AEROBIC MEMBRANE BIOLOGICAL REACTOR TREATMENT

OF RECIRCULATED MECHANICAL NEWSPRINT WHITEWATER

AT HIGH TEMPERATURES

by

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ABSTRACT

The membrane biological reactor (MBR) is a robust and stable biological treatment process which integrates biological oxidation with ultrafiltration for treating wastewaters. A lab scale MBR consisting of a 10 L aerobic reactor, a cross-flow tubular ultrafiltration unit (molecular weight cut-off = 75 kDaltons) and a progressive cavity pump was operated at temperatures ranging from 40 to 55°C, hydraulic retention times (HRT) of 2.8, 1.1 or 0.7 days, a solids retention time of 25 days and a transmembrane pressure of 79 kPa to treat a synthetic closed-mill mechanical newsprint whitewater. The mixed-liquor volatile suspended solids concentration in the MBR varied with the operating conditions, ranging from 2 to 9 g/L. In another study, the effectiveness of the ultrafiltration component of the MBR alone was investigated. The synthetic whitewater was ultrafiltered to a concentration factor of 37 using the ultrafiltration unit at a transmembrane pressure of 69 kPa and a cross-flow velocity of 1.7 m/s (same velocity as the MBR). These two treatment processes were assessed for the removal efficiency of total solids (TS), total dissolved solids (TDS), total chemical oxygen demand (TCOD), dissolved chemical oxygen demand (DCOD), dissolved organic carbon (DOC), colour, cationic demand, resin acids (RA) and fatty acids (FA).

The MBR achieved similar removal efficiencies for all operating temperatures and hydraulic retention times. It was particularly effective at removing FA (100% removal), RA (average removal $\geq$ 98%), TCOD (82% average removal), DCOD (78% average removal) and DOC (76% average removal). The reduction of the whitewater cationic demand was good (64% average removal). The average removal efficiencies for TS (36%) and TDS (27%) were fair, while the MBR was ineffective at removing colour (-5% average removal). Ultrafiltration alone was not nearly as effective at removing the target contaminants from the synthetic whitewater. The high removal efficiencies of RFA achieved with the MBR may be due to the fact that RFA have a tendency to be adsorbed by the biosolids, which are retained by the ultrafiltration membrane. This and other inherent advantages of the MBR suggest much potential for this process in treating recirculated whitewater internally in pulp and paper mills.

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LIST OF ABBREVIATIONS AND ACRONYMS

AC	Alternating current
ADUF	Anaerobic digestion ultrafiltration
adt	Air-dried tonne
ASB	Aerated stabilization basin
BCTMP	Bleached chemi-thermomechanical pulp
BOD	Biochemical oxygen demand
BOD_5	Biological oxygen demand (5 day)
CD	Cationic demand
CF	Concentration factor
cfu	Colony forming units
COD	Chemical oxygen demand
col.	Colour
CTMP	Chemi-thermomechanical pulp
d	Day(s)
DCOD	Dissolved chemical oxygen demand
DCS	Dissolved and colloidal substances
DDPM	1,5-dimethyl 1-1,5 diazaundecamethylene polymethylobromide
DHA	Dehydroabietic acid
DO	Dissolved oxygen
DOC	Dissolved organic carbon
E_1	1st caustic extraction stage
F/M	Food to microorganism
FA	Fatty acids
HRT	Hydraulic retention time
ID	Internal diameter
lab	Laboratory
M-10	Minisette polyethersulfone ultrafiltration unit with a MWCO of 10 kDaltons (manufactured by Filtron Inc. of Northborough, MA, USA)
M-100	Minisette polyethersulfone ultrafiltration unit with a MWCO of 100 kDaltons (manufactured by Filtron Inc. of Northborough, MA, USA)
MBR	Membrane biological reactor
MF	Microfiltration
MIM	Minimum impact mill
ML	Mixed liquor
MLSS	Mixed liquor suspended solids
MLTDS	Mixed liquor total dissolved solids
MLVSS	Mixed liquor volatile suspended solids
MST	Membrane sewage treatment
MW	Molecular weight
N	Nitrogen

NF	Nanofiltration
OUR	Oxygen uptake rate
P	Phosphorus
P	Pressure
PAPRICAN	Pulp and Paper Research Institute of Canada
PCI	Paterson Candy International, Inc.
PF-75	Permaflow-1 tubular ultrafiltration unit with a MWCO of 75 kDaltons (manufactured by Zenon Environmental Inc. of Burlington, Ontario, Canada)
psi	Pounds per square inch
PVC	Polyvinyl chloride
PVSAK	Polyvinyl sulphuric acid potassium salt (K)
RA	Resin acids
RFA	Resin and fatty acids
RO	Reverse osmosis
rpm	Revolutions per minute
S_0	Influent COD or BOD concentration
SBR	Sequencing batch reactor
SOUR	Specific oxygen uptake rate
S_R	Substrate removed
SRT	Solids retention time
T	Temperature
TBO	Toluidine blue O
TCF	Totally chlorine free
TCOD	Total chemical oxygen demand
TDS	Total dissolved solids
TEF	Totally effluent free
TMP	Thermomechanical pulp
TOC	Total organic carbon
TS	Total solids
TSS	Total suspended solids
U	Specific substrate utilization rate
UASB	Upflow anaerobic sludge blanket
UBC	University of British Columbia
UF	Ultrafiltration
VDS	Volatile dissolved solids
VS	Volatile solids
VSS	Volatile suspended solids
Y_{obs}	Observed growth yield

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1. INTRODUCTION

1.1. Motivation of Research

The pulp and paper industry is working to reduce the amounts of fresh water used and the volume of effluent discharged to the environment, by recycling process water more extensively in pulp and paper mills. In order to maximize whitewater re-use within integrated thermo-mechanical newsprint mills, dissolved and colloidal substances (DCS) that may affect paper quality or compromise paper machine runnability must be maintained at acceptable concentrations. An internal form of whitewater treatment capable of purging excess DCS could allow an increase in the recirculation of whitewater.

A long term research project comparing various treatment processes for the removal of contaminants from recirculated whitewater from integrated thermo-mechanical newsprint mills with excess flows of 2 to 5 cubic meters per air dried tonne of product (m^3/adt) was initiated in 1992 at the University of British Columbia's Pulp and Paper Centre. This thesis focuses on the effectiveness of aerobic membrane biological reactor technology, a high performance treatment process integrating aerobic biological treatment and ultrafiltration, for this application. Some of the results have been published in Tardif and Hall (1996b) and Tardif and Hall (1996c).

Other studies, also completed at the Pulp and Paper Centre, were conducted with the aim of comparing various technologies for the treatment of the same whitewater. Johnson first investigated the treatability of the whitewater using a sequencing batch reactor (SBR) (Johnson, 1995; Johnson and Hall, 1996). Elefsiniotis then investigated the effectiveness of ultrafiltration for the treatment of the same whitewater, particularly whether ultrafiltration of the SBR effluent resulted in the additional removal of contaminants (Elefsiniotis, 1994; Elefsiniotis et al., 1995). A paper comparing all the treatment alternatives studied this far at the Pulp and Paper Centre as part of this on-going research project has recently been presented (Tardif and Hall, 1996a).

1.2. Thesis Organization

Background information as well as a literature review of subjects related to the applicability of membrane bioreactor treatment to remove DCS from recirculated thermo-mechanical newsprint whitewater are presented in Chapter 2. Chapter 3 outlines the objective of the research carried out for this study. Chapter 4 describes the materials and methods used while the results and a discussion of these results are presented in Chapter 5. Finally, Chapter 6 reviews the major conclusions stemming from this work and lists recommendations for future research in this area. The Appendix describes how to retrieve the raw experimental data and graphs presented in this thesis from the attached computer disk, as well as instructions on how to create new graphs from these.

2. BACKGROUND AND LITERATURE REVIEW

In this section, the whitewater system of thermo-mechanical newsprint mills is explained. Possible treatment alternatives for purging contaminants accumulated from increased whitewater recirculation are reviewed. An overview of membrane filtration processes and the applications of the aerobic membrane biological reactor process for treating wastewaters are also presented.

2.1. The Trend Towards Systems Closure in the Pulp and Paper Industry

The pulp and paper industry is currently working towards reducing the use of fresh water in its operations, thus minimizing the volume of effluent discharged to the environment. This trend towards the closure of operations seems to be accelerating. Recently, the first-ever symposium concerned entirely with the closure of pulp and paper mills was held: the 1996 TAPPI Minimum Effluent Mills Symposium (held in Atlanta, GA, USA) attracted a large group of consulting and process engineers, mill operators, scientists and other people interested in this "hot topic", the term used to describe mill closure at the opening of the symposium. Numerous papers have also been published recently on this topic, including a six-part series of articles in the periodical *Pulp and Paper*. In the first article of this series (Dexter, 1996), the author points out that "most people in the paper industry know that water closure is in the industry's future" and concludes that "water closure represents a competitive advantage, particularly in the environmentally conscious pulp and paper industry".

However, in order to achieve greater mill closure, separation technologies are needed to purge critical contaminants which currently leave in the effluent (Gerbasi *et al.*, 1993b; Wearing, 1992 and 1993b). Current separation technologies for removing dissolved and colloidal substances from thermo-mechanical newsprint whitewater are presented in Section 2.5, after a brief review of whitewater recycling strategies (Section 2.3) and an overview of the problems associated with whitewater recirculation (Section 2.4) are presented.

2.2. Water Use in Mechanical Newsprint Mills

In typical integrated newsprint mills, large amounts of effluent are discharged, currently ranging from 10 to 150 m^3/adt (Wearing *et al.*, 1985b). Older mills, which were designed to flush out contaminants using large volumes of fresh water, use 50 to 200 m^3/adt, while new mechanical pulping configurations are designed for 10 to 20 m^3/adt (Wearing, 1992). The drive towards increased water conservation can be linked to several factors (Wohlgemuth *et al.*, 1996):

- increasing end-of-pipe effluent treatment costs and more stringent discharge limits;

- limited water supply, especially in urban areas;

- competition in the industry with respect to environmental performance and waste minimization;

- company-wide environmental strategic goals towards closed-cycle operation, evident through industry-initiated concepts such as MIM (Minimum Impact Mill), TEF (Totally Effluent Free), TCF (Totally Chlorine Free);

- government incentives for use of new, effluent-free technology; and

- energy conservation efforts, particularly related to heat conservation.

At current water usages of 10 to 20 m^3/adt, it is most economical to discharge excess whitewater to the recipient after biological treatment (Wearing, 1993b). However, the development of new "kidneys", or internal treatment systems designed to purge contaminants from various systems, may be the key to further volume reductions which could lead to the complete closure of integrated thermo-mechanical newsprint mills. If, by using such an internal treatment system, total water usage in these mills can be reduced to 2 to 5 m^3/adt, than it becomes economically viable to evaporate the remaining effluent and incinerate the concentrate (Wearing, 1992). Such a mill would not require end-of-pipe biological treatment as no liquid effluent would be left to treat externally and would be considered a TEF

(Totally Effluent Free) or zero-effluent mill. At least two TEF pulp mills have been introduced in the past few years: a BCTMP (bleached chemi-thermo-mechanical pulp) mill located in Meadow Lake, Saskatchewan, Canada (Fromson and Leslie, 1994) and a BCTMP mill located in Chetwynd, British Columbia, Canada (Young, 1994). Both mills currently use evaporation-based treatment of the external effluent for water re-use within the mill. However, these are not integrated pulp and paper mills: they only produce pulp to be used as furnish in other mills.

2.3. Whitewater Recycling Strategies

In a pulp and paper mill, the whitewater system is defined as a system of tanks, pumps and piping for handling all recirculated process water streams that contain fiber fines (Smook, 1990). For the paper machine, whitewater is formed during the forming and dewatering of the web during paper formation. A whitewater system is said to be "open" if a large proportion of the water flow is sewered and "closed" if only a small proportion leaves the system. In the thermo-mechanical pulping process, whitewater is responsible for a large proportion of the total fresh water usage. Closing the whitewater system tightly, would therefore be beneficial in attaining the goal of reducing the total water usage in integrated thermo-mechanical newsprint mills to 2 to 5 m^3/adt. However, attempts to close up an existing whitewater system often meet with serious difficulties relating to paper machine runnability, and, often, product quality (Wahren, 1985).

A tightly closed whitewater system would produce several benefits, which are listed below (Panchapakesan, 1995; Pietschker, 1996):

- reduced loss of fiber, fines and filler;

- reduced chemical consumption;

- reduced energy consumption as heat is conserved;

- reduced freshwater consumption;

- reduced end-of-pipe effluent treatment costs.

Although the costs associated with closed cycle technologies are significantly higher than the cost for treatment of the effluent for subsequent discharge (Gerbasi *et al.*, 1993a), systems closure is considered more attractive than biological treatment and discharge for satisfying society's future demand for environmentally friendly pulp and paper mill operations (Francis, 1995). Complete closure may, in fact, represent the only alternative if a new mill is to be built where the receiving waters have a very limited assimilative capacity, as was the case for the Meadow Lake closed pulp mill (Fromson and Leslie, 1994). Problems associated with the closure of the whitewater systems are reviewed in the following section.

2.4. Problematic Dissolved and Colloidal Substances Present in Recirculated Whitewater

Tightly closed whitewater systems differ from conventional whitewater systems in that large quantities of fresh water cannot be used to flush out contaminants. By closing the whitewater system, these contaminants, or dissolved and colloidal substances, which can be detrimental to the paper machine operation or the product quality, tend to accumulate in the recirculated whitewater. Many papers list these detrimental substances and explain their effects on the paper machine or on the product (Geller and Göttsching, 1982; Springer *et al.*, 1985; Wearing *et al.*, 1985a; Thornton *et al.*, 1993; Welkener *et al.*, 1993; Pietschker, 1996; Thompson and Garner, 1996). Closing a mill's whitewater system typically leads to the following problems (Panchapakesan, 1992):

- higher suspended solids concentrations in the whitewater;

- higher dissolved substances concentration in the whitewater;

- the higher incidence of deposits on the papermaking equipment and the product;

- more biological growth in the whitewater system; and

- corrosive effects.

These problems are described in greater details below.

2.4.1. Effects of Detrimental Dissolved and Colloidal Substances

Whitewater is usually composed of wood fibers, fines, soluble and colloidal organics, salts and metals. The soluble and colloidal organics consist mainly of lignin, carbohydrates and wood extractives (Järvinen et al., 1985). Approximately half of the dissolved organic material has been reported to be of high molecular weight (MW > 10,000 - by ultrafiltration) (Wearing et al., 1985a). With the exception of valuable wood fibers, which can be recovered to make paper products, the accumulation of substances in the whitewater may have deleterious effects on the product quality or on the paper machine operation (Järvinen et al., 1985).

Total dissolved solids. The total dissolved solids in the whitewater can be categorized into organics and inorganics. The higher concentrations of dissolved organics in recirculated whitewater result mainly in higher biological growth in the system, causing slime, corrosion and odor problems in the paper machine, as well as possibly giving an odor to the paper product (Panchapakesan, 1995). Dissolved inorganics can cause corrosion and wear of the equipment (sulfates and chlorides, for example, are detrimental to equipment and hardware made of bronze, cast iron and mild steel). Other dissolved inorganics, such as carbonates and silicates, contribute to scaling. Cations, such as Fe^{2+} and Al^{3+}, also contribute to corrosion and may decrease brightness of the paper product (Panchapakesan, 1995). However, the presence of some solids in the whitewater seems desirable. According to Welkener et al. (1993), the presence of fines and fibers in thermo-mechanical pulp (TMP) whitewater can reduce the extent of pitch and stickies deposition by adsorbing the colloidal pitch onto the fines. That adsorbed pitch is less prone to deposition. According to an estimate from the Pulp and Paper Research Institute of Canada (PAPRICAN), an acceptable concentration of total dissolved solids in a closed mechanical newsprint mill could be in the range of 3000-4000 mg/L (Wearing, 1993a).

Resin and fatty acids. Resin and fatty acids (RFA), which are sparingly soluble organic extractives present in the furnish, may pose a significant problem in the closure of whitewater systems. These substances are considered to be among the most detrimental, as they will form deposits, specks or holes on the product or pitch on the paper machine, which may cause a break of the sheet during production (Welkener *et al.*, 1993). The total RFA concentration could be maintained at 12-15 mg/L (or less) in a closed whitewater system, a level judged acceptable according to one estimate from PAPRICAN (Wearing, 1993a).

Anionic trash. Another category of contaminants which becomes dissolved during papermaking operations is known as "anionic trash". These substances are anionic in nature and are capable of consuming cationic retention aids, which are costly additives used to improve the retention of fines and short fibers in the papermaking process. The accumulation of anionic trash in whitewater might therefore have to be controlled in tightly closed systems. A recent study (Thornton *et al.*, 1993) determined that polygalacturonic acids released from Norway spruce TMP accounted for a major part of the potential anionic trash released in bleached TMP suspensions. The removal of this anionic trash could lead to significant savings in the costs associated with cationic additives, a large proportion of which are inhibited by the anionic trash before they can perform their role as retention aids (Alince, 1987; Linhart *et al.*, 1987; Springer *et al.*, 1987; Sundberg *et al.*, 1993).

2.4.2. Biological Growth in the Whitewater System

As mentioned earlier, the accumulation of dissolved organic solids may lead to increased microbiological growth in the paper machine, which can result in several types of problems. The increase in microbiological growth in closed whitewater systems is also a consequence of increased incubation, as the whitewater is recirculated more times than for an open whitewater system. The runnability of the paper machine may be affected by microbiological growth in several ways (Gudlauski, 1996):

- breaks in the paper sheet due to microbiological (slime) deposition;

- downtime to wash up or boil deposition;

- sewering of fibers or additives due to degradation;

- reduced production capacity due to screen plugging; and

- downtime for repair due to deposit corrosion.

Even the safety of the mill workers may become an issue when anaerobic bacteria produce toxic or explosive gases, such as hydrogen sulfide (H_2S), hydrogen (H_2) and methane (CH_4), in stock or water chests (Gudlauski, 1996). Slime deposition can also make catwalks and machine surfaces slippery, causing lost time accidents.

In view of the various detrimental effects caused by microbiological growth in the whitewater system, any "kidney" developed for purging contaminants accumulating in whitewater should be able to control this problem by retaining or destroying these microorganisms. The use of ultrafiltration in such an internal treatment application may prove beneficial by retaining microorganisms. The control of the concentration of microorganisms in whitewater from a recycled paper mill using ultrafiltration was one of the principal objectives of a recent study conducted in Denmark to increase whitewater recirculation (Knudsen et al., 1996). It is hoped that as temperatures in the closed whitewater system increase with closure, from the current 45-60°C (Panchapakesan, 1992) to possibly 70°C (Wearing, 1993a), some of the biological growth in the whitewater system could be suppressed (Wenzl, 1981). The use of biocides (Geller and Göttsching, 1982) might have to be limited if the internal whitewater treatment process involved biological treatment.

2.4.3. Corrosion

Corrosion can occur in the paper machine equipment and affect efficiency and maintainability. The downtime experienced if no spare part is readily available (e.g. for a major component like a suction roll) can be considerable (Thompson and Garner, 1996). As discussed previously, microbiological activity is likely to increase after whitewater systems closure, increasing the likelihood of microbiological corrosion. In addition, the concentration of ionic species will also increase in closed whitewater systems. This is likely to have an impact on the choice of materials used as greater whitewater closure is achieved. For example, Thompson and Garner (1996) report that 304L stainless steel will become a marginal or unacceptable choice of material in many closed whitewater systems, although this will be mill specific.

2.5. Alternatives for Treating Recirculated Whitewater

As discussed previously, in order for integrated TMP newsprint mills to become totally effluent-free by evaporating their excess water flows, the total water usage for these mills should be reduced to approximately 2 to 5 m^3/adt. It would then become economically viable to evaporate the effluent to produce high-quality water for re-use in the mill and to incinerate the resulting concentrate. For many integrated TMP newsprint mills, the reconfiguration of the whitewater system and proper stream segregation, as discussed by Wearing *et al.* (1985b), might be sufficient to reduce freshwater consumption and the resulting effluent. However, the use of a "kidney", or internal treatment process, to purge contaminants from the recirculated whitewater, might be necessary for integrated TMP newsprint mills to reduce their total water consumption to 2 to 5 m^3/adt. One possible configuration for integrating such a kidney in a TMP newsprint mill is illustrated on Figure 2.1. The kidney could treat a sub-stream of water from the TMP mill to produce water to replace or supplement freshwater at various points in the integrated mill. However, because the kidney would likely not remove all contaminants which accumulate in recirculated whitewater, some effluent would still have to be evaporated to produce a high-quality condensate that would also be used at various points in the integrated mill. The evaporator

and kidney concentrates could then be incinerated, resulting in the complete closure of the integrated mill.

Potential internal treatment processes designed to purge contaminants from recirculated whitewater should be able to handle high temperatures, as temperatures in the whitewater system are likely to increase from the current 45 - 60°C to 70°C, as discussed previously. This is especially important for treatment processes involving the use of biological treatment, which may be sensitive to such high temperatures. Investigations of the highest feasible working temperatures for biological treatment of recirculated whitewater are therefore important in determining whether cooling of the whitewater would be necessary prior to biological treatment.
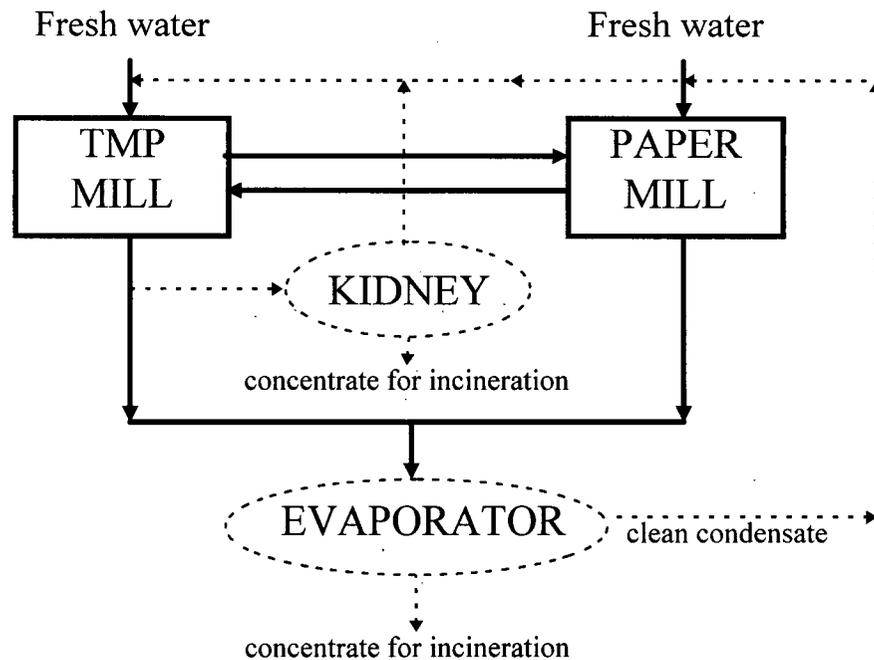
Figure 2.1. Proposed internal treatment system in a integrated TMP newsprint mill to purge contaminants from recirculated whitewater. The "kidney" would enable the reduction of the total mill water usage to 2 to 5 m³/adt, rendering evaporation a viable means for treating the remaining effluent. The resulting concentrates could be disposed of by incineration.

Possible alternatives for internal whitewater treatment processes are discussed below. They include: freeze crystallization, evaporation, chemical additions, membrane filtration, biological treatment and a combination of biological treatment and membrane filtration.

2.5.1. Freeze Crystallization

Freeze crystallization, a process commonly used for the concentration of fruit juices, is a separation process that can be used to freeze relatively uncontaminated water crystals for water recovery. The resulting slurry, or concentrate, can then be disposed of by further evaporation and/or incineration. This process was applied to the Louisiana-Pacific mill located in Chetwynd, BC, Canada. However, due to operational difficulties, it was later replaced by evaporation (Young, 1994). Freeze crystallization, described briefly by Gerbasi *et al.* (1993a) in a paper comparing several closed cycle technology alternatives for an existing TMP-newsprint mill, may prove unacceptable for use for the treatment of recirculated whitewater, as resin and fatty acids begin to attach to the ice crystals when total dissolved solids concentrations in the slurry exceed 15%. This limitation means that large volumes of concentrate would have to be disposed of, resulting in high operating costs, in addition to the high capital costs.

2.5.2. Evaporation

Evaporation may be the least costly closed-cycle alternative for TMP-newsprint mills with a low water usage. It is also a well proven technology (Gerbasi *et al.*, 1993a). Evaporation and condensation are used to recover relatively uncontaminated water, while the effluent is disposed of after further concentration, usually by incineration. This technology has been reported to work satisfactorily at the closed BCTMP mill located in Meadow Lake, Saskatchewan, Canada (Fromson *et al.*, 1994). However, as stated previously, to make this process economically viable in integrated TMP newsprint mills, the total consumption of water should first be reduced to excess flows of 2 to 5 m^3/day before evaporation can become an economically viable closed-cycle alternative for integrated newsprint mills.

2.5.3. Chemical Addition

A wide range of chemicals can be utilized in the papermaking process, including biocides, slimicides, pitch dispersants, corrosion inhibitors, retention aids, sizing agents, defoamers, etc. (Smook, 1992). These chemical additives can be helpful in the successful operation of papermaking equipment when the whitewater system is more tightly closed. However, they are usually costly and are limited to the control of specific problems. Their utility in closed whitewater systems should remain unchanged, but they are only part of the solution in order to achieve a greater closure of the whitewater system.

2.5.4. Membrane Filtration

Membrane-based separation processes are used for concentrating aqueous solutions containing suspended solids, colloids, macromolecules and microorganisms. These processes have traditionally been used on high value products (e.g. for biotechnology, the dairy industry, etc.), but the development of robust and inexpensive membrane modules has opened up new applications for membrane technology, such as wastewater treatment. It appears that membrane-based separation processes, such as ultrafiltration and nanofiltration, could be used as kidneys to purge contaminants from whitewater, as discussed in Section 2.6. For this reason, ultrafiltration has been investigated as a possible alternative for the removal of contaminants from integrated TMP newsprint recirculated whitewater by Elefsiniotis et al. (1995). Only modest (< 45%) resin acid removal efficiencies were reported in that study, as well as for total dissolved solids (TDS), dissolved chemical oxygen demand (DCOD) and dissolved organic carbon (DOC) (25 to 45% removal). The use of nanofiltration in a similar study (Jokinen et al., 1993a) achieved significantly higher contaminant removal efficiencies. Since ultrafiltration was specifically studied in this thesis, research in this area is reviewed in greater detail in Section 2.6.

One of the disadvantages of membrane separation processes is that they only retain contaminants. They do not destroy them. This may pose a problem, as pitch caused by the concentration of resin and fatty acids can deposit in the concentrate tank when high (> 10) concentration factors are achieved. In addition, large volumes of concentrate would still have to be evaporated and/or incinerated.

Despite these potential problems, the use of membrane separation processes as a kidney to purge contaminants from integrated TMP newsprint mills appears feasible.

2.5.5. Aerobic Biological Treatment

Yet another method of treating integrated TMP newsprint whitewater would be to use biological treatment. Aerobic biological treatment has long been known to remove RFA and organic contaminants which contribute to the chemical oxygen demand (COD) in other pulp and paper effluents (Lo et al., 1994). Liu et al. (1993b) have shown that treatment of a CTMP effluent using laboratory (lab) scale aerobic treatment can result in excellent removal efficiencies (>98%) of resin and fatty acids, about 94 to 98% of the 5-day biochemical oxygen demand (BOD_5) and 70 to 80% of the COD. However, the performance of the aerobic treatment, which was investigated at various operating temperatures ranging from 13 to 50°C, significantly decreased in efficiency at temperatures above 30°C, in part due to poor sludge settling. This finding was also reported by Johnson and Hall (1996) in their investigation of the treatment of a synthetic recirculated mechanical newsprint whitewater using a lab scale aerobic sequencing batch reactor. They found that poor sludge settleability and low biomass growth were responsible for low DCOD, TDS and resin acids (RA) removal efficiencies at temperatures above 40°C. For most contaminants, the best removal efficiencies were obtained at an operating temperature of 30°C: 100% of the RA, 96% of the fatty acids (FA) and 76% of the COD were removed at that temperature. Since the same synthetic mechanical newsprint whitewater was used in the present study, the results of the Johnson and Hall study (1996) are compared to those obtained in this study in Section 5.8.

Biological treatment to remove contaminants from recirculated newsprint whitewater, although effective at temperatures of 40°C and below, should be combined with ultrafiltration, since microorganisms should be retained or destroyed by any internal treatment scheme used to treat whitewater to be re-used internally. The release of seed microorganisms to the whitewater system would only increase the various problems associated with the presence of microorganisms. In addition, in an integrated biological-membrane treatment process, such as the membrane bioreactor used in the present

study, poor sludge settleability and low biomass growth are no longer problems as all microorganisms are retained by the membrane and returned to the reactor. Combined treatment processes involving both the use of ultrafiltration and biological treatment are discussed in Section 2.5.7 and 2.5.8.

2.5.6. Anaerobic Biological Treatment

Anaerobic treatment, used alone, is not considered a suitable process for the treatment of TMP and CTMP whitewater. Lo *et al.* (1994) reached that conclusion by reviewing results from bench and pilot scale studies (Anderson *et al.*, 1987; Wilson *et al.*, 1987) and from plant operations (Gunnarson *et al.*, 1989; Maclean *et al.*, 1990), which have shown that, unlike aerobic treatment, anaerobic treatment is unable to detoxify TMP and CTMP effluents. A maximum of 70 to 80% of the BOD_5 can be removed using anaerobic digestion, which is insufficient to meet effluent regulations (Jurgensen *et al.*, 1985; Lo *et al.*, 1994). In addition, chemical compounds present in the effluent, such as RFA , are toxic to anaerobic bacteria in the treatment system and cause operational upsets (McCarthy *et al.*, 1990). A similar finding was also reported by Liver and Hall (1996) in their study of the interaction of RA with unacclimated aerobic and anaerobic biomass. They found that non-acclimated anaerobic biomass was not capable of significant degradation of RA under batch conditions while unacclimated aerobic biomass was capable of rapid degradation of high initial concentrations of RA to non-detectable levels under similar conditions. Furthermore, they found that RA were inhibitory to methanogens in non-acclimated anaerobic batch assays with resin acid/biomass ratios of more than 0.0031 mg RA/mg VSS, while the presence of RA did not measurably alter the growth characteristics of the activated sludge biomass utilized in the aerobic batch reactors. Schnell *et al.* (1990) also noted that a considerable risk is associated with high rate anaerobic treatment of an integrated newsprint mill effluent, due to the potential of important losses of suspended sludge. They found that, under certain operating conditions, the anaerobic sludge became unusually buoyant due to a gas buildup within the sludge granules and concentrations of up to 2 g/L of TSS were measured in the effluent. Such releases of anaerobic sludge in the whitewater system from an

internal whitewater treatment system, which should be designed to retain microorganisms, not release additional seed organisms, would be unacceptable.

Despite these reported drawbacks for the use of anaerobic processes to treat TMP and CTMP effluents as well as RA-containing water streams, anaerobic treatment has recently been studied as an alternative for the treatment of whitewater from a thermo-mechanical pulping process (Rintala *et al.*, 1991; Rintala and Lepistö, 1992; Jahren and Rintala, 1996), from waste paper processing mills (Huster *et al.*, 1991; Barascud *et al.*, 1992 and 1993) and pulping wastewaters (Sierra-Alvarez *et al.*, 1990). A combined anaerobic and nanofiltration process has also been studied at a lab scale to treat thermo-mechanical clear whitewater (Nuortila-Jokinen *et al.*, 1996). Resin and fatty acids were not specifically analyzed in these studies.

Jahren *et al.* (1996) have shown that 68% of the COD present in a TMP whitewater could be removed at 55°C (55% at 70°C) using a UASB (upflow anaerobic sludge blanket) reactor with a hydraulic retention time of 9 hours. Similar results were reported by Rintala *et al.* (1991) using a UASB at 55°C and retention times of 1.1 to 3.2 hours, with the highest observed COD removal reported to be 65%. Barascud *et al.* (1992) have shown that by inserting a two-phase anaerobic system in a closed waste paper water circuit, and by treating a limited part of the flow, COD reductions of 75% could be achieved in the water circuit. The hydraulic residence time was kept constant at 12 hours and the temperature at 35°C during the study. In another study, the use of nanofiltration as a secondary polishing step to UASB reactor treatment of TMP clear whitewater improved the removal efficiency of the UASB reactor used alone (Nuortila-Jokinen *et al.*, 1996). COD removal efficiencies with the UASB alone were 55 and 65% (at temperatures of 55 and 70°C, respectively). The nanofiltration removed an additional 78-81% of the COD.

In a theoretical study involving the treatment of waste paper mill whitewater, Huster *et al.* (1991) point out that both aerobic and anaerobic processes can be used, in principle, to remove organic

substances which accumulate in closed whitewater systems. However, there is an advantage in using an anaerobic process since acidification usually begins within the water circuits due to the low concentrations of dissolved oxygen. Huster *et al.* believe that aerobic processes are inferior to anaerobic systems because of the energy required and the distinctly higher production of biological sludge. However, they add that an aerobic polishing step may be appropriate in some cases to further break down organic substances contained in the process water and in order to oxidize impurities from the anaerobic process.

Although anaerobic treatment is not efficient at removing RFA, anaerobic treatment used in combination with nanofiltration or another polishing step could be a viable treatment alternative for the treatment of recirculated TMP newsprint whitewater.

2.5.7. Aerobic Biological Treatment Combined with Ultrafiltration

Aerobic biological treatment combined with ultrafiltration has been considered as a potential closed cycle technology in a recent techno-economic assessment comparing three alternatives to treat and re-use the effluent from an existing TMP-newsprint mill (Gerbasi *et al.*, 1993a). In this case, the effluent would first be treated using aerated stabilization basin (ASB) technology. The biologically treated effluent would then be treated by UF and RO membrane filtration to remove the remaining contaminants. For flows lower than 20 m^3/adt, anaerobic treatment followed by an aerobic polishing step was found to minimize capital and operating costs. Some of the permeate from the UF system could be used directly back in the mill without RO treatment. A portion of the total mill effluent would need to be treated by RO to purge inorganic constituents. It was assumed that water recoveries ranging from 85 to 95% could be achieved. However promising, the biological-membrane treatment alternative was considered yet an unproven technology. However, it was determined that the estimated capital and operating costs of biological treatment combined with ultrafiltration were comparable to evaporation, a closed-cycle technology that is well proven (Gerbasi *et al.*, 1993a).

The combination of aerobic biological treatment followed by or integrated with ultrafiltration would offer interesting advantages such as the retention of suspended solids, microorganisms and problematic contaminants, such as RFA, which can be adsorbed to larger solids or microorganisms which can be rejected by the membrane. As pointed out earlier, Zaidi *et al.* (1991) have also shown that RA can also be retained by an interaction of these compounds with ultrafiltration membranes. When ultrafiltration is integrated to an aerobic membrane biological reactor, as described in Section 2.7, the loss of biomass in the aerobic reactor becomes a non-issue, as all suspended solids are retained by the membrane for return to the bioreactor. The advantages and operation of integrated aerobic membrane bioreactors are reviewed in more detail in Section 2.7.

Using the same recirculated mechanical newsprint whitewater that was used in the present study, Elefsiniotis *et al.* (1995) have shown that aerobic biological treatment followed by ultrafiltration as a polishing step could significantly enhance the removal efficiency of COD, TDS and DOC. However, because of poor sludge settling in the aerobic biological reactor at temperatures above 40°C, the biological treatment and the ultrafiltration should be integrated into one process for use at higher temperatures. The results of the Elefsiniotis *et al.* (1995) study are compared to the present study in Section 5.8, since the same whitewater was used in both studies.

2.5.8. Aerobic Membrane Bioreactor Treatment

The aerobic membrane bioreactor (MBR) process, schematically represented on Figure 2.7 (on page 30), is essentially a modification of the activated sludge process. The secondary clarifier is replaced by an ultrafiltration step. The ultrafiltration permeate is the treated effluent while the retentate or concentrate, containing all the biosolids, is returned to the bioreactor. This process, described in greater detail in Section 2.7, combines the advantages of both ultrafiltration and biological treatment. Because of this, and since the sequential combination of biological treatment and ultrafiltration were successful at removing target contaminants from recirculated TMP newsprint whitewater at temperatures of up to 40°C (Elefsiniotis *et al.*, 1995), the aerobic MBR appears to be a promising treatment alternative

for purging contaminants internally in integrated TMP newsprint mill. Since the aerobic MBR process is the focal point of this thesis, the MBR is explained in greater detail and reviewed in Section 2.7.

2.6. Membrane Filtration Processes

Many recent papers have been published on the use of membrane separation processes for treating various streams in pulp and paper mills including kraft extraction or bleach effluents (Muratore *et al.*, 1975; Lundhal and Mansson, 1980; Muratore *et al.*, 1983; Dorica, 1986; Dorica *et al.*, 1986; Bindoff *et al.*, 1987; Jönsson, 1987; Jönsson *et al.*, 1988; Ekengren *et al.*, 1991; Buisson *et al.*, 1992; Nichols, 1992; Zaidi *et al.*, 1992; Bryant and Sierka, 1993; Ekengren *et al.*, 1993; Frostell *et al.*, 1994), chemi-thermo-mechanical pulp (CTMP) screw press filtrates (Frostell *et al.*, 1994; Ramamurthy *et al.*, 1995), paper coating effluents (Pichon *et al.*, 1992; Strisberg *et al.*, 1992) and other effluents (Okamoto *et al.*, 1985; Zaidi and Buisson, 1991; Sierka *et al.*, 1992; Pejot and Pelayo, 1993). Ultrafiltration has also been used in the pulp and paper industry to fractionate and purify the lignin in kraft black liquor (Pepper and Tingle, 1983; Jönsson and Wimmerstedt, 1985; Kirkman and Gratzl, 1986; Woerner and McCarthy, 1987; Uloth and Wearing, 1989a and 1989b) and for the recovery of spent sulfite liquor (Forss *et al.*, 1979; Gaddis *et al.*, 1991). Of particular interest for this thesis are studies on the effectiveness of membrane separation processes for the removal of contaminants from whitewater. There are several such papers in the literature (Jönsson and Wimmerstedt, 1985; Nyström *et al.*, 1992; Nuortila-Jokinen *et al.*, 1993a; Nuortila-Jokinen *et al.*, 1994; Paleologou *et al.*, 1994; Sierka *et al.*, 1994; Elefsiniotis *et al.*, 1995; Nuortila-Jokinen *et al.*, 1995). After a brief overview of membrane separation processes, this review will focus on the use of ultrafiltration for the treatment of mechanical newsprint whitewater.

2.6.1. Overview of Membrane Separation Processes.

Modern membrane separation technologies originated from the development of a synthetic asymmetric membrane by Sourirajan and Loeb in 1960 at the University of California, Los Angeles

(Cheryan, 1986). Asymmetric membranes (Figure 2.2) consist of a very dense top layer or skin with a thickness of less than 0.5 μm supported by a porous sublayer with a thickness of about 50 to 200μm (Mulder, 1991). These membranes combine the high selectivity associated with a dense membrane with the high permeation rate of a very thin membrane. Since the development of these membranes over thirty years ago, many applications have been spawned, including desalination and water treatment by reverse osmosis, probably the best-known and earliest application. In this section, an overview of membrane processes is presented, with a particular emphasis on ultrafiltration (UF).
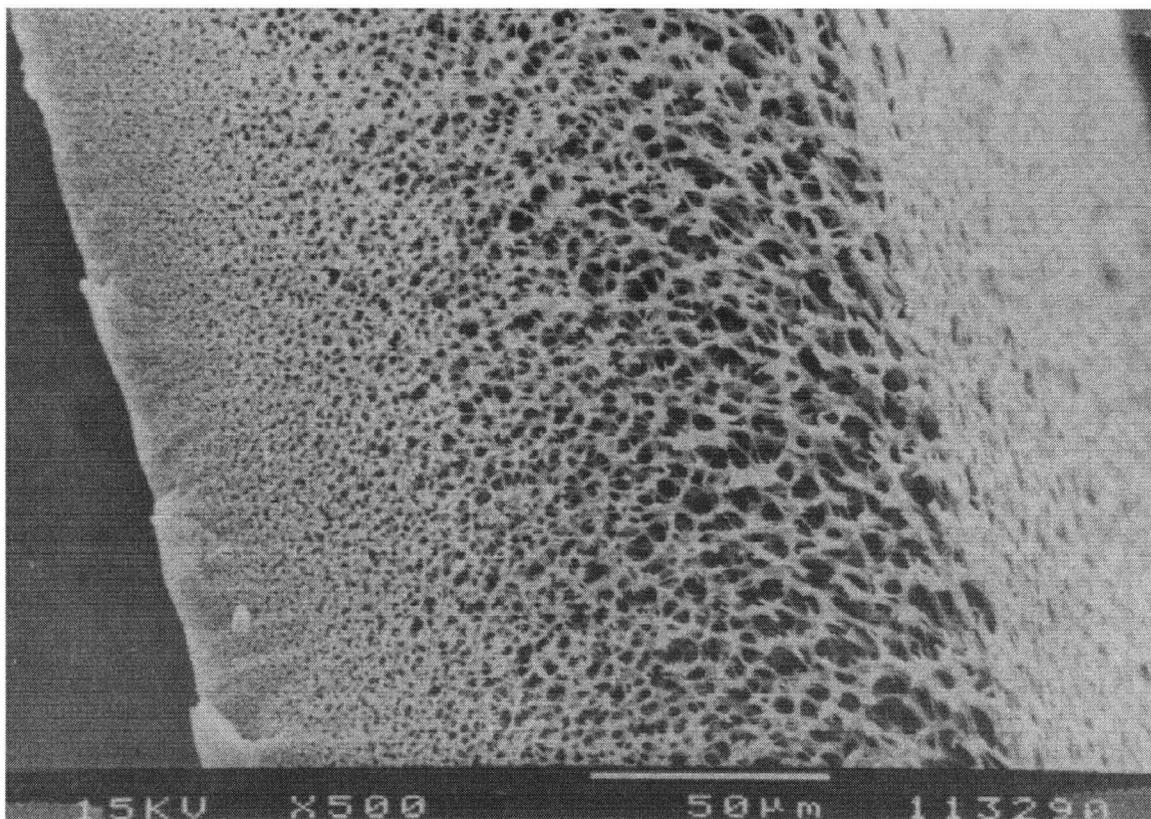
Figure 2.2.   Cross-section of an asymmetric polysulfone ultrafiltration membrane (from Mulder, 1991).

Pressure-driven membrane separations are based on the principle of selective permeability of one or more components of a liquid mixture through a membrane barrier. They can be used as concentration or fractionation processes to produce two liquid streams of different characteristics. There are two types of pressure-driven filtration: dead-end and cross-flow (Howell, 1993). Cross-flow filtration differs from traditional dead-end filtration by using a feed flow parallel to the membrane surface (Figure 2.5), which

tends to remove the deposited layers from the membrane surface, thus helping to keep it clean. The feed solution is circulated through the membrane module under pressure at a given recirculation rate using a pump. The solution which passes through the membrane is called the permeate while the more concentrated solution which doesn't pass through the membrane is called the retentate or concentrate. The membrane pore size and the material of construction are important in determining which compounds are retained or rejected by the membrane. Typically, pressure-driven membrane processes are classified as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF), depending on the rejection characteristics of the membrane (Figure 2.3). The main driving force in these processes is pressure. Transmembrane pressure is defined as the difference between the average pressure of the feed solution and the back-pressure of the permeate. If the permeate side is open to the atmosphere, than the back-pressure of the permeate is zero (Cheryan, 1986), and the transmembrane pressure is equal to the average feed pressure in the module.

	ST Microscope	Scanning Electron Microscope	Optical Microscope	Visible To Naked Eye
	Ionic Range	Molecular Range	Macro Molecular Range	Micro Particle Range	Macro Particle Range

Micrometers (Log Scale): 0.001 | 0.01 | 0.1 | 1.0 | 10 | 100 | 1000

Angstrom Units (Log Scale): 1 | 10 | 100 | 1000 | 10^4 | 10^5 | 10^6 | 10^7

Approx. Molecular Wt. (Saccharide Type—No Scale): 100 | 200 | 1000 | 10,000 | 20,000 | 100,000 | 500,000

Relative Size of Common Materials: Aqueous Salt, Carbon Black, Paint Pigment, Giardia Cyst, Human Hair, Endotoxin/Pyrogen, Yeast Cell, Beach Sand, Metal Ion, Synth Dye, Virus, Bacteria, Mist, Tobacco Smoke, Coal Dust, Gelatin, Red Blood Cell, Pin Point, Sugar, Colloidal Silica, Blue Indigo Dye, Pollen, Granular Activated Carbon, Atomic Radius, Albumin Protein, A.C. Fine Test Dust, Latex/Emulsion, Asbestos, Milled Flour

PROCESS FOR SEPARATION: REVERSE OSMOSIS (Hyperfiltration), ULTRAFILTRATION, PARTICLE FILTRATION, NANOFILTRATION, MICROFILTRATION

Figure 2.3. **Pressure driven processes in relation to the size and type of particles rejected (from Osmonics, 1993).**

In its ideal definition, RO (or hyperfiltration) retains all components other than the solvent (water) itself, while UF retains only macromolecules or particles larger than about 5 to 100 nm

(molecular weight cut-off (MWCO) = 1,000 to 200,000). NF falls in between RO and UF, while microfiltration processes are designed to retain particles in the micron range. The upper and lower limits of NF, UF and MF may vary. One author, using a pressure-driven filtration process at a MWCO of 8,000, may refer to it as a UF process, while another may refer to it as NF. Membranes are usually rated according to their molecular weight cut-off, which is the molecular weight at which 90% of the (macro)molecular solutes are rejected by the membrane (Mulder, 1991). A membrane can have a "sharp cut-off" or a "diffuse cut-off", as illustrated in Figure 2.4, depending on the distribution of its pore sizes.
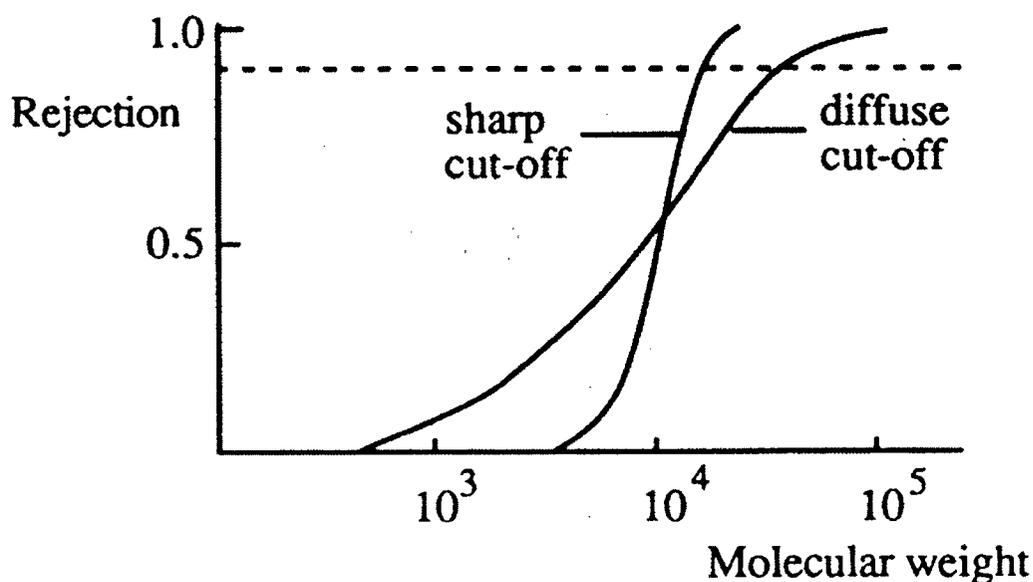
Figure 2.4. Rejection characteristics of two membranes having the same MWCO rating (from Mulder, 1991).

Other factors have to be considered which affect the manufacturer-specified molecular weight cut-off: interactions between the membrane and the solute depend on the membrane material, physical and chemical conditions of the feed solution and solute chemistry (Zaidi and Buisson, 1991).

Concentration polarization of solutes at the membrane surface also plays a very important role in the rejection of solutes using ultrafiltration. As the solvent passes through the membrane, a local region of higher concentration of solutes develops at the membrane surface. This "boundary layer", illustrated on Figure 2.5, acts as a secondary membrane and may reject solutes which would normally pass through

the ultrafiltration membrane. Concentration polarization can be severe in ultrafiltration because the flux through the membrane is high. When the solute concentration at the membrane surface reaches a maximum, a gel layer is formed at the membrane surface. The formation of a boundary layer and a gel layer is usually considered a highly undesirable phenomenon, since they produce a decrease in the measured flux. The flux is defined as the volumetric flow of permeate produced per unit time per unit area of the membrane (common units are $L/m^2 \cdot h$). The thickness of the boundary layer, and thus the membrane flux, depends on the velocity, viscosity, density, transmembrane pressure and turbulence of the flow (Cheryan, 1986). In order to minimize the boundary layer thickness, a cross-flow velocity in the membrane module sufficient to maintain a turbulent flow should be used. Increasing the transmembrane pressure will lead to an increase in membrane flux, but only up to a certain point (Figure 2.6). If the concentration of solutes is high enough, an increase in transmembrane pressure may not result in an increase in flux. Rather, the gel polarized layer will only become thicker and denser and the flux will remain constant. In this region, the membrane flux is controlled solely by mass transfer.
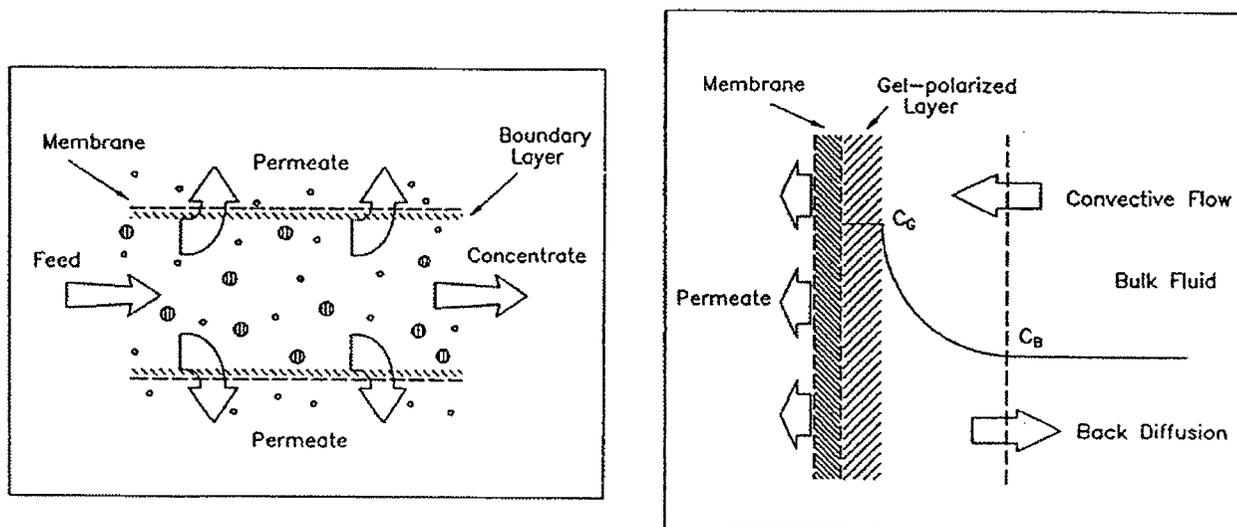
Figure 2.5. **Schematic of concentration polarization and gel layer during cross-flow ultrafiltration (from Onysko, 1992).**

Another mechanism affecting the membrane flux is fouling. Membrane fouling is due to the deposition and accumulation of submicron particles and/or bacteria on the membrane surface and the

crystallization and precipitation of smaller solutes on the surface or within the pores of the membrane itself (Cheryan, 1986). The effects of membrane fouling can usually be reversed, at least partially, by means of chemical cleaning of the membrane at high feed velocities. Proprietary cleaning solutions are commercially available for different types of membranes and applications.

Membrane filtration of solutions is usually done in a batch mode. The feed solution is concentrated until a certain concentration factor (CF), or volume reduction factor, is obtained. The concentration factor is defined as the total feed volume divided by the final retentate volume. The concentration factor achieved during membrane filtration may be limited by fouling of the membrane or by the desired quality of the permeate. As the concentration factor increases, the permeate collected may contain higher concentrations of undesirable solutes.
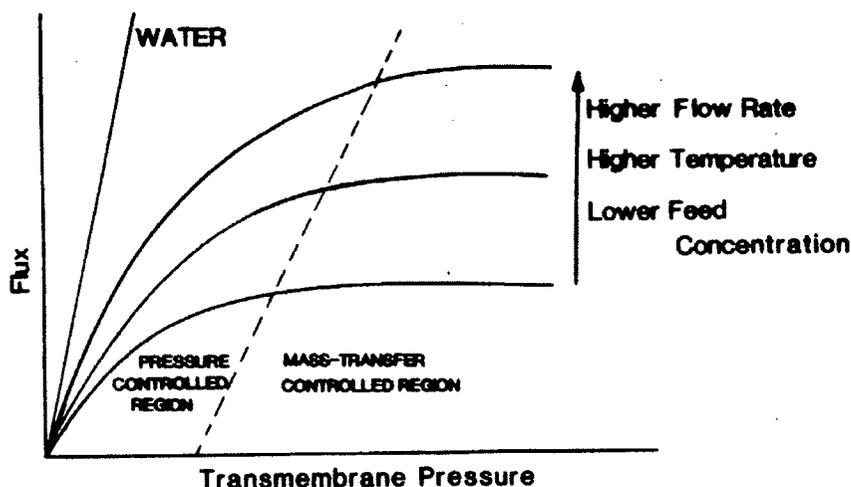
Figure 2.6. Generalized correlation between operating parameters and flux, indicating the areas of pressure control and mass transfer control (from Cheryan, 1986).

Ultrafiltration systems are commercially available in a number of configurations. The most common ones are listed in Table 2.1. The most appropriate ultrafiltration membrane modules for the use in wastewater treatment containing sludge or suspended solids are tubular modules, because their relatively large internal diameter allows the filtration of solutions containing suspended solids without any risk of plugging. They are also inexpensive and are easily replaced. However, the associated

pumping costs are higher than with most other membrane configurations because high recirculation rates are needed to create velocities sufficient to generate a turbulent flow over the membrane.

Table 2.1. Common commercially available ultrafiltration membrane modules (adapted from Raycheba, 1990).

Module	Description	Advantages	Disadvantages
Plate and frame	Stacks of membrane support plates and spacers held together by a central bolt.	1. Low hold-up volume per unit area. 2. Only damaged membranes need to be replaced. 3. Good for viscous feeds.	1. Susceptible to fouling. 2. Difficult to clean.
Tubular	Membrane coated on tubular support which is encased in an outer shell.	1. Easy to clean. 2. Modules easy to replace. 3. Good for turbid solutions.	1. High hold-up volume per unit area. 2. Low density packing. 3. High pumping costs.
Spiral-wound	Membrane layers are separated by a woven support, wound around a perforated tube and inserted in a tubular vessel.	1. High packing density. 2. Low manufacturing costs. 3. Easy to clean. 4. Low hold-up volume per unit area.	1. Susceptible to fouling - pretreatment necessary. 2. Dead-end space is susceptible to fouling and bacterial growth.
Hollow- fibre	Bundles of hollow, hair-like fibres are inserted in a tube.	1. High packing density. 2. High product recovery. 3. Inexpensive to build.	1. Susceptible to fouling. 2. Cleaning difficult. 3. Cannot treat feeds that are viscous or high in solids.

2.6.2. Membrane Separation Processes for Treating Whitewater.

According to a comprehensive review on the use of UF for removing organics from pulp and paper mill effluents (Zaidi and Buisson, 1991), one of the first pulp and paper process waters studied for membrane treatment was the alkaline E_1 (1st caustic extraction stage) bleaching effluent of a kraft mill, which contributes most of the colour in the total wastewater discharge and has a very high chemical oxygen demand. Recognizing this, researchers in the 1970's focused on the segregation and treatment of the E_1 kraft effluent. Two issues prompted the investigation of membrane filtration to remove this colour: (i) biological effluent treatment systems were not very effective in removing colour-causing

compounds and (ii) membranes seemed to have the potential to remove the high molecular weight chlorolignins which contributed most of the colour (Zaidi and Buisson, 1991). The research on membrane processes focused on extraction stage kraft bleaching effluent until the late 1980's, when researchers in Scandinavia evaluated the treatment of effluent streams from various bleaching stages at kraft mills as well as effluents from CTMP mills (Zaidi and Buisson, 1991). Because of (i) the increasing pressure on the pulp and paper industry to reduce the discharge of effluents containing toxic organics, with the long term expectation of eliminating those discharges, and (ii) the availability of improved membranes and membrane systems suitable for effluent treatment applications, there appears to be a revival of interest in the use of membrane processes to treat various effluent streams (Zaidi and Buisson, 1991). Specifically, the use of membrane separation to treat and reuse selected effluent streams in TMP and CTMP mills has recently been studied (Zaidi and Buisson, 1991; Nuortila-Jokinen *et al.*, 1993b; Nuortila-Jokinen *et al.*, 1994; Elefsiniotis *et al.*, 1995). These studies are reviewed in this section.

In a recent laboratory scale study on the ultrafiltration of whitewater (Nuortila-Jokinen *et al.*, 1994), paper machine clear whitewater with an initial COD of 1000 mg O_2/L was ultrafiltered using a tubular ultrafiltration module with a MWCO of 8 kDaltons. The COD removal, which was dependent on the pH and the modification of the membrane prior to the ultrafiltration of the whitewater using an anionic agent, ranged from 19 to 52%. The cationic demand (CD) removal ranged from 40 to 93%. The membrane flux achieved ranged from 30 to 65 L/m^2·h (Nuortila-Jokinen *et al.*, 1994), for pressures ranging from 150 to 250 kPa and feed velocities in the membrane module of 0.45 to 0.71 m/s. In one experiment, the microbe count after ultrafiltration using the 8 kDaltons tubular membrane unit was determined to be 10^3 colony forming units per mL (cfu/mL), from an initial count of 10^6 cfu/mL. Nanofiltration of the same paper machine clear whitewater with a flat sheet module with several negatively charged membranes resulted in COD removals ranging from 47 to 74 % and CD removals of 100% in all cases (Nuortila-Jokinen *et al.*, 1993b). The permeate flux, which was dependent on the

membrane used, ranged from 15 to 48 $L/m^2 \cdot h$ for pressures of 600 kPa and feed velocities of 2 m/s. For the nanofiltration experiment, the reduction of selected ions was also reported. Chloride ions (Cl^-) were partly rejected (12 to 19%, depending on the membrane used), while 59 to 98% of sulfate (SO_4^{2-}) ions were rejected. Most cations (Na^+, Fe^{3+}, Ca^{2+}, Mg^{2+}, Mn^{2+}) were well rejected, with an total rejection rate for cations ranging from 38 to 72%. Some cations were completely or almost completely (98-100%) retained with some membranes, particularly Fe^{3+}, Ca^{2+}, and Mg^{2+}. This is important, since some of these may have negative impacts on the paper machine or paper machine equipment. For example, Fe^{3+} causes increased corrosion and ions like Ca^{2+} form large insoluble colloidal calcium soaps which end up as stickies in the pipe lines and spots on the paper (Nuortila-Jokinen et al., 1993b). In the same study, the paper machine whitewater was also ultrafiltered and then nanofiltered. It was found that nanofiltration used alone was more efficient than a combination of ultrafiltration and nanofiltration. The authors concluded that removing ligneous material together with COD and anionic trash could result in an increase of the brightness of the product in closed paper mills. They also found that membrane modification with anionic agents could enhance the reduction of long-chained negatively charged substances, thus improving the brightness. Finally, they found that although nanofiltration could not generate enough flux for an industrial application, it could remove most of the brightness decreasing substances as well as corrosive and colloid forming ions.

Researchers from the same university also completed pilot scale studies on the ultrafiltration and nanofiltration of whitewater at the same mill that had provided the whitewater for the lab scale study (Nuortila-Jokinen et al., 1995). Using a PCI (Paterson Candy International, Inc.) ultrafiltration module with a MWCO of 100 kDaltons (FP100), the clear paper machine whitewater was ultrafiltered at a pressure of 200 kPa, with a flow rate of 14.2 L/min (for a velocity in the membrane module of 2 m/s) at 40°C. The stabilized membrane flux was approximately 50-60 $L/m^2 \cdot h$. Removal efficiencies were low for total dissolved solids (3 to 10%), COD (8 to 20%) and ionic material (sulfate, sodium, manganese, magnesium, calcium, iron and aluminium removal efficiencies were usually less than 10%), but good for

colour (50 to 85%) and CD (70 to 78%). Much better removal efficiencies were obtained using NF. Removal efficiencies varied with the membrane used and ranged from 65 to 90% for TDS, 60 to 75% for COD, 80 to 90% for colour for acidic low brightness grades. The removal of the CD was complete in the studies involving both NF membranes used for the acidic low brightness grades. Significantly lower removal efficiencies were obtained during NF experiments of clear whitewater of high brightness grades. The authors concluded that NF without pre-treatment using UF could be a more economic way to purify the paper mill whitewater.

Investigative work carried out on ultrafiltration of mechanical newsprint whitewater was completed at the University of British Columbia's Pulp and Paper Centre by Elefsiniotis *et al.* (1995). A lab scale ultrafiltration unit using cassette-type ultrafiltration membranes was used at various temperatures ranging from 20 to 60°C. The MWCO of the membranes used was either 10 or 100 kDaltons. The results did not vary significantly with the operating temperature. However, the higher MWCO membrane could not generally remove contaminants as effectively as the 10 kDaltons membrane. The membrane removal efficiencies for TDS, dissolved COD and dissolved organic carbon were modest, ranging from 10 to 37%. Resin acids removal efficiencies were also modest, ranging from 25 to 45%. However, except in one case, over 90% of the fatty acids were removed. The rejection of dehydroabietic acid was the lowest, with a 10% efficiency. Since the same simulated mechanical newsprint whitewater was used in the present study, the results of the Elefsiniotis *et al.* study (1995) are compared to those obtained in this study in Section 5.8.

Zaidi *et al.* (1991) have characterized the rejection characteristics of several membranes using a standard protocol developed at the Wastewater Technology Centre (Burlington, Ontario). They determined the MWCO of several membranes experimentally by using polyethylene glycols and dextrans. They found that the manufacturer-specified MWCO often differed significantly from their experimental MWCO, probably due to differences in experimental protocols. More importantly, they found that, contrary to what is generally believed, the membranes could reject compounds with a

molecular weight substantially smaller than the MWCO of the membrane. For example, they quantified the rejection efficiency of dehydroabietic acid (DHA), which has a molecular weight of 298, using several membranes with MWCO ranging from 1.5 to 150 kDaltons at a feed pressure of 0.4 MPa. Most membranes rejected over 75% of the DHA. The lowest rejection efficiency was 40%. Similar findings were reported for other compounds of molecular weights similar to DHA, with rejection efficiencies usually in the range of 40 to 90% for compounds with molecular weights of 179 to 333, using the same membranes. It had been assumed, in previous studies, that the high rejection of resin acids was due to the adsorption of these compounds to larger molecules (such as lignins) or wood fibres normally present in pulp mill effluents (Zaidi and Buisson, 1991). However, the authors point out that larger molecules which could have provided adsorption sites for the DHA were not present in their test solutions. Therefore, they concluded that resin acids can be rejected due to interaction between the resin acids and the membrane.

One way to dispose of ultrafiltration concentrates was recently investigated by Nichols (1991; 1992). He pointed out that while studies have shown ultrafiltration to be a potentially viable treatment technology for mill closure, no generally accepted means of disposal of the ultrafiltration concentrate exists. He has therefore investigated the feasibility of incineration of UF concentrates from acid-stage (C+D) stage and caustic stage (first extraction or E_1 stage) effluents from two bleached-kraft mills. He concluded that the incineration of E_1 stage effluent concentrate appears feasible, but the (C+D) concentrates, due to their high inorganic and lower carbon content, appear to be less amenable to thermal destruction. It is possible that concentrates from ultrafiltration of TMP newsprint whitewater could be more suitable, since they would likely have a high carbon content. However, the feasibility of thermal destruction of UF concentrates from TMP newsprint whitewater has not been studied.

In summary, the treatment of recirculated TMP newsprint whitewater appears feasible using membrane processes, however, large amounts of concentrate would still have to be disposed of, possibly by incineration.

2.7. The Aerobic Membrane Bioreactor Process

Aerobic membrane bioreactor (MBR) treatment of wastewater originated from a modification of the conventional activated sludge process. In order to improve the solids-liquid separation stage, the secondary clarifier of the activated sludge process is replaced by an ultrafiltration stage. The clear permeate is the process effluent, while the UF retentate, which contains all the biological and suspended solids, is returned to the bioreactor (Figure 2.7). The quality of the permeate no longer depends on the quality of the floc, as it does for conventional activated sludge treatment. In addition, the space requirement for the ultrafiltration equipment is much less than that required by a secondary clarifier (Zaloum *et al.*, 1994). The MBR process also enables the precise control of the solids retention time (SRT) and allows the possibility of operating the bioreactor with high mixed liquor volatile suspended solids (MLVSS) concentrations, as no biological solids are lost in the effluent.
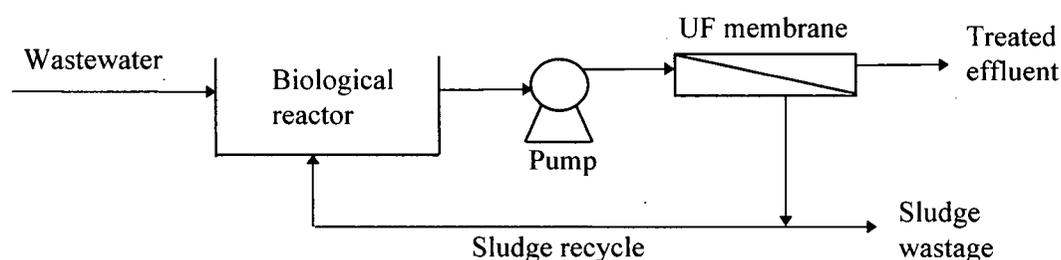
Figure 2.7. Schematic of an aerobic membrane biological reactor.

The MBR system was first developed in the 1970s for the treatment of sanitary wastewater by Dorr-Oliver Inc. Smith *et al.* (1969) were the first to report the use of ultrafiltration in combination with activated sludge to treat wastewater. Bemberis *et al.* (1971) produced the first review of the commercial use of the MBR technology, which was by then a patented process called the Membrane Sewage Treatment (MST) system (Budd and Okey, 1969). Two commercial MST systems were installed by Dorr-Oliver in the US from 1967 to 1971, for the treatment of less than 18.9 m^3/day. System economics dictated against application of the MST system in the USA at higher wastewater flows (Mishra *et al.*, 1994). The Dorr-Oliver work resulted in a licensing agreement with Sanki Engineering Company, Ltd.

of Tokyo Japan. Sanki installed approximately 20 membrane sewage reclamation systems using the MST technology from 1974 to 1987. Many are installed in buildings in Japan to recycle grey water. In North America, Thetford Systems of Ann Arbor, MI, USA (now part of Zenon Environmental Inc.) introduced their commercial embodiment of the MBR process configuration, which they called the Cycle-Let system. Over 80 Cycle-Let systems have been installed since the 1970s for aerobic and anoxic treatment of municipal wastewaters (Mishra et al., 1994).

Since the early 1980s, several researchers have applied aerobic versions of the MBR configuration for the treatment of industrial and municipal wastewaters. The two largest aerobic MBR systems currently in use in North America are for treating oily wastewaters at General Motors automotive manufacturing plants located in Mansfield, OH, USA and Windsor, Ontario, Canada (Mishra et al., 1994). The system at the Mansfield plant was designed to treat 151 m^3/day with two 144 m^3 aerobic reactors. The full scale process was started in 1991, has exceeded expectations in terms of membrane flux (64 to 72 L/m^2·h) and has achieved COD removal efficiencies greater than 90% with MLVSS concentrations ranging from 19 to 29 g/L. The MBR full scale system planned for the Windsor plant was designed to treat 864 m^3/day using two 757 m^3 aerobic reactors (Mishra et al., 1994). Results obtained for the pilot tests for these MBR systems have been published (Hare et al., 1990; Knoblock et al., 1994).

Results from a pilot scale study (Zaloum et al., 1994) involving the use of aerobic MBR technology to treat wastewater from an aluminium transformation mill located at Cap-de-la-Madeleine, Québec, Canada, have shown that an aerobic MBR was much more efficient at removing the BOD$_5$ and toxicity (measured with Microtox) than ultrafiltration alone. The MBR flux obtained during this study was approximately 40 L/m^2·h at a transmembrane pressure of 340 kPa.

In France, studies have been completed on the use of aerobic MBR systems to treat landfill leachates and municipal wastewater. In their pilot scale study of an aerobic MBR process to treat

municipal wastewater, Trouve *et al.* (1994) found that at an HRT of 24 hours and a SRT of 25 days, a steady-state was reached after 50 days of operation. The MLVSS was then approximately 3 g/L. The researchers noted that the sludge production was less than that of conventional activated sludge, because of the high SRT. The COD removal efficiency was over 96% and over 99.9% for the BOD_5. Nitrification in the MBR was established in only 6 days, due to the retention of autotrophic bacteria with the membrane. The measured membrane flux of 80 to 100 $L/m^2 \cdot h$ (at a transmembrane pressure of 100 kPa and velocities of 1.5 to 3.5 m/s) was higher than values commonly reported in the literature and could be maintained for longer than 15 days without chemical cleaning.

Other researchers have studied the use of aerobic MBR technology for municipal wastewater treatment at a lab scale (Krauth and Staab, 1986; Magara and Itoh, 1991; Sato and Ishii, 1991; Krauth and Staab, 1993; Lübbecke *et al.*, 1995).

In their lab scale study on the treatment of a synthetic wastewater containing glucose as the main carbon source, Lübbecke *et al.* (1995) have reported excellent BOD_5 removal efficiencies (>99.5%) with their impinging-stream loop MBR at an operating temperature of 27°C, HRT of 7.6 to 24h, SRT of 1.5 to 8 days and MLVSS concentrations of up to 40 g/L. They noted it is possible to work with high reaction rates and very low effluent concentrations using an MBR with dramatically lower (70%) excess sludge production than activated sludge. They reported an observed net growth yield (Y_{obs}) of 0.2-0.3 kg mixed liquor suspended solids (MLSS)/kg BOD_5 $_{removed}$). Furthermore, they remarked that there are no anaerobic zones or sludge settling problems in as in the clarifier of the conventional activated sludge process. The average membrane flux achieved was 45 $L/m^2 \cdot h$ at a transmembrane pressure of 210 kPa and a velocity of 4.5 m/s. Cleaning intervals were relatively long (3.5 weeks).

One interesting advantage of a modified MBR system designed for biological denitrification of municipal wastewater noted by Magara *et al.* (1991) is the complete retention of bacteria and suspended solids. Therefore, they concluded, if useful micro-organisms can be developed by genetic engineering,

they could be used in wastewater treatment because the risk of discharging these new micro-organisms to the environment can be overcome by the membrane filtration component of the system.

Other researchers have used a vacuum pump to draw the permeate from the membrane filters, which can then possibly be immersed in the aerobic bioreactor (Suwa *et al.*, 1989; Yamamoto *et al.*, 1989; Chiemchaisri and Yamamoto, 1993a, 1993b and 1994). This set-up can further reduce the space requirements of this wastewater treatment process and can reduce the energy requirements for pumping by 85 to 90% of that required by the recirculating tubular design (Lee, 1994 p. 17). This MBR configuration has been used for a lab scale study aiming at comparing MBR technology and conventional activated sludge treatment of a CTMP effluent at an SRT of 15 days, HRT of 48, 36 and 24 hours and an operating temperature of 35°C (Dufresne *et al.*, 1996). The COD and toxicity removal efficiencies were reported to be significantly better with the MBR treatment than with conventional activated sludge. The average COD removal efficiencies ranged from 68 to 82% for the MBR compared to 40 to 68% for the activated sludge.

The use of an anaerobic MBR has also been reported to treat segregated bleach plant wastewater (Onysko and Hall, 1993) at a lab scale. In South Africa, anaerobic MBR technology (referred to as the anaerobic digestion ultrafiltration (ADUF) process) has been applied for the full scale treatment of a maize processing effluent (Ross *et al.*, 1992). Although anaerobic treatment processes do not degrade organic contaminants as effectively as aerobic processes, the lower costs of operation and the production of methane as a valuable by-product are important considerations in the application of these processes to treat wastewater.

In summary, the aerobic MBR is a compact high performance treatment system which has many interesting operating advantages, despite higher operating costs than conventional activated sludge treatment due to pumping requirements. These advantages are summarized below (Onysko, 1992).

- The absolute retention of biomass and suspended solids is possible;

- the system is compact due to the absence of secondary clarifiers;

- the initial process start-up is rapid due to the retention of all biomass;

- high biomass concentrations and high operating temperatures are possible without concern for sludge bulking and poor sludge settling;

- there is minimal effect of varied loadings on treatment efficiency;

- the process is stable and simple;

- lower food to mass ratios (F/M) are possible;

- the precise control of the SRT is possible, as well as the use of long SRTs;

- the rejection of pathogenic organisms is possible;

- particulate and higher molecular weight organics are retained by the membrane, providing increased opportunity for biodegradation;

- excellent removal efficiencies can be achieved since only lower molecular weight recalcitrant organics will remain in the effluent; and

- modular ultrafiltration units allow for expansion of the treatment capacity.

3. OBJECTIVES OF THE RESEARCH

The thesis question proposed when this project was initiated was *"does an aerobic membrane biological reactor offer significant advantages for removing contaminants found in recirculated newsprint whitewater ...?"* (Tardif, 1994). Specifically, the aim of the thesis was to compare the aerobic MBR process to either ultrafiltration, biological treatment, or, the sequential combination of aerobic biological treatment and ultrafiltration, to treat a synthetic recirculated thermo-mechanical newsprint whitewater at high temperatures. These other treatment processes were investigated at the University of British Columbia's Pulp and Paper Centre by Johnson (1995), Johnson and Hall (1996), Elefsiniotis (1994) and Elefsiniotis *et al.* (1995). In the first of those studies, involving the use of biological treatment, low concentrations of biomass in the biological reactor were measured at temperatures over 40°C, due to poor sludge growth and poor sludge settleability. The second study, involving the use of ultrafiltration to treat the whitewater and to polish the biologically treated effluent, showed that the use of ultrafiltration alone was not as efficient as biological treatment at removing most contaminants, but resulted in significantly better contaminant removal efficiencies when used to polish the biologically treated effluent. In addition, for the sequential combination of biological treatment and ultrafiltration, both waste sludge *and* UF concentrate waste was generated.

Since the MBR can retain all biological solids, it was thought that the integrated use of ultrafiltration and aerobic biological treatment could allow better contaminant removal efficiencies than biological treatment or ultrafiltration at temperatures above 40°C, while generating less waste to dispose of by incineration than the sequential combination of biological treatment and ultrafiltration. The MBR could possibly allow the treatment of the whitewater at high temperatures (50 to 60°C), which would also minimize any costs associated with cooling the whitewater before its treatment. The following research objectives were thus established:

1. To investigate the efficiency of a lab scale aerobic MBR for the removal of resin and fatty acids (RFA), chemical oxygen demand (COD), dissolved organic carbon (DOC), colour, cationic demand and solids from a synthetic recirculated mechanical newsprint whitewater of the same composition as the one used in the previous studies conducted at the UBC Pulp and Paper Centre.

2. To determine the effects of varying the operating temperature on the process and the efficiency of the process for temperatures ranging from 40°C to 55°C.

3. To determine the effects of varying the hydraulic retention time on the process and the efficiency of the process for HRTs ranging from 0.7 to 2.8 days.

4. To investigate the fate of the RFA throughout the experimental period.

5. To compare the performance of the MBR to the previous studies on biological and/or ultrafiltration treatment of recirculated newsprint whitewater completed at the UBC Pulp and Paper Centre.

4. MATERIALS AND EXPERIMENTAL METHODS

In this section, descriptions of all materials and experimental methods used for this study are given. Section 4.1 describes the experimental apparatus used while Sections 4.2 and 4.3 describe the procedures and the analytical techniques and equipment used during the study, respectively.

4.1. Description of the Experimental Apparatus Used

4.1.1. Membrane Biological Reactor System

The membrane biological reactor used in this study, illustrated in Figure 4.1, was composed of an aerobic reactor, a progressive cavity pump and an ultrafiltration unit, coupled with reinforced collapse-resistant tubing as well as polyvinyl chloride (PVC) schedule 80 fittings (such as elbows and adapters). The contents of the bioreactor were pumped through the ultrafiltration unit under pressure, forcing solids-liquid separation. The permeate could be recycled to the reactor or wasted. This was controlled using a three-way valve, a level controller and floating switches as described below. The mixed liquor volume in the reactor ranged from 9 to 11 L while the recirculation pump, tubing, ultrafiltration units and fittings held up 4 L of the mixed liquor, for a total liquid operating volume of 13 to 15 L (14 L average).

Aerobic Reactor. The 18 L size aerobic reactor was constructed from a transparent acrylic cylinder with a height of 64.0 cm, an internal diameter of 19.1 cm and a wall thickness of 6.4 mm. It was glued to a square acrylic base of 25 cm X 25 cm X 2.5 cm for stability. Air was supplied through a perforated acrylic tube of internal diameter (ID) 6.4 mm (1/4 in), which was glued to the bottom of the reactor and connected to a central air compressor using 8.0 mm ID (3/8 in) flexible vinyl tubing. The air was delivered at flow of 2 L/min. This flow was monitored using a Lab-Crest Mark III air flow meter (Fischer & Porter of Warminster, Pa.). Little aeration was needed since most of the air bubbles delivered to the reactor were entrained in the recirculation pump and broken down into very fine bubbles, often causing foaming problems in the bioreactor.
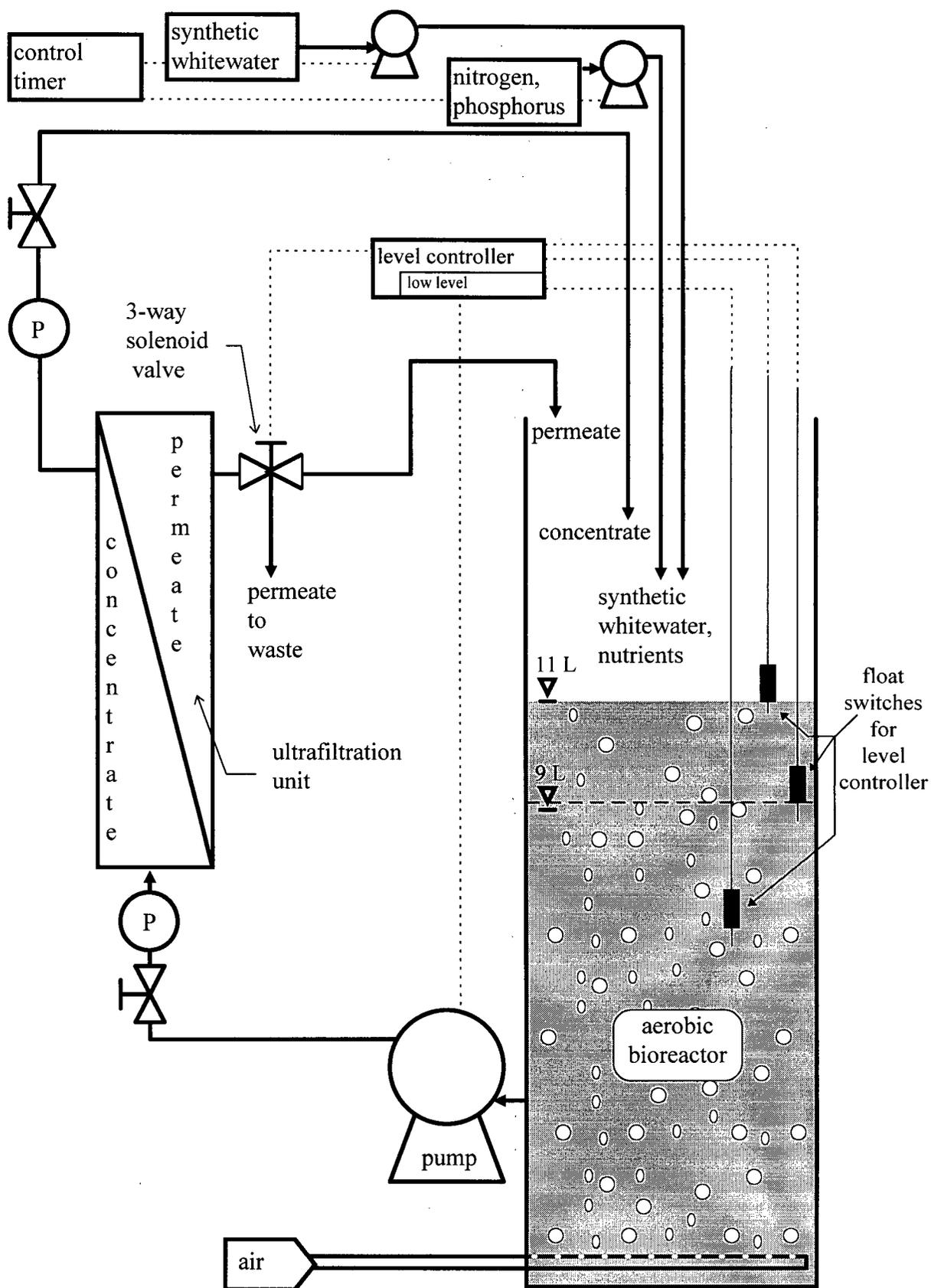
Figure 4.1. Aerobic membrane biological reactor used in this study.

In order to keep the foaming under control, a defoaming device was installed on the open top of the bioreactor. This defoaming device consisted of a continuous duty AC motor, spinning a 21 cm shaft at 1550 revolutions per minute (rpm) at the end of which was installed a piece of plastic wire (the type usually used for hand-held lawn trimmers). This spinning plastic wire created, in effect, an invisible barrier which broke down the foam whenever it reached the wire.

Water Bath for Temperature Control. The aerobic reactor was kept in a water bath in order to maintain the membrane biological reactor system at a constant operating temperature, ranging from 40°C to 55°C. The water bath consisted of an aluminium box, open at the top, with a length and width of 47 cm and a height of 66 cm. In order to insulate the water bath effectively, the outside of this box was lined with a 5 cm (2 in) thick polystyrene foam board and was encased in a polyethylene box, also lined with polystyrene foam board on the outside. The water bath was kept at constant temperatures using a Haake (of Paramus, New Jersey) D8 immersion circulator. The water bath temperature usually had to be set at a temperature a few degrees below the desired temperature in the membrane biological reactor, since the MBR recirculation pump generated heat. For example, in order to maintain the MBR system at a constant temperature of 47.5°C, the water bath was set at a temperature of approximately 43°C. The water level in the water bath was kept at a constant level by replacing the evaporated water with tap water as needed. In order to minimize evaporation losses of the water in the bath, polystyrene foam board was used to cover the exposed water surfaces.

Ultrafiltration Unit Used for the System. The cross-flow ultrafiltration unit used for the system was a Permaflow-1 (PF-75) tubular membrane module, supplied by Zenon Environmental Inc. of Burlington, Ontario. The unit, illustrated in Figure 4.2, had a length of 1.46 m (5 feet) and an internal diameter of 25 mm (1 inch), giving a membrane area of 0.109 m^2 (1.18 ft^2). The manufacturer-specified molecular weight cut-off was 75,000 Daltons, while the nominal pore size was 0.08 μm. Other specifications and operating limits of the membrane module are given in Table 4.1. Noteworthy is the maximum recommended operating temperature (45°C), which was exceeded for this study, as the same

membrane was used throughout the study at operating temperatures ranging from 40°C to 55°C. According to the manufacturer (Kozachenko, 1994), this was acceptable because of the low trans-membrane pressure used for the MBR study (79 kPa or 11.5 psi). The membrane itself can tolerate a 55°C operating temperature, but there is a slight risk that some membrane module components or adhesives may fail at this temperature if the module is used at pressures close to the maximum recommended operating pressure of 620 kPa (90 psi).
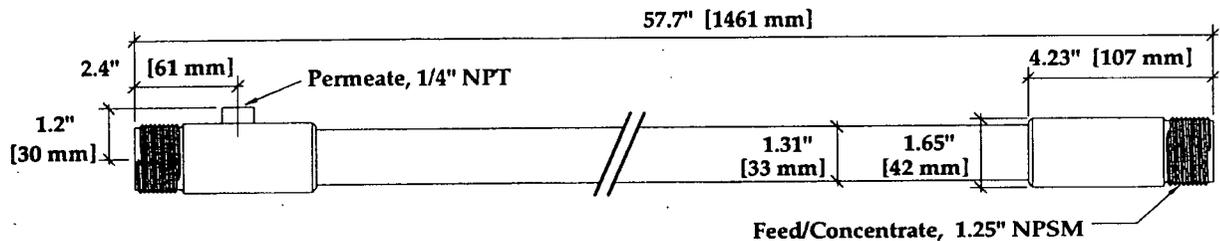
Figure 4.2. Zenon Permaflow-1 tubular membrane module
(source: Zenon Environmental Inc., 1994)

Table 4.1. Specifications and operating limits of the Zenon Permaflow-1 ultrafiltration membrane used in this study

Model	5 ft Permaflow™-1, UF75
Nominal membrane pore size	0.08 μm
Nominal molecular weight cut-off	75,000 Daltons
Configuration	Single 25 mm (1.00") internal diameter tube
Nominal membrane surface area	0.109 m^2 (1.18 ft^2)
Weight of module (drained)	0.75 kg (1.65 lb)
Tube (feed/concentrate) hold-up volume	0.70 L (0.19 US gal)
Shell (Permeate) hold-up volume	0.04 L (0.01 US gal)
Maximum operating pressure	620 kPa (90 psi) at 45°C (113°F)
Maximum recommended operating temperature	45°C (113°F)
Recommended feed flow	95 - 130 litres/min (25-35 US gal/min)
Maximum trans-membrane back pressure	30 kPa (5 psi)
Minimum concentrate pressure	69 kPa (10 psi)
Feed pH range (continuous operation)	3 - 10.5
Feed pH range (cleaning: < 1 hr at T < 50°C)	2 - 11

The construction of the ultrafiltration unit is thoroughly described in a US patent (Langerak *et al.*, 1993). The unit could easily be removed for cleaning or inspection by disconnecting the 3.8 cm (1 1/2 in) hand-tightened PVC schedule-80 unions installed at each end of it. Pressure gauges, with an operating range of 0 to 200 kPa (0 to 30 psi), were installed at the membrane inlet and outlet to measure the pressure drop across the membrane. These gauges were protected from clogging by the use of a diaphragm seal (type 12000-20) obtained from Bellofram of Newell, West Virginia.

Pump Used for the MBR. The pump used for the membrane biological reactor was a Moyno type 34401 progressive cavity pump, distributed by Robbins-Myers of Springfield, Ohio. The pump generated a recirculation rate of 50 L/min (velocity in the membrane unit = 1.7 m/s) at a trans-membrane pressure of 79 kPa (11.5 psi).

Delivery and Make-up of the Synthetic Whitewater Feed to the Reactor. Since recirculated whitewater typical of closed mills was not available at the time of the study, a synthetic closed-mill whitewater was made up by using 1 L of screw pressate obtained from a TMP mill (Howe Sound Pulp and Paper Ltd. of Port Mellon, B.C.) and 35 mL of evaporator concentrate (35% w/w) from a closed cycle BCTMP mill (Millar Western Pulp Ltd. of Meadow Lake, Sask.) and adding tap water to a total volume of 5 L. Both the screw pressate and the evaporator concentrate were stored in carboys in a cold room at a temperature of 4°C. In order to remove any large particles, the synthetic whitewater was passed through a 0.4 mm mesh screen. The concentrations of the various contaminants of interest present in the whitewater are listed in Table 5.1 on page 63.

The whitewater was prepared every 48 hours and placed in a cleaned feed tank stored at room temperature. In order to simulate continuous-flow conditions, the whitewater was added to the reactor by batches of 104 mL at intervals ranging from 7.5 to 30 minutes, yielding a total daily feed of 20 to 5 L or an HRT of 0.7 to 2.8 days. The whitewater was delivered to the reactor using a variable speed Masterflex peristaltic pump and speed controller (obtained from Cole-Parmer Instrument Company of

Niles, Illinois) which was linked to a timer (Chrontrol table top model CD-4, from Lindburg Enterprises Inc. of Ronson, Connecticut).

In order to prevent bacterial growth in the feed tank, nutrient solutions were delivered separately to the reactor, also using a Masterflex pump and speed controller linked to a timer. More details regarding nutrient additions to the MBR are given in Section 4.3.8.

Reactor Level Control. The level in the reactor was maintained between 9 and 11 L, using two float switches, a controller designed and assembled by the UBC Department of Civil Engineering support staff, as well as a three-way solenoid valve placed at the permeate outlet of the ultrafiltration membrane. At any given moment, the three-way valve could be either: 1) recycling the permeate to the reactor; or 2) wasting the permeate to a large effluent container. The level of mixed liquor in the reactor was thus controlled as follows: when the level in the reactor reached 11 L, the highest floating switch rose and triggered the three-way valve to waste the permeate to the effluent container. When the mixed liquor level decreased to 9 L, the second floating switch triggered the three-way valve to recycle the permeate to the reactor. The recycling of the permeate back to the reactor was necessary because the output of permeate exceeded the influent whitewater flow rate.

The controller also limited any spills by interrupting the main MBR pump if a float switch located at the 7 L mark of the reactor opened an electrical circuit. This interruption was useful on several occasions, listed in Table 4.2 on page 50. Usually, two types of incidents led to the interruption of the recirculating pump: in some cases, one of the float switches did not return to its normal position as the liquid level was lowering in the reactor, while in others, a leak developed in a PVC fitting.

4.1.2. Membrane Cleaning System

The membrane cleaning system shown on Figure 4.3 consisted of a centrifugal pump, a 50 L sink, one pressure gauge and two ball valves. An additional three-way valve was placed under the sink

to direct the water or cleaning solution to the recirculating pump or to the sewer drain. The pump was a

corrosion resistant centrifugal CMNP-12T pump made by Sherwood (of Detroit, Michigan).
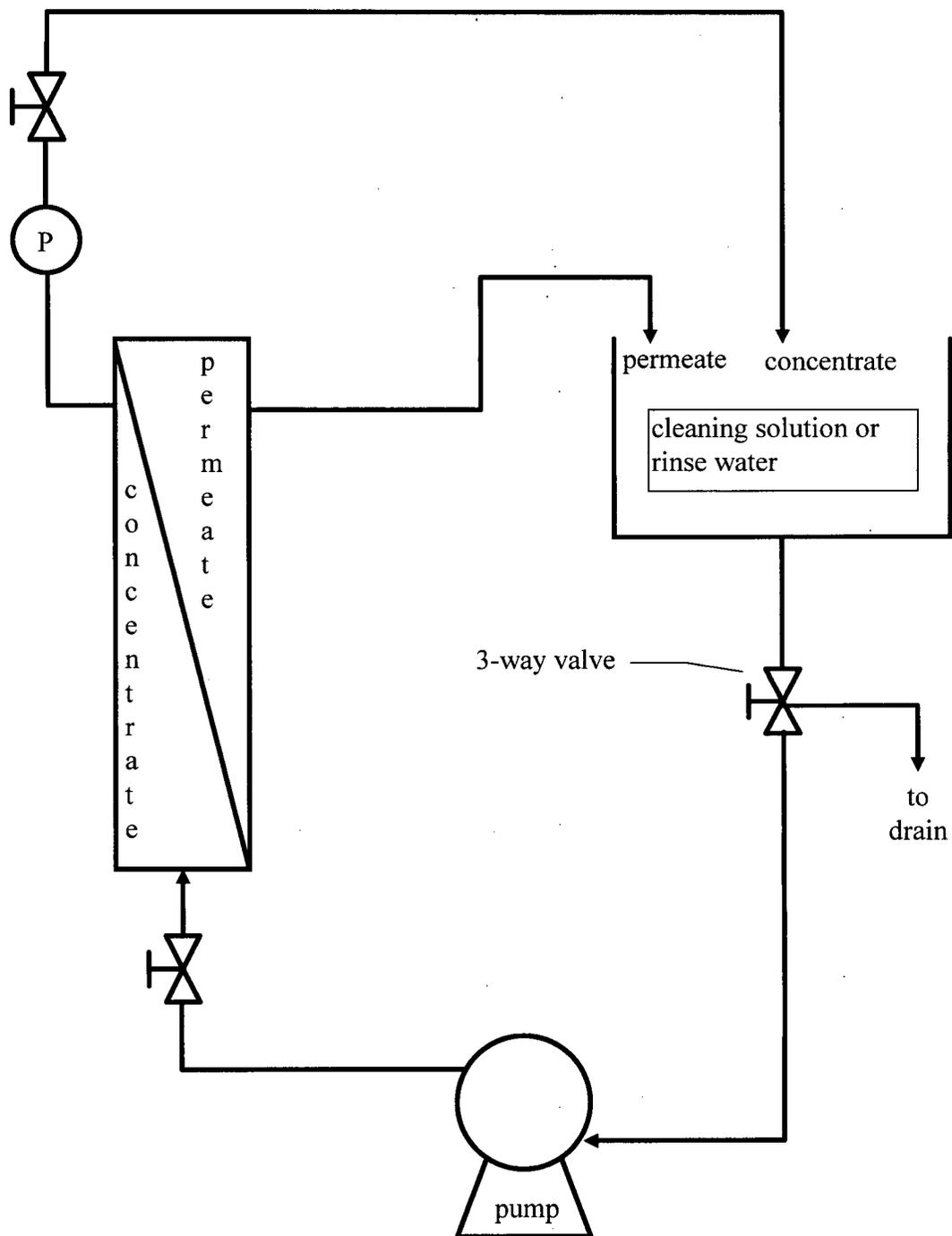
Figure 4.3.   Membrane cleaning system.

4.2. Procedures Used During Studies

4.2.1. Characterization of the Ultrafiltration Membrane

Before using the MBR in a continuous-use process with active biomass, the MBR system was operated without biomass, to assess the effectiveness of ultrafiltration alone for the treatment of the whitewater. The Zenon Permaflow-1 ultrafiltration unit was used in the MBR system, as described in Section 4.1.1, but without biomass, nutrients and aeration in order to evaluate the efficiency of the ultrafiltration membrane alone for removal of contaminants of interest. The membrane was first tested with distilled water to determine the permeate flux of the membrane at various operating average concentrate pressures ranging from 2.5 kPa to 275 kPa (0.5 psi to 40 psi), a recirculation rate of 50 L/min (velocity in the membrane unit = 1.7 m/s) and operating temperatures usually ranging from 35°C to 40°C.

The system was started at 10:15 AM on September, 30 1994 with 14 L (total system volume) of synthetic whitewater (the level in the reactor ranged from 9 to 11 L) and synthetic whitewater was added to the reactor at a rate of 40 L/d for 13 days. The contents of the reactor were allowed to concentrate up to a concentration factor of 37: no wasting of the contents of the reactor was practiced (except for concentrate sampling). The concentration factor was calculated using Equation 4-1.

$$\text{Concentration Factor} = \frac{\text{Volume of influent added to the system}}{\text{Total system volume}} \qquad \textbf{Equation 4-1}$$

Samples of the permeate and of the reactor concentrate were taken every day at 10:15h, 16:15h and 22:15h for the duration of this trial run. The sample volumes of the reactor concentrate samples were limited to 250 mL.

4.2.2. Cleaning of the Zenon Permaflow-1

During the operation of the MBR, the permeate flux across the membrane sometimes approached a rate that was insufficient to accommodate the influent flow rate. The recirculating pump of the MBR

was then temporarily halted and the membrane was removed and cleaned using the system shown in Figure 4.3. The cleaning procedure outlined below took approximately 6 hours to complete. The Permaflow-1 ultrafiltration module was easily placed in the cleaning system using hand-tightened unions. The membrane was then cleaned as follows:

1. The system was rinsed out by recirculating tap water at a temperature of 40°C for ten minutes. The pump generated a recirculation rate of 40 L/min with a back pressure of 34.4 kPa (5 psi). The system was then flushed. This process was repeated at least five times and was successful at removing parts of the gel layer cake present on the membrane. Operating conditions and the permeate flow rate were recorded.

2. Forty litres of a solution containing 3 g/L of MC-4 cleaner (obtained from Zenon Environmental Inc.) and 250 ppm of sodium hypochlorite (NaOCl) were recirculated for 60 minutes, again at a recirculation rate of 40 L/min at a back pressure of 34.4 kPa. The temperature of the solution ranged from 35°C to 40°C.

3. The system was drained and thoroughly flushed with tap water.

4. Tap water was recirculated (as in step 1) and operating conditions and permeate flow rates were recorded.

4.2.3. Start of the MBR and Biomass Acclimatization

The organisms used to seed the reactor were obtained from Johnson (1995), who had just completed a study on the treatment of the same synthetic whitewater using a sequencing batch reactor (SBR). Throughout the MBR study, this SBR was kept under operation in case any sludge was needed to re-seed the MBR. A second SBR, operating at room temperature was also kept under operation for the same reason.

The MBR operation was initiated as follows: settled sludge (2.5 L) from a sequencing batch reactor, that had been operating at a temperature of 39°C for over 2 months, was combined with 3.0 L of settled sludge from another SBR that had been operating at 23°C for several months, and added to 4.5 L of synthetic whitewater containing nutrients, all in the MBR system. The main pump was started: this moment, at 20:30 on November 11, 1994, was day 1 (time 0) for the MBR. For the next 2 days, the MBR was fed at a rate of 2 L of influent per day (HRT = 7 days) at an operating temperature of 25°C. From day 2 to day 65, whitewater was added at a rate of 3 L/d and the operating temperature was maintained at 25°C. On day 66, the whitewater addition rate was increased to 5 L/d (HRT = 2.8 days). On day 69, the temperature of the MBR was brought up to 30°C by using the water bath. The operating temperature was slowly increased to reach 40°C on day 84. The first day of the sampling program outlined in the next section was day 84, at which time the HRT was 2.8 days and the operating temperature was 40°C.

4.2.4. MBR Operating Parameters

As discussed in Section 3, the two main parameters varied in this study of the MBR were the hydraulic retention time and the temperature. These operating parameters were varied according to the experimental design illustrated in Figure 4.4. During the five experimental runs (each one being represented by the round markers on Figure 4.4, the hydraulic retention time was set at either 0.70, 1.12 or 2.80 days, while the temperature was set at either 40°C, 47.5°C or 55°C. A relatively long HRT of 2.8 days was chosen for the first run (T = 40°C) as well as the initial run at a temperature of 55°C to allow the MBR biomass to adapt to the new temperatures. Similarly, the HRT was increased from 0.70 d to 1.12 d when the MBR operating temperature was increased from 40°C to 47.5°C. The experimental conditions represented below were maintained for a duration of at least four weeks for each one of the runs.

Temperature. As indicated previously, the temperature in the MBR was maintained at a steady state at one of three temperature settings: 40°C, 47.5°C or 55°C. Figure 4.5 shows the design operating
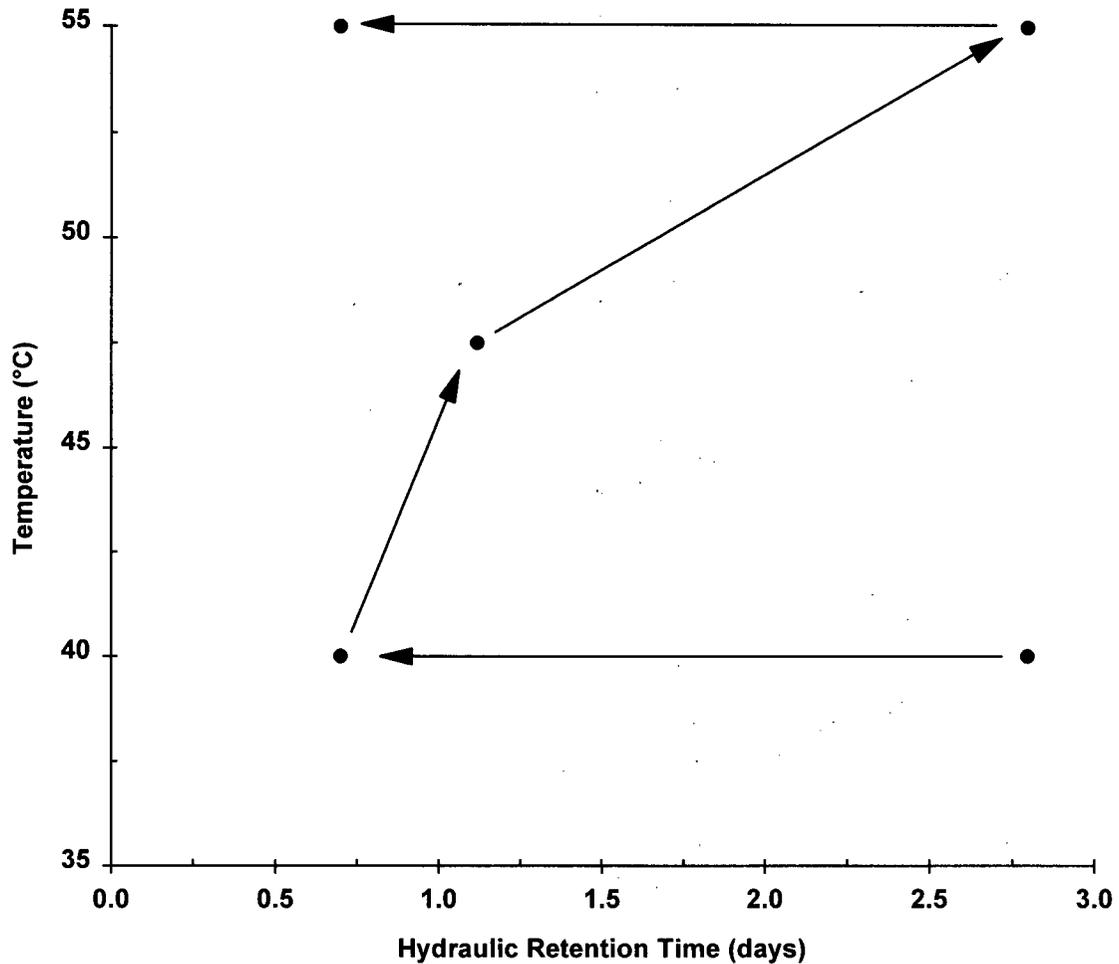
Figure 4.4. **Experimental design used to investigate the effects of the HRT and the temperature on the treatment of synthetic whitewater using an MBR.**

temperatures over the experimental period. Vertical lines were added to the graph to show the beginning

of each run. When the temperature had to be increased, it was done over the course of a few days in

order to allow the microorganism population to adapt to the rising temperature. Even though most of the

MBR system was insulated, the MBR temperature did vary daily during the runs due to variations in the

laboratory temperature. The measured temperature over the experimental period is given in Figure 5.23

on page 88.

Hydraulic Retention Time. The hydraulic retention time was varied as shown in Figure 4.6. The HRTs, corresponding to feeding rates of 20.0 L/d, 12.5 L/d and 5.0 L/d, were changed abruptly between the runs. Vertical lines show the beginning of each run. The end of each run is not shown.

SRT. The solids retention time was maintained at approximately 25 days, by wasting 0.5 L of mixed liquor on a daily basis. However, when the HRT was decreased, wasting was discontinued for several days in order to allow the MBR biomass to increase. In addition, numerous accidental losses of mixed liquor from the MBR, described below, made it impossible to maintain an exact SRT. When such spills occurred, the mixed liquor wasting from the reactor was halted for the period of time which would otherwise have been necessary to remove an equivalent amount of mixed liquor through regular wasting.
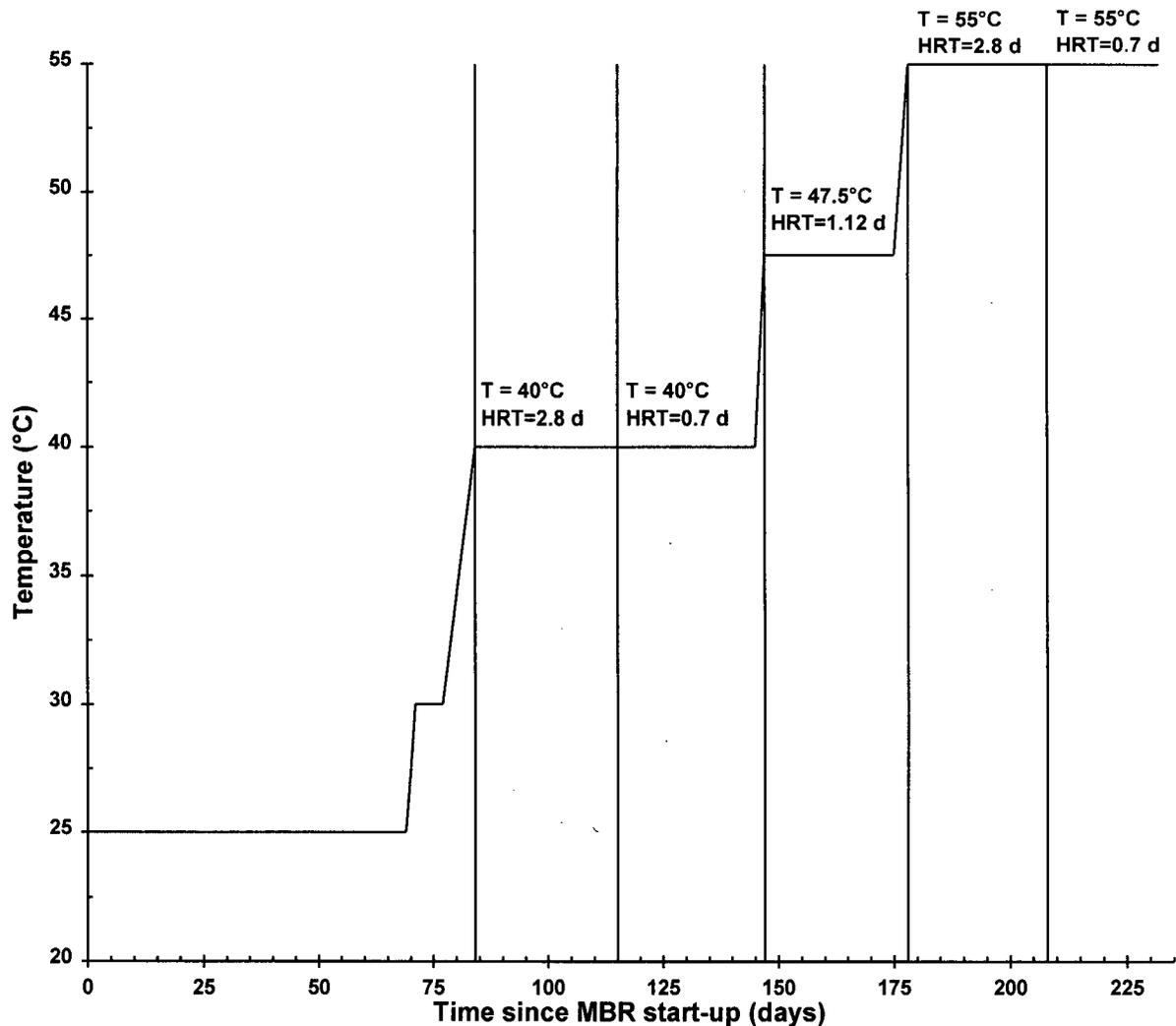
Figure 4.5. Design temperature settings of the MBR over the experimental period.

When samples of mixed liquor were taken from the reactor, the wasting volume was reduced accordingly for that day.

Nutrient Additions. Nitrogen and phosphorus were added every 30 minutes from stock solutions containing ammonium chloride (145.2 mg NH_4Cl / L) and sodium phosphate (77.7 mg $Na_2PO_4 \cdot 12H_2O$ / L) at a ratio in excess of COD:Nitrogen:Phosphorus of 200:5:1. This nutrient addition was slightly excessive and could have been reduced in order to limit the concentration of nutrients present in the treated permeate. The concentration of orthophosphate and ammonia nitrogen were
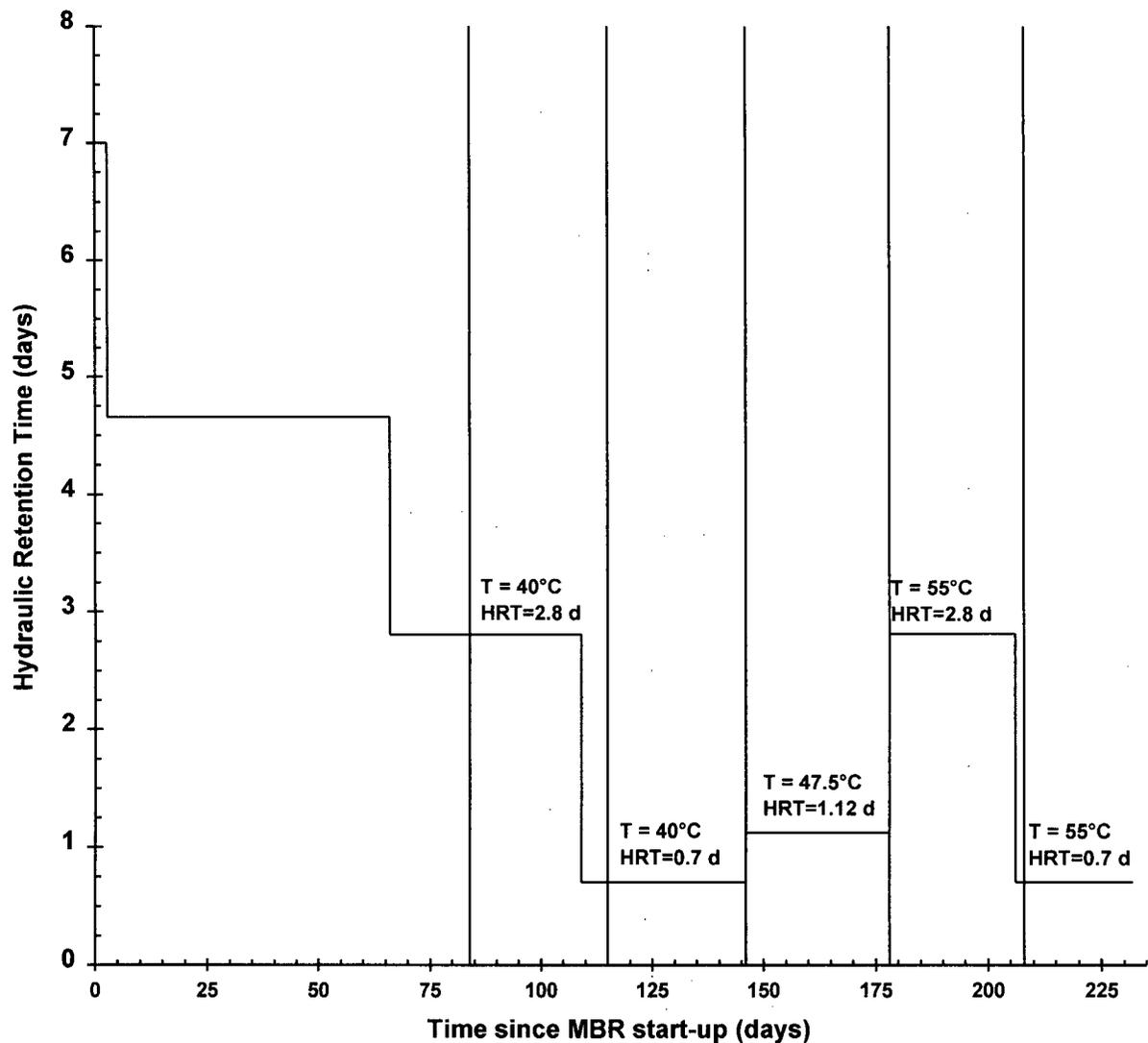
Figure 4.6. Actual hydraulic retention time of the MBR over the experimental period.

monitored regularly to ensure that nutrients were available in sufficient concentrations in the MBR.

Dissolved Oxygen Level in the Reactor. The dissolved oxygen concentration in the MBR was maintained above 2.0 mg O_2/L during normal operation. However, when the operation of the recirculation pump was interrupted, the dissolved oxygen (DO) concentration did occasionally drop below this level for short periods of time, to values as low as 0.1 mg/L.

MBR Operating Incidents. Various incidents occurred while operating the membrane biological reactor. The most important were spills due to leaks in a PVC fitting or in the recirculating pump seal which led to a loss of mixed liquor and an interruption of the recirculating pump. The PVC fittings cracked because of vibrations in the system caused by the recirculating pump. In other less serious cases, the main recirculating pump was shut down due to a stuck level control switch or, in one case, a building power failure. Other significant incidents, such as a period when no nutrients were added to the reactor for a few days due a programming error of the timer controlling the nutrient additions, are reported as well. These incidents are listed in Table 4.2 and are reported because they impacted the mixed liquor volatile suspended solids concentration in the reactor as well as the efficiency of the MBR treatment of the whitewater.

Table 4.2.   MBR operating incidents

Date	Day #	Run #	Problem
March 8, 1995	117	2	A programming error in the control timer caused the discharge of all the nutrient solutions on February 27 (day 108) in the mixed liquor. Since the containers containing the nutrient solutions are empty, no nutrients are added from day 108 to day 117.
March 15, 1995	124	2	The permeate recycle line falls outside the reactor and the permeate drains until the level in the reactor drops to 8 L. The MBR recirculation pump is automatically turned off, and remains off for several hours. The DO level in the reactor falls below 2 mg O_2/L.
March 19, 1995	129	2	The mechanical seal of the recirculation pump fails and 2 L of MBR mixed liquor are lost. The mixed liquor is replaced by an equal amount of mixed liquor obtained from the SBR operating at

Date	Day #	Run #	Problem
			40°C.
March 25, 1995	134	2	Foam cutting wire broke: loss of solids through foaming resulted in recirculation pump shut-down for several hours. The loss may be equivalent to the loss of 1 L of mixed liquor.
March 26, 1995	136	2	Influent prepared using a new batch of evaporator concentrate. The different composition of the influent may have resulted in decreased removal efficiencies.
April 12, 1995	152	3	Power shortage on UBC campus resulted in pump shut-down for over 15 hours and in the loss of several liters of mixed liquor. The DO level falls below 2 mg O_2/L and the operating temperature drops to a low of 42°C.
April 14, 1995	154	3	The recirculation pump's mechanical seal fails and 2 L of MBR mixed liquor are lost.
May 11, 1995	181	4	Worn bearings in the recirculation pump cause vibrations which result in cracks developing in plastic fittings. Several liters of mixed liquor lost over the course of several days until the source of the problem is corrected.
May 20, 1995	190	4	More plastic fittings crack, resulting in the loss of several more liters of mixed liquor. Some fittings are replaced with brass or steel fittings.
May 28, 1995	198	4	A defective level control results in pump shut-down for several hours, causing a drop in the dissolved O_2 concentration.
May 30, 1995	200	4	A defective level control results in pump shut-down for several hours, causing a drop in the dissolved O_2 concentration.
June 8, 1995	208	5	Ultrafiltration control valve wrongly set, resulting in a transmembrane pressure of over 100 kPa (15 psi). The recirculation pump provides more heat to the system, and the MBR operating temperature reaches 65°C and remains at over 60°C for over 8 hours.
June 23, 1995	224	5	The permeate 3-way valve sticks in the recycle position. The level in the reactor increases to the level of the foam cutter, causing splashing and the lost of some mixed liquor.

4.2.5. Sampling and Sample Preservation

Permeate samples were collected daily and analyzed promptly as described in Section 4.3. The influent and mixed liquor samples were collected weekly. The influent samples were collected from the feed tank at room temperature, while mixed liquor samples were collected from the reactor itself using a glass beaker. Samples were collected as follows (daily for the permeate, weekly for the influent and mixed liquor):

- 400 mL (Nalgene containers) of permeate, influent and mixed liquor for COD, DOC, solids, pH, cationic demand and colour.

- 30 mL (glass container) of mixed liquor for the OUR measurement.

- 75 mL (Nalgene containers) of permeate and influent for ammonia and ortho-phosphate analysis.

- 50 mL (amber glass containers with a Teflon-lined cap) of permeate, influent and mixed liquor for RFA analysis. Duplicates were taken for each sample.

4.2.6. Quality Control / Quality Assurance Program

All samples were analyzed in-house, following the analytical methods outlined below. Standard, blanks, duplicates and in some cases triplicates were analyzed as part of a quality control program. More details are given in Section 4.3.

4.3. Analytical Techniques and Equipment

4.3.1. Resin and Fatty Acid Analysis

Resin and fatty acids (RFA) concentrations were measured bi-monthly using a method adapted from Voss and Rapsomatiotis (1985) and adapted by staff of the Pulp and Paper Research Institute of Canada (1988). Immediately following the collection of the samples in amber glass vials with Teflon-lined caps, their pH level was adjusted to 10 using a stock solution of 1 N sodium hydroxide. The samples were then preserved for up to two weeks at 4°C. All samples were analyzed in duplicate, and

occasionally in triplicate. A blank was also analyzed for every set of samples. The permeate and influent samples were extracted without further preparation, while the mixed liquor samples were centrifuged at 3000 rpm for 30 minutes. The supernatant was collected and then extracted. The pellet, containing the biomass, was resuspended in distilled water to a volume equal to the original sample volume of mixed liquor, pH adjusted to 10 and then extracted. Hence, RFA concentrations in the mixed liquor were broken down into two fractions: the fraction bound to the solids and the fraction in solution.

In order to minimize solvent use, and since resin and fatty acid concentrations were high, a sample volume of 5 mL was extracted with two 5 mL volumes of methyl-t-butyl-ether, as opposed to the prescribed sample volume of 50 mL and two extractions using 50 mL of solvent. The solvent extracts were then concentrated by allowing the methyl-t-butyl-ether to evaporate (sometimes with nitrogen gassing) and 0.1 mL of methanol and 1.0 mL of diethyl ether were added. Methylation of the resin and fatty acids was then carried out using diazomethane gas carried by nitrogen gas. The methylated extracts were once again concentrated using a stream of nitrogen gas and were diluted to 1.0 mL with methyl-t-butyl-ether before being transferred to Teflon-lined glass vials.

The analysis of the samples prepared as above was carried out on a Hewlett-Packard 5880A gas chromatograph, equipped with a flame ionization detector and a 30 m DB-1 fused silica column of internal diameter of 0.32 mm and of film thickness of 0.25 μm (J&W Scientific, Folsom, CA). The carrier gas used was helium at a linear velocity of 20 cm/s at 290°C. The flame ionization detector makeup gas was composed of helium, hydrogen and purified air (flows of 20, 30 and 400 mL/min, respectively). The temperature regime used was the same as Johnson (1995): the injection temperature was 275°C and the detector temperature was 290°C. The temperature program, of a length of 48.16 minutes, is detailed in Table 4.3. The method detection limit was approximately 0.1 mg/L for each individual resin or fatty acid.

The specific resin and fatty acids listed in Table 4.4 were measured in the samples analyzed. All RFA concentration values reported in this study are given in mg/L as dehydroabietic acid (DHA), since DHA was used as the methylation standard. This approach has been justified by Voss and Rapsomatiotis, (1985). Palustric and levopimaric acid concentrations are reported as a pair because separating their respective peaks was not feasible.

Table 4.3.   Temperature program used in the gas chromatograph analysis of RFAs.

Duration (min)	Temperature (°C)	Temperature change rate
2.00	45	0
9.66	increasing at this rate →	15
1.00	190	0
25.00	increasing at this rate →	1
0.50	215	0
5.00	increasing at this rate →	15
5.00	290	0

Table 4.4.   Specific resin and fatty acids measured in the samples.

Resin Acids	Fatty Acids
Pimaric	Palmitic
Sandaracopimaric	Linoleic
Isopimaric	Linolenic
Palustric + Levopimaric	Oleic
Dehydroabietic	Stearic
Abietic	
Neoabietic	

4.3.2. Dissolved Organic Carbon

The permeate samples were preserved at 4°C for up to 7 days while the influent and mixed liquor samples were analyzed within a few hours of their collection. Analysis was done weekly using an automatic Shimadzu Total Organic Carbon Analyzer (model TOC-500). Influent and mixed liquor samples were pre-filtered using Whatman 934-AH 1.5 μm microfiber filters. The TOC analyzer was

calibrated with each set of samples as described in the instruction manual (Shimadzu Corporation, 1987).

A distilled water blank was analyzed with each set of samples.

4.3.3. Chemical Oxygen Demand

The permeate samples were preserved at 4°C for up to 7 days and analyzed weekly using the closed reflux colorimetric procedure (standard method 5220D) adopted by American Public Health Association *et al.* (1989). Influent and mixed liquor samples were analyzed within hours of their collection for both total COD (TCOD) and dissolved COD (DCOD). The DCOD was obtained by pre-filtering the samples using Whatman 934-AH 1.5 μm microfiber filters. In the case of the permeate samples, the DCOD was equivalent to the TCOD, since the permeate was ultrafiltered (nominal pore size of the UF membrane = 0.08 μm). Therefore, the permeate samples were only analyzed unfiltered. Since chloride was present in the permeate and mixed liquor samples due to the regular addition of ammonium chloride to the mixed liquor, the standard method with addition of mercury was used. Following digestion in a Hach COD reactor, the absorbance of the samples (duplicates and sometimes triplicates were used) and standards was measured using a Hach DR-2000 spectrophotometer set at 600 nm. A standard curve was plotted for every batch digested, using five standards (including a distilled water blank) and the COD of the samples were then calculated by the use of a spreadsheet computer application.

4.3.4. Cationic Demand

The cationic demand was measured using a method obtained from the Pulp and Paper Research Institute of Canada (Kwong, 1994). The permeate samples were preserved for up to a week at 4°C, while the influent and mixed liquor samples were analyzed within a few hours of their collection. The samples were centrifuged and a cationic polymer, 1,5-dimethyl 1-1,5 diazaundecamethylene polymethylobromide (DDPM, also known as polybrene) was added to the supernatant. The excess cationic polymer in the sample was titrated with an anionic polymer, polyvinyl sulphuric acid potassium salt (PVSAK), using

toluidine blue O (TBO) as a colour indicator. The equipment used in the cationic demand titration was limited to 2 burettes and 2 magnetic stirrers and stir bars.

1. A solution of 0.1 % toluidine blue O was prepared by dissolving 0.05 g of TBO in deionized water in a 50 mL volumetric flask.

2. A 0.01 N solution of DDPM was prepared by adding 2.000 g of DDPM (obtained from Sigma of St-Louis, Missouri) to 1.0 L of deionized water in a volumetric flask. From this stock solution, a 0.001 N solution for titration was prepared by diluting 100 mL of the stock solution in a 1.0 L volumetric flask. This titration solution was used to standardize the PVSAK solution as detailed below. According to Kwong (1994), the approximate equivalent weight of DDPM is 187.11, while the average equivalent weight with respect to cationic charge is 200.

3. A stock solution of approximately 0.01 N of PVSAK was prepared by diluting 1.6221 g of PVSAK (obtained from Kodak of Rochester, New York) in 1.0 L of deionized water using a volumetric flask. From this stock solution, a titration solution of approximately 0.001 N was prepared by diluting 100 mL of the stock solution in a 1.0 L volumetric flask. This solution was then standardized as detailed below.

4. The PVSAK solution was standardized as follows:

   a) A blank titration was carried out before the standardization by adding 100 mL of deionized water to a 250 mL beaker and adding 3 drops of the 0.1 % TBO solution and mixing the solution with a magnetic stirrer for 1 minute. This solution was titrated with the PVSAK solution until a pink end point was reached. This volume corresponds to $V_{water\ blank}$ in the calculations below.

   b) The PVSAK solution was then standardized: 10.00 mL of 0.001 N DDPM and 3 drops of TBO were added to 100 mL of deionized water in a 250 mL beaker. This solution was mixed for one

minute and titrated using the "0.001 N" PVSAK solution until the pink end point. This volume

corresponds to $V_{PVSAK\ blank}$ in Equation 4-2. This end point was verified by adding 2.0 mL of the

PVSAK solution and back titrated with DDPM until a blue end point was reached.

$$N_{PVSAK} = \frac{N_{DDPM} \times V_{DDPM}}{V_{PVSAK\ blank} - V_{water\ blank}}$$

Equation 4-2

Where N_{PVSAK} =   Normality of the PVSAK solution

$V_{PVSAK\ blank}$ =   Volume of PVSAK consumed for titrating 10.00 mL of DDPM in a deionized water blank

V_{DDPM} =   10.00 mL

N_{DDPM} =   0.001 N

$V_{water\ blank}$ =   volume PVSAK necessary to titrate a 100 mL of deionized water containing three drops of TBO.

Following the centrifugation of the process samples at 1500 rpm for 30 minutes, 10 mL of the

supernatant was diluted to 100 mL using a volumetric flask (in the case of the reactor samples, 10 mL

were diluted in 1000 mL using a volumetric flask). One hundred mL of the diluted sample were then

placed in a 250 mL beaker to which was added 3 drops of 0.1 % TBO and 10.00 mL of 0.001 N DDPM

standard. Following one minute of mixing, the solution was titrated with the PVSAK titration solution to

a pink end point. This volume (V_{PVSAK}) was recorded. Finally, the end point was verified by adding 2

mL of PVSAK and titrating to a blue end point using DDPM. The cationic demand of the sample could

then be calculated using Equation 4-3. The cationic demand is expressed in mg of DDPM/ L of sample.

It can also be expressed in terms of eq/L by not multiplying by the factor of $2 \cdot 10^5$ mg/L in the Equation

4-3.

$$Cationic\ demand = \frac{N_{PVSAK} \times (V_{PVSAK\ blank} - V_{PVSAK}) \times 2 \cdot 10^5\ mg\ /\ L}{V_{sample}}$$

Equation 4-3

Where N_{PVSAK} = Normality of the PVSAK solution (as determined from Equation 4-2)

$V_{PVSAK\ blank}$ = Volume of PVSAK consumed for titrating 10.0 mL of DDPM in a deionized water blank (as in Equation 4-2)

V_{PVSAK} = Volume of PVSAK consumed for titrating 10.0 mL of DDPM in the diluted sample

V_{sample} = Actual volume of sample present in the beaker (equal to 10.00 mL for permeate and influent samples and 1.00 mL for mixed liquor samples)

4.3.5. Colour

The colour of the permeate, influent and mixed liquor samples was evaluated using the CPPA standard method H.5 (Canadian Pulp and Paper Association, 1993). The samples were preserved for up to a week at 4°C. The mixed liquor samples were diluted (usually 1:10) to bring their colour into the range of the method. The pH of the samples was then adjusted to 7.6 (± 0.1) and prefiltered using Whatman 934-AH 1.5 μm microfiber filters. The pH of the samples was readjusted to 7.6 (± 0.1) and filtered using a Sartorius cellulose nitrate membrane filter having a nominal pore size of 0.8 μm. Finally, the absorbance of the samples was measured with a Pye-Unicam SP8-100 double beam spectrophotometer set at a wavelength of 465 nm. These values were then translated into colour units, by measuring the absorbance of standard platinum-cobalt solutions of 500 colour units and 100 colour units.

4.3.6. Solids

The total solids (TS), volatile solids (VS), