CLEANING AND PRE-TREATMENT TECHNIQUES FOR ULTRAFILTLRATION MEMBRANES FOULED BY PULP AND PAPER EFFLUENT

Final Report

to the
Water Research Commission

by

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WRC Report No. 1035/1/01
ISBN 1-86845-839-3

JANUARY 2003

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EXECUTIVE SUMMARY

1.1 INTRODUCTION

The development of inert durable membranes over the past three decades saw pressure-driven processes, like microfiltration, ultrafiltration and reverse osmosis, develop into viable options for the treatment of large volumes of industrial effluents from various origin. The chemical stability and physical properties of membrane polymers, such as poly(ethersulphone) PES, made the design and manufacture of membrane plants, capable of clarifying extremely reactive and "hostile" effluents, possible. The most challenging obstacle in the way of full implementation of modern pressure-driven filtration processes, however, is the fouling phenomenon, an inherent consequence of any membrane filtration process used for the clarification of industrial effluent or polluted water.

The diversity of the effluents and water being treated by pressure-driven filtration processes rules out any single method as a total solution to membrane fouling. This problem is usually addressed by a combination of effluent pre-treatment and differential flow techniques in conjunction with chemical and physical cleaning of the fouled membranes. For the development of the most effective physical and chemical membrane cleaning methods, information on the physical and chemical properties of membrane foulants is important. During the past decade the membrane research group at the University of Stellenbosch, comprising the Institute for Polymer Science and the Department of Biochemistry, focussed on foulant characterisation and foulant removal from UF membranes used in industrial effluent treatment.

1.2 OBJECTIVES

In a previous WRC project (WRC no. 660) methods for effluent and foulant characterisation, membrane cleaning and membrane pre-treatment techniques were developed and successfully applied to membranes fouled by pulp and paper effluent under laboratory-scale conditions. This effluent came from cascading dams at the Mondi Kraft paper mill at Piet Retief, which were part of the effluent pre-treatment process prior to ultrafiltration. The reason for the investigation into this specific effluent was the deterioration in the performance of the membrane plant due to extensive fouling. During these studies spectrophotometric analyses showed that pulp and paper effluent, from the Mondi Kraft mill, contained unsaturated aromatic compounds and that ultraviolet-visible spectroscopy (UV-Vis spectroscopy) could

be used to estimate the concentration of these potential foulants in the effluent. Combining pure-water flux (PWF) measurements and phenolic staining techniques with UV-Vis analyses, foulant adsorption onto PES ultrafiltration membranes was studied and partial identification of foulants was possible. Pre-coating of the membranes with Pluronic® F108 resulted in a significant reduction in foulant adsorption over a 90 h filtration period under cross-flow conditions, and the flux through fouled membranes was successfully restored by cleaning with the non-ionic detergent Triton X100® and sponge balls. To build on and extend the previous work, the initial aims of this project were the following:

1. Development of a pilot scale filtration unit at Weir Envig (Pty) Ltd. (Paarl).
2. Characterisation of dam effluent to confirm previous results.
3. Implement membrane cleaning techniques developed under laboratory conditions at the pilot plant.
4. Evaluate cleaning techniques in terms of cleaning efficiency and cost effectiveness.
5. Implement non-covalent membrane pre-treatment techniques on a pilot scale.
6. Evaluate the feasibility of membrane pre-treatment techniques on the basis of cleaning frequency and cost effectivity.
7. Transfer technology to the industry for large-scale implementation.

As mentioned earlier, the performance of the membrane plant at Piet Retief deteriorated after an initial period of normal operation. This deterioration was subsequently 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 sulphur production. The "*sulphur problem*" prompted by-passing of the dams and feeding of paper machine effluent directly from the pulp and paper factory to the ultrafiltration plant. This change in feed composition resulted in a rapid and total blockage of the membranes due to the presence of fibres in the effluent. To overcome this problem the installation of a dissolved air flotation (DAF) clarifier was commissioned. Lower operating fluxes were, however, attained with the clarified paper machine effluent (DAF product) than with the dam effluent. This prompted an investigation into a decrease in the operating fluxes.

In addition to the installation of the DAF clarifier, changes in the paper production process, the mill, and the pre-treatment regimes implemented before flotation, also altered the

composition of the UF-feed. These changes to the UF-feed necessitated a shift in emphasis from the goals originally set for the current project. It was decided by the Steering Committee that the group at Stellenbosch would take a more fundamental approach to solving the fouling problem, while the work at the mill would take a incremental improvement approach and that progress in each approach could complement the other in search of an effective solution to the fouling problem. The altered aims for the Stellenbosch group were:

1. Characterisation of the DAF effluent and foulants on PES membranes using UV-Vis spectroscopy, gel permeation chromatography (GPC), inductively coupled plasma (ICP), atomic force microscopy (AFM) and scanning electron microscopy (SEM).
2. Static fouling of PES membranes with flocculants and coagulants used in the pre-treatment of paper machine effluent prior to DAF-clarification, to determine their respective roles in fouling.
3. Characterisation of membrane foulants on membranes from a flat-sheet test rig that was used to test different approaches to fouling reduction at the mill.

1.3 DISCUSSION

The laboratory analyses, carried out at the University of Stellenbosch, were designed to answer the following questions:

1. What are the fouling characteristics of the DAF effluent?
2. What is the influence of flocculants and coagulants, added to the effluent to enhance the DAF process, on membrane performance?
3. What are the most obvious fouling characteristics of the effluent prior to UF, and do the DAF clarifier and microstrainer add to the fouling potential of the effluent?
4. How is the character of the membrane surface influenced by foulant deposition?

These studies, and the results obtained, are given in **Chapters 2** to **5** of this report. The conclusions drawn from these results 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 the organic compounds present in the effluent to the surface of the hydrophobic PES membranes. Pluronic® F108 coated

membranes fouled with DAF product yielded a slightly higher PWF compared to 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 papermaking process in the Kraft mill showed that none of the agents adsorb irreversibly onto the membranes. The results also showed that none of the flocculants and coagulants used in the DAF clarifier fouled 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 elevated pH. These changes can be 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 hours. 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 the chelating agent. These results supported the idea that polymeric substances in the effluent complexed 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. 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 fibers as prominent components of the fouling layer. Indicating that a more efficient microstrainer should be used after the DAF clarifier.

A large number of experiments were carried out at the Piet Retief mill. These experiments

and the results obtained are given in **Chapter 6** and conclusions to this 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 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 character due to ionisation. Increasing the pH of the effluent feed to the 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 cleaning in place (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 (PSFP), 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 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 X-100®, a non-ionic surfactant (Wilbert *et al.*, 1998), as a CIP reagent in some instances increased the operating flux after CIP to values higher than that of the original membrane.
- Osmonics membranes, negatively charged polysulphone membranes, successfully resisted the formation of a foulant layer on the membrane surface. The 5 kDa molecular mass cut-off (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 the dam effluent. 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 for 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 that 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. To prove this hypothesis conclusively, however, further extensive experimentation is needed.

1.4 RECOMMENDATIONS

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

As elevation of the pH of the effluent feed to the UF plant reduced the rate and degree of membrane fouling considerably. Future operations should be at pH 10. Precipitation at elevated pH values greater than 10 resulted in the clarification of the effluent and

consideration could be given to the inclusion of an alkaline pH 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.

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

LIST OF FIGURES

Abbreviations

AFM	**atomic force microscopy**
CIP	**cleaning in process**
Da	**daltons**
DAF	**dissolved air flotation**
EDTA	**ethylene diamine tetra-acetic disodium salt**
GPC	**gel permeation chromatography**
HPLC	**high performance liquid chromatography**
ICP	**inductively coupled plasma**
$L/m^2.h$	**litres per square meter per hour**
MM_{av}	**molecular mass averages**
MMCO	**molecular mass cut-off**
MM_d	**molecular mass distribution**
NTU	**nephelometric turbidity unit**
PEO	**polyethylene oxide**
PES	**poly(ethersulphone)**
PF	**product flux**
PS	**polysulphone**
PWF	**pure water flux**
RO	**reverse osmosis**
SEM	**scanning electron microscopy**
UF	**ultrafiltration**
UV-Vis	**ultraviolet-visible spectroscopy**

REPORT ON CAPACITY BUILDING

All of the work done in the Biochemistry Department at the University of Stellenbosch, was carried by Mr. Garth Domingo who is also an M.Sc. student. Mr. Domingo, who is from a previously disadvantaged community, was not only exposed to research at the bench during this project but also had the opportunity to interact closely with industry. He acquired additional skills such as report writing, verbal communication and liaison with industry. I believe that this WRC project offered Mr. Domingo the unique opportunity to gain insight into the academic as well as the applied facets of research and this experience should be of great value to him in his future careers. In addition to Mr. Domingo, a former employee of the ML Sultan Technikon in Durban also worked on related aspects of this project.

TECHNOLOGY TRANSFER

As mentioned in the report this project was done in very close collaboration with the paper mill at Piet Retief. The fouling problem, as far as the UF-plant goes, has been largely solved by incorporation of sponge balls in the cleaning regime. In this sense technology transfer took place during the course of the project.

For future technology transfer, the implementation of Ca^{2+} removing suspended solids before UF should be considered.

CHAPTER 1

INTRODUCTION AND OBJECTIVES OF THIS STUDY

The Piet Retief Mondi Kraft paper mill (The Mill) produces effluent with a potential biological impact (Figure 1.1). Currently this effluent is disposed of 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 must therefore be found to reduce wastewater discharge as a step towards the implementation of mill effluent closure. 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 ultrafiltration (UF) (Dorica *et al.*, 1986; Jönsson, 1987; Zaidi *et al.*, 1992).

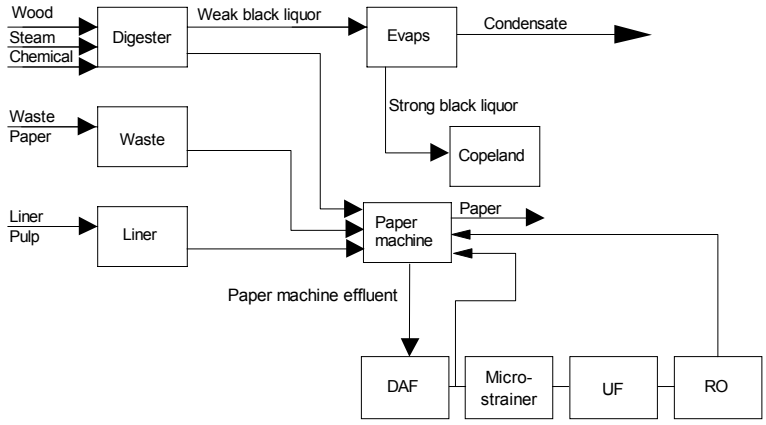


Figure 1.1. Flow diagram of The Mill illustrating mill effluent closure (DAF: dissolved air flotation, RO: reverse osmosis).

Treatment of pulp and paper effluent (PPE) 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 Mondi Kraft paper mill at Piet Retief 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 $L/m^2.h$ 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 mill to address the fouling problem and increase the efficiency of the UF plant.

1.1 PROCESS DESCRIPTION AND ORIGIN OF EFFLUENT

The Mondi Kraft Piet Retief integrated pulps 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 dissolved air flotation (DAF) clarifier before ultrafiltration.

1.1.1 Wood supply

Wood from pine and gum trees, is used in the production of paper. The former is obtained from sawmills in the surrounding area and occasionally chipped at the mill. The latter are supplied as whole logs, which are debarked 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 monitor the chip size and remove dirt, bark and metal pieces. Thereafter, the pine and gum chips are combined in a 1:1 ratio before transportation to the digester.

1.1.2 Digester

The wood chips are cooked in a continuous vapour phase digester at 175ºC in a mixture of sodium sulphite (Na_2SO_3), sodium carbonate (Na_2CO_3) [10%] and anthraquinone as a catalyst. A proportion of the lignin in the wood is split and converted to lignosulphonate. Under neutral sulphite pulping conditions the lignin is "softened" rather than dissolved to produce a high yield pulp (Helm, 1997)[1]. The yield target at the 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"

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

(pyrolyzed) in the Copeland reactor where combustion of the organic compounds takes place 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. The "dried" pulp is stored on noodle piles.

1.1.3 Waste plant

Waste paper, mainly cardboard boxes made from Kraft linerboard, is purchased and recycled at the 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 (COD) of the effluent.

1.1.4 Noodle/Baled pulp

Kraft pulp, obtained from the 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).

1.1.5 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 "Boxliner 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. Broken, trimmed edges of the paper, from the paper machine, are returned to the bottom liner and can supply up to 5% of the bottom liner.

1.1.6 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 entered into a press section where pressure nips and felts are used to press water from the sheet. The sheet then enters steam heated drying cylinders to remove any remaining moisture.

1.1.7 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 collection of fines and trash as well as to retain "size", a water repelling agent which makes the paper water resistant, in the sheet. 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.

1.1.8 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 makedown 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.

1.1.9 Membrane plant

Paper machine effluent is clarified by a DAF clarifier and polished by a 30 μm micro-strainer before UF with PES membranes. The tubular membranes (12.7 mm internal diameter) are encased in modules of 19 parallel flow tubes per module as shown in (Figure 1.2). 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 40ºC. The system is operated in a feed and bleed mode at 92%

recovery.

Figure 1.2. UF membrane plant in the Mondi Kraft paper mill at Piet Retief.

1.2 OBJECTIVES

In the original plant design the paper machine effluent from the paper machine was pumped into a series of 15 cascading dams. 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 an optimal depth of 1,2 m to allow for effective evaporation. With the implementation of the UF plant, paper machine effluent directly from the paper machine 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 most suitable. 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 would allow for the 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 membrane 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. The "*sulphur problem*" prompted the feeding of paper machine effluent directly into the UF plant. This change in feed resulted in a rapid and total blockage of the membranes due to the presence of fibres in the effluent. To overcome this problem a DAF clarifier was installed. Lower operating fluxes were, however, attained with the clarified paper machine effluent (DAF

product). This prompted an investigation into the sharp decrease in the operating fluxes.

In a previous WRC project (no. 660), the University of Stellenbosch research team investigated new methods to clean UF membranes used in the pulp and paper industry. Dam effluent that was used as feed at the time, was also characterised. The conclusions of that study were:

1. UV-absorbance analysis of pulp and paper effluent indicated the presence of unsaturated aromatic compounds in the effluent.
2. Pure-water flux (PWF) measurements, in combination with a phenolic-specific staining method, were successfully used to measure foulant adsorption and to identify specific foulants adsorbed onto the membranes.
3. Pre-coating polysulphone (PS) membranes with Pluronic® F108 resulted in almost no foulant adsorption over a 90 h filtration period under cross-flow conditions.
4. The flux through fouled membranes was successfully restored by cleaning with Triton® X100 (a non-ionic detergent) and sponge balls.

The initial aims of this project were to build on, and continue the work previously done. The following goals were set:

1. development of a pilot-scale filtration unit at Weir Envig (Pty) Ltd. (Paarl);
2. characterisation of dam effluent to confirm previously obtained results;
3. implementation of membrane cleaning techniques developed under laboratory conditions at the pilot plant;
4. evaluation of cleaning techniques in terms of cleaning efficiency and cost effectiveness;
5. implementation of non-covalent membrane pre-treatment techniques on a pilot scale;
6. evaluation of membrane pre-treatment techniques on the basis of its cleaning frequency and cost effectivity; and
7. transfer of the technology to the industry for large-scale implementation.

With the implementation of the DAF clarifier, dam effluent was no longer required as feed to the UF plant and was subsequently replaced with DAF product. The operating fluxes for DAF product, however, unexpectedly turned out to be substantially lower than that attained

with dam effluent. In addition, changes in the paper production process, the mill, and the pre-treatment regimes implemented before DAF, altered the composition of the UF feed. These changes to the UF feed necessitated a shift in emphasis and a change in the goals originally set for the current project. The Steering Committee decided that the group at Stellenbosch would take a fundamental approach to solving the fouling problem while the work at The Mill would take a incremental improvement approach. Progress in each approach had to complement the other for an effective solution to the fouling problem. The altered aims of the Stellenbosch group were:

1. characterisation of the DAF effluent and foulants on PES membranes using ultraviolet-visible (UV-Vis) spectroscopy, gel permeation chromatography (GPC), inductively coupled plasma (ICP), atomic force microscopy (AFM) and scanning electron microscopy (SEM);
2. static fouling of PES with flocculants and coagulants used in the pre-treatment of paper machine effluent prior to DAF-clarification, to determine their role in fouling; and
3. characterisation of membrane foulants on membranes from a flat-sheet test rig that was used to test different approaches to fouling reduction at the mill.

CHAPTER 2

STATIC FOULING OF FLAT-SHEET MEMBRANES WITH DAF EFFLUENT

As mentioned in **Chapter 1**, The Mill recently installed a dissolved air flotation (DAF) unit. One of the functions of the DAF clarifier was to remove suspended solids present in the excess backwater coming from the paper machine. The clarified backwater is returned to the paper machine where it is used as shower water. The DAF clarifier also provides the UF unit with clarified feed for additional purification. The UF purified water is forwarded to specific sections at the mill for further use. This advanced form of paper mill wastewater treatment has become a necessity when considering the stringent regulations governing the protection of receiving waters (Möbius and Cordes-Tolle, 1994[a]; Möbius and Cordes-Tolle, 1994[b]). In Southern Africa, DAF also plays a pivotal role in the reclamation of sewage effluents, sludge thickening, treatment of eutrophic waters and various industrial effluents (Offringa, 1995). The objective of the static fouling experiments was twofold: (1) to evaluate the change in the pure-water flux (PWF) before and after fouling and (2) to establish whether pre-treatment with Pluronic® F108, a non-ionic surfactant, could reduce long-term membrane fouling. Maartens *et al.* (1996) showed that results obtained from static fouling experiments can be compared to results from dynamic fouling experiments.

2.1 EXPERIMENTAL

Uncoated and Pluronic® F108 pre-treated PES membranes were statically fouled with DAF product (clarified effluent), provided by The Mill.

2.1.1 Materials and methods

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 stripes were placed in beakers with 600 mL of 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 of 20 ± 0.2 ºC. 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.

2.1.2 Results

The values presented in Figure 2.1 are the arithmetic mean and the standard deviation, for three determinations. The results displayed show a 21% reduction in flux after static fouling of the uncoated PES membranes with DAF product. Pre-treatment of the unmodified PES membranes with the hydrophilic 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.

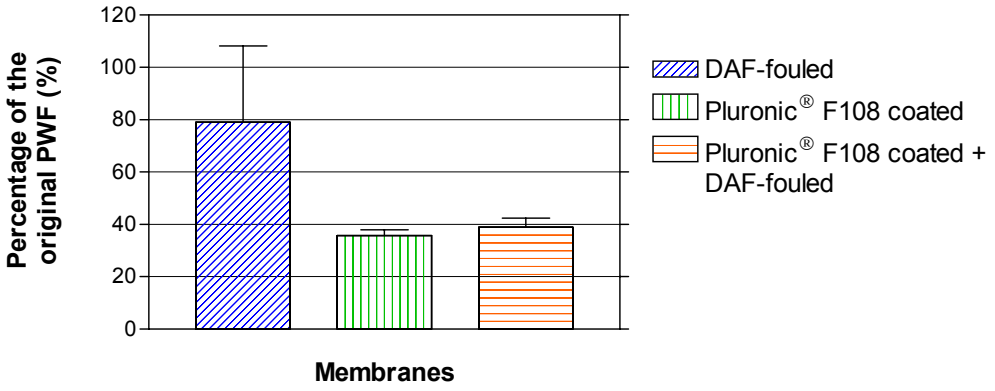


Figure 2.1: Changes in the PWF values, obtained with uncoated and Pluronic® F108 pre-coated membranes, fouled in DAF product.

2.2 PRE-TREATMENT WITH VARIOUS SURFACTANTS

In addition to Pluronic® F108, several other surfactants were evaluated to establish to what extent they could improve the surface character of the UF membranes. This was done to reduce membrane fouling and enhance the flux during the UF of paper mill effluent. The surfactants selected varied with regard to their PEO chain length, the hydrophilic/lipophilic block length ratio and molecular mass. The following block copolymers, shown in Table 1, where chosen for the investigation:

Table 1: Range of block copolymers chosen for the investigation

SURFACTANT	AVE MM[1]	HLB[2]	Physical Form	Solubility in H_2O	AGR[3] (mg/L)
Tetronic - 701	3600	3	Liquid	Insoluble	
Tetronic - 704	5500	15	Liquid	>10%	
Pluronic - L35	1900	19	Liquid	>10%	2000-100000
Pluronic - F38	4700	31	Solid	>10%	
Pluronic - F68	8400	29	Solid	>10%	
Pluronic - F77	6600	25	Solid	>10%	
Pluronic - F87	7700	24	Solid	>10%	
Pluronic - F88	11400	28	Solid	>10%	
Pluronic - F98	13000	28	Solid	>10%	
Pluronic - P103	4950	9	Paste	>10%	50-1000
Pluronic - F108	14600	27	Solid	>10%	400-50 000

[1] Average molecular mass [2] Hydrophilic/lipophilic balance [3] Aggregation concentration range

Tetronic® surfactants are tetra-functional block copolymers, as opposed to the Pluronic® surfactants which are difunctional block copolymers. The amine moiety in Tetronic surfactants provides a slightly cationic property. When a membrane is rendered more hydrophilic by modification with the Pluronic® and Tetronic® surfactants, the hydrophobic nature of the membrane is shielded and adsorption due to hydrophobic interaction becomes less favourable.

For this experiment UF membranes were statically coated with a range of surfactants and the PWF and UF of PEG 12K determined. From the data the most effective surfactant would then be chosen for further investigation on the paper and pulp effluent.

2.2.1 Experimental

The UF membrane tubes were soaked in a coating solution of 5 g/L for the various surfactants at room temperature (25°C) for 18 h. The tubes were rinsed with RO water to remove any unbound surfactant molecules. The PWF and the product flux (PF) during UF of PEG 12 K solutions were measured using a cross-flow laboratory module at constant temperature (20°C), pressure (100 kPa) and a linear flow rate of 500 L/h. The PWF was determined at 100 kPa at 20°C after 10 min of contact and the PF was determined after 20 min.

2.2.2 Results and Discussion

The results from the coating experiments are presented in Table 2.

Table 2: PWF and UF data achieved during the coating experiments

Coating	PWF Average	Standard Deviation	UF Average	Standard Deviation
F68	64.49	21	44.16	12
F98	43.6	6	40.8	8
F108	53.0	7	49.4	9
P103	49.7	8	44.5	9
L35	62.5	14	44.5	6
F87	45.1	14	38.0	13
F88	80.7	26	60.3	16
701	73.2	6	65.5	4
704	44.7	13	38.3	11
F77	51.8	17	43.9	14
F38	79.4	27	51.5	12

From the results shown in Table 2, certain trends were established in terms of molecular mass and hydrophobe footprint. These trends are presented in Figures 2.2 and 2.3.

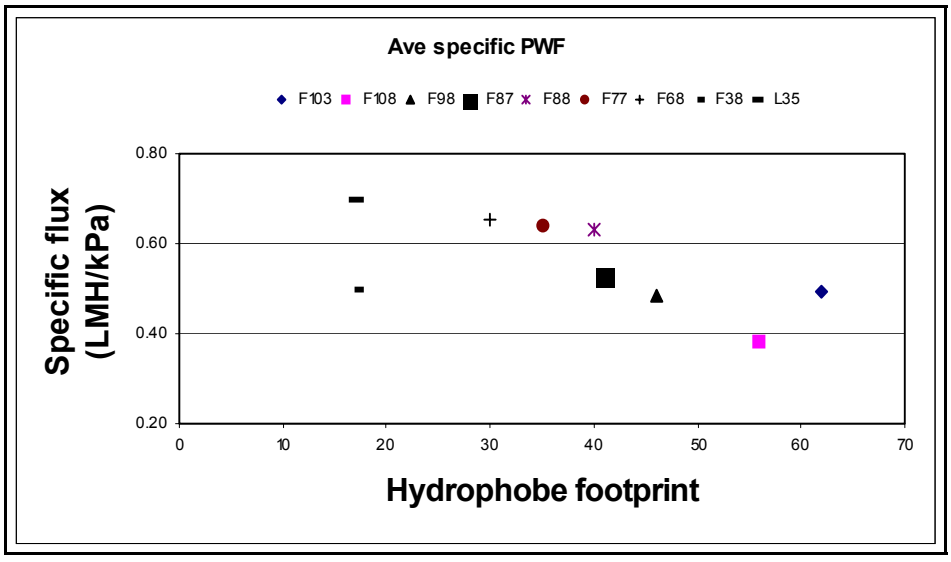


Figure 2.2: Variation in the PWF with changes in the molecular mass of the surfactant.

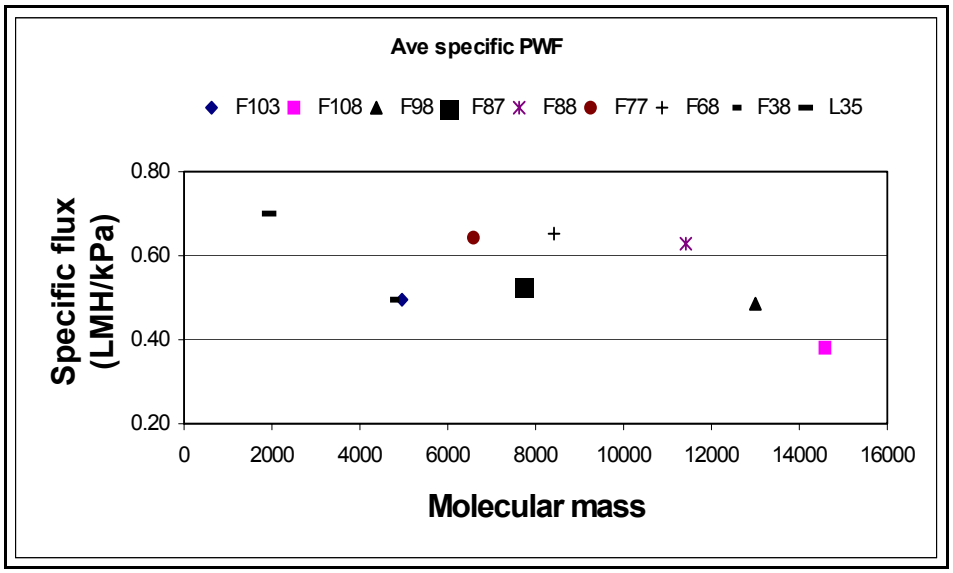


Figure 2.3: Variation in PWF with variations in the size of the hydrophobe footprint.

In general, as the molecular mass increases or the hydrophobe footprint increases the specific flux decreases, except with F38. The reason for this deviation is unknown. It is possible that the concentration of the coating solution was above its critical micelle concentration and the membrane was therefore not well coated. From these results, one surfactant from the Pluronic® range and one from the Tetronic® range were chosen for further investigation. Pluronic® F68 which gave the highest flux and had an 80% hydrophile content was chosen. From the Tetronic® range, 701 gave higher fluxes and in addition it was the only surfactant that was not soluble in water. It was assumed that this characteristic would result in a stronger adsorption between the membrane and the surfactant, with a lower probability of desorption.

2.3 INFLUENCE OF SURFACTANTS ON EFFLUENT FLUX

The objective of the experiments described in this section was to test the effect of membrane modification, using the surfactants previously chosen, on the flux of the pulp and paper effluent. A higher operating pressure (500 kPa) was selected for these experiments to effectively compress the membranes.

2.3.1 Materials and methods

Tubular membranes were modified by static/passive adsorption as previously described. The PWF and the effluent flux during UF of pulp and paper effluent were measured using a cross-flow laboratory module at constant temperature (20°C), pressure (500 kPa) and a linear

flow rate of 500 L/h. The PWF was determined at 500 kPa at 20°C after 10 min of contact and the effluent flux was determined after 20 min.

2.3.2 Results and Discussion

The PWF of the membrane coated with F68 was monitored at specific timed intervals. In Figure 2.4 it can be seen that the PWF reaches a steady state within an hour. Hence, for all further experiments the membranes were pre-compacted for 1 hour at 500 kPa, prior to determining the PWF.

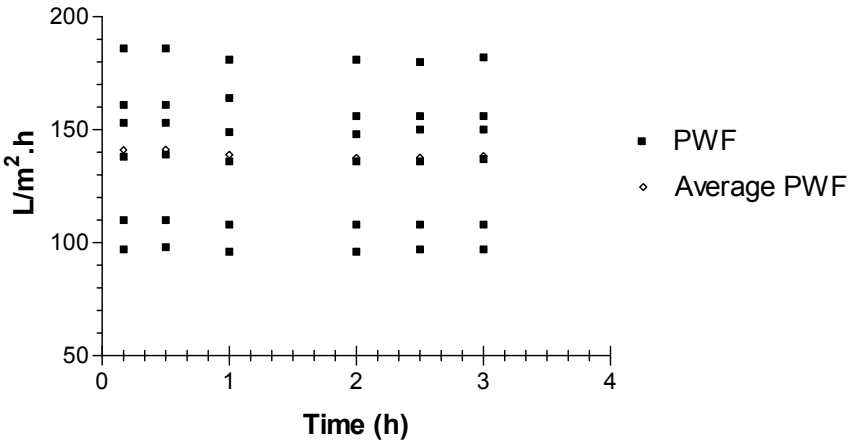


Figure 2.4: Variation in PWF with time at 500 kPa

Pre-compacted membranes were then subjected to the effluent under conditions previously used. The product flux of the effluent was determined after 20 min of contact with the effluent and at regular intervals throughout the experiment.

The results from the experiments are presented in Table 3. It is interesting to note that the effluent flux for the uncoated membrane is the lowest.

Table 3: Effluent flux achieved during the coating experiments

Coating Material	Effluent Flux after 20 min ($L/m^2.h$)	± Standard Deviation
F68	47.89	1
701	48.71	8
Uncoated	43.48	0

The effect of the different membrane modifications on fouling can be correlated to a decrease in hydrophobicity of the membranes in the case of the Pluronic surfactants and perhaps to electrostatic repulsion in the case Tetronic® 701.

Figure 2.5 depicts the variation of the effluent flux over time for the membrane coated with Pluronic® F68.

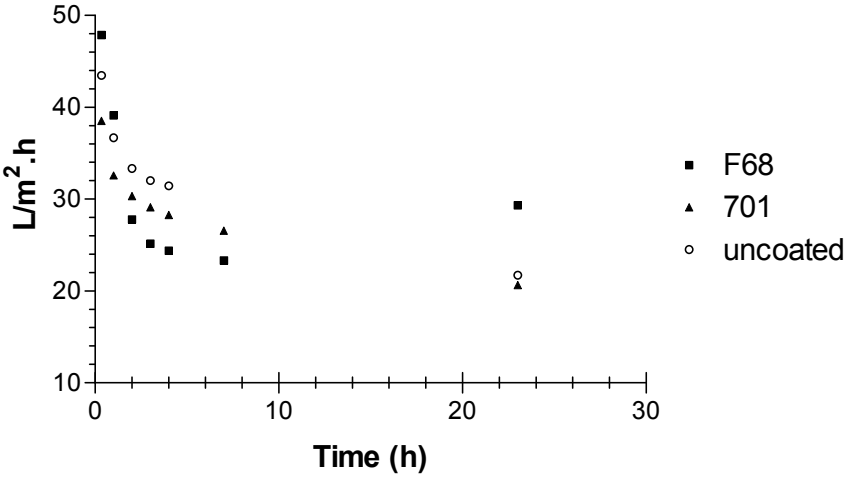


Figure 2.5: Effluent flux decline as a function of time for uncoated and coated membranes.

An initial drop in flux was observed followed by a slower decline. However, an increase in flux was observed at the last reading. This increase was attributed to the fact the system was switched off overnight before the last three hours of the run. The flux drop with time is probably because of the adsorption of particles on the membrane surface as well as concentration polarization. During the time the system was idle, diffusion of the foulants probably occurred. Another possibility is that it could have been due to aeration of the feed solution as a result of the low volume reached towards the end of the experiment.

Similar results were achieved for the membranes coated with Tetronic® 701 and the uncoated membranes i.e. a flux of approximately 25 L/m^2.h after 24 hours of contact with the effluent. No significant difference was observed between the coated and uncoated membranes.

2.4 CONCLUSIONS

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

- The reduction in PWF through the uncoated DAF fouled membranes can be attributed to the adsorption of the organic compounds, present in the effluent, to the hydrophobic membrane surface of the PES membranes. (This result corresponds with the results obtained at the mill.)
- Coating of native PES membranes with Pluronic® F108 reduces the PWF through the membranes considerably.
- The PWF of Pluronic®-coated membranes fouled with DAF was slightly higher than the unfouled Pluronic®-coated membranes.
- Coated membranes showed advantages with respect to fouling prevention and productivity increase.

CHAPTER 3

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 Mill, Bubond® 123 (resin) and Bubond® 127 (polyethylene oxide (PEO) (both provided by Buckman Chemicals, Johannesburg, 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 site 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 this study was to establish whether the flocculants and coagulants used at The 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.

3.1 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, at the Institute of Polymer Science, University of Stellenbosch. The test rig was operated at an operational pressure of 200 kPa, a linear velocity of 1 m/s and 20ºC. 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. Native unfouled PES UF membranes were placed in the various bentonite suspensions for 48 h at room temperature. The membranes were then thoroughly rinsed in reverse osmosis (RO) water and the PWF was determined.

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

Results and discussion - experiment 1

The results presented in Figure 3.1 indicated that static fouling of the PES membranes with bentonite had no significant effect on the permeate flow through the membranes. Bentonite was, therefore, not a possible foulant of the UF membranes at The Mill.

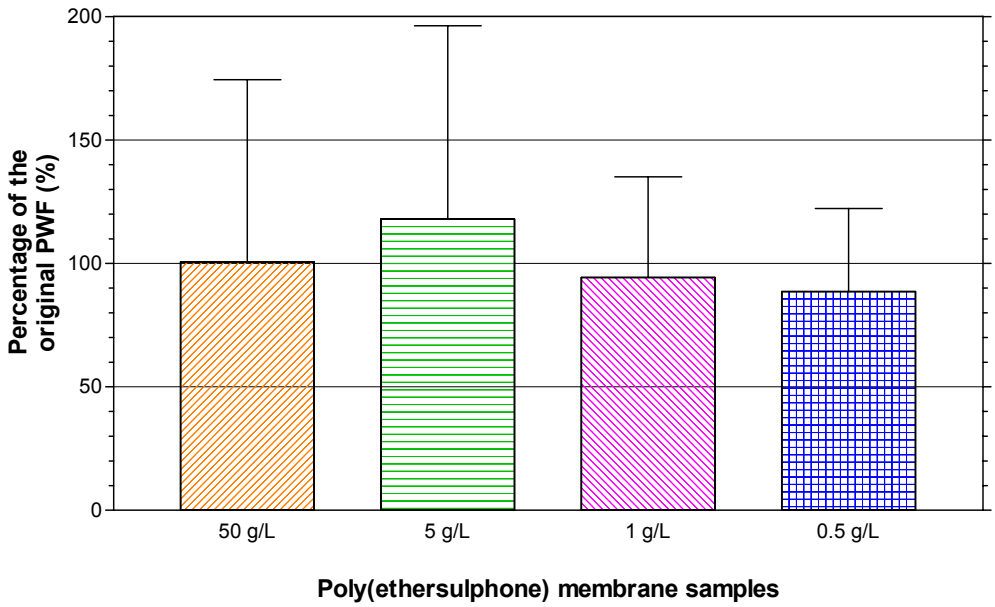


Figure 3.1: The PWF values obtained for PES membranes fouled in bentonite suspensions, varying in their respective concentrations.

Experiment 2

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

facilitated the fouling of the UF membranes. The membranes were fouled for 48 h at room temperature, rinsed in reverse osmosis water, before the PWF was determined.

Results and discussion - Experiment 2

The results displayed in Figure 3.2 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).

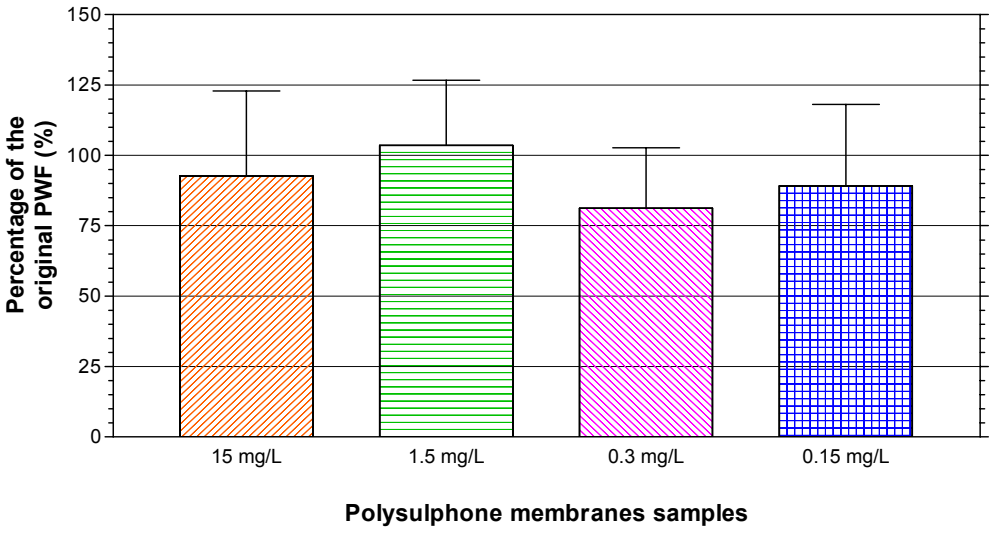


Figure 3.2: PWF values obtained for PES membranes fouled in 15, 1.5, 0.3 and 0.15 mg/L Bufloc® 5031 cationic coagulant suspensions.

Experiment 3

Resin (Bubond® 123), a coagulant, is currently being used in the pre-treatment of the DAF feed at the 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 ºC), 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 3.3). 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.

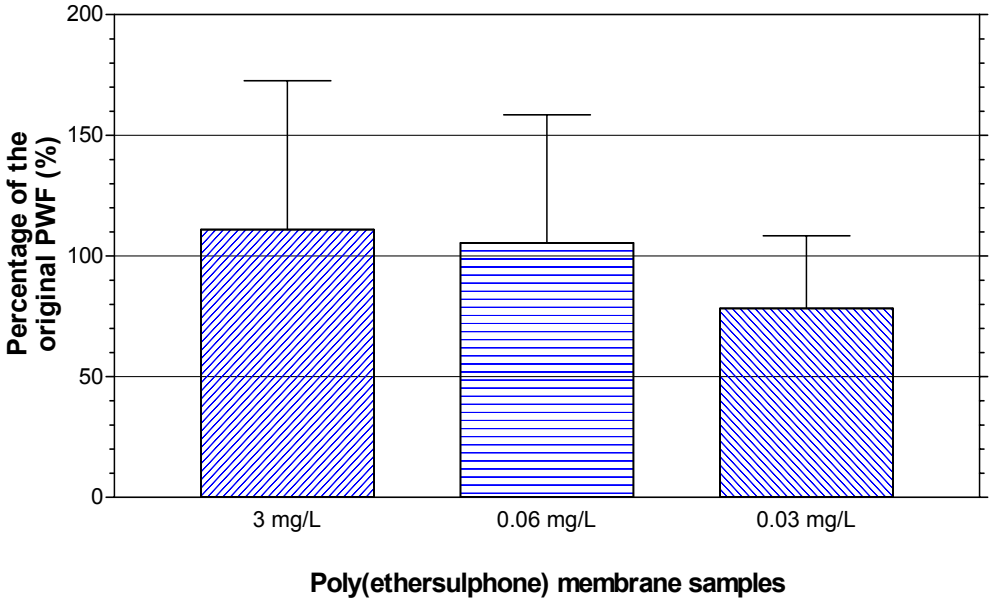


Figure 3.3: PWF values obtained for PES membranes fouled in various Bubond® 123 suspensions, differing in their respective concentrations.

Experiment 4

PEO (Bubond® 127) 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 final concentrations of 1, 0.02 and 0.01 mg/L. 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 3.4 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.

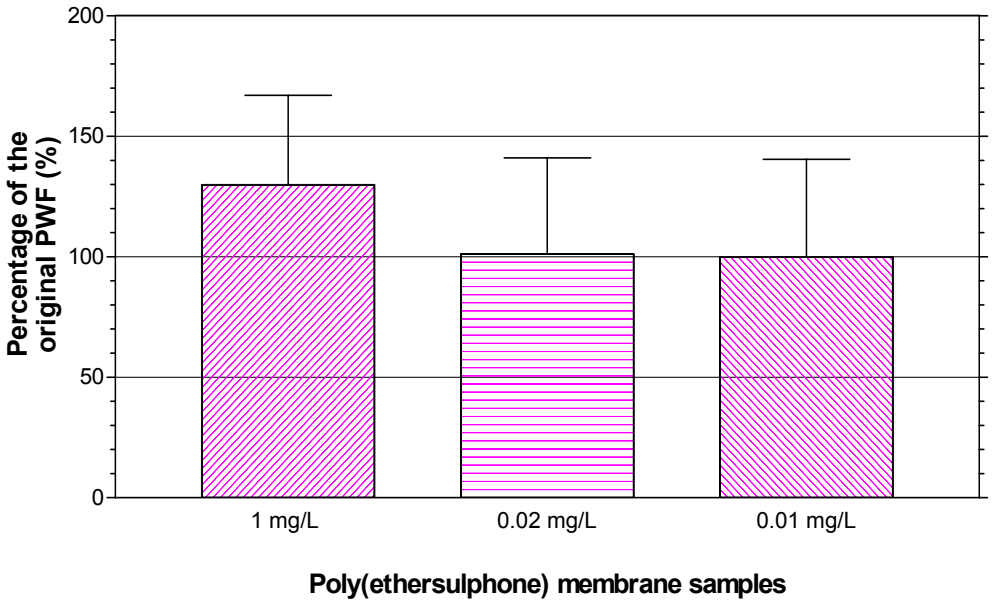


Figure 3.4: PWF values for PES membranes fouled in a solution containing 1, 0.02 and 0.01 mg/L of a 1.5% (m/v) Bubond® 127 stock solution.

3.2 CONCLUSIONS TO FLOCCULANT AND COAGULANT EVALUATION

- The static fouling experiments carried out on the flocculants and coagulants in this study show that not one of the agents adsorb onto the membranes irreversibly.
- The results also show that flocculants and coagulants used to assist clarification of effluent in the DAF clarifier, do not act as fouling agents of the UF membranes tested.

CHAPTER 4

ULTRAVIOLET-VISIBLE SPECTROPHOTOMETRIC ANALYSIS OF EFFLUENT SAMPLES

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 ultrafiltration 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.

4.1 UV-VIS ANALYSES OF EFFLUENTS GENERATED IN THE MILL

As shown in Figure 4.1, 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 mill were carried out.

4.1.1 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 4.1. 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.

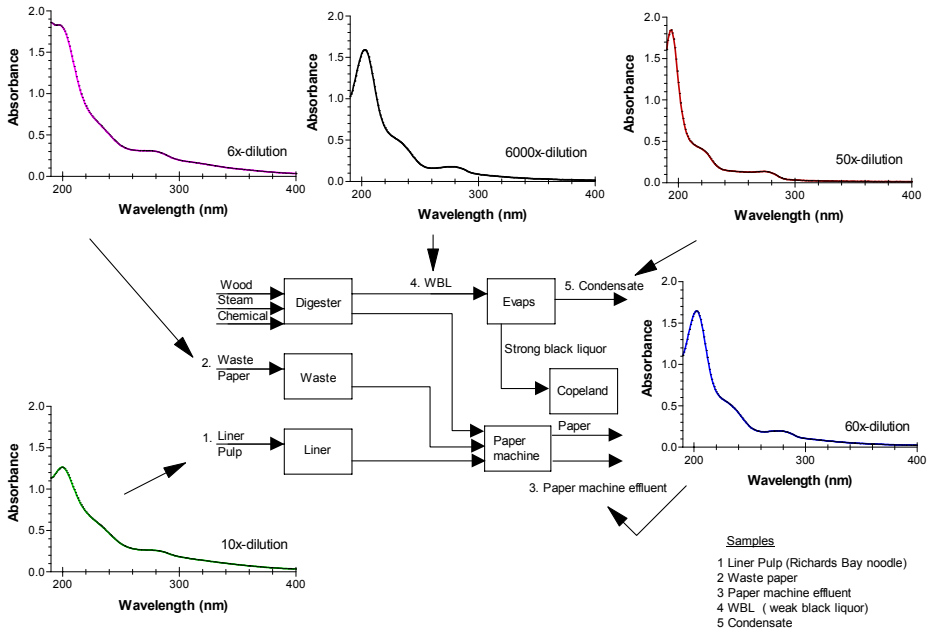


Figure 4.1: Schematic representation of the origin of different effluent streams generated in the paper mill and their respective UV-spectra.

4.1.2 Results

The absorbance maxima at 230 and 280 nm in UV-Vis spectra of all the effluents analysed indicate the presence of aromatic substances (Figures 4.1). 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 Figure 4.1, black liquor and paper machine effluent have identical UV-Vis characteristics, indicating similarity in composition. In addition to the absorbance 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 4.2 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)[1]. 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. This spectrum is shown in Figure 4.3. The absorption spectra displayed in Figure 4.2 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.

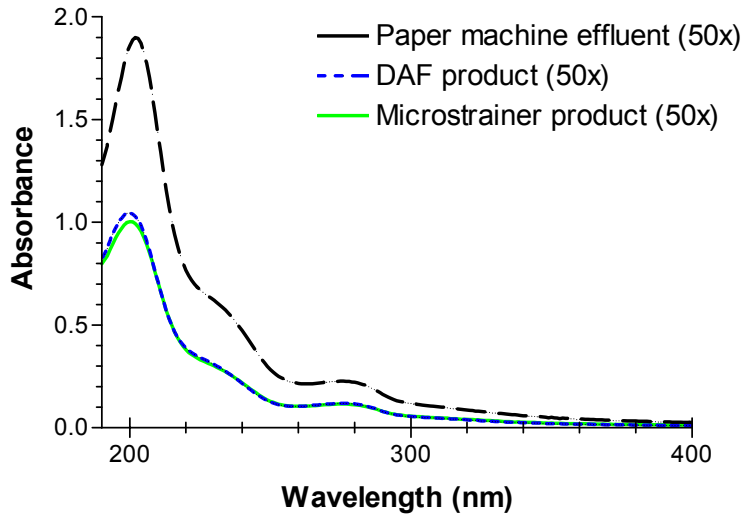


Figure 4.2: Spectral analyses of paper machine effluent, DAF and microstrainer product (i.e. before and after purification of the paper machine effluent on the DAF clarifier).

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

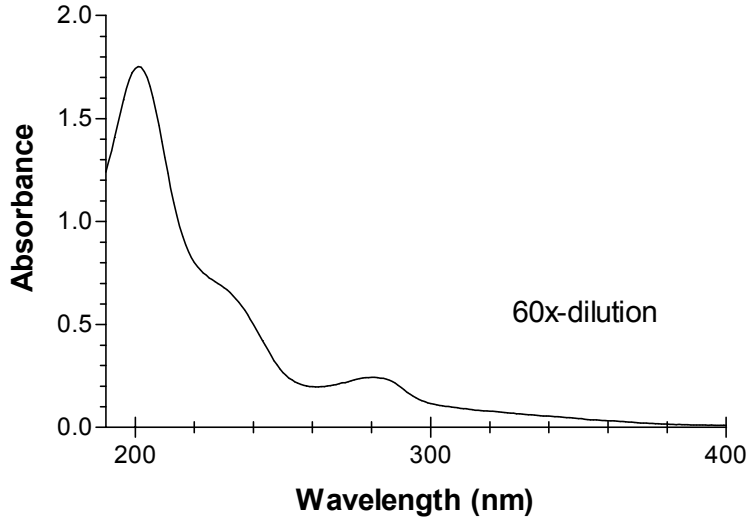


Figure 4.3: Wavelength scan of a diluted 0.1% m/v commercial lignosulphonate solution at pH 7.

4.1.3 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 the PES membranes at alkaline pH. This prompted an investigation into the influence of pH on the character of the effluent.

4.1.4 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**.**

4.1.5 Results

An absorption maximum in the region 240 to 260 nm, was observed with an increase in the pH for all three effluents (Figure 4.4). 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 4.4 (A-C).

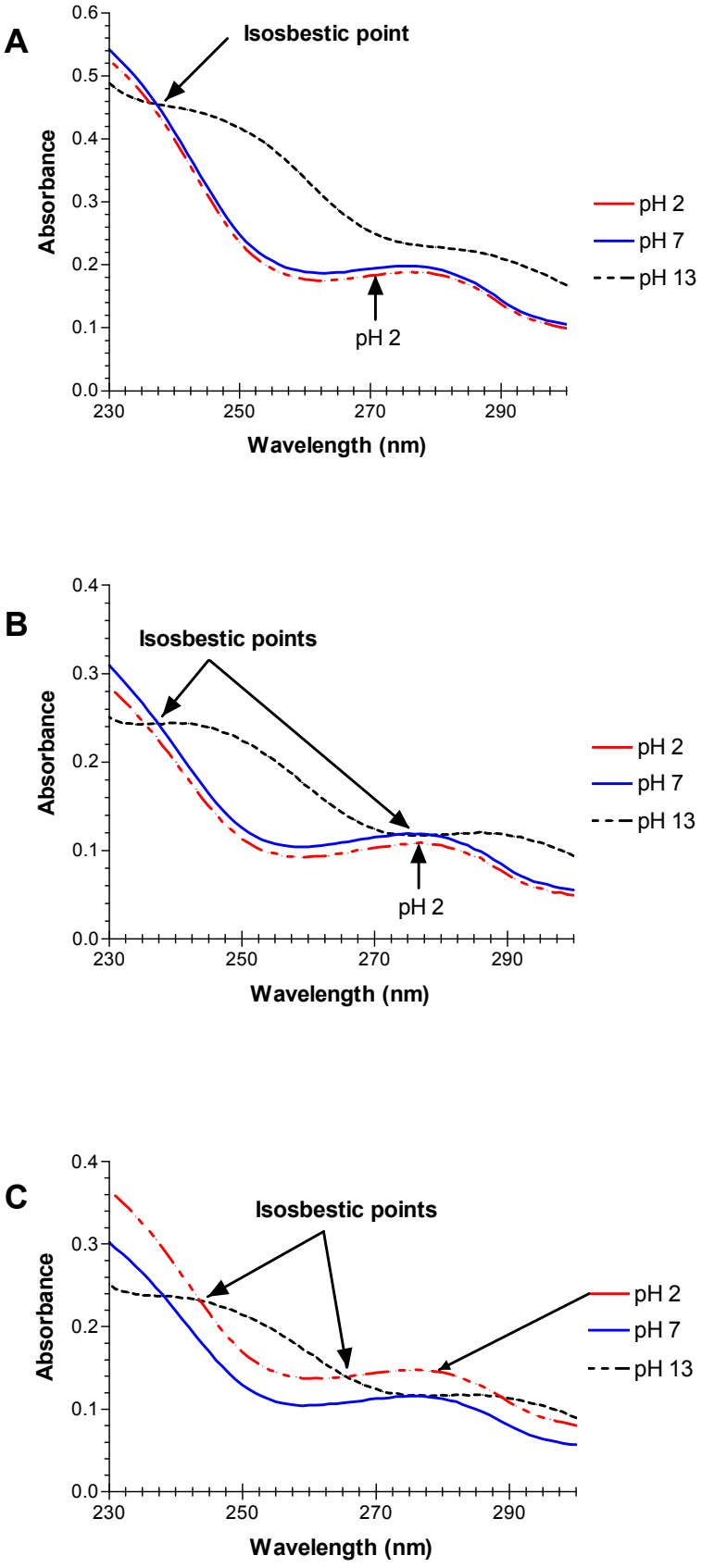


Figure 4.4: Change in the absorption spectra of (A) paper machine effluent, (B) DAF product and (C) microstrainer product with a change in the pH.

4.1.6 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.

4.2 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).

4.2.1 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.

4.2.2 Results

The analytical wavelengths used for the detection of the various elements plus the results of

the analyses are listed in Table 4.1. 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.

Table 4.1: 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	394.401	37.6	37.5	4.1	-**	4.4	35.3
Ca	317.933	113.6	102.2	176.7	145.4	171.2	101.9
K	769.896	11	16.1	15.8	22.6	15	22
Li	323.263	1.2	0.8	0.9	1	1.9	1.9
P	214.914	0.9	1.4	0.4	0.2	0.4	0.3
Si	250.69	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 mill.

4.2.3 Discussion

It is evident from the results displayed in Table 4.1 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.

4.3 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.

4.3.1 Experimental

The effluent (microstrainer product) used in this experiment was obtained from the Piet Retief Mondi Kraft paper mill. EDTA was supplied by Saarchem-Holpro Analytic (Pty) Ltd 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.

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 4.5).

4.3.2 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.

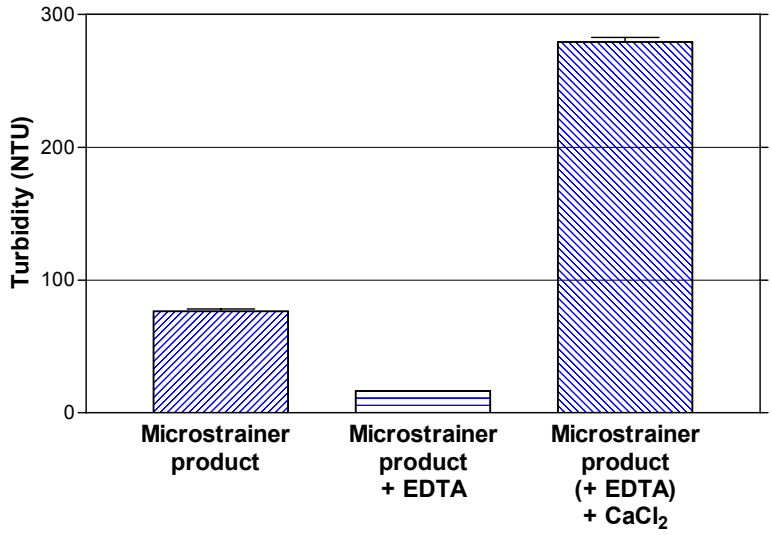


Figure 4.5: Influence of EDTA and Ca^{2+} on the turbidity of microstrainer product at pH 13.

4.4 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 gel permeation chromatography (GPC). GPC is a powerful tool to determine of molecular mass averages (MM_{av}) and 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).

4.4.1 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 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.

4.4.2 Results

Figure 4.6 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 4.7 to 4.12 were obtained 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:

1. The GPC column was calibrated by determining the elution volumes required to displace several PEO standards of known molecular mass from the column.
2. The elution volume for the unknown compounds, present in the effluent, were then determined under the same operating conditions.
3. 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 4.7).

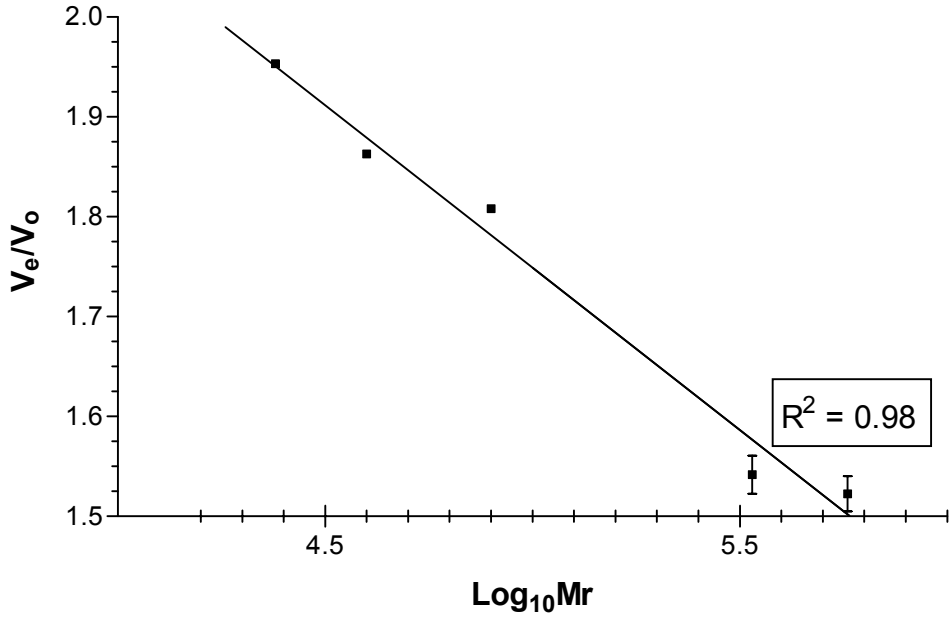


Figure 4.6: GPC standard curve for PEO standards (molecular mass 24 to 850 kDa).

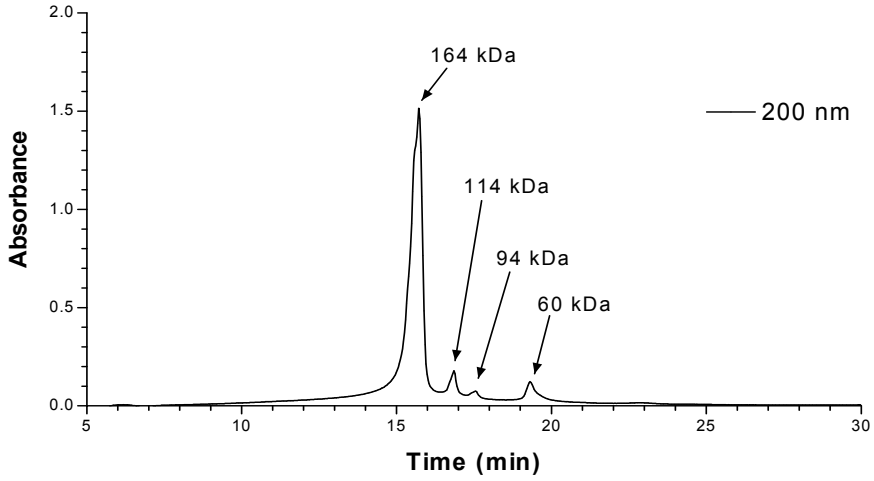


Figure 4.7: GPC-analysis of microstrainer product (pH 4.4). Detection was at the wavelength indicated on the chromatogram.

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 (Figure 4.8). It was interesting to note that at pH 13 an additional peak at 28 kDa was observed.

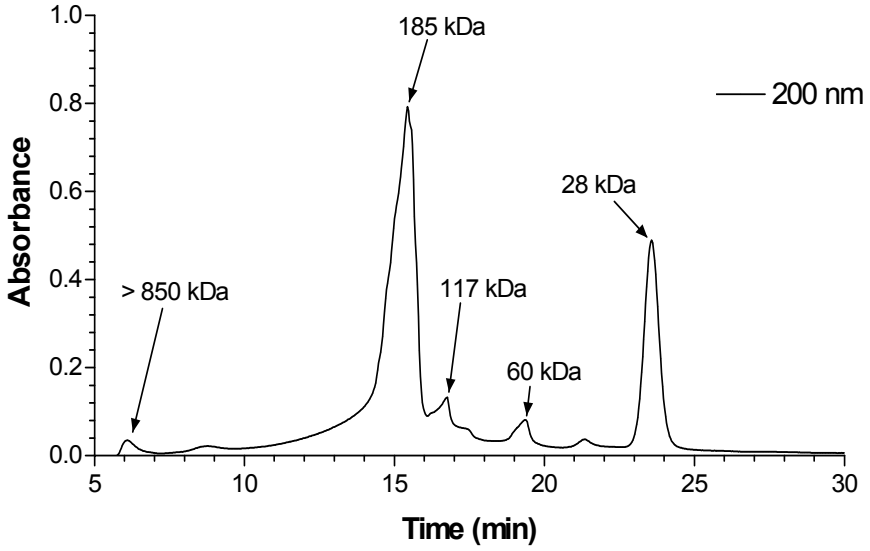


Figure 4.8: GPC-analysis of microstrainer product (pH 13) at various wavelengths. Detection was at the wavelength indicated on the chromatogram.

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 MW_{av} of 90 kDa and a minor peak at 333 kDa and were observed (Figure 4.9). The 28 kDa peak present in Figure 4.8 was absent and it can therefor 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.

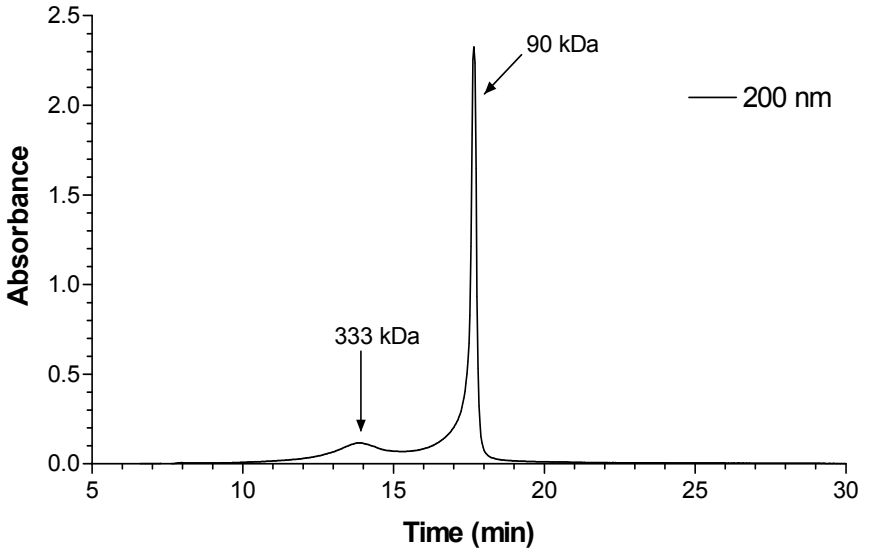


Figure 4.9: Microstrainer product (pH 13) was adjusted to pH 4 and analysed to establish whether the 28 kDa peak, present in Figure 4.8, would be affected. No peak was observed at 24 min which corresponded to the 28 kDa fraction.

To establish whether the formation of the 28 kDa fragment shown in Figure 4.8 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 4.10. 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 4.9. The microstrainer product sample analysed in Figure 4.9 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 4.1). 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.

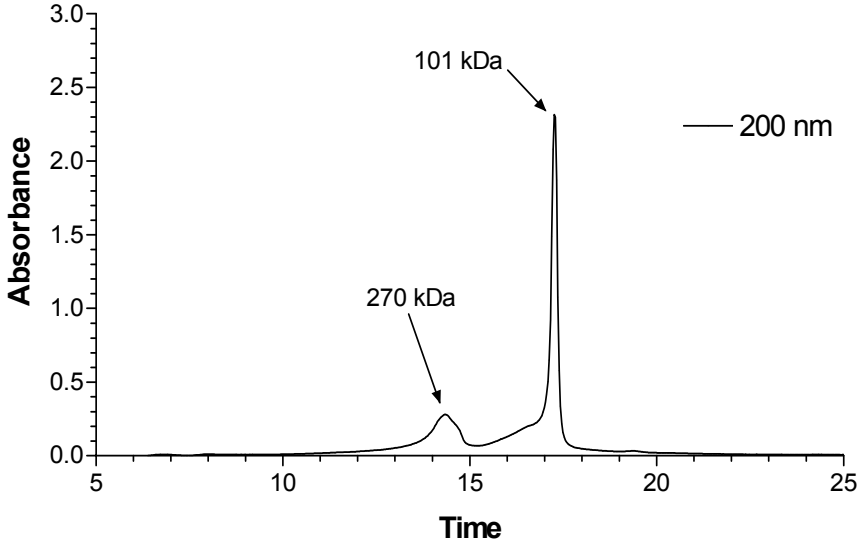


Figure 4.10: GPC of microstrainer product (pH 4.4) after addition of NaCl (0.2g per 50 mL of effluent) to establish whether the Na^+ (in NaOH) or the solution pH was responsible for the 28 kDa peak observed in Figure 4.8.

The 28 kDa peak was still present after the addition of EDTA to the microstrainer product (pH 13) as shown in Figure 4.11. This confirmed the involvement of the alkaline pH with the

formation of the 28 kDa peak.

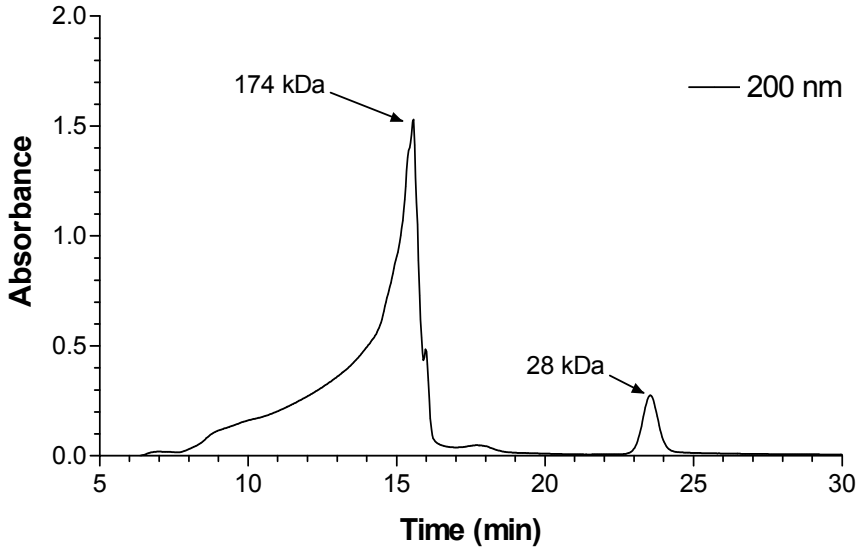


Figure 4.11: GPC-analysis of microstrainer product (pH 13) after the addition of EDTA (0.4 g per 50 mL effluent).

The subsequent addition of $CaCl_2$ (dehydrated) to the microstrainer product (pH 13), containing EDTA, resulted in the formation of an additional peak (MW_{av} of 208 kDa) at 15 min, indicating complex formation as shown previously. The peak at 28 kDa remained (Figure 4.12).

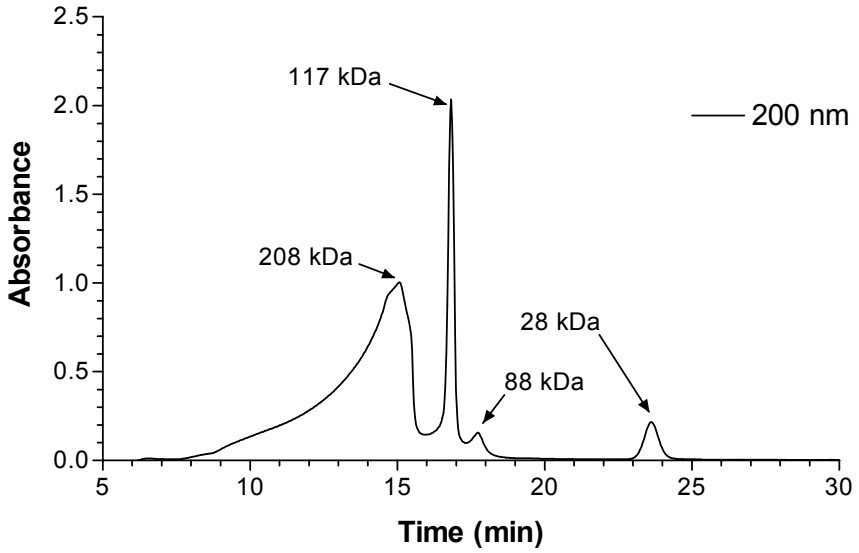


Figure 4.12: GPC of microstrainer product (pH 13) after addition of EDTA (0.4 g) and $CaCl_2$ (0.2g) per 50 mL effluent.

4.4.3 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.

4.5 CONCLUSIONS

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

- The effluents analysed contain aromatic compounds and unsaturated polymers which can act as potential foulants.
- All the samples analysed contain the same type of compounds of which lignosulphonate is 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 can be 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 a number of hours. 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.
- Any future cleaning regimes or fouling prevention measures will be more successful if the

above properties of the effluent are considered.

CHAPTER 5

MEMBRANE FOULANT CHARACTERISATION BY ATOMIC FORCE MICROSCOPY AND SCANNING ELECTRON MICROSCOPY

5.1 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 atomic force microscopy (AFM). Similar work has been performed by Allie (1999) who evaluated the surface roughness of modified and unmodified PES membranes before and after fouling.

5.1.1 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).

5.1.2 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 5.1). The following parameters were obtained with the analysis: the average roughness, R_a, defined as:

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

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

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

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 5.2). 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)

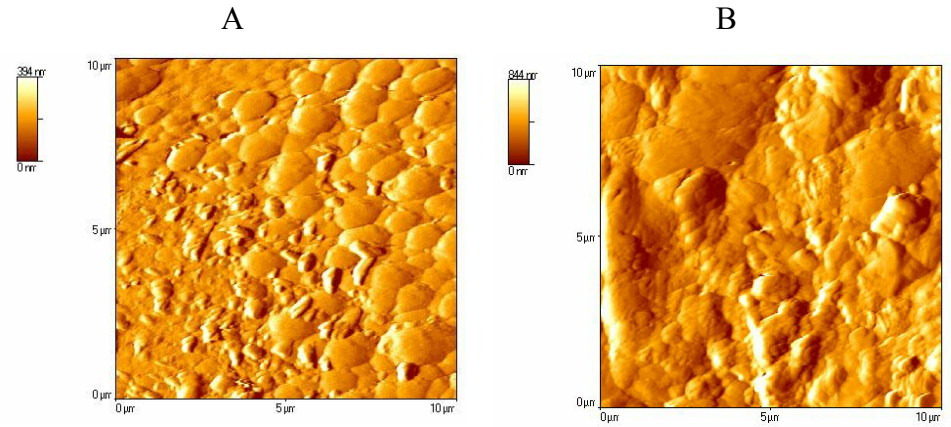


Figure 5.1: AFM images of unfouled (A) and fouled (B) PES membranes. The bar on the left of the images indicate the vertical deviation.

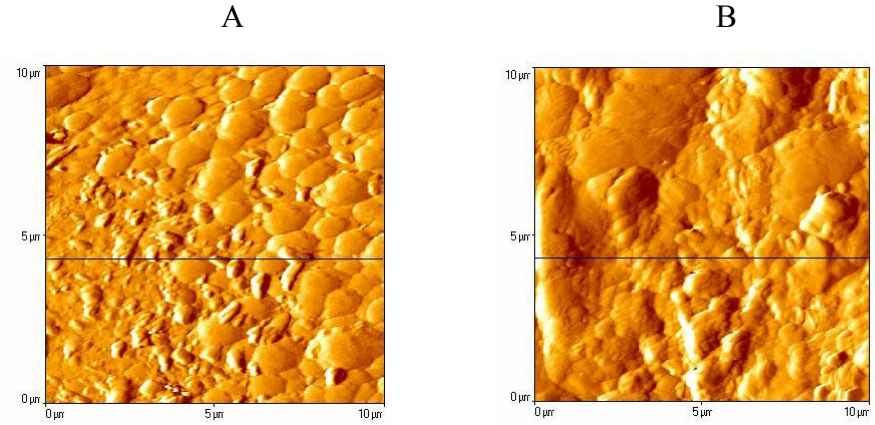
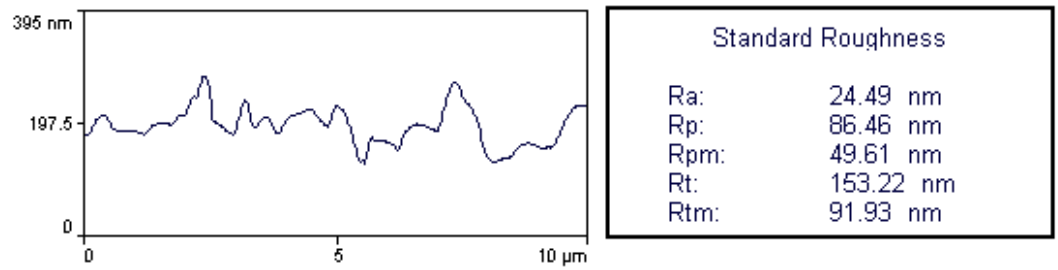


Figure 5.2: Previously shown 2-D AFM images (Figure 5.1) of unfouled and fouled PES membranes, indicating the lines that were analysed during horizontal line analyses

5.1.3 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 5.3. 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

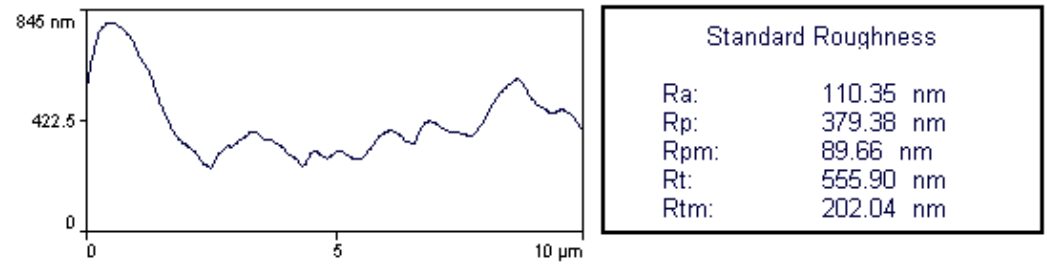


Figure 5.3: Data obtained for the line analysis of unfouled (A) and fouled (B) PES membranes.

5.2 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.

5.2.1 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 1 000 magnification.

5.2.2 Results

Examination of the micrographs (Figure 5.4) 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.* (1998) showed that hydrophobic membranes exposed to plug screw feed pressate (PSFP) were initially fouled by lignin sulphonates that formed an insoluble compact layer on the membrane surface that allowed for the accumulation of cellulosic species on the modified surface. 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.

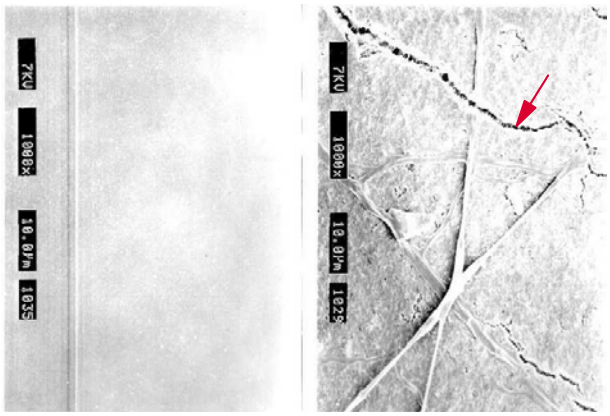


Figure 5.4: SEM micrographs of 40 kDa MMCO (a) unfouled and (b) fouled PES UF membranes at 1 000 magnification.

The crevice in the solid layer (indicated with the arrow in Figure 5.4) developed when the tubular membrane was unfolded during sample preparation.

Fritzsche *et al.* (1992) were able to detect and determine the size of the pores in UF membranes with a MMCO of 30 kDa or greater using a SEM. Because of the low magnification of the images in Figure 5.4 it was not possible to investigate the membrane pores.

5.2.3 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.

5.3 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 Mill.
- SEM analyses supported the findings of the AFM experiments showing fibers as prominent components of the fouling layer.

CHAPTER 6

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

6.1 INTRODUCTION

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 a serial configuration. The following experiments were done at the mill.

1. The hydrophobicity of the membranes was changed using Pluronics®, surfactants and Osmonic® membranes.
2. The hydrophobicity of dissolved species was reduced by changing the pH, solvents, and 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.

6.1.1 Experimental

Experiments performed at the UF-plant of the Mondi Kraft Piet Retief 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 controlled at 40 ºC by means of a heating element and regulator. 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 at the University of Stellenbosch

The membranes 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

The Piet Retief paper mill is supplied with water from the Hlelo river which is clarified with a conventional alum and chlorinated before use. A PWF of the UF membranes was determined on the test rig with this water. The flux obtained during this experiment served as a control for subsequent experiments. The results of the PWF determinations are summarised in Figure 6.1

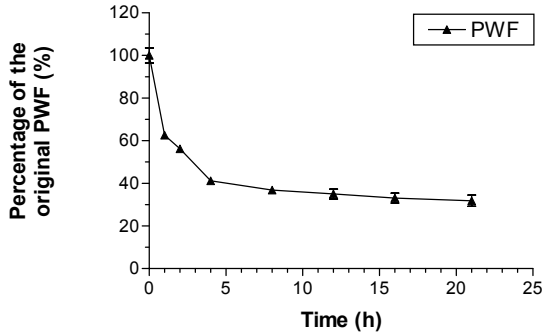


Figure 6.1: PWF decline over a period of 22 h. Feed water from the Hlello river was pre-treated with alum and chlorine before UF.

Experiment 2

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, a 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 6.2.

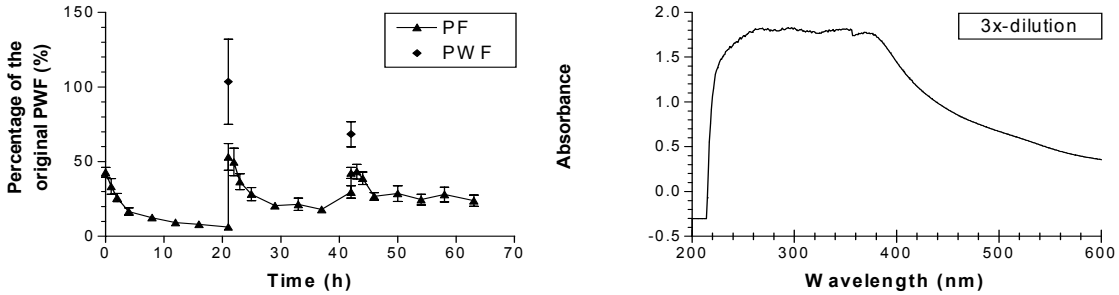


Figure 6.2: PES membranes were fouled with DAF product, pre-treated with a cationic coagulant and flocculant. The product flux (PF) and PWF obtained through the membranes (left) and UV-Vis analysis performed on the membrane extracts (right) are shown.

Experiment 3

In the past, the effluent feed to the membrane plant was a combination of primary and paper machine effluent. The primary effluent was wash water from the digester which contained black liquor (washings). The combined effluent feed had a pH 8, whereas the paper machine effluent had a pH of 4.5. The rate and degree of fouling of the UF membranes were much lower for the combined effluent compared to when only paper machine effluent was used. It was suggested that the black liquor may have surfactant properties, by virtue of the lignosulphonate present in the liquor, that may have a cleaning effect on the membranes or retain some of the organics in solution during UF. For this reason the addition of black liquor to the paper machine effluent was investigated on the test rig. The results obtained are displayed in Figure 6.3.

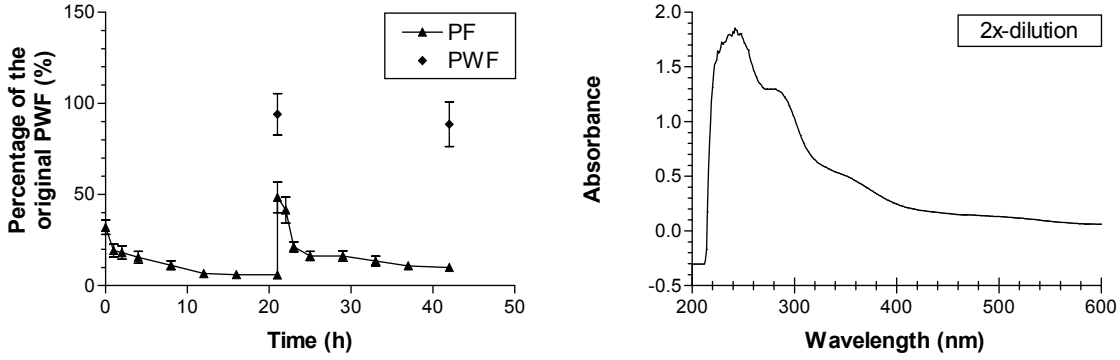


Figure 6.3: PF and PWF determinations (left) for membranes fouled with paper machine effluent, containing black liquor. The absorbance spectrum of the membrane extracts is shown on the right hand side.

Experiment 4

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 effluent. This phenomenon was investigated on the test rig (Figure 6.4).

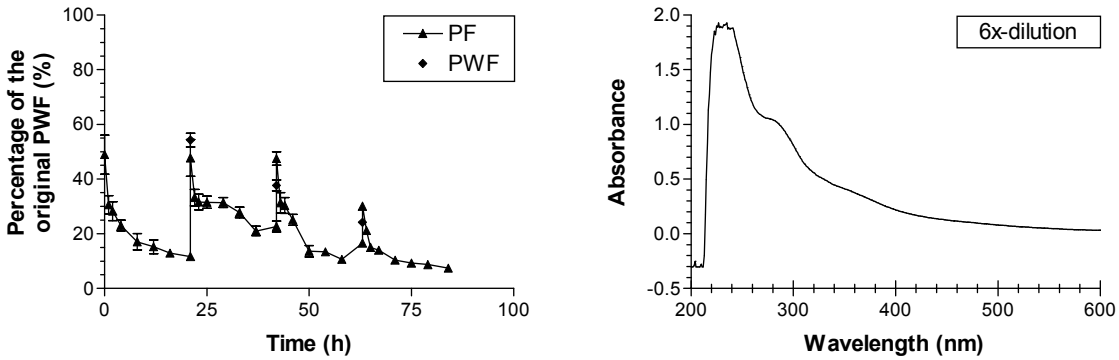


Figure 6.4: PF and PWF determinations for membranes fouled with dam effluent (left) and the UV-Vis analysis (right) of the membrane extracts.

Experiment 5

This experiment involved the evaluation of DAF effluent, chemically treated with S.A. Paper Chemicals (Pty) Ltd. (Sapco) products. The chemical program used bentonite 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 6.5.

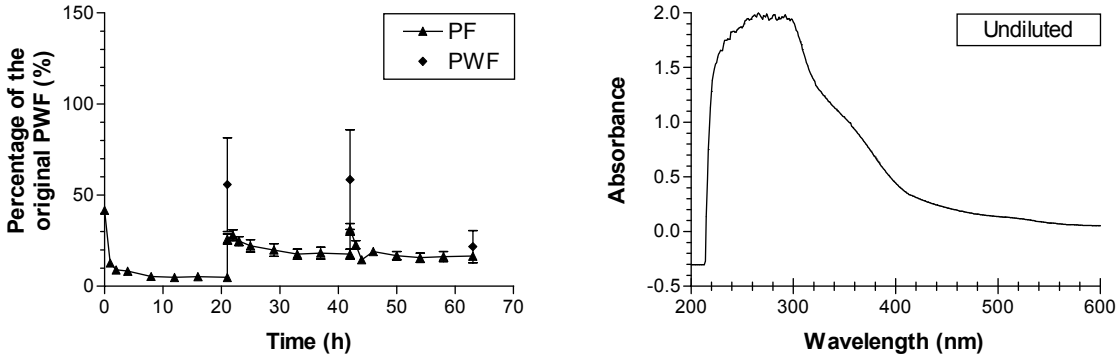


Figure 6.5: Evaluation of membranes fouled with DAF product and subsequently chemically treated with Sapco products (left). A wavelength scan of the membrane extracts is shown on the right.

Experiment 6

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. Due to the difficulty involved in controlling the pH of the direct feed to the test rig, it was decided to operate the test rig in a batch concentration mode. This involved recirculating the concentrate back to the feed tank so that a constant pH could be maintained.

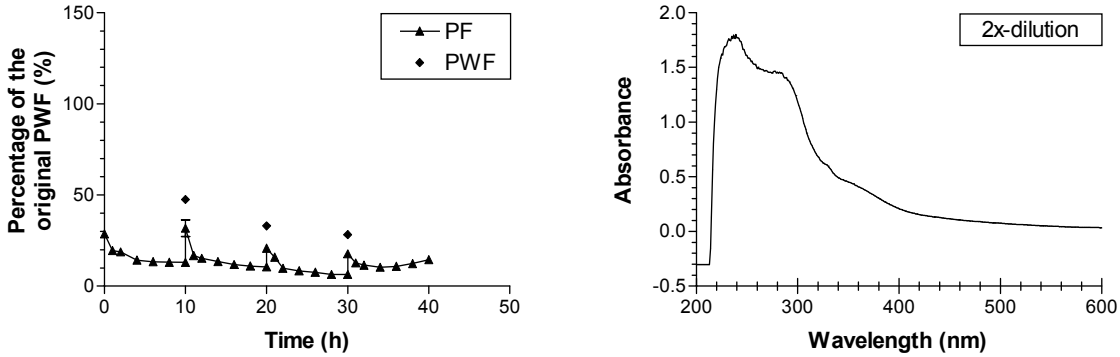


Figure 6.6: Flux measurements (left) obtained for membranes fouled with DAF product (pH 8) and the UV-Vis analysis (right) of the membrane extracts are displayed.

Experiment 7

This trial was a repeat of Experiment 6. In the previous experiment recirculation of the concentrate to the feed tank was maintained to ensure a constant feed pH of 8, but a larger feed tank, a 200 L drum filled with effluent pre-treated to the required pH, made concentration recirculation unnecessary. The results obtained for this experiment are presented in Figure 6.7.

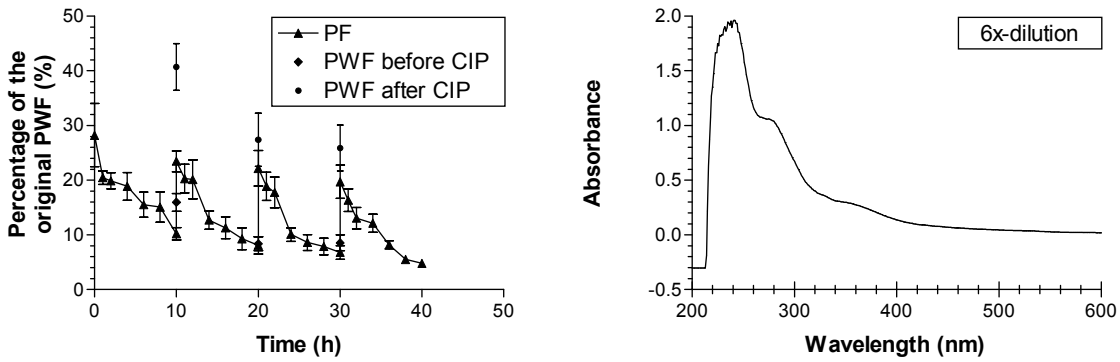


Figure 6.7: A repeat of experiment 6. CIP was performed with sodium

hexametaphosphate.

Experiment 8

The idea behind this experiment was the same as for Experiment 7, 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 for the experiment are displayed in Figure 6.8.

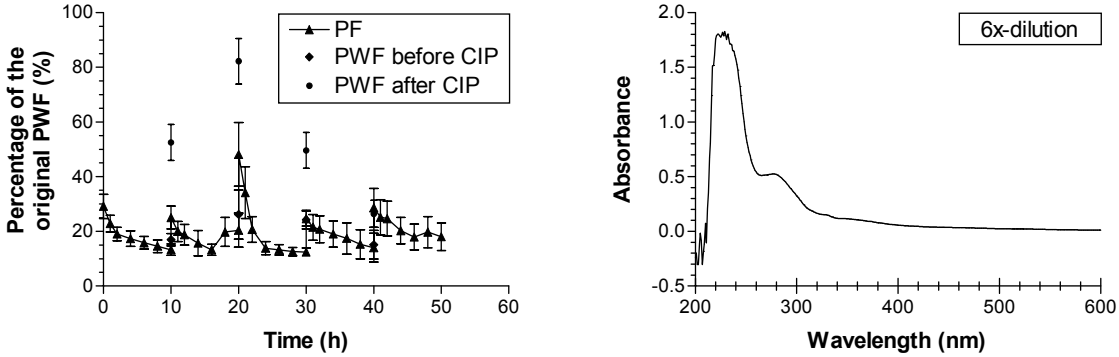


Figure 6.8: PES membranes were fouled with DAF product (pH 10) and evaluated on the basis of their PF and PWF, before and after CIP. UV-Vis analysis of the membrane extracts is shown on the right hand side.

Experiment 9

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 6.9.

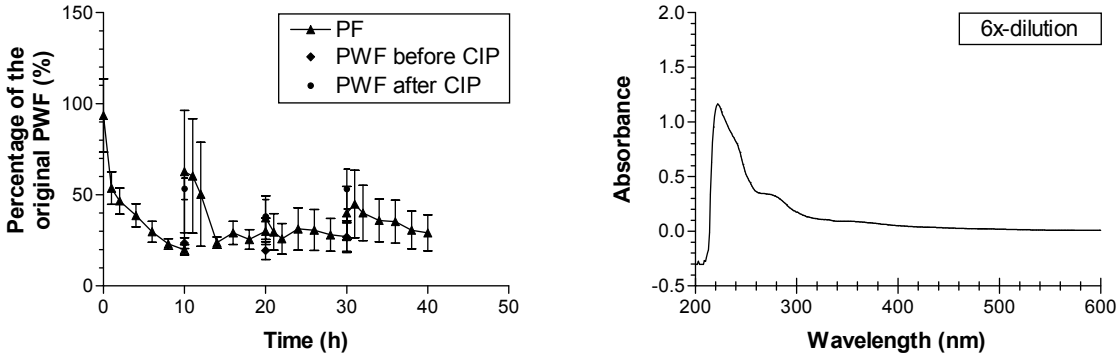


Figure 6.9: Flux measurements of membranes fouled with DAF product, passed through an activated carbon column (left) and an absorbance spectrum of the membrane

extracts (right).

Experiment 10

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 for the experiment are presented in Figure 6.10.

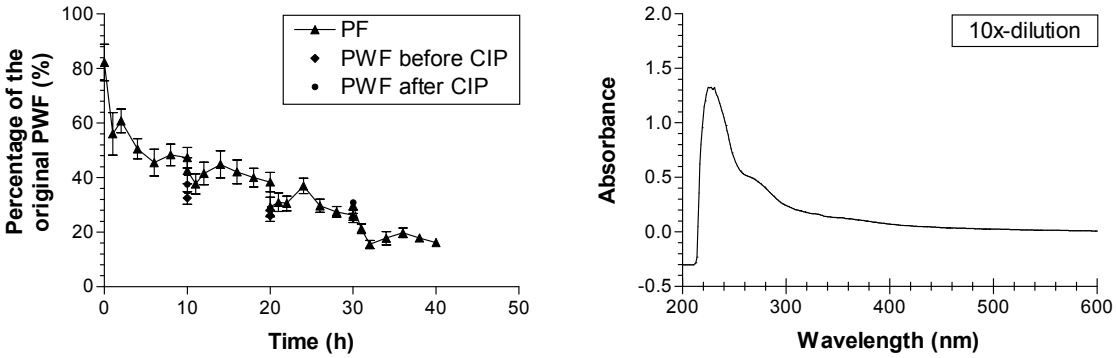


Figure 6.10: Flux measurements (left) of membranes fouled with DAF product, passed through an ion exchange column, and a wavelength scan of the membrane extracts (right) are shown.

Experiment 11

BL® 2085 (wire conditioner), a proprietary chemical supplied by Buckman, 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 6.11 summarises the results obtained for the experiment.

Experiment 12

Busperse® 59LO (pitch dispersent), provided by Buckman, 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 6.12.

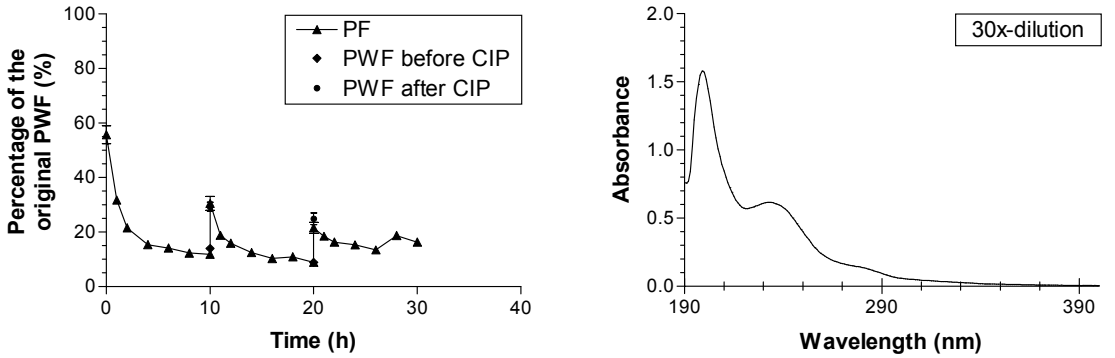


Figure 6.11: Results obtained for PES membranes pre-treated with BL® 2085 (wire conditioner). Flux determinations (left) of the membranes and UV-Vis analysis (right) of the membrane extracts are displayed.

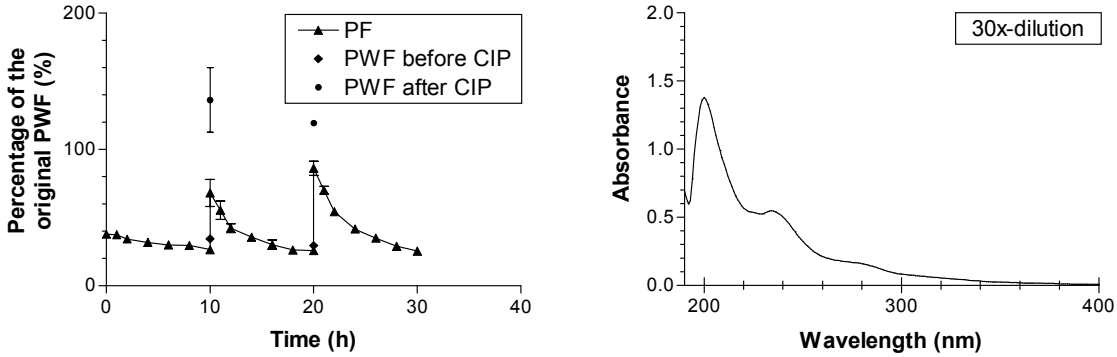


Figure 6.12: Membranes were pre-treated with Busperse® 59LO (pitch dispersent) in an attempt to modify the membrane surface. Results obtained for flux determinations (left) and UV-Vis analysis of the membrane extracts (right) are shown.

Experiment 13

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 6.13.

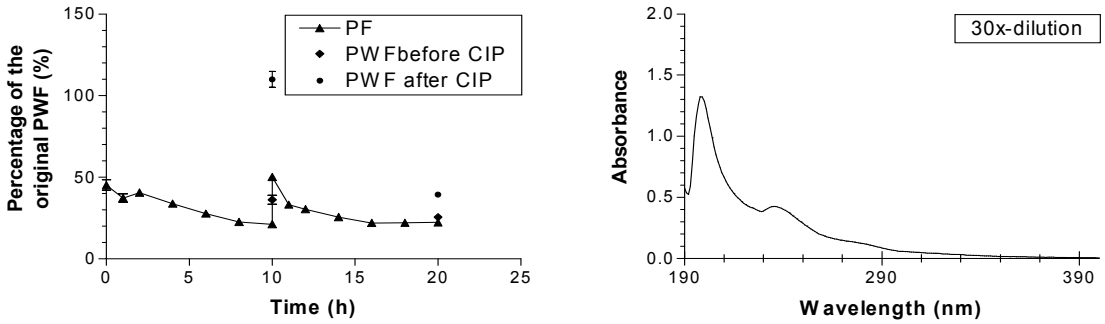


Figure 6.13: The effectiveness of lignosulphonate as a dispersent was evaluated. Flux determinations (right) and UV-Vis analysis of the membrane foulants (left), were performed.

Experiment 14

The chemical treatment program for the DAF clarifier was changed to Bubond® 123 (resin) and Bubond® 127 (PEO), which were provided by Buckman. 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 6.14.

Experiment 15

The pH of the effluent feed to the test rig was raised to pH 10 and the inlet pressure reduced to 400 kPa compared to the normal 600 kPa. The objective of the experiment was to maintain the solubility of the foulants while simultaneously reducing the rate of foulant adhesion onto the membrane surface by operating at a lower pressure differential. Results obtained for the experiments are presented in Figure 6.15.

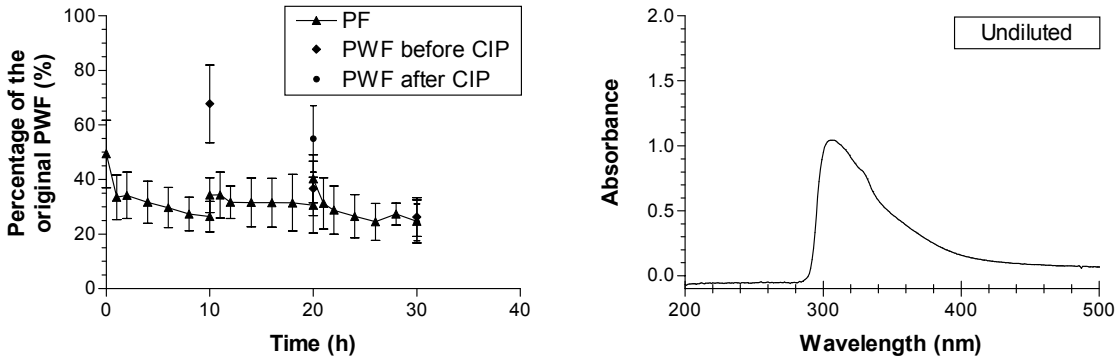


Figure 6.14: PES membranes were fouled with pre-treated microstrainer product. Flux determinations of the membranes (left) and UV-Vis analysis of the membrane extracts (right) were performed.

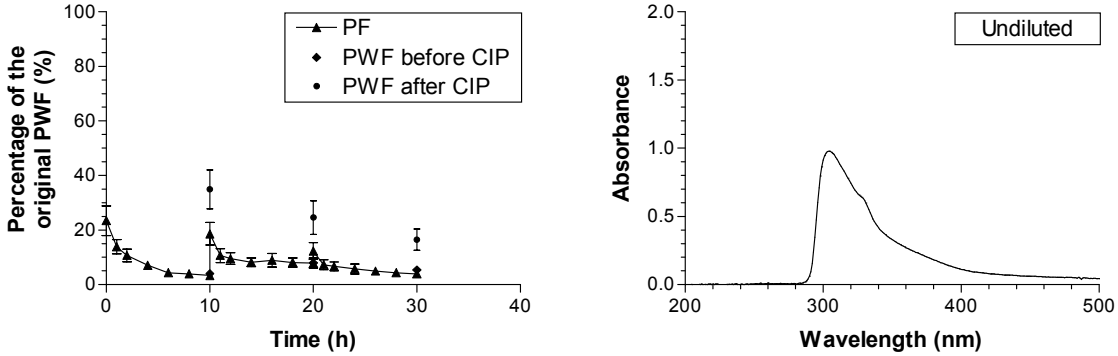


Figure 6.15: The pH of the microstrainer product was elevated to pH 10 and the inlet pressure to the rig reduced to 400 kPa. Flux determinations of the fouled membranes (left) and UV-Vis analysis of the membrane foulants (right) are displayed.

Experiment 16

The purpose of this experiment was to investigate the mechanical cleaning action of spongeballs on the membrane surface. Membranes were removed every hour, cleaned by wiping the membrane surface with a spongeball and replaced. The pH of the effluent feed to the test rig was increased to pH 10. Figure 6.16 summarises the results obtained for the experiment.

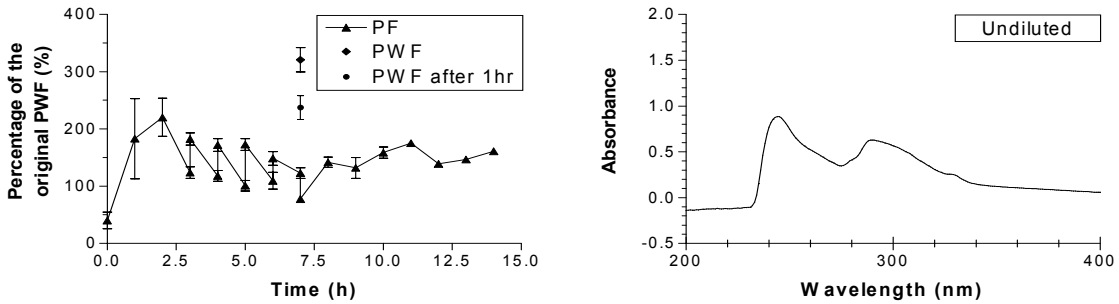


Figure 6.16: The effectiveness of membrane cleaning with spongeballs was evaluated by means of flux determinations (left) and UV-Vis analysis of the membrane foulants (right).

Experiment 17

The use of lignosulphonate as a dispersant, in combination with an elevated feed pH, was investigated on the test rig (see Figure 6.17). The lignosulphonate concentration in the feed was 5%.

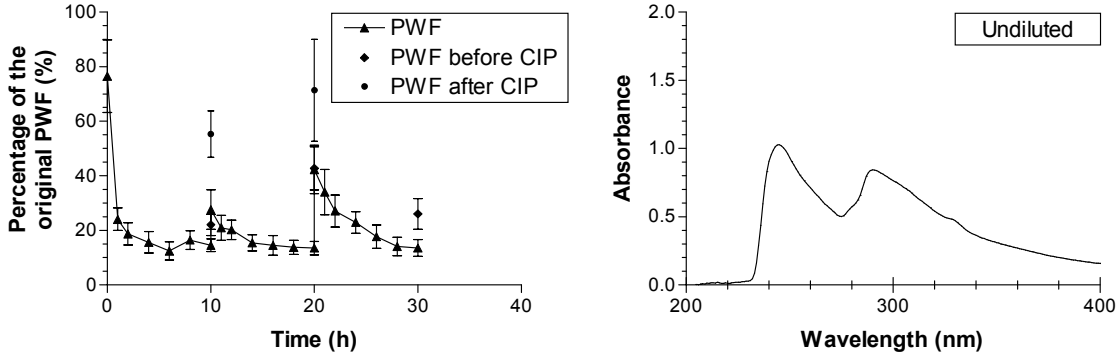


Figure 6.17: The effectiveness of lignosulphonate as a dispersant, in combination with an elevated pH, was examined on the test rig. Results obtained for flux determinations through the membranes (left) and UV-Vis analysis of the membrane foulants (right) are presented.

Experiment 18

When the membrane plant was first commissioned, the feed to the plant consisted of black liquor washings from the digester and paper machine effluent. According to plant data, higher product fluxes were obtained with the combined effluent than those obtained with DAF product. 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 6.18.

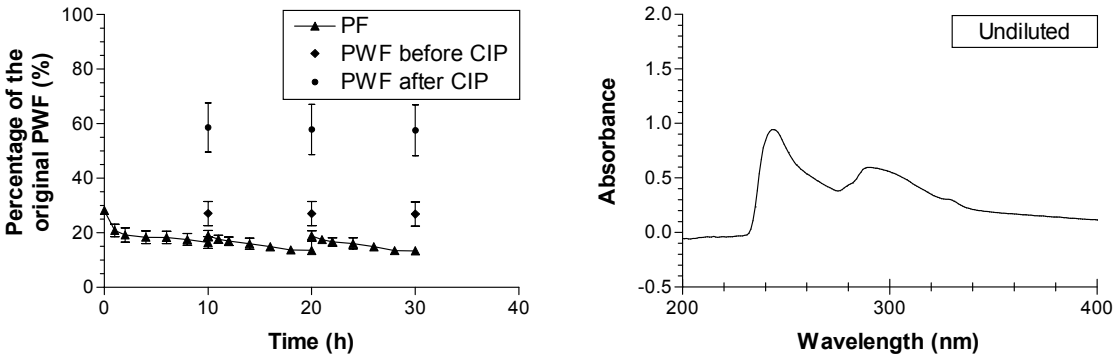


Figure 6.18: PES membranes were fouled with a combined effluent, consisting of paper machine effluent and black liquor. Flux determinations performed on the membranes (left) and UV-Vis analysis of the membrane extracts (right) are shown.

Experiment 19

Triton X100® (supplied by Sigma Chemical co.) is a non-ionic surfactant that has been effectively used as a cleaning agent on untreated and pre-treated tubular PES membranes, fouled with pulp and paper effluent (Swart *et al.*, 1999). For this experiment a 5% Triton X100® solution was used as a cleaning agent during the CIP of fouled test rig membranes. The results obtained are presented in Figure 6.19.

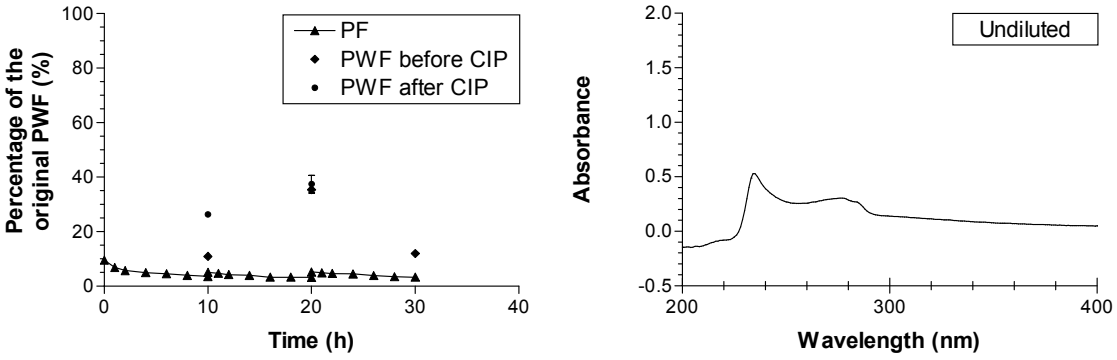


Figure 6.19: Triton X100® was evaluated as a membrane cleaning agent and its effectiveness evaluated by means of flux determinations through the membranes (left) and UV-Vis analysis of the membrane foulants (right).

Experiment 20

Sodium dodecyl sulphate (SDS), provided by Saarchem, was used in conjuntion with NaOH as a cleaning agent for tubular PES membranes (Swart *et al.*, 1999). A 1% SDS solution was prepared in water and evaluated on the test rig. Figure 6.20 displays the results obtained for the experiment.

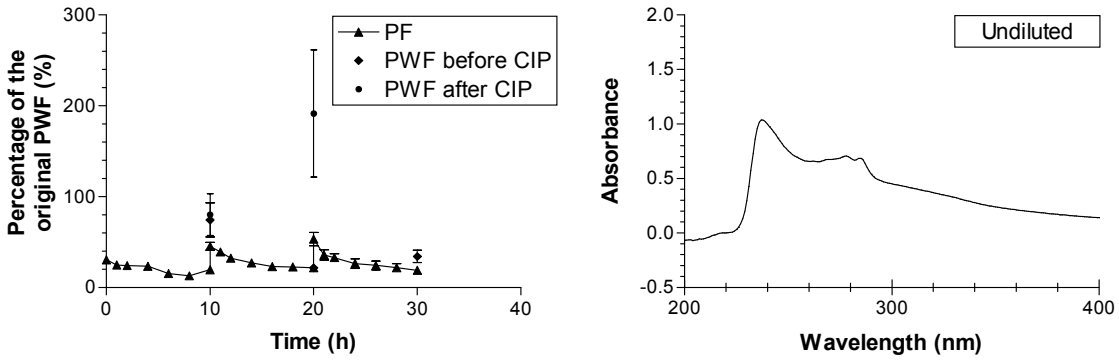


Figure 6.20: SDS, in combination with NaOH, was evaluated as a membrane cleaning agent. Flux measurements through the membrane (left) and UV-analysis of the membrane foulants (right) are presented.

Experiment 21

Experiment 14 was repeated to verify background results. Results obtained are shown in Figure 6.21.

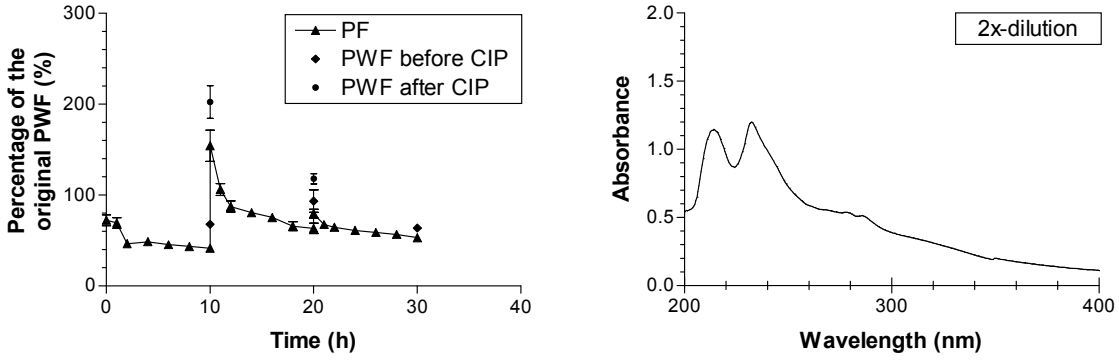


Figure 6.21: Repeat of experiment 14, see Figure 6.14.

Experiment 22

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) 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. Discs of flat-sheet membranes were pre-treated in a 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 6.22.

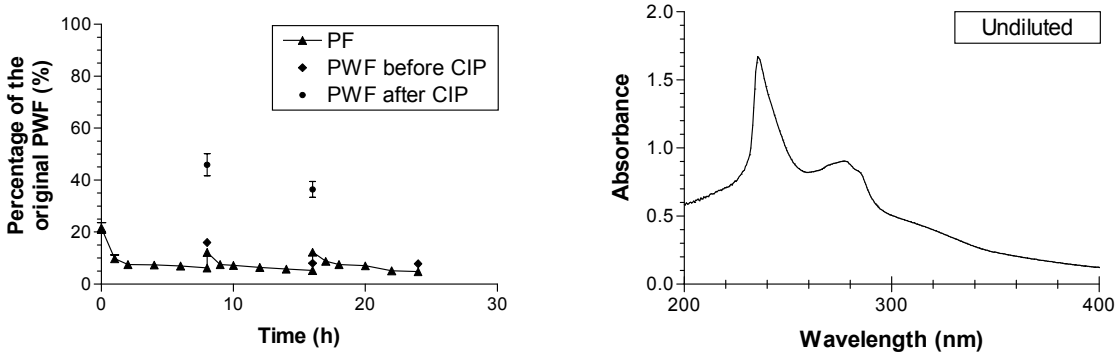


Figure 6.22: The ability of Pluronic® F108 to prevent membrane fouling was evaluated. Results obtained for the flux measurements through pre-treated membranes (left) and UV-Vis analysis of the membrane foulants (right) are presented.

Experiment 23

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 that had a MMCO of 5 kDa and 15 kDa, 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 in conjuction with an elevated effluent feed pH of 10. The results for the experiment are summarised in Figure 6.23.

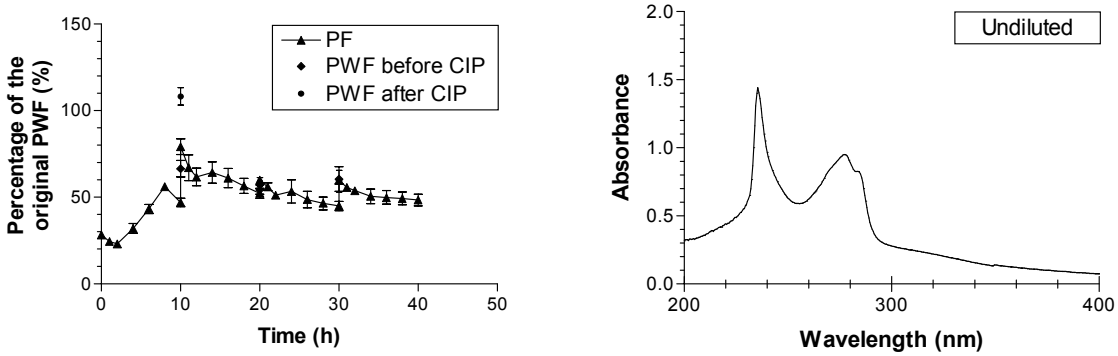


Figure 6.23: An Osmonics membrane, a negatively charged PS membrane, with MMCO of 5 kDa was fouled with microstrainer product (pH 10) at an inlet pressure of 1 MPa. Flux measurements were performed on the membranes (left) and UV-Vis analysis was performed on the membrane extracts (right).

Experiment 24

The Osmonics membrane with the 15 kDa MMCO was used in this experiment. The pH of the effluent feed was raised to pH 10 and the feed pressure to the test rig was raised to 600 kPa. Figure 6.24 summarises the results of the experiment.

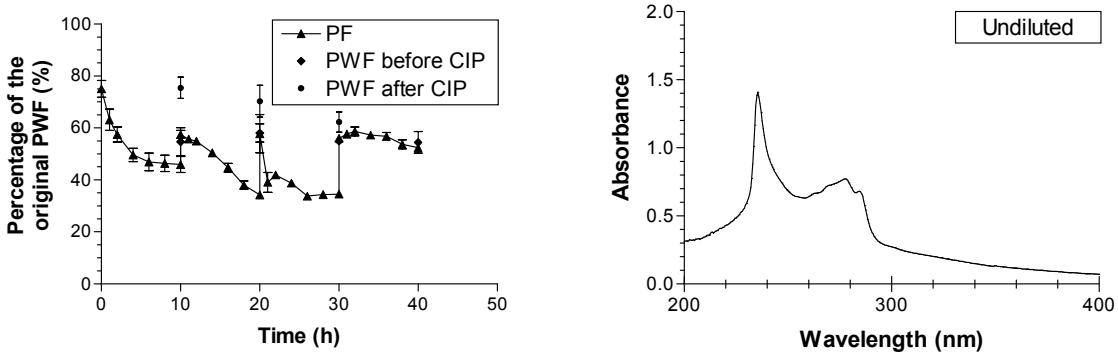


Figure 6.24: Osmonics membranes, MMCO of 15 kDa, were fouled with microstrainer product (pH 10) at an inlet pressure of 600 kPa. Flux measurements were performed on the membranes (left) and the membrane foulants were analysed by means of UV-Vis spectrophotometry (right).

Experiment 25

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 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 a

1% v/v Triton X100®. The results of the experiment are displayed in Figure 6.25.

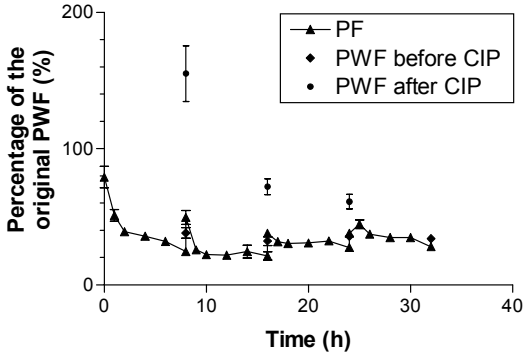


Figure 6.25: PES membranes were coated with 1% m/v Pluronic® F108, fouled with microstrainer product and cleaned with 1% v/v Triton X100®. Flux measurements were performed on the membranes and are displayed above.

Experiment 26

This experiment was the same as Experiment 25, but with the pH of the effluent feed increased to pH 10. Figure 6.26 summarises the results obtained for the experiment.

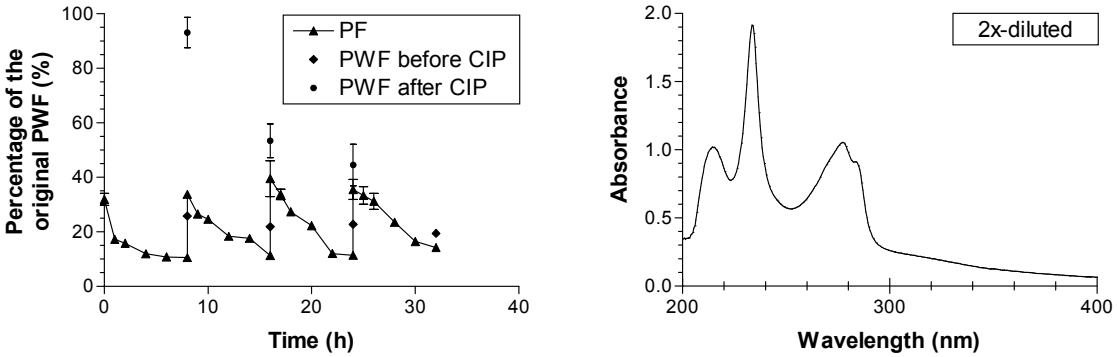


Figure 6.26: A repetition of Experiment 25 performed at an elevated pH of 10. Flux measurements were performed on the membranes (left) as well as UV-Vis analysis of the membrane extracts (right).

Experiment 27

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 6.27.

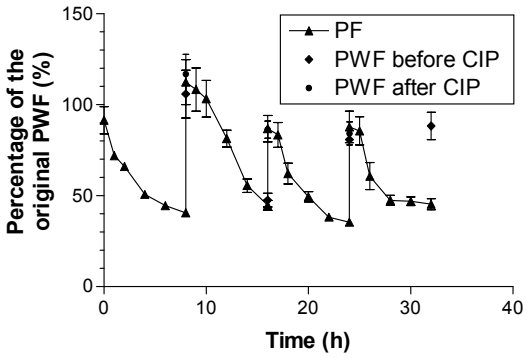


Figure 6.27: Osmonics membranes, with a MMCO of 5 kDa, were pre-coated in a 1% m/v Pluronic® F108 solution and fouled with microstrainer product (pH 10) at an inlet pressure of 1 MPa and cleaned with 1% v/v Triton X100®. Results obtained for flux measurements are presented (above).

Experiment 28

The experimental conditions and procedures were the same as for Experiment 27 but for this experiment the 15 kDa MMCO Osmonics membrane was used. The results obtained are displayed in Figure 6.28.

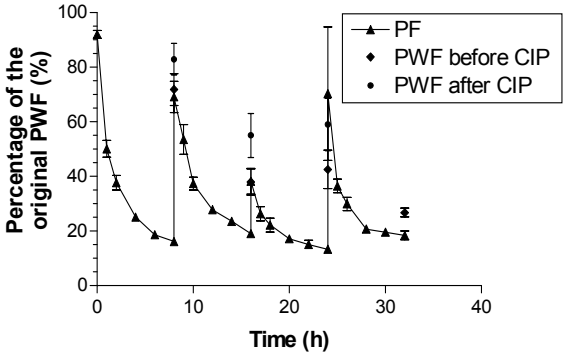


Figure 6.28: Osmonics membrane, with MMCO of 15 kDa, were operated under the same experimental conditions as discussed in Experiment 27. Results obtained for flux measurements are presented (above).

Experiment 29

A 100 mg/L Pluronic® F108 [concentration 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 6.29 summarises the results obtained for the experiment.

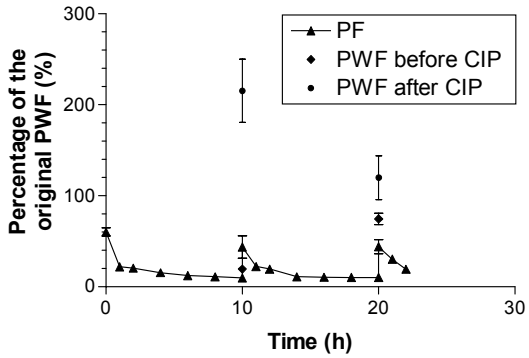


Figure 6.29: PES membranes were dynamically coated with a 0.01% Pluronic® F108 solution under standard operating conditions. Triton X100® (1% v/v) was used as a cleaning reagent. Flux measurements are presented.

Experiment 30

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 6.30.

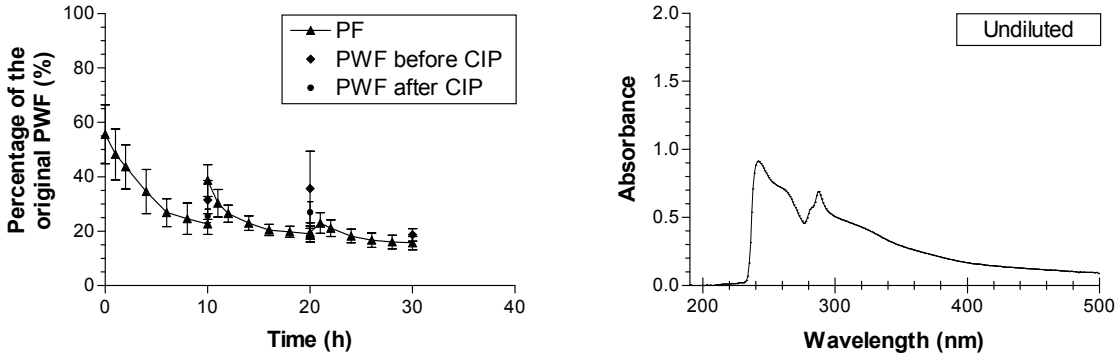


Figure 6.30: PES membranes were fouled with dam effluent (natural pH) and cleaned with 1% v/v Triton X100®. Flux measurements performed on the membranes (left) including UV-Vis analysis of the membrane foulants are shown on the right hand side.

Experiment 31

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 6.31.

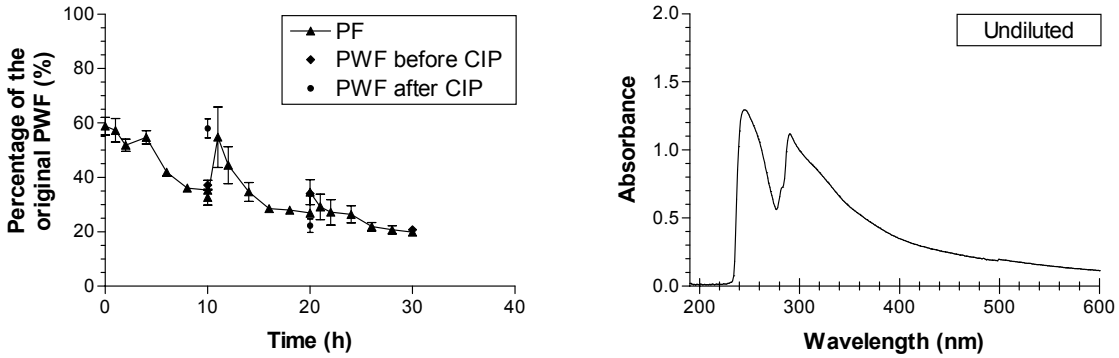


Figure 6.31: PES membranes were fouled with dam effluent (pH 10) and cleaned with 1% v/v Triton X100®. Flux measurements performed on the membranes (left) including UV-Vis analysis of the membrane foulants are shown (right).

Experiment 32

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

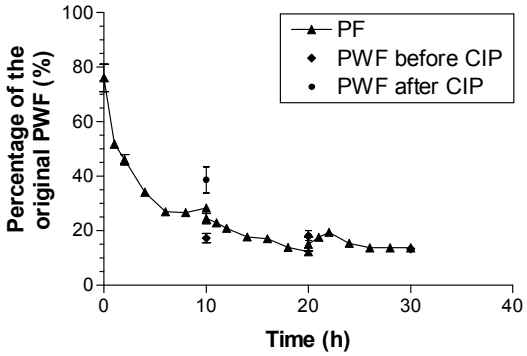


Figure 6.32: Flux measurements obtained for membranes fouled with microstrainer product, which had been passed through a column of membrane staples.

6.2 CONCLUSIONS FROM TEST RIG EXPERIMENTS

The results obtained from the studies are summarised in Figure 6.33. The following overall conclusions can be made from the data obtained from the experiments described in section 6.1.1.

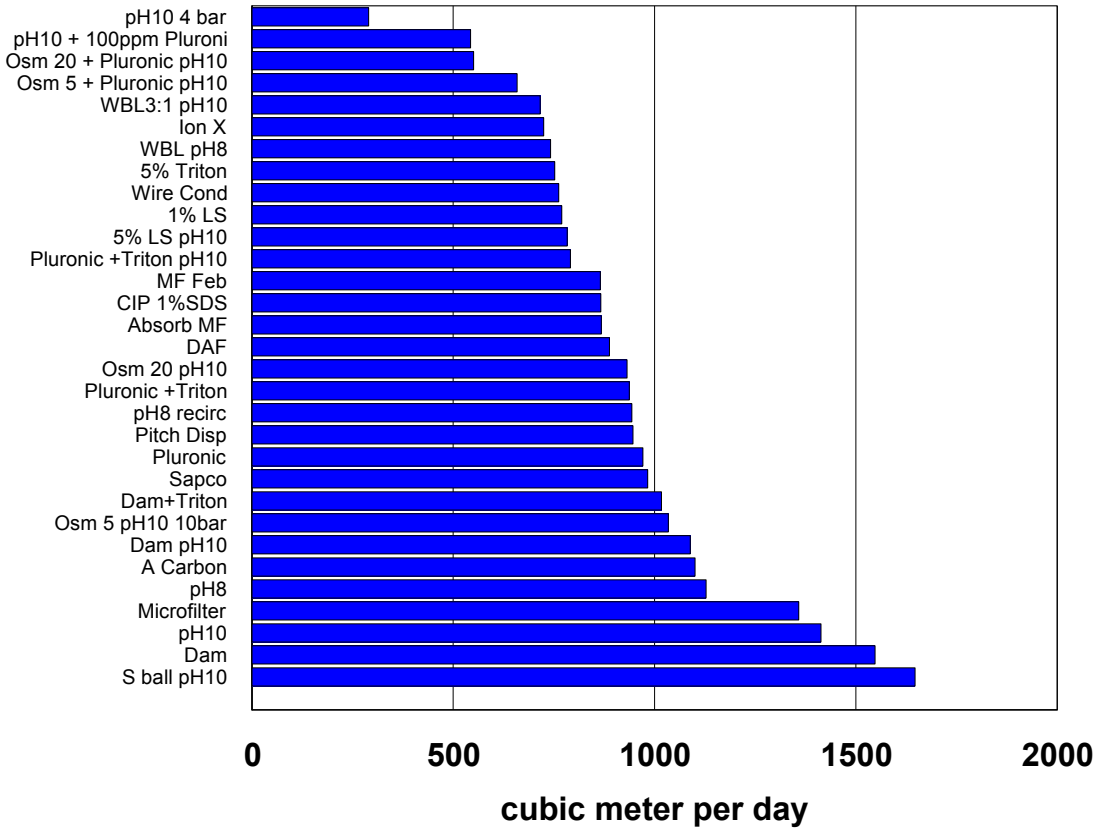


Figure 6.33: Summary of results obtained from cleaning experiments conducted at the mill in Piet retief. Results are presented as the integrated permeate flow.

- 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, with the 30 μm opening, 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 (PSFP), 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 PES membranes 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 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 for all the experiments. It was found that

the dam effluent contained reduced sulphur compounds that could not easily be removed from the membranes during CIP.

- 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 4.2.2, Figure 4.3). 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 4.2 and 4.3). 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. To prove this hypothesis conclusively, however, further experimentation is needed.

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