the pH for all three effluents (Figure 6.5). Furthermore, the increase in the pH caused a "shift" in the absorbance from a lower to a higher wavelength. The changes in pH value resulted in a spectral shift for all three samples analysed, with isosbestic points at approximately 238, 238 and 275, 245 and 265 nm, respectively, as displayed in Figure 6.5 (A-C).

6.2.6 Discussion

The increase in the absorption maxima, in the 240 to 260 nm region, indicates the presence of a new ionised species emerging as a result of the increased pH. The shift in absorbance can be attributed to the ionisation (deprotonation) and subsequent delocalization of electrons in the phenolic groups of the lignin breakdown products present in the various effluent samples.

The results also clearly indicate the presence of ionizable groups which would significantly influence the solubility of these substances, a factor that could play an important role in effluent pre-treatment for fouling prevention.

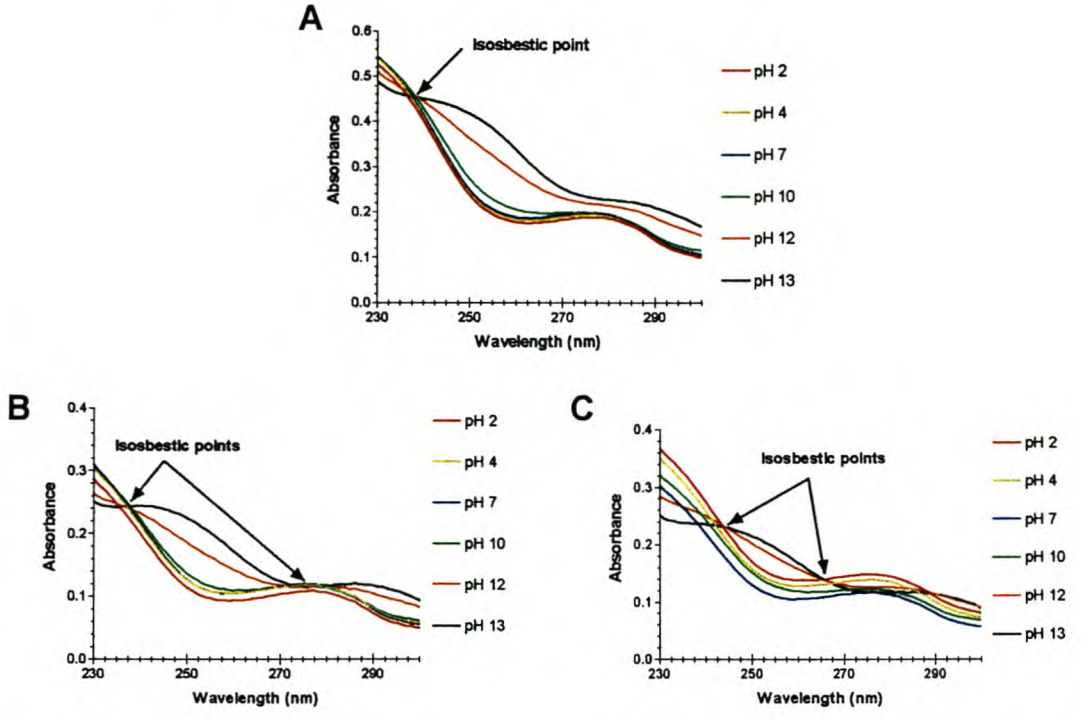


Figure 6.5: Change in the absorption spectra of (A) paper machine effluent, (B) DAF product and (C) microstrainer product with a change in the pH.

6.3 INDUCTIVELY COUPLED PLASMA ANALYSES OF VARIOUS EFFLUENT SAMPLES

It was observed that an increase in the pH of the solution was accompanied by an increase in the turbidity in several of the effluent samples. Given the presence of ionizable groups and mono or divalent metal ions in the effluent, the possibility of metal ion complex formation with lignin breakdown products was investigated. In an attempt to associate complex formation with the increase in turbidity at alkaline pH, several effluent samples were analysed by means of ICP spectroscopy to determine the levels of metal ions in the various effluents at different pH values. The technique allows for the rapid multi-element analysis of water samples for the determination of major, minor and trace elements, with high accuracy and low detection limits (Nham, 1991[a]; Nham, 1992). Plasma spectrometry is also widely used in the analysis of environmental samples e.g. air (Nham, 1991[b]), geological samples (Liberatore, 1993; Liberatore, 1994) and in the food industry (Robb *et al.*, 1999).

6.3.1 Experimental

The overnight supernatant of two samples of paper machine effluent, DAF product and microstrainer product, of which the pH values were corrected to 7 and 13, respectively, were analysed by means of ICP. A Varian Liberty Vacuum 200 Inductively Coupled Plasma Atomic Emission Spectrometer was used for all the measurements. The spectrometer was calibrated with calibration standards prepared from a 1 000 mg/L stock standard.

6.3.2 Results

The analytical wavelengths used for the detection of the various elements plus the results of the analyses are listed in Table 6.1.

Table 6.1: ICP analysis of paper machine effluent, DAF and microstrainer product.

		Detected values (mg/L)					
		Paper machine effluent		DAF product		Microstrainer product	
Elements	**Wavelength (nm)**	**pH 7**	**pH 13**	**pH 7**	**pH 13**	**pH 7**	**pH 13**
Al	394.4	37.6	37.5	4.1	-**	4.4	35.3
Ca	317.9	113.6	102.2	176.7	145.4	171.2	101.9
K	769.9	11	16.1	15.8	22.6	15	22
Li	323.3	1.2	0.8	0.9	1	1.9	1.9
P	214.9	0.9	1.4	0.4	0.2	0.4	0.3
Si	250.7	7.7	15	3.6	10.9	5.3	38.1

** Paper machine effluent, DAF and microstrainer product were received on separate occasions and were subjected to different pre-treatment regimes at the paper mill.

Mono and polyvalent metal ions were found to be present in the three effluent samples with Ca^{2+} having the highest concentration. The level of Ca^{2+} in the supernatant decreased significantly with an increase in the pH compared to the levels of Al^{3+} (in microstrainer product), K^{+} and Si^{4+} which increased with an increase in pH.

6.3.3 Discussion

It is evident from the results displayed in Table 6.1 that a significant amount of Ca^{2+} is present

in the various effluents. An increase in pH resulted in an initial increase in turbidity. If the samples were allowed to settle overnight, the Ca^{2+} levels of the supernatant decreased significantly, indicating that Ca^{2+} was bound to the material that settled out at elevated pH. These results supported the hypothesis that Ca^{2+} might contribute to complex formation with a resultant decrease in solubility and a subsequent increase in turbidity of the effluent.

6.4 THE INFLUENCE OF A CHELATING AGENT ON THE TURBIDITY OF THE EFFLUENT AT ELEVATED pH

If complex formation at alkaline pH values was enhanced by Ca^{2+}, addition of a chelating agent, such as ethylene diamine tetra-acetic acid disodium salt (EDTA), should remove the Ca^{2+} and prevent complex formation and lower the turbidity associated with elevated pH.

6.4.1 Experimental

The effluent (microstrainer product) used in this experiment was obtained from the paper mill. EDTA was supplied by Saarchem-Holpro Analytic (Pty) Ltd (Krugerdorp, RSA) and $CaCl_2$ provided by Merck, Darmstadt. The pH of the microstrainer product was adjusted to 13, the samples were stirred well and the turbidity was measured with a portable turbidity meter (Hach model 2100P). To bind all Ca^{2+} in the effluent sample, EDTA was added to a final concentration of 0.02 M. To reverse the effect of EDTA and precipitate colloidal and suspended solids, $CaCl_2$ was added to the EDTA containing effluent samples to yield a final concentration of 0.04 M.

6.4.2 Results

The microstrainer product (pH 13) had a turbidity of 76.4 ± 1.9 NTU. The addition of EDTA to the microstrainer product at pH 13 dissolved the precipitate and considerably reduced the turbidity to 16.5 ± 0.2 NTU. The subsequent addition of $CaCl_2$ again induced precipitation thereby increasing the turbidity to 279.3 ± 3.2 NTU (Figure 6.6).

6.4.3 Discussion

The increase in turbidity, which accompanied the increase in pH of the microstrainer product, can be ascribed to complex formation between the deprotonated carboxylic and phenolic groups of the foulants with divalent Ca^{2+} ions present in the effluent. The addition of EDTA, a chelating agent, to the effluent solution at pH 13, bound the Ca^{2+} and redissolved the

precipitate, thereby reducing the turbidity significantly. The subsequent addition of $CaCl_2$ saturated the EDTA and again induced precipitation with a concomitant increase in turbidity. These results confirmed the role of Ca^{2+} in complex formation and indicates that the removal of Ca^{2+} before the UF step might reduce fouling of the UF membranes significantly. A second option would be to increase the pH of the effluent and to add sufficient Ca^{2+}, to promote precipitation of all residual potential high molecular mass foulants from the DAF effluent.

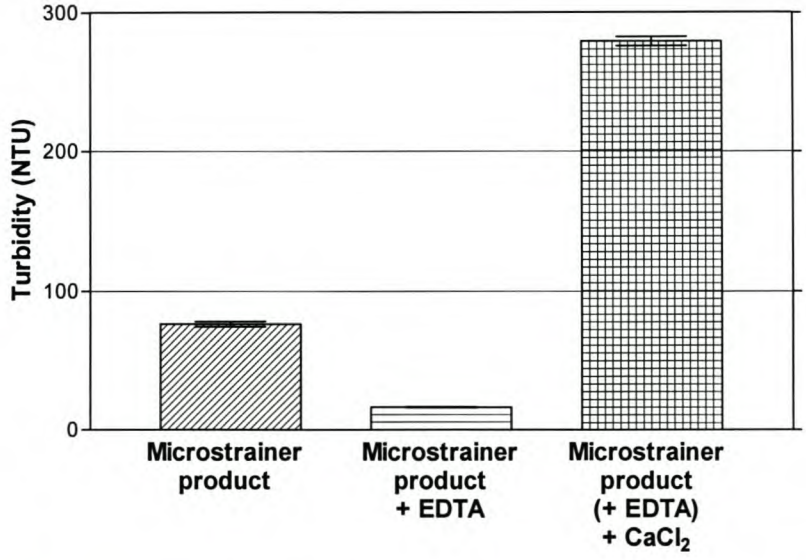


Figure 6.6: Influence of EDTA and Ca^{2+} on the turbidity of microstrainer product at pH 13. The values presented are the arithmetic mean for three determinations ± SD represented by the error bars.

6.5 GEL PERMEATION CHROMATOGRAPHY ANALYSIS OF MICROSTRAINER PRODUCT SAMPLES

To ascertain if elevation in the pH of the microstrainer product led to complex formation, samples with different pH values and Ca^{2+} concentrations were analysed by GPC. GPC is a powerful tool for the determination of the molecular mass averages (MM_{av}) and the molecular mass distribution (MM_d) of polymers (Yau *et al.*, 1979). It is used in various industries, for example, the motor industry for the quantitative determination of aromatic groups in lubricant oils (Varotsis and Pasadakis, 1997) as well as in the food industry for the analysis of components from complex mixtures such as chewing gum and fruit juices (Meyer, 1998). GPC can also be used for on-line product quality control (Yau *et al.*, 1979), the analysis of

synthetic polymers and characterisation of samples of biological origin (Meyer, 1998).

6.5.1 Experimental

The high-pressure liquid chromatography (HPLC) system used in this study consisted of a solvent delivery system (Waters model 6000A), an automated gradient controller (Waters model 680), a photodiode array detector (Waters 991) and LOTUS 1-2-3 software (Lotus, Cambridge, MA, USA) for data analysis. The chromatography was carried out using a 7.8 × 300 mm Ultrahydrogel™ 500 GPC column supplied by Waters. The mobile phase, degassed analytical grade water, was filtered through a 0.45 μm membrane filter (supplied by Millipore) and passed through the column at a flow rate of 0.6 mL/min. PEO standards (provided by Microsep), with molecular masses ranging from 24 kDa to 850 kDa were used to establish a molecular mass calibration curve. All the samples used during this study were centrifuged on a Heraeus bench centrifuge for 5 min and the supernatant filtered through a 0.45 μm membrane filter (supplied by Millipore) before loading it onto the column.

6.5.2 Results

Figure 6.7 represents a standard curve obtained with PEO molecular mass standards. In this system each standard had a characteristic elution volume. The molecular mass values for the compounds present in the effluent as presented in Figures 6.8 to 6.13 were interpolated from the standard curve. Each component in each of the chromatographic profiles was identified by its elution volume (V_e), the volume collected that corresponds to the apex of a peak. The molecular mass of these unknown compounds were determined as follows:

7. The GPC column was calibrated by determining the elution volumes required to displace several PEO standards of known molecular mass from the column.
8. The elution volume for the unknown compounds, present in the effluent, were then determined under the same operating conditions.
9. The data obtained were compared by means of a linear empirical relationship between the logarithm of relative molecular mass ($Log_{10}Mr$) and V_e/V_o.

V_o represented the void volume, that is the total space surrounding the gel particles in the packed column. This volume was determined by measuring the volume of solvent required to elute a solute (850 kDa PEO standard) that is completely excluded from the gel matrix (Bohinski, 1987; Boyer, 1993).

Untreated microstrainer product (pH 4.4) produced peaks with MM_{av} of 164, 114, 94 and 60 kDa, respectively (Figure 6.8).

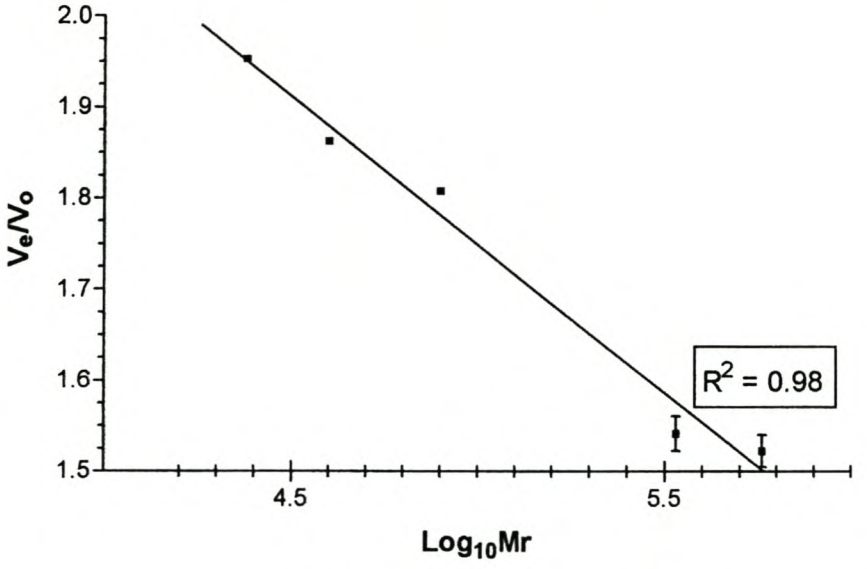


Figure 6.7: GPC standard curve for PEO standards (molecular mass of between 24 to 850 kDa).

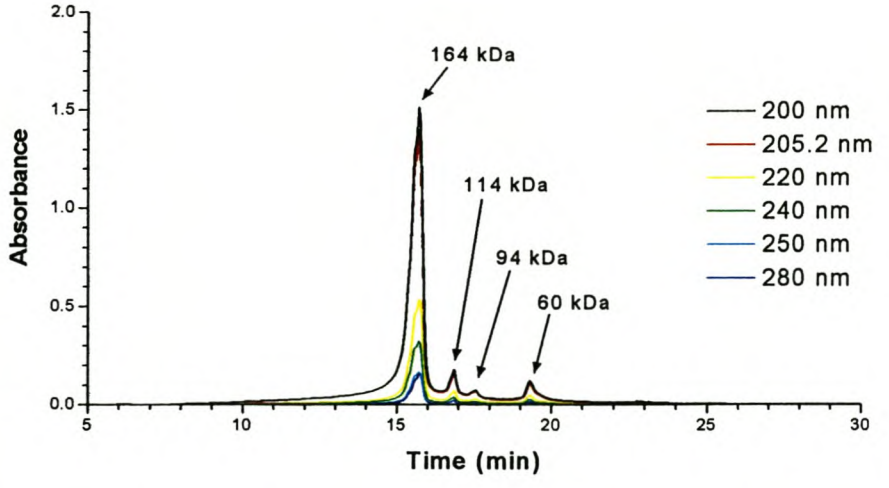


Figure 6.8: GPC-analysis of microstrainer product (pH 4.4). Detection was at the wavelengths indicated on the chromatogram.

To establish the effect of an alkaline pH on the compounds present in the effluent, the MM_{av} and MM_d was determined after adjusting the pH of the microstrainer product to pH 13. Peaks with a MM_{av} larger than 850, 185, 117, 60 and 28 kDa were obtained (Figure 6.9). It was interesting to note that at pH 13 an additional peak at 28 kDa was observed.

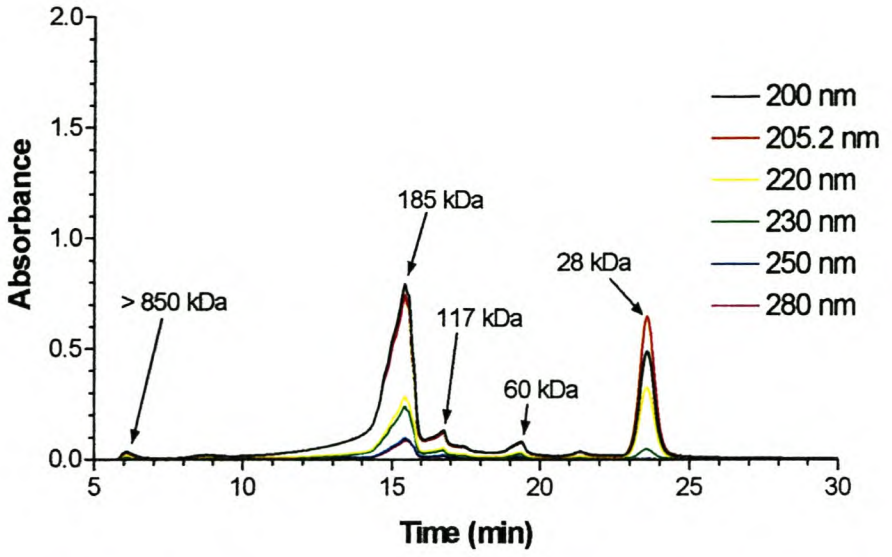


Figure 6.9: GPC-analysis of microstrainer product (pH 13) at various wavelengths. Detection was at the wavelengths indicated on the chromatogram.

The pH of the microstrainer product (pH 13) sample was subsequently adjusted to 4 to establish whether the peak observed at 28 kDa, at pH 13, was an artefact of the procedure or whether a new species was formed due to the change in pH. A major peak with an MM_{av} of 90 kDa and a minor peak at 333 kDa and were observed (Figure 6.10). The 28 kDa peak present in Figure 6.9 was absent and it can therefore be assumed that the 28 kDa peak is a new complex which forms when the pH of the effluent is adjusted from 4 to 13.

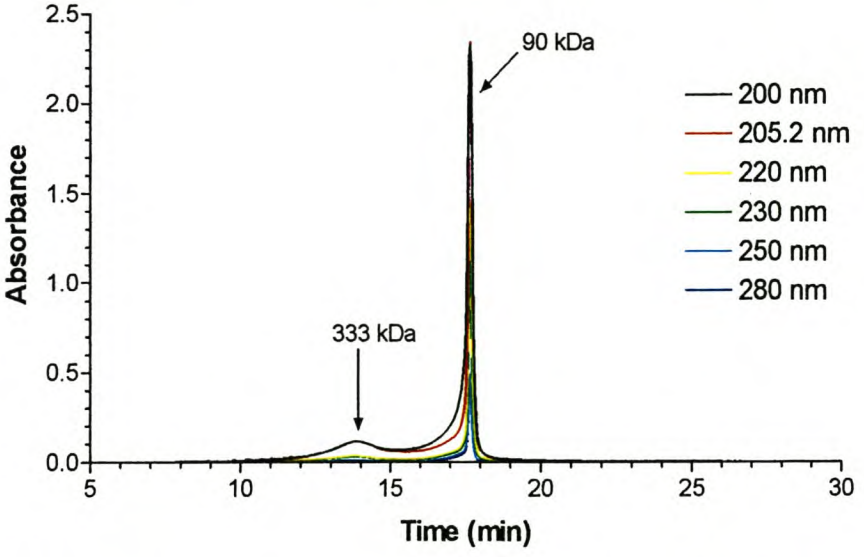


Figure 6.10: Microstrainer product (pH 13) was adjusted to pH 4 and analysed to establish whether the 28 kDa peak, present in Figure 6.9, would be affected. No peak was observed at 24 min which corresponded to the 28 kDa fraction.

To establish whether the formation of the 28 kDa fragment shown in Figure 6.9 was caused as a result of Na^+, introduced with the addition of NaOH to elevate the pH of the effluent to 13, NaCl (equivalent to the amount of NaOH added for pH adjustment, 0.2 g per 50 mL of effluent) was added to the effluent at pH 4.4. The NaCl containing sample was subsequently analysed by GPC and the result is shown in Figure 6.11. The profile obtained after the addition of NaCl to the effluent sample was similar to that obtained when the pH of the effluent sample was reduced from 13 to 4, as shown in Figure 6.10. The microstrainer product sample analysed in Figure 6.10 had a high Na^+ concentration prior to the addition of HCl to reduce the pH. After the addition of HCl to the sample the major counter ions were Na and Cl. All ionizable species would therefore have had the same counter ions associated with it in contrast to the original sample which had a number of different counter ions forming complexes (Table 6.1). The molecular mass of any ionizable complex will be dependent on the type of counter ions involved and, hence, different peaks were observed in the GPC of native effluent. The adjustment of the pH from 4.4 to 13 and back to 4 required the introduction of NaOH and HCl. In both cases the multiple ion complexes were replaced with Na^+ and Cl^- yielding single counter ion complexes reducing the complexity of the chromatograms considerably.

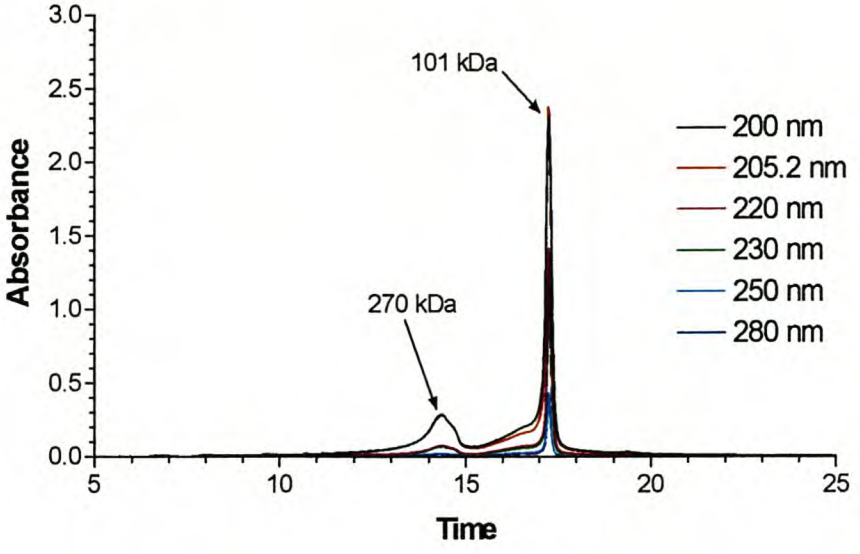


Figure 6.11: GPC of microstrainer product (pH 4.4) after addition of NaCl (0.2g per 50 mL of effluent) to establish whether the Na^+ (in NaOH) or the solution pH was responsible for the 28 kDa peak observed in Figure 6.9.

The 28 kDa peak was still present after the addition of EDTA to the microstrainer product (pH 13) as shown in Figure 6.12. This confirmed the involvement of the alkaline pH with the

formation of the 28 kDa peak.

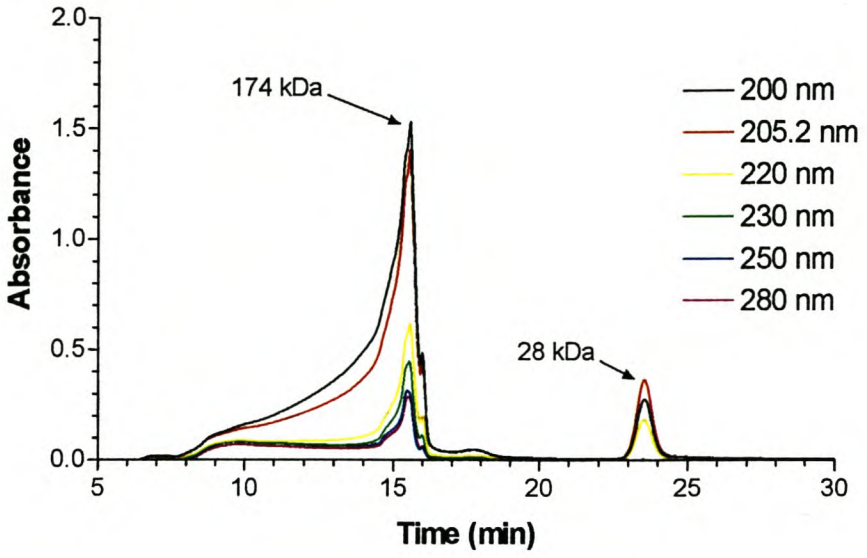


Figure 6.12: GPC-analysis of microstrainer product (pH 13) after the addition of EDTA (0.4 g per 50 mL effluent).

The subsequent addition of $CaCl_2$ (dehydrated) to the microstrainer product (pH 13), containing EDTA, resulted in the formation of an additional peak (MM_{av} of 208 kDa) at 15 min, indicating complex formation as shown previously. The peak at 28 kDa remained (Figure 6.13).

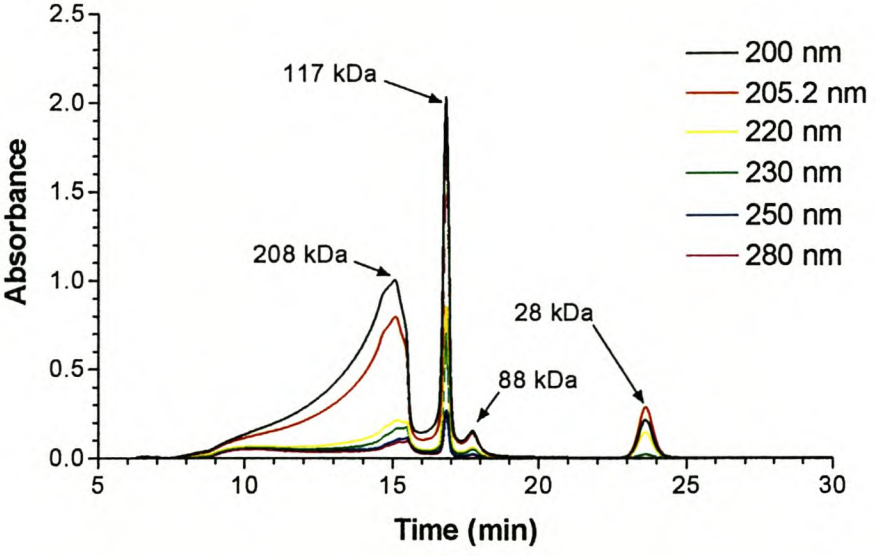


Figure 6.13: GPC of microstrainer product (pH 13) after addition of EDTA (0.4 g) and $CaCl_2$ (0.2g) per 50 mL effluent.

6.5.3 Discussion

GPC analyses of the microstrainer product at pH 4.4 and 13, in the presence and absence of Ca^{2+}, Na^{+} and Cl^{-}, confirmed the complex formation indicated by UV-Vis, turbidity and ICP analyses. The GPC results showed the formation of high molecular mass complexes when the pH was adjusted to 13 and when Ca^{2+} was added. In addition, the elevation of pH to 13 led to the formation of an additional 28 kDa complex which could only be removed by lowering the pH to 4. The GPC results therefore support the idea that the microstrainer product still contains a number of high molecular mass complexes which could act as foulants for the PES UF membranes and that the complexes can be removed by manipulation of the pH as well as the Ca^{2+} levels in the effluent.

6.6 DIRECT COUPLING OF A GPC TO AN ES-MS

The photodiode array detector (Waters 991) used in conjunction with the GPC column, provided limited information on the chemical composition of the foulants present in the effluent. Consequently, a more powerful detector, a mass spectrometer (MS) was used with the GPC to obtain additional structural information on the polymers (e.g. the end groups and repeating units) based on the size and molecular mass of the compounds present in the effluent (Aaserud *et al.*, 1999; Fei and Murray, 1996). Combining GPC with MS furthermore eliminated any "unreliable calibration" commonly associated with size exclusion chromatography (SEC) (Nielen, 1996).

6.6.1 Experimental

GPC separations were performed on a 7.8 × 300 mm Ultrahydrogel™ 500 column (supplied by Waters). The mobile phase, deionised water, was delivered by a Pharmacia LKB Gradient Pump 2249 at a flow rate of 100 μl/min. The GPC eluent was directed through the flow cell of a multiwavelength detector (Model M-490). MassLynx software was used to convert the analogue output from the detector to digital output. The solvent delivery system from the flow cell of the detector was directly coupled to a coaxial probe fitted to the electrospray ionisation source of a Micromass Quattro triple quadrupole mass spectrometer. Acetonitrile, containing 1% (v/v) formic acid, was added at the tip of the capillary at a flow rate of 100 μl/min. This resulted in the formation of a 50/50/0.5 acetonitrile/water/formic acid (v/v/v) mixture in the ionisation source which promoted ionisation in the positive mode. A

make-up flow consisting of acetonitrile/ammonia (25%) (100/0.5:v/v) was used for experiments performed in the negative mode. For the detection of ions in either positive or negative mode, a capillary voltage of 3.5 kV was applied and the cone voltage set at 50 V. The source temperature was 100 °C and all lenses were set for maximum detection. Data was acquired in the continuum mode by scanning the first analyser through m/z = 100-1500 at a scan rate of 2 sec/scan.

6.6.2 Results

Figures 6.14 and 6.15 represent chromatograms and mass spectra obtained during LC-MS analysis of microstrainer product at pH 4.36 and pH 13, respectively, with a quadropole mass analyzer. The chromatograms displayed in Figures 6.14 (A) and 6.15 (A) are the total-ion currents (TIC) for the respective microstrainer product samples. Figure 6.14 (A) indicates the presence of a peak emanating from the column after 93.47 min. The mass spectrum in Figure 6.14 (B) obtained after averaging the scans acquired during the elution of the sample indicated a polymer with a repetitive unit of 44 Da resembling PEO. A similar mass spectrum was observed in Figure 6.15 (B).

6.6.3 Discussion

The mass spectra, displayed in Figures 6.14 (B) and 6.15 (B), indicate the presence of PEO in the microstrainer product. PEO is used as a flocculant during the pre-treatment program prior to the DAF process. Detection of any other compounds with the quadropole mass analyzer was impossible due to the inability of the compounds to ionise. It is, however, important to note that polysaturated non-conjugated molecules will not readily ionise and will therefore not be detected by ES-MS. The presence of these compounds was, however, confirmed by UV- analysis as characterised by absorption maxima at below 205 nm (see Figure 6.2).

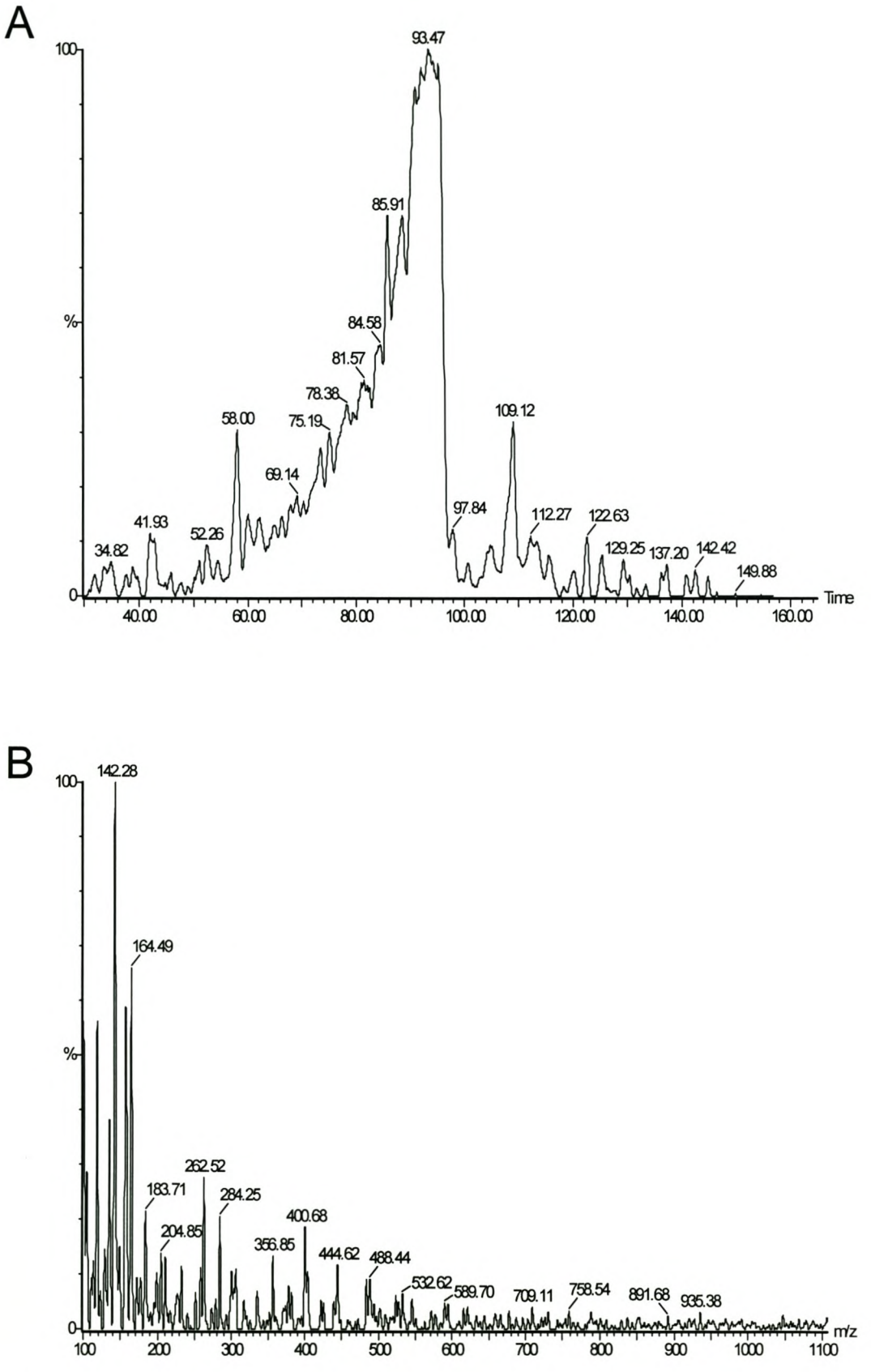


Figure 6.14: (A) Chromatogram of microstrainer product (pH 4.36) obtained by GPC with ES-MS detection (TIC). (B) Averaged mass spectrum between 86 and 96 min as recorded by the MS.

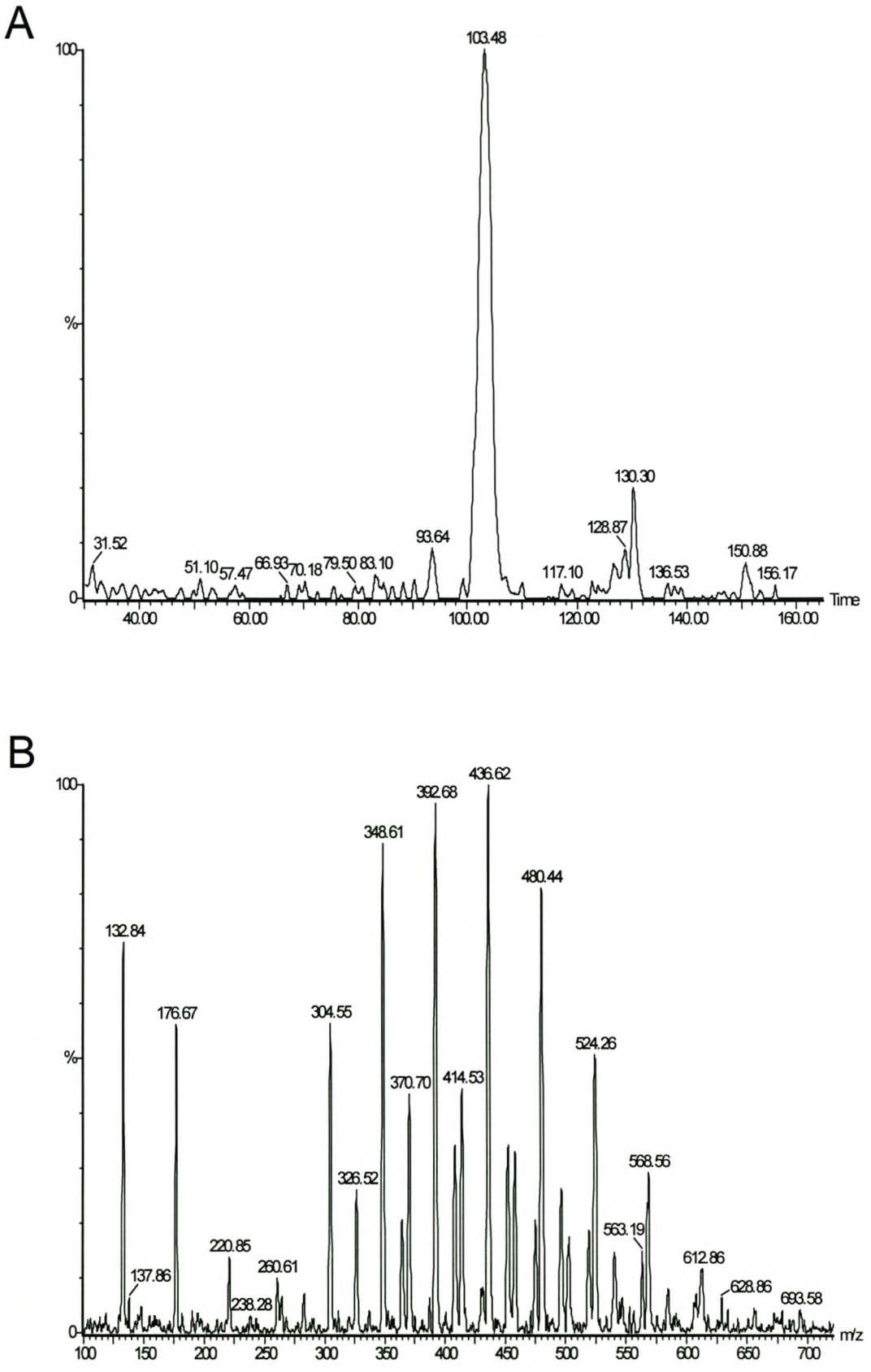


Figure 6.15: (A) Chromatogram of microstrainer product (pH 13) obtained by GPC with ES-MS detection (TIC). (B) Averaged mass spectrum between 100 and 110 min as recorded by the MS.

6.7 CONCLUSIONS

The use of spectroscopy and GPC yielded valuable information about potential membrane foulants in the pulp and paper effluent. The following conclusions were drawn from these experiments:

- The effluents analysed contained aromatic compounds and unsaturated polymers which could act as potential foulants.
- All the samples analysed contained the same type of compounds of which lignosulphonate was the main constituent.
- The pH of the solution had a marked effect on the UV-Vis characteristics with a shift to higher absorbance maxima being induced by elevated pH. These changes were ascribed to de-ionisation of functional groups (carboxylic and phenolic) on the foulants present in the effluent.
- Precipitation was observed in effluent samples with an elevated pH when left undisturbed for 2 h. This increase in turbidity could be attributed to complex formation between negatively charged foulants and metal ions present in the effluent.
- Complex formation could be enhanced by the addition of Ca^{2+} and reversed by the addition of EDTA, a chelating agent.
- GPC analyses confirmed conclusions drawn from the UV-Vis data and indicated the formation of high molecular mass complexes at pH 13.
- Mass spectra indicated the presence of PEO in the microstrainer product. Detection of any other compounds with the quadropole mass analyzer was, however, impossible because of the inability of the compounds to ionise.
- Any future cleaning regimes or fouling prevention measures will be more successful if the above-mentioned properties of the effluent are considered. For example, as a pre-treatment step the effluent can be conditioned at an alkaline pH for a period before UF. This will induce complex formation between the divalent metal ions and the negatively charged compounds in the effluent, and promote flocculation as a means towards clarifying the effluent.

Currently, pre-treatment of the paper machine effluent has a limited effect on the fouling tendency of the UF membranes. As part of the investigation as to what the possible foulants

might be, fouled tubular membranes were obtained from the Piet Retief paper mill and characterised by means of AFM and SEM. These findings are discussed in Chapter 7.

CHAPTER 7

MEMBRANE FOULANT CHARACTERISATION BY ATOMIC FORCE MICROSCOPY AND SCANNING ELECTRON MICROSCOPY

Paper machine effluent was pre-treated on a DAF clarifier and passed through a microstrainer before UF. Yet, extensive fouling still persisted. In an attempt to understand more about what the foulants are and how they affect the surface character of the membrane, fouled tubular PES membranes were obtained from the Piet Retief paper mill and analysed by means of AFM and SEM.

7.1 ATOMIC FORCE MICROSCOPY

AFM images have previously been used to determine the pore size, pore size distribution, surface porosity and surface roughness of membranes (Singh *et al.*, 1998). The technique, furthermore, allows for the imaging of the non-conducting material in air and in liquid (Clark and Lucas, 1998) without special sample preparation (Singh *et al.*, 1998). Force-distance experiments have also been successfully performed with AFM to determine the biocompatibility between compounds and rapid screening of surface-engineered surfaces (McGurk *et al.*, 1999). The adhesive force that exists between a colloidal probe and membrane material has also been directly quantified by means of AFM. The quantification of such interactions can assist in the screening of new membrane materials and provides valuable information on process behaviour, e.g. membrane fouling (Bowen *et al.*, 1998). In this study the surface character of unfouled and fouled PES membranes was evaluated by means of AFM. Similar work has been performed by Allie (1999) who evaluated the surface roughness of modified and unmodified PES membranes before and after fouling.

7.1.1 Experimental

AFM imaging of the samples was performed with a TMX 2000 Explorer (Topometrix, Santa Barbara, CA) in contact mode using V-shaped cantilevers (Topometrix) 200 μm in length and 18 μm in width. The cantilevers were operated at a force constant of 0.032 N/m and a resonance frequency of 5 to 15 kHz. Si_3N_4 pyramidal light force tips were used and imaging forces were adjusted to a set point of -30 nA. A 165 nm step height standard topometrix grid was used for the calibration of the height (z) and lateral (x,y) measurements of the stage. Data analysis was performed by means of Topometrix SPM Lab (Version 3.06.06).

7.1.2 Results

An unfouled PES membrane and a PES membrane fouled in microstrainer product were analysed by means of AFM to determine their surface roughness before and after fouling.

Roughness

AFM roughness analysis was performed over a 100 μm^2 sample area for both unfouled and fouled membranes (Figure 7.1). The following parameters were obtained with the analysis: the average roughness, R_a, defined as:

$$R_a = \frac{1}{N} \sum_{i=0}^{N} |Z_i - \bar{Z}|$$

Where N is the total number of points in the image matrix and $\bar{Z}$ is given by:

$$\bar{Z} = \frac{1}{N} \sum_{i=0}^{N} Z_i$$

Z_i is the height of the ith point over a reference value. The corresponding values for both the unfouled and fouled images were: R_a = 24.95 nm and 110.35 nm, $\bar{Z}$= 178.69 nm and 414.76 nm and Z_{max} = 394.73 nm and 844.32 nm, respectively.

A roughness analysis was performed for lines arbitrarily chosen on the surface of the unfouled and fouled membranes (Figure 7.2). The parameters R_p and R_t were used considering the statistical distributions of heights on a certain profile. R_p is defined as the maximum height of the profile above a mean line

$$R_p = Z_{max} - \bar{Z}$$

and R_t is the maximum peak to valley height in the profile.

$$R_t = Z_{max} - Z_{min}$$

By using the mean values of R_p and R_t a more descriptive profile can be obtained for the entire line profile. The above mentioned values are defined as:

$$R_{pm} = \frac{1}{Y} \sum_{i=0}^{y} (R_p)_i$$

$$R_{tm} = \frac{1}{Y} \sum_{i=0}^{y} (R_t)_i$$

Y represents the 20 highest features in the profile and therefore equals 20 (Prádanos *et al.*, 1996).

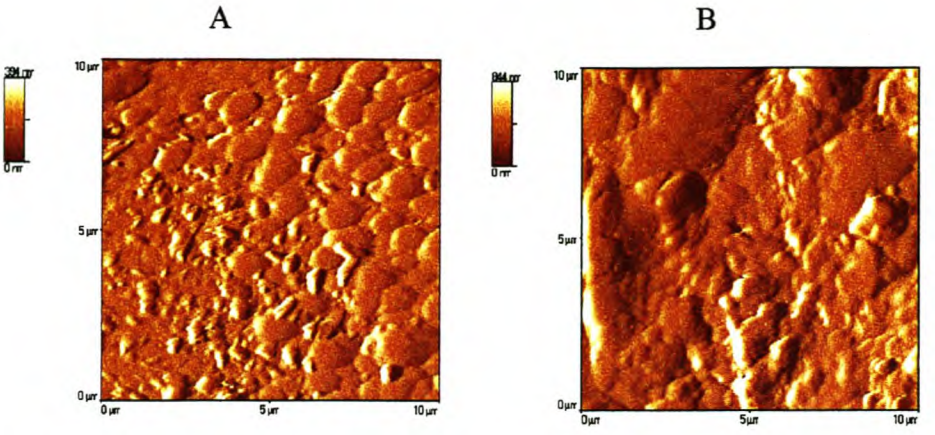


Figure 7.1: AFM images of unfouled (A) and fouled (B) PES membranes. The bar on the left of the images indicate the vertical deviation.

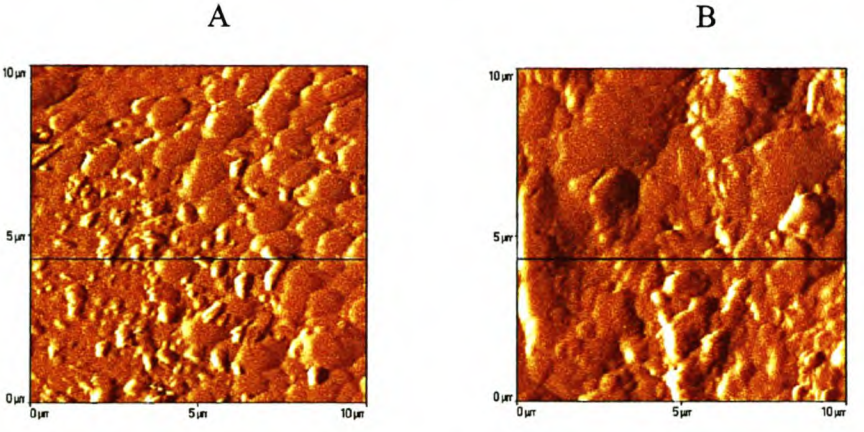
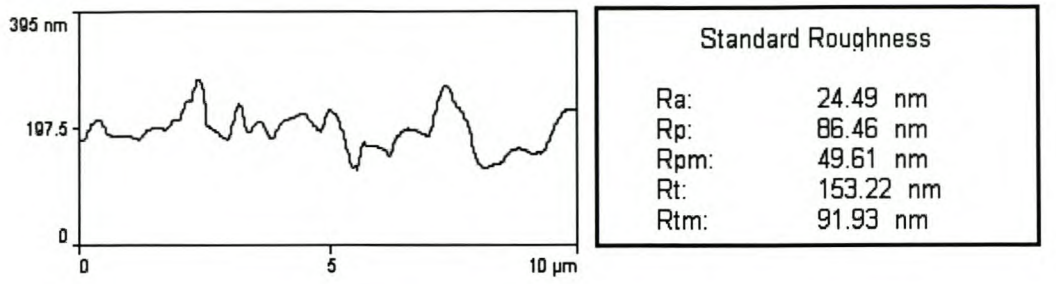


Figure 7.2: Previously shown 2-D AFM images (Figure 7.1) of unfouled and fouled PES membranes, indicating the lines that were analysed during horizontal line analyses

7.1.3 Discussion

A 10% 10 μm membrane surface of a fouled membrane had a total surface area of 108.6 μm^2 compared to the 104.2 μm^2 obtained for the unfouled membrane surface of the same size. The increase in the surface area can be attributed to the deposition of membrane foulants onto the PES membrane surface. Adsorption of the membrane foulants onto the hydrophobic membrane surface also increased the average surface roughness (R_a) shown in Figure 7.3. The increase in surface roughness promotes the deposition of other constituents in the effluent onto the membrane surface resulting in the blockage of the membrane pores and subsequent reduction in membrane flux.

A



B

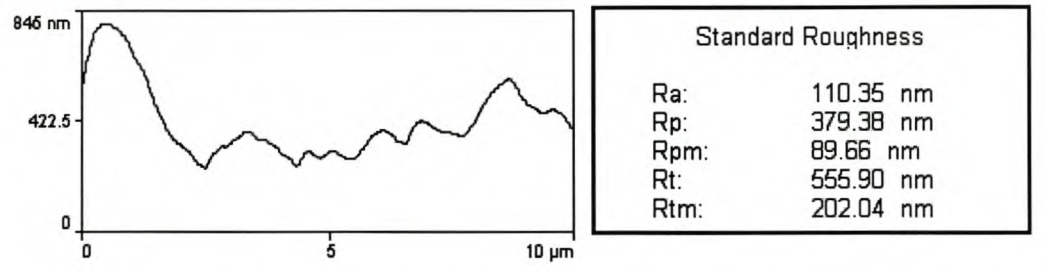


Figure 7.3: Data obtained for the line analysis of unfouled (A) and fouled (B) PES membranes.

7.2 SCANNING ELECTRON MICROSCOPY

SEM yields images over a wide range of magnifications to provide morphological, physical and chemical information about any given specimen (Postek et al., 1980). The technique is used in many industrial manufacturing processes to assist in production quality control of various products for example, photographic materials, paints, pigments and polymers (Watt, 1997). In this study PES membranes were subjected to SEM analyses in an attempt to attain more information on the change(s) in topography before and after fouling of the membrane surface.

7.2.1 Experimental

Unfouled and fouled 40 kDa MMCO PES UF membranes were viewed with a Topcon (SEM ABT-60) scanning electron microscope and analysed with a Link EDS analyzer using AN10000 software to produce the SEM images. The samples were prepared by precoating the membranes with gold to eliminate charging (Fritzsche *et al.*, 1992) and examined at 1 000x magnification.

7.2.2 Results

Examination of the micrographs (Figure 7.4) indicated the presence of a solid compact layer on the PES membrane fouled with microstrainer product (compared to the unfouled membrane surface). Carlsson *et al.* showed that hydrophobic membranes exposed to plug screw feed pressate were initially fouled by lignosulphonates that formed an insoluble compact layer on the membrane surface that allowed for the accumulation of cellulosic species on the modified surface (Carlsson *et al.*, 1998). Embedded fibres, probably wood particles, were also visible on the surface of the fouled membrane. The presence of the fibres on the UF membrane surface indicated that neither DAF nor microstraining was able to effectively remove microfibres from the UF feed water.

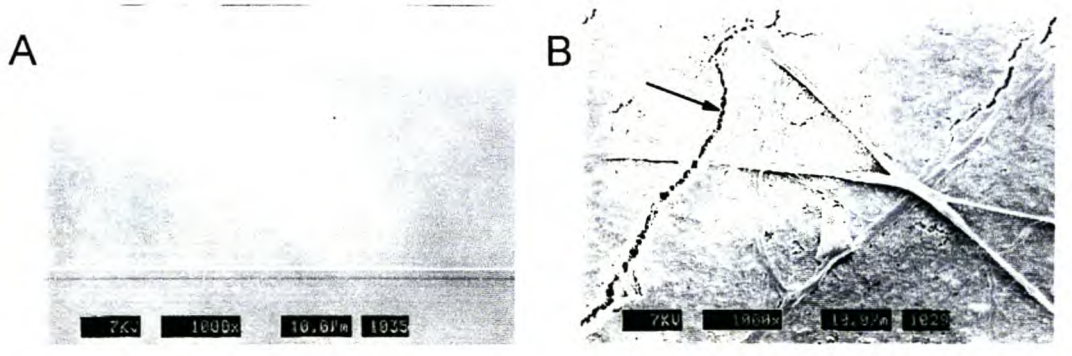


Figure 7.4: SEM micrographs of 40 kDa MMCO (A) unfouled and (B) fouled PES UF membranes at 1 000x magnification.

The crevice in the solid layer (indicated with the arrow in Figure 7.4) developed when the tubular membrane was unfolded during sample preparation.

7.2.3 Discussion

The SEM analyses of the fouled and unfouled membranes show that the microstrainer product still contains a substantial amount of particulate matter. The presence of these particles will effect UF membrane performance adversely and, even if it is too large to enter the membrane pores, will allow for the adsorption and build-up of other foulants present in the effluent.

7.3 CONCLUSIONS

The results obtained from the AFM and SEM experiments may be summarised as follows:

- A clear distinction between fouled and unfouled membranes could be made on the basis of surface roughness analyses with AFM.

- AFM showed significant deposits of foulants on membranes received from the paper mill.
- SEM analyses supported the findings of the AFM experiments showing fibres as prominent components of the fouling layer.

The AFM and SEM findings confirmed the need for a more integrated approach to counter the fouling problem. Various options were considered, applied and evaluated to improve the performance of the UF plant at the mill in Piet Retief. The experiments performed and the results obtained are discussed in Chapter 8.

CHAPTER 8

TEST RIG EXPERIMENTS PERFORMED AT THE PIET RETIEF MONDI KRAFT PAPER MILL

The primary interest of the production team at the UF plant was to produce purified process water at the design flow rate. The task was, however, severely hampered because of the extensive fouling of the UF membranes. In an attempt to solve the fouling problem at the UF plant a joint effort was launched between the University of Stellenbosch, the Water Research Commission (WRC) and personnel at the Mondi Kraft Piet Retief paper mill.

It was decided by the WRC Steering Committee that the research group at the University of Stellenbosch would take a fundamental approach to solving the fouling problem, while the work at the mill would take an incremental improvement approach. The aim was that the progress in each approach would complement the other in search of an effective solution to the fouling problem.

Research at the UF plant was conducted by Mr. Graham Burch and Mr. Victor Sibiya. The urgent need for a solution to the fouling problem demanded that the reasons behind the failure of certain experiments could not be explored in great depth, but that only the more successful experiments be investigated in more detail. The successful experiments were built upon with new ideas to optimise the performance of the UF plant. This was done through discussion and in open forum with experts in the field of membranes, including: Prof. Chris Buckley, Mr. Chris Brouckaert, Mr. John Hunt, Dr. Ed Jacobs, Prof. Pieter Swart as well as the personnel at the Mondi Kraft Piet Retief paper mill: Mr. Graham Burch, Mr. Victor Sibiya, Mr. Bruce Strong and the late Mr. Al Edkins.

This chapter describes the work done at the paper mill in Piet Retief. The tests were conducted on a flat-sheet rig with three cells in series. The following experiments were carried out.

1. The hydrophobicity of the membranes was changed using Pluronics®, surfactants and Osmonics® membranes.
2. The hydrophobicity of dissolved species was reduced by changing the pH and adding surfactants.
3. Foulants were removed in pre-treatment steps using activated carbon, ion exchange and

adsorption.

4. Improved mechanical and chemical cleaning techniques were implemented.

The membranes used during the various experiments were sent for UV-Vis spectral analyses to the Department of Biochemistry, University of Stellenbosch.

8.2 EXPERIMENTAL

Experiments performed at the UF plant of the paper mill

A 3-cell test rig that could accommodate flat-sheet membranes, was provided by the Pollution Research Group, University of Natal, Durban. The test rig was operated at a feed pressure of 600 kPa and the feed temperature was controlled at 40 °C by means of a heating element and temperature controller. The permeate flow through the membranes was measured using a measuring cylinder and stopwatch. The system was operated at zero recovery and the concentrate discarded and not fed back to the feed tank. All experiments were performed under the same operating conditions, unless otherwise stated.

UV-Vis analyses of membrane foulants

The membrane samples obtained from Mondi were incubated in an ammonia solution (7 mL, 0.1% Triton X100®, 1.5% NH_4OH) for 2 h at 40 °C, whereafter the extracts were diluted with analytical grade water and analysed by UV-Vis spectrophotometry. The absorbance of the diluted extracts was measured between 190 and 400 nm as previously described.

Experiment 1

Paper machine effluent emanating from the paper mill was pre-treated in a DAF clarifier to remove colloidal and other suspended solids (fibres) before UF. The normal pre-treatment protocol consisted of neutralising all anionic material in the effluent with Bufloc® 5031, a cationic scavenger, and subsequent flocculation with Bufloc® 590, an anionic flocculant. This protocol was temporarily suspended and replaced with a new pre-treatment program that involved using a cationic coagulant and flocculant. The effectiveness of this program was evaluated on the test rig and the results are presented in Figure 8.1.

Experiment 2

When the membrane plant was first commissioned, the feed to the plant consisted of black liquor washings from the digester and paper machine effluent. The combined effluent feed

had an alkaline pH, compared to the paper machine effluent which had a pH of 4.5. According to plant data, higher product fluxes were obtained with the combined effluent than those obtained with DAF product. It was suggested that the black liquor may have surfactant properties, by virtue of the lignosulphonate present in the liquor (Eykamp, 1995), that may have a cleaning effect on the membranes or retain some of the organics in solution during UF. In an attempt to reproduce these results, weak black liquor was combined with paper machine effluent in a 1:3 ratio and the pH raised to pH 10. The combined effluent was then evaluated on the test rig and the results summarised in Figure 8.2.

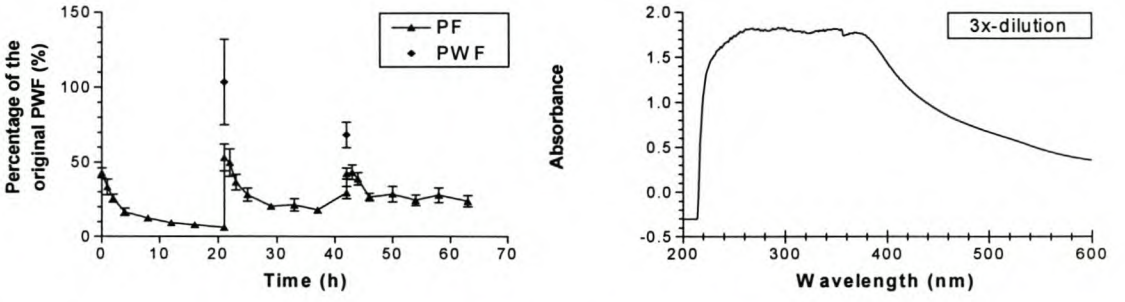


Figure 8.1: PES membranes were fouled with DAF product, pre-treated with a cationic coagulant and flocculant. The PF and PWF obtained through the membranes (left) and UV-Vis analysis performed on the membrane extracts are shown (right).

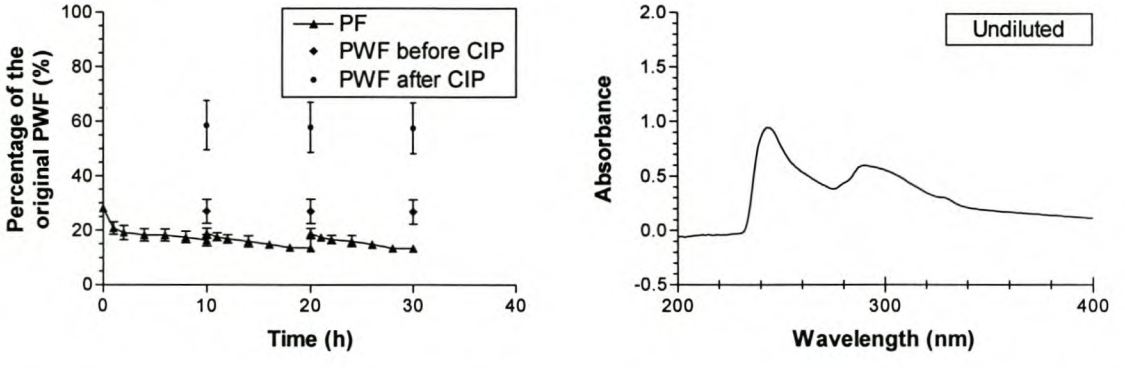


Figure 8.2: PF and PWF determinations (left) for membranes fouled with paper machine effluent, containing black liquor. The absorbance spectrum of the membrane extracts is shown on the right hand side.

Experiment 3

Previously, paper machine effluent was drained into the cascading dams surrounding the

paper mill. The subsequent UF of the dam effluent yielded higher operating fluxes compared to those obtained with DAF product. This experiment involved running dam effluent on the test rig to verify earlier findings (Figure 8.3).

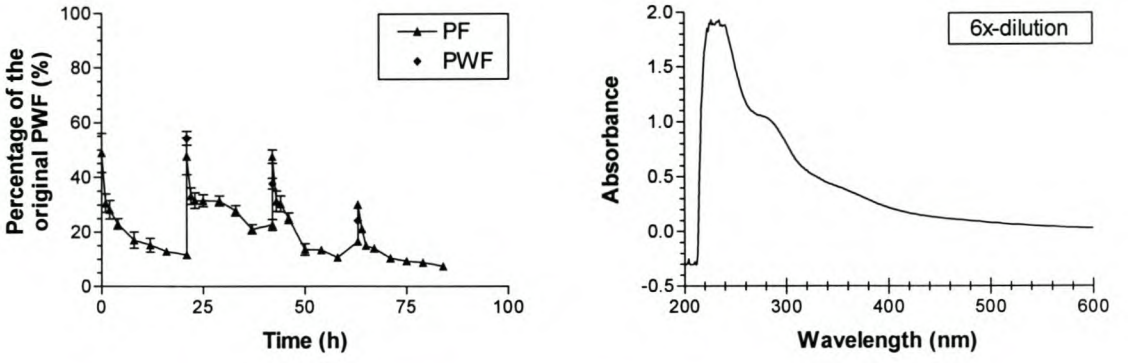


Figure 8.3: PF and PWF determinations for membranes fouled with dam effluent (left) and the UV-Vis analysis (right) of the membrane extracts.

Experiment 4

This experiment involved the evaluation of DAF product, chemically treated with S. A. Paper Chemicals (Pty) Ltd (Sapco) products. The chemical program used bentonite clay as a scavenger for anionic material in conjunction with Magnafloc E10, a non-ionic flocculant that would aid in the precipitation of the suspended particles, to produce a clearer effluent. The results obtained for the experiment are displayed in Figure 8.4.

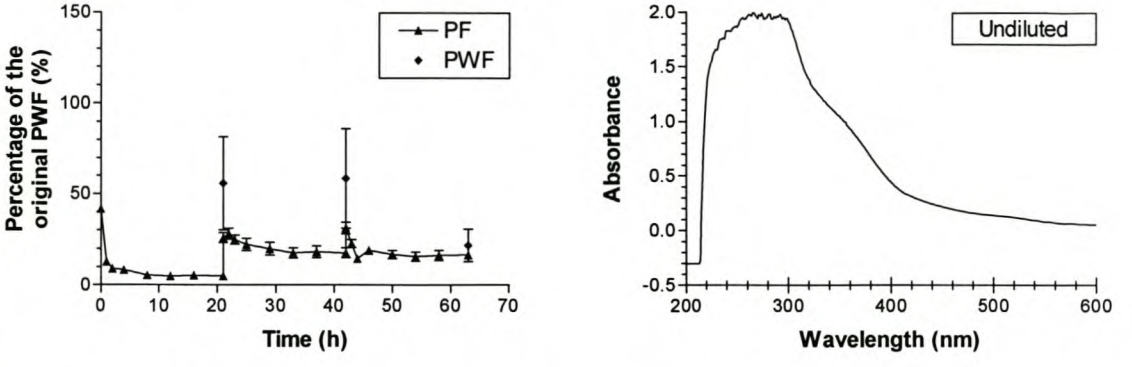


Figure 8.4: Evaluation of membranes fouled with DAF product and subsequently chemically treated with Sapco products (left). A wavelength scan of the membrane extracts is shown on the right.

Experiment 5

Ionisation of the foulants present in the effluent was expected to increase solubility, thereby

reducing the rate of membrane fouling. For this reason the pH of the effluent feed was increased from pH 4.5 to pH 8. A 200 L drum filled with effluent pre-treated to the required pH was used as a feed tank to ensure a constant feed pH of 8. The results obtained for this experiment are presented in Figure 8.5.

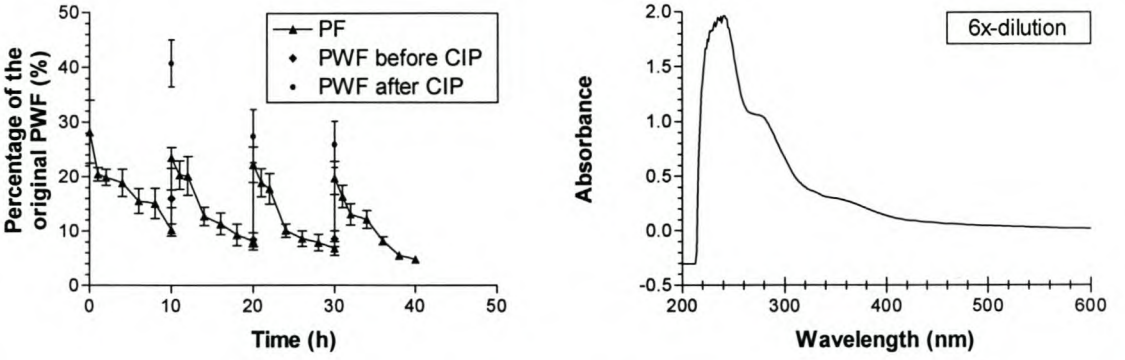


Figure 8.5: Flux measurements (left) obtained for membranes fouled with DAF product (pH 8) and the UV-Vis analysis (right) of the membrane extracts are displayed.

Experiment 6

The idea behind this experiment was the same as for Experiment 5, but the pH of the feed was increased to 10. A higher pH would increase the solubility of the foulants through ionisation, thereby reducing the rate of membrane fouling. The results obtained in the experiment are displayed in Figure 8.6.

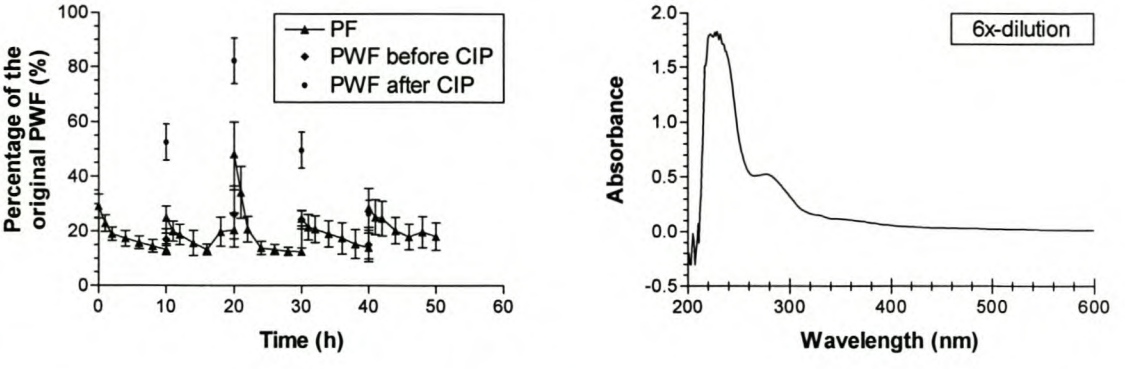


Figure 8.6: PES membranes were fouled with DAF product (pH 10) and evaluated on the basis of their PF and PWF, before and after CIP. UV-Vis analysis of the membrane extracts is shown on the right hand side.

Experiment 7

DAF product was passed through an activated carbon column in an effort to reduce residual

organic material, remaining soluble in the effluent after clarification, that might adsorb onto and foul the UF membranes. The efficiency of the activated carbon column in effluent pre-treatment was evaluated on the test rig and the results are summarised in Figure 8.7.

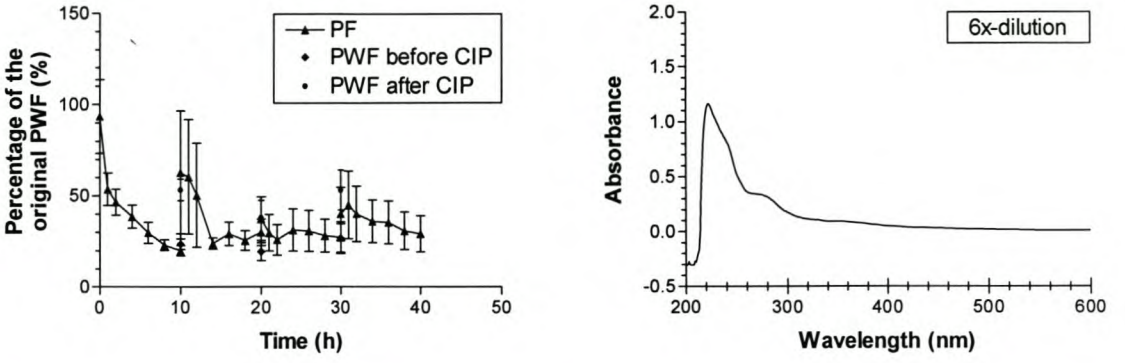


Figure 8.7: Flux measurements of membranes fouled with DAF product, passed through an activated carbon column (left) and an absorbance spectrum of the membrane extracts (right).

Experiment 8

DAF product was passed through an ion exchange column, containing a weak base anion exchange resin, to remove ionised species present in the effluent before running it on the test rig. The ion exchange column is normally used between the UF and RO sections of the membrane plant. The purpose of this exercise was to determine whether the ion exchange column could contribute towards reducing membrane fouling. The data obtained in the experiment are presented in Figure 8.8.

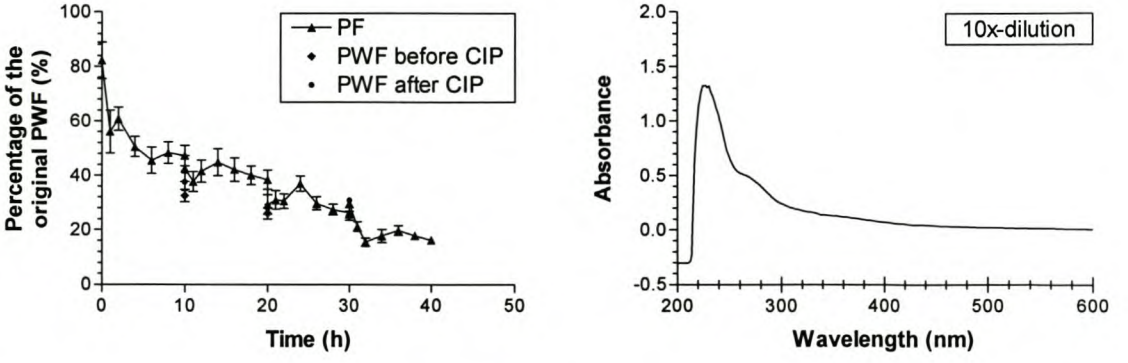


Figure 8.8: Flux measurements (left) of membranes fouled with DAF product, passed through an ion exchange column, and a wavelength scan of the membrane extracts (right) are shown.

Experiment 9

BL® 2085 (wire conditioner), a proprietary chemical supplied by Buckman Laboratories International, is applied to the paper machine wires to prevent fouling by glue-like substances (*"stickies"*), pitch and waxes present in the paper machine backwater. For the purpose of this experiment, BL® 2085 was added to the test rig feed with the aim of modifying the membrane surface to prevent membrane fouling. Figure 8.9 summarises the results obtained in the experiment.

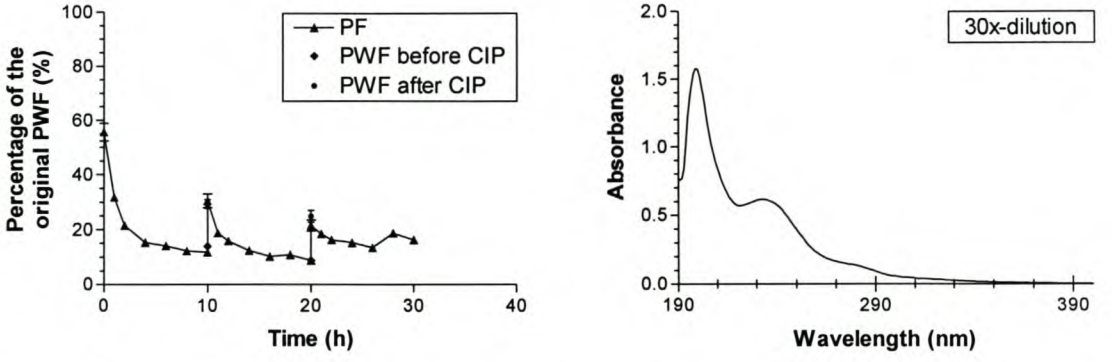


Figure 8.9: Results obtained for PES membranes pre-treated with BL® 2085 (wire conditioner). Flux determinations (left) of the membranes and UV-Vis analysis (right) of the membrane extracts are displayed.

Experiment 10

Busperse® 59LO (pitch dispersent), provided by Buckman Laboratories International, is used to solubilize and remove glue-like substances (*"stickies"*), pitch and waxes from the paper machine surface. Busperse® 59LO was added to the effluent feed (test rig feed) at a concentration of 5 mg/L in an attempt to modify the membrane surface and reduce fouling. The results obtained for the experiment are displayed in Figure 8.10.

Experiment 11

Sodium lignosulphonate, a byproduct of the Kraft cooking process, is the component of black liquor that provides the dispersent properties to the liquor. Commercially obtained pure sodium lignosulphonate (provided by Borregaard) was added to the test rig feed at a concentration of 1% of the feed to disperse the organics responsible for fouling the UF membranes. The effectiveness of the lignosulphonate as a dispersent was evaluated and the results presented in Figure 8.11.

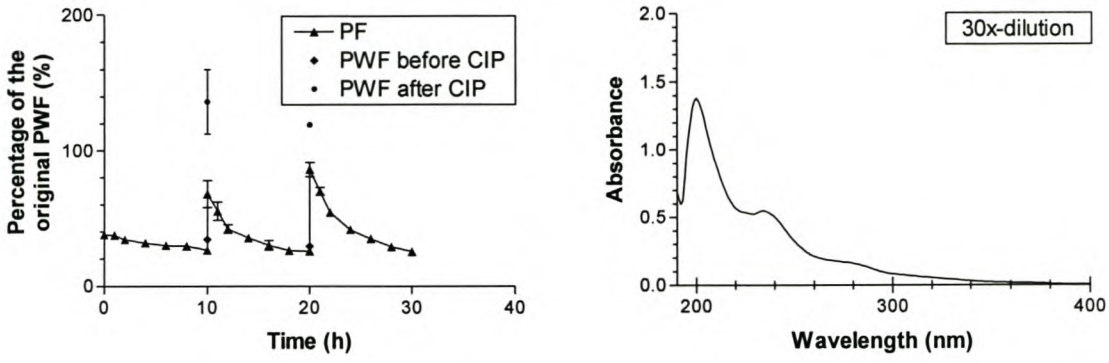


Figure 8.10: Membranes were pre-treated with Busperse® 59LO (pitch dispersent) in an attempt to modify the membrane surface. Results obtained for flux determinations (left) and UV-Vis analysis of the membrane extracts (right) are shown.

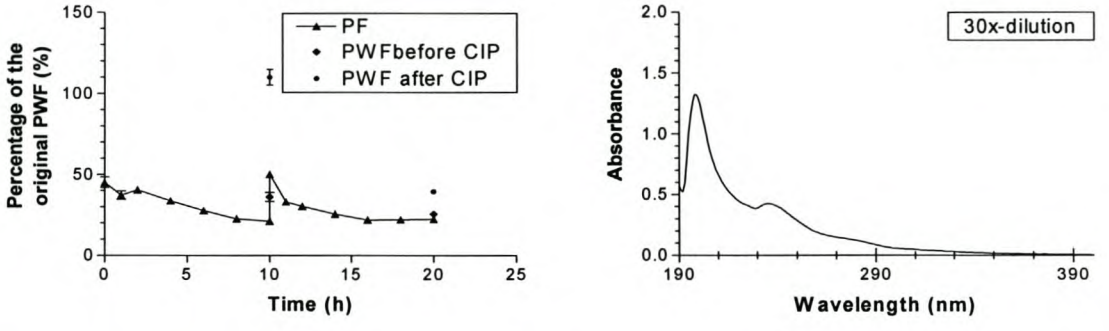


Figure 8.11: The effectiveness of lignosulphonate as a dispersent was evaluated. Flux determinations (right) and UV-Vis analysis of the membrane foulants (left), were performed.

Experiment 12

The chemical treatment program for the DAF clarifier was changed to Bubond® 123 (resin) and Bubond® 127 (PEO), which were provided by Buckman Laboratories International. At the same time, the use of a microstrainer was introduced for the removal of residual fibres from the DAF product. The microstrainer had a woven plastic screen with 30 μm openings. From this experiment onwards, all the feed to the test rig was clarified by means of the Bubond® 123 and Bubond® 127 program and filtered through the microstrainer. Results obtained for the experiment are presented in Figure 8.12.

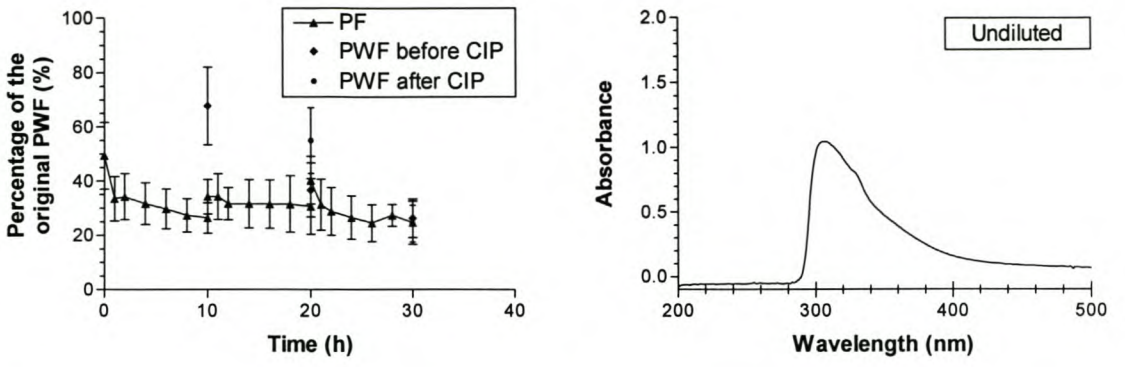


Figure 8.12: PES membranes were fouled with pre-treated microstrainer product. Flux determinations of the membranes (left) and UV-Vis analysis of the membrane extracts (right) were performed.

Experiment 13

The purpose of this experiment was to investigate the mechanical cleaning action of spongeballs on the membrane surface. The flat-sheet membranes were removed every hour, cleaned by wiping the membrane surfaces with a spongeball and replaced. The pH of the effluent feed to the test rig was increased to pH 10. Figure 8.13 summarises the results obtained for the experiment.

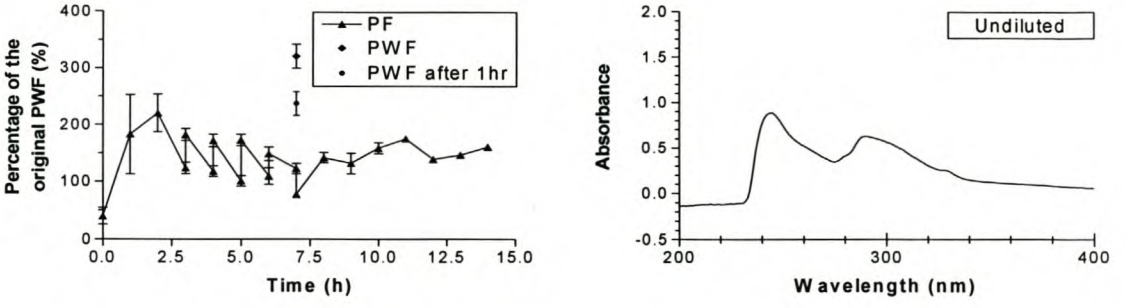


Figure 8.13: The effectiveness of membrane cleaning with spongeballs was evaluated by means of flux determinations (left) and UV-Vis analysis of the membrane foulants (right).

Experiment 14

The use of lignosulphonate as a dispersant, in combination with an elevated feed pH, was investigated on the test rig (see Figure 8.14). The lignosulphonate concentration in the feed was 5%.

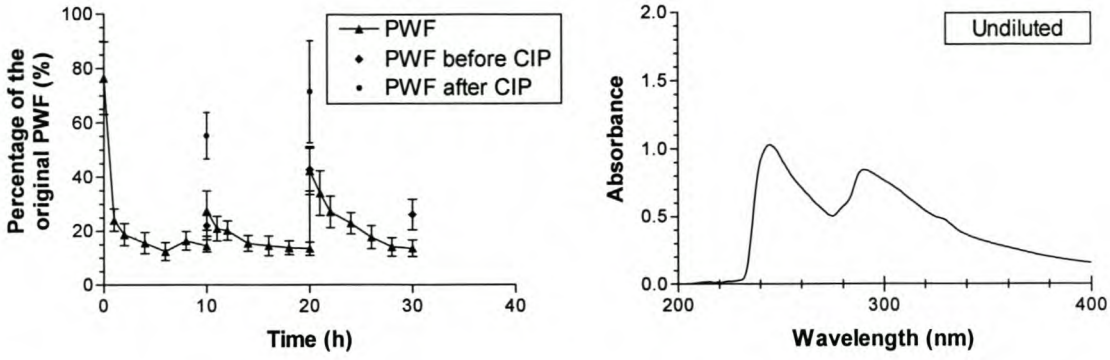


Figure 8.14: The effectiveness of lignosulphonate as a dispersant, in combination with an elevated pH, was examined on the test rig. Results obtained for flux determinations through the membranes (left) and UV-Vis analysis of the membrane foulants (right) are presented.

Experiment 15

Maartens (1998) showed that pre-treatment of the UF membranes with Pluronic® F108, a non-ionic surfactant, significantly reduced foulant adsorption onto the membranes. This surfactant, a tri-block copolymer, consists of one hydrophobic poly(propylene oxide) anchor group, located in the middle of the molecule, and two hydrophilic poly(ethylene oxide) blocks situated on both ends of the molecule. The hydrophobic section of the molecule attaches itself to the hydrophobic membrane surface and orientates the hydrophilic end-groups of the molecule towards the aqueous phase. Discs of flat-sheet membranes were pre-treated in an aqueous 1% Pluronic® F108 solution for 8 h and exposed to pulp and paper effluent on the test rig. Sodium hexametaphosphate was used as the chemical cleaning agent during CIP. The results obtained are displayed in Figure 8.15.

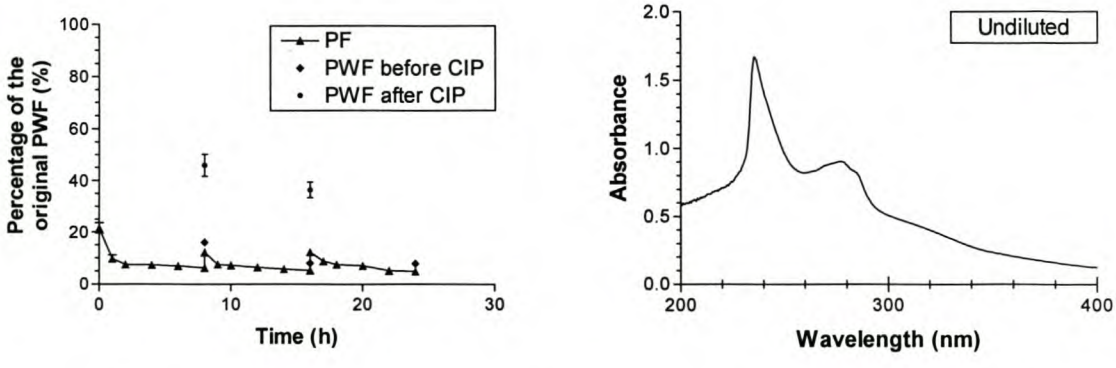


Figure 8.15: The ability of Pluronic® F108 to prevent membrane fouling was evaluated. Results obtained for the flux measurements through pre-treated membranes (left) and UV-Vis analysis of the membrane foulants (right) are presented.

Experiment 16

Samples of a new Osmonics® membrane were used as a replacement for the standard PES membranes. The tubular PES membrane had a molecular mass cut-off (MMCO) of 40 kDa, compared to the two sets of Osmonics® membranes used that had a MMCO of 5 kDa (G-type membrane) and 15 kDa (GH-type membrane), respectively. The Osmonics® membranes are made of PS and were negatively charged. To compensate for the possible reduction in product fluxes that might occur due to the lower MMCO of the Osmonics® membranes, the inlet pressure was increased to 1 MPa. The Osmonics® membrane with the 5 kDa MMCO was used in this experiment at a feed pH of 10. The results for the experiment are summarised in Figure 8.16.

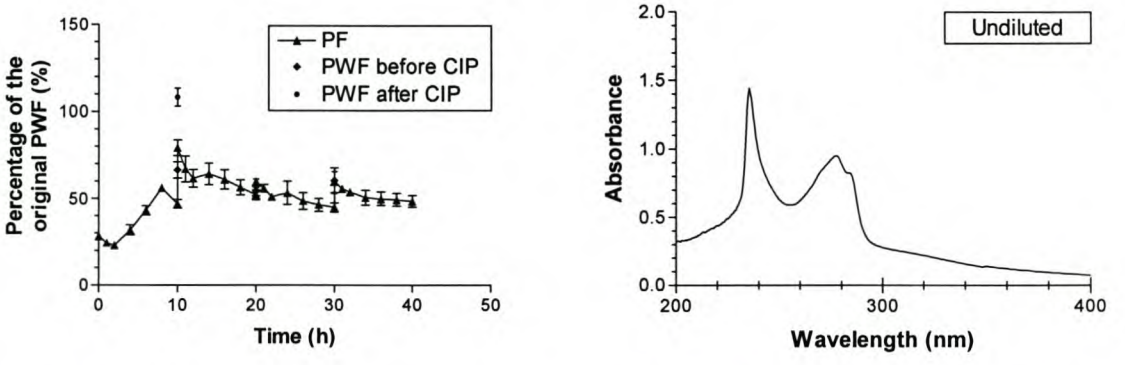


Figure 8.16: An Osmonics membrane, a negatively charged PS membrane, with MMCO of 5 kDa was fouled with microstrainer product (pH 10) at an inlet pressure of 1 MPa. Flux measurements are shown (left) and UV-Vis analysis (right).

Experiment 17

The Osmonics membrane with the 15 kDa MMCO was used in this experiment. The pH of the microstrainer product used as feed was raised to pH 10 and the feed pressure to the test rig was raised to 600 kPa. Figure 8.17 summarises the results of the experiment.

Experiment 18

Swart *et al.* (1999) showed that tubular PES membranes pre-treated and fouled with Pluronic® F108 and microstrainer product, respectively, could effectively be cleaned with a non-ionic surfactant, Triton X100®. Standard PES membranes were soaked in a 1% m/v Pluronic® F108 solution for 8 h and used under standard operating conditions. The membranes were cleaned with 1% v/v Triton X100®. The results of the experiment are displayed in Figure 8.18.

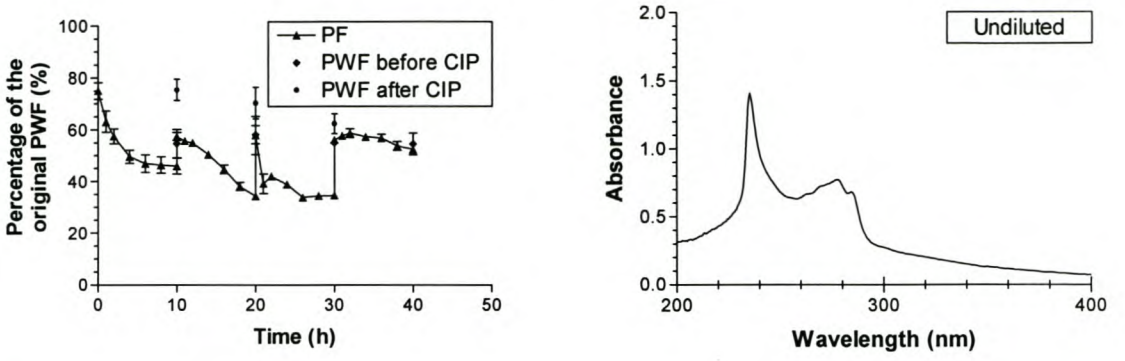


Figure 8.17: Osmonics membranes, MMCO of 15 kDa, were fouled with microstrainer product (pH 10) at an inlet pressure of 600 kPa. Flux measurements (left) and UV-Vis analysis (right).

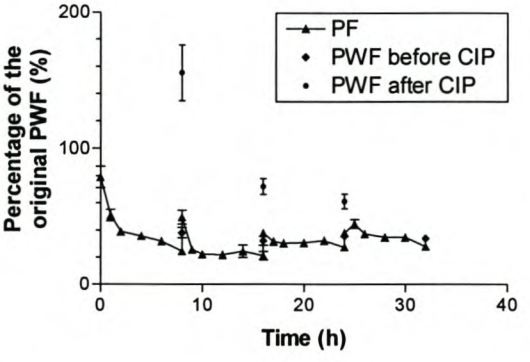


Figure 8.18: Flux performance of PES membranes coated with 1% m/v Pluronic® F108, fouled with microstrainer product and cleaned with 1% v/v Triton X100®.

Experiment 19

This experiment was the same as Experiment 18, but the pH of the microstrainer product as feed increased to pH 10. Figure 8.19 summarises the results obtained for the experiment.

Experiment 20

Osmonics membranes, with a 5 kDa MMCO, were pre-coated in a 1% m/v Pluronic® F108 solution for 3 h before they were tested. The test rig was operated at 1 MPa in conjunction with an elevated effluent pH of 10. Triton X100® (1% v/v) was used as the CIP reagent. The results obtained for the experiment are shown in Figure 8.20.

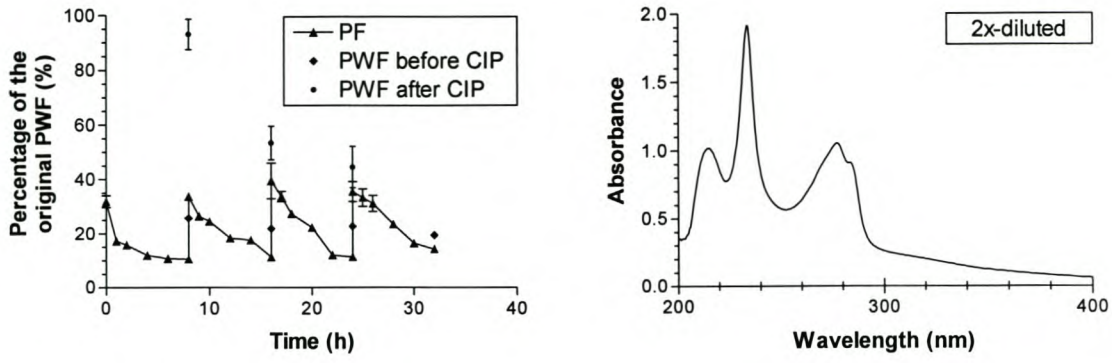


Figure 8.19: A repetition of Experiment 18 performed at an elevated pH of 10. Flux measurements (left) and UV-Vis analysis (right) are shown.

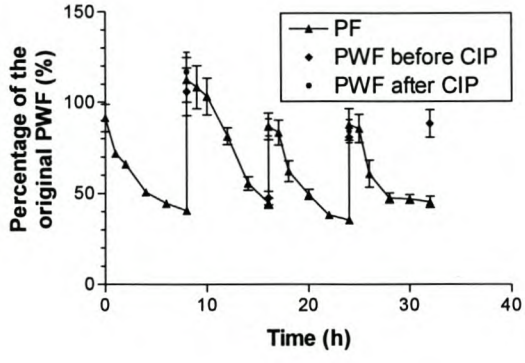


Figure 8.20: Osmonics membranes (MMCO 5 kDa) were pre-coated in a 1% m/v Pluronic® F108 solution and fouled with microstrainer product (pH 10) at an inlet pressure of 1 MPa and cleaned with 1% v/v Triton X100®.

Experiment 21

The experimental conditions and procedures were the same as for Experiment 20 but for this experiment the 15 kDa MMCO Osmonics membrane was used. The results obtained are displayed in Figure 8.21.

Experiment 22

A 100 mg/L Pluronic® F108 [0.01% (m/v)] solution was added to the effluent feed to dynamically coat disks of PES membranes under standard operating conditions. Triton X100® (1% v/v) was used as the CIP reagent. Figure 8.22 summarises the results obtained for the experiment.

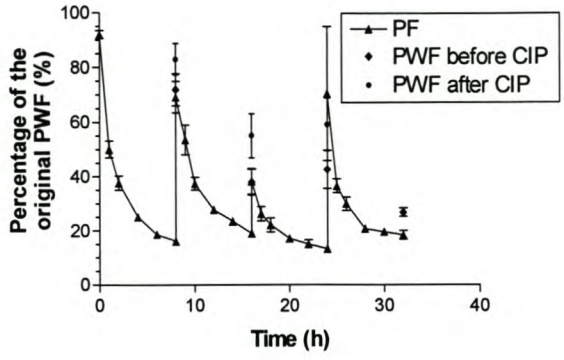


Figure 8.21: Osmonics membrane (MMCO 15 kDa) were operated under the same experimental conditions as discussed in Experiment 20.

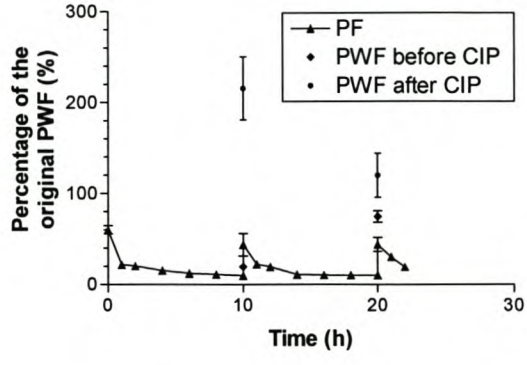


Figure 8.22: Flux performance of PES membranes dynamically coated with a 0.01% m/v Pluronic® F108 solution under standard operating conditions. Triton X100® (1% v/v) was used as a cleaning reagent.

Experiment 23

Dam effluent, at its natural pH, was used as feed to the test rig with 1% v/v Triton X100® as the CIP chemical. The results for the experiment are summarised in Figure 8.23.

Experiment 24

Dam effluent, with an increased pH of 10, was evaluated on the test rig in conjunction with 1% v/v Triton X100® as the CIP chemical. The results obtained for the experiment are displayed in Figure 8.24.

Experiment 25

PES membranes were fouled with microstrainer product, which had passed through a column of membrane staples (short lengths of PS capillaries). Triton X100® (1% v/v) was used as the CIP reagent (Figure 8.25).

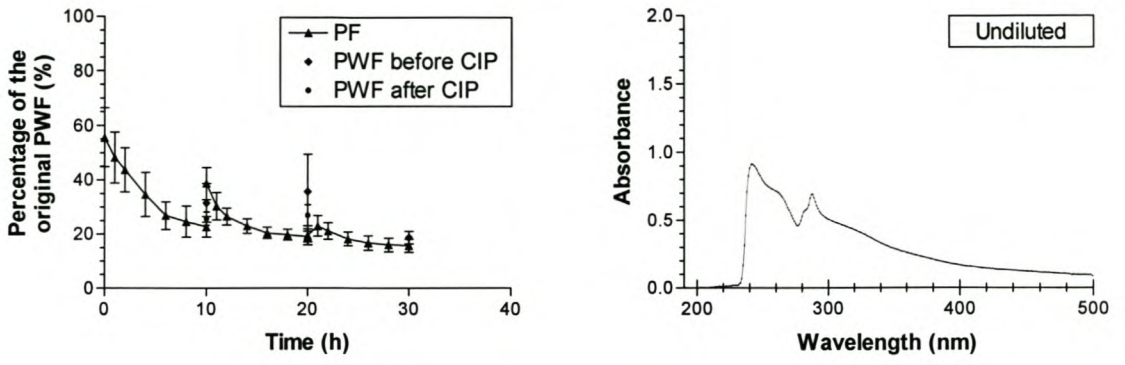


Figure 8.23: PES membranes were fouled with dam effluent (natural pH) and cleaned with 1% v/v Triton X100®. Flux measurements (left) and UV-Vis analysis (right) are shown.

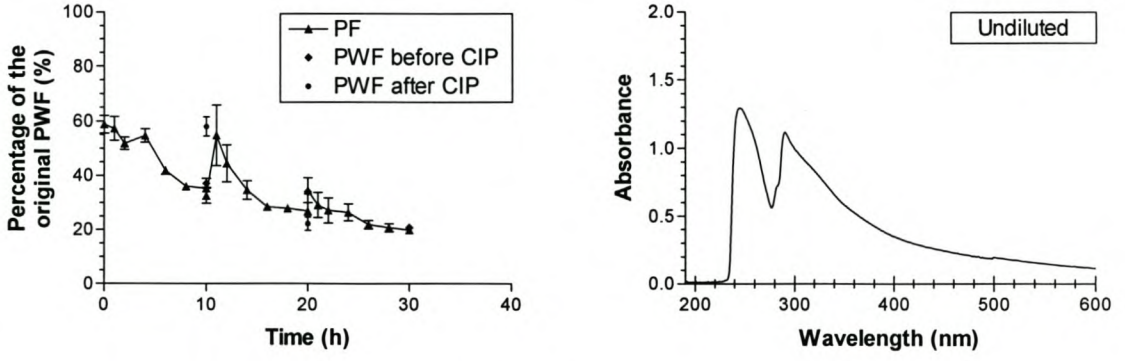


Figure 8.24: PES membranes were fouled with dam effluent (pH 10) and cleaned with 1% v/v Triton X100®. Flux measurements (left) and UV-Vis analysis (right) are shown.

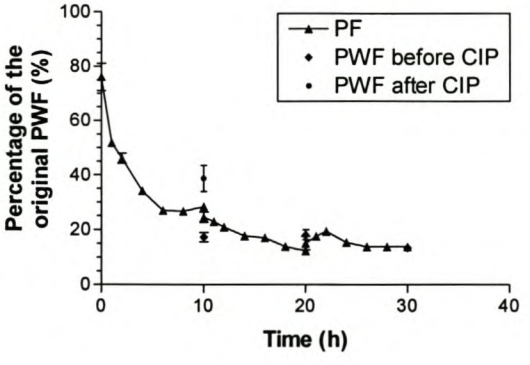


Figure 8.25: Flux measurements obtained for membranes fouled with microstrainer product, which had been passed through a column of membrane staples.

8.2 CONCLUSIONS FROM TEST RIG EXPERIMENTS

The results obtained from the studies are summarised in Figure 8.26. The following overall conclusions can be made from the data obtained from the experiments described in section 8.1.1.

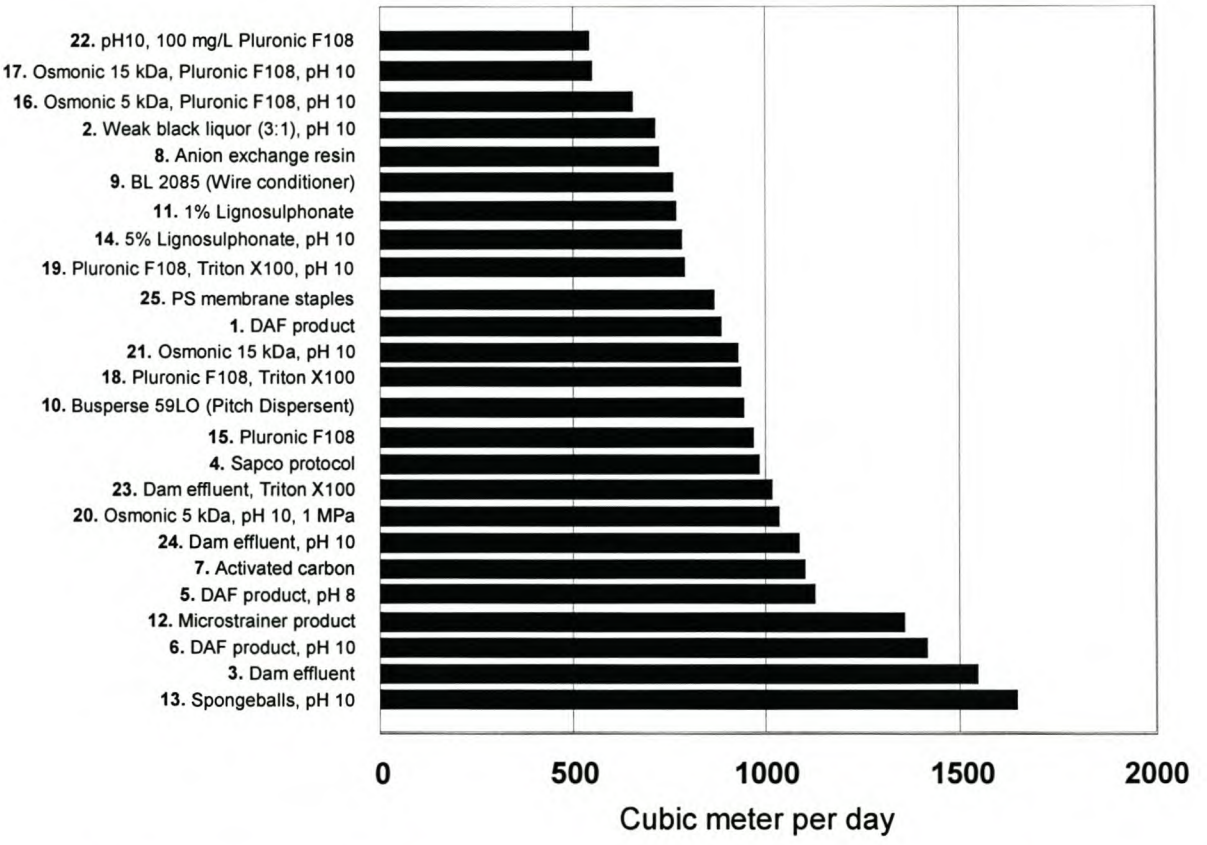


Figure 8.26: Summary of results obtained from experiments (**1-25**) conducted at the paper mill in Piet retief. Results are presented as the integrated permeate flow.

- DAF product had the same fouling tendency regardless of the pre-treatment program being used to promote flocculation and scavenging of suspended solids in the effluent. The microstrainer (30 μm) installed to remove residual fibres had limited success as it did not change the fouling tendency of the DAF product.

- An increase in the pH of the effluent feed to the test rig reduced the rate of membrane fouling. The reduction in the rate of membrane fouling can be attributed to the increased solubility of the foulants, after ionisation of their functional groups, brought about by the increase in pH.

- Membranes used for the filtration of effluent, with added black liquor, showed a significant flux recovery after CIP. Unfortunately, the operating fluxes decreased

considerably during production. Sodium lignosulphonate, a component of black liquor, was thought to be responsible for the lower fluxes. Carlsson *et al.*, 1998 showed that hydrophobic membranes treated with plug screw feed pressate, originating from the sulfite digestion of wood chips, were initially fouled by lignin sulphonates as free acids or salts. Deposition and dehydration of the lignosulphonates on the hydrophobic membrane surface resulted in the formation of an insoluble compact layer, followed by the progressive accumulation of cellulosic species on the modified surface. The recovery in flux after CIP can thus be attributed to the effective hydration and subsequent removal of the lignosulphonates from the hydrophobic membrane surface (Carlsson *et al.*, 1998).

- Attempts to remove foulants from the effluent stream by means of activated carbon, ion exchange resin or PS beads were unsuccessful.
- The use of Triton X100®, a non-ionic surfactant (Chapman *et al.*, 1998), as a CIP reagent in some instances increased the operating flux after CIP to values greater than that of the original clean membrane.
- Negatively charged PS membranes from Osmonics, successfully resisted the formation of a foulant layer on the membrane surface. The 5 kDa MMCO Osmonics membrane was operated successfully for several days without a significant loss in flux, indicating that hydrophilic or negatively charged membranes withstood membrane fouling more effectively than hydrophobic PES membranes, under the same operating conditions. Mechanical cleaning ("wiping") of the PES membrane surface with spongeballs, proved to be one of the most effective and successful methods to control fouling and prevent flux loss.
- Pre-treatment of the PES membranes with Pluronic® F108, a non-ionic surfactant, only marginally reduced membrane fouling. The pattern of the operating flux loss with time, however, remained unchanged.
- High operating fluxes were obtained with the dam effluent. This can be attributed to the very long retention time and favourable anaerobic conditions that allowed for the biodegradation of the organic material and clarification of the dam effluent to very low levels of suspended solids. The flux loss experienced with dam effluent after several CIP sessions was, however, the highest for all the experiments.
- UV-Vis analysis showed that the majority of samples had strong absorbance in the UV

region pointing to the presence of aromatic compounds in the effluent. Lignosulphonate was found to be a major constituent in the various effluent samples (as shown in Section 6.2.2, Figure 6.4). It is, however, interesting to note that the UV-Vis spectra of most of the membrane extracts did not show the absorbance maxima below 210 nm that was seen with the paper machine effluent, DAF and microstrainer products as well as the lignosulphonate (Figures 6.3 and 6.4). This observation indicates that the compounds absorbing at the lower wavelengths (unconjugated olefinic compounds) did not foul the membranes to the same extent as the aromatic substances with absorbance maxima between 230 and 400 nm. Further experimentation is needed to conclusively prove this hypothesis.

CHAPTER 9

GENERAL CONCLUSIONS

Membrane fouling is generally not completely reversible and as the number of filtration cycles increases, the degree of irreversible fouling increases. Chemicals are required to remove adsorbed material from the membrane surface in order to restore the initial flux of the system. Chemical CIP is, however, time consuming and costly in terms of chemical consumption, labour and energy. Chemicals used during CIP often react with the membrane, shortening the membrane life and increasing the frequency of membrane replacement which is a major cost in UF (Kennedy *et al.*, 1998).

To enhance the performance and reduce the operating costs of the UF process, the optimal operating conditions need to be established. In an attempt to reach these objectives the following areas were investigated: (1) the fouling characteristics of the DAF effluent, (2) the influence of flocculants and coagulants on membrane performance, (3) fouling characteristics of the effluent prior to UF, (4) the ability of the DAF clarifier and microstrainer to reduce the fouling potential of the effluent, (5) the change in surface characteristics of the membrane with an increase in foulant deposition, as well as (6) pre-treatment and cleaning (chemical and mechanical) of the PES membranes.

CONCLUSIONS OF THIS STUDY

The conclusions drawn from results obtained for experiments discussed in Chapters 4 to 7 can be summarised as follows:

Unused membranes statically fouled with DAF effluent showed a reduction in PWF. The reduction in PWF was attributed to the adsorption of some of the organic compounds present in the effluent onto the surface of the hydrophobic PES membranes. Pluronic® F108 coated membranes fouled with DAF product yielded a slightly higher PWF than that obtained for unused Pluronic® F108 coated membranes. Coating membranes with Pluronic® F108, however, had no apparent advantage for fouling prevention and productivity enhancement.

Static fouling experiments carried out on the flocculants and coagulants used during the paper-making process in the Kraft mill showed that none of the agents adsorb irreversibly onto the membranes. The results also show that none of the flocculants and coagulants used in the DAF clarifier foul the UF membranes.

Effluent analyses showed that all effluents analysed contained aromatic compounds and unsaturated polymers which could act as potential foulants. The same type of compounds were indicated in all the samples (liquid and membrane) analysed, and lignosulphonate appeared to be the main constituent.

The pH of the solution had a marked effect on the UV-Vis characteristics of the compounds in the effluent with a shift to higher absorbance maxima being induced at higher pH values. These changes can be ascribed to de-ionisation of functional groups (carboxylic and phenolic) on the foulants present in the effluent. Precipitation was observed to occur in effluent samples with elevated pH levels when left undisturbed for 2 h. This increase in turbidity could be attributed to complex-formation between negatively charged foulants and cations present in the effluent.

ICP analyses confirmed the presence of high levels of calcium in the effluent. Complex formation, and a subsequent increase in turbidity, could be enhanced by the addition of calcium and reversed by the addition of EDTA, a chelating agent. These results supported the idea that polymeric substances in the effluent formed large complexes with metal ions at elevated pH. Further GPC analyses of the effluent at different pH and calcium concentrations confirmed conclusions drawn from the UV-Vis data and indicated the formation of high molecular mass complexes at pH 13. The exact molecular mass of these complexes could not be determined by ES-MS because of their poor ionisation ability. From these studies it is apparent that any future cleaning regimes or fouling prevention measures will be more successful if these properties of the effluent are considered.

AFM analyses of unfouled and fouled membranes, showed a distinct difference in the surface roughness of the two samples. Significant deposits of foulants could be observed on membranes received from the mill at Piet Retief. These results were confirmed by SEM analyses which showed fibres as prominent components of the fouling layer, perhaps indicating that a more efficient microstrainer should be used after the DAF clarifier.

A number of experiments were carried out at the Piet Retief mill. These experiments and the results obtained are given in Chapter 8 and conclusions to that part of the study may be summarised as follows:

- The DAF product had the same fouling tendency regardless of the pre-treatment program being used to promote flocculation and scavenging of suspended solids in the effluent.

The 30 μm microstrainer, installed downstream of the DAF unit to remove residual fibres, had limited success as it did not change the fouling tendency of the DAF product. These results are supported by the laboratory experiments carried out in Stellenbosch.

- The UV-Vis analyses of the effluent showed pH-associated changes in characteristics due to ionisation. Increasing the pH of the effluent feed to the UF test rig from 4.5 to 10 reduced the rate of membrane fouling.
- Membranes used for the filtration of effluent, with added black liquor, showed a significant flux recovery after CIP. Unfortunately, the operating fluxes decreased considerably when filtration was resumed. Sodium lignosulphonate, a component of black liquor, was thought to be responsible for the lower fluxes. Carlsson *et al.*, (1998) showed that hydrophobic membranes treated with plug screw feed pressate, originating from the sulphite digestion of wood chips, were initially fouled by lignin sulphonates as free acids or salts. Deposition and dehydration of the sodium lignosulphonates on the hydrophobic membrane surface resulted in the formation of an insoluble compact layer, followed by the progressive accumulation of cellulosic species on the modified surface. The recovery in flux after CIP can thus be attributed to the effective hydration and subsequent emulsification of the lignosulphonates from the hydrophobic membrane surface (Carlsson *et al.*, 1998). Attempts to remove foulants from the effluent stream through adsorption by means of activated carbon, anion exchange resin or PS beads were unsuccessful.
- The use of Triton X100® as a CIP reagent in some instances increased the operating flux after CIP to values higher than that of the original membrane.
- Membranes from Osmonics (negatively charged PS membranes) successfully resisted the formation of a foulant layer on the membrane surface. The 5 kDa MMCO Osmonics membrane was operated successfully for several days without a significant loss in flux, indicating that hydrophilic or negatively charged membranes withstood membrane fouling more effectively than hydrophobic PES membranes under the same operating conditions.
- Mechanical cleaning of the PES membrane surface with spongeballs proved to be one of the most effective and successful methods to prevent flux loss caused by fouling.
- Pre-treatment of the PES membranes with Pluronic® F108, a non-ionic surfactant, only marginally reduced membrane fouling. The pattern of the operating flux loss with time,

however, remained unchanged.

- High operating fluxes were obtained with effluent taken from the cascading dams. This can be attributed to the very long retention time and favourable anaerobic conditions that allowed for the partial biodegradation of the organic material and complete clarification of the dam effluent to very low levels of suspended solids. The flux loss experienced with dam effluent after several CIP sessions was, however, the highest of all the experiments. It was found that the dam effluent contained reduced sulphur compounds that could not easily be removed from the membranes.
- UV-Vis analysis provided very little information on the chemical composition of the foulants present in the effluent. The majority of the samples analysed showed absorbance in the UV region, indicating the presence of aromatic compounds in the effluent. Lignosulphonate was found to be a major constituent in the various effluent samples. It is, however, interesting to note that the UV-Vis spectra of most of the membrane extracts did not show the absorbance maxima below 210 nm that was seen for the paper machine effluent, DAF and microstrainer products as well as the lignosulphonate. This observation indicates that the compounds absorbing at the lower wavelengths (unconjugated olefinic compounds) did not foul the membranes to the same extent as the aromatic substances with absorbance maxima between 230 nm and 400 nm.

Recommendations

From the results obtained in laboratory studies as well as work performed on the test rig at the Piet Retief paper mill the following recommendations for future research can be put forward:

- Precipitation at pH values greater than 10 resulted in the clarification of the effluent and consideration could be given to conditioning the effluent at an alkaline pH for a period before UF. Chelating agents can be added to the DAF clarifier to remove any divalent metal ions, e. g. Ca^{2+}, which promote membrane fouling.
- Elevation of the pH of the UF feed promotes complex formation between the divalent metal ions and the breakdown products in the effluent. This will result in the precipitation of the complexes and subsequent fouling of the UF membranes. In this way Ca^{2+} is used to promote flocculation of the negatively charged compounds in the effluent. The fouled membranes can be cleaned with spongeballs to effectively remove the foulants from the membranes. Through this exercise the Ca^{2+} content in the effluent can be

reduced considerably, which also reduces the possibility of scaling in the RO membranes caused by calcium oxalate. (This protocol is currently in use at the UF plant at the Piet Retief paper mill and contributes considerably to a reduction in the organic load in the effluent and scale formation in the RO membranes.)

- The use of an anionic surfactant as a membrane pre-coat to hydrophilise the membranes should be investigated.
- The use of a microstrainer with smaller apertures to remove any residual fibres from the DAF product, should be considered.

From this study it was concluded that the coagulants and flocculants used in the pre-treatment of the paper machine effluent did not contribute to the fouling of the UF membranes. Characterisation of various effluent samples indicated the presence of a high Ca^{2+} content which formed complexes with the ionised sulphonated compounds present in the effluent, at higher pH values. This, combined with other findings for example the effective cleaning of the UF membranes with spongeballs, has been shown to be very useful in optimising the current operating conditions at the UF plant at the Piet Retief paper mill.

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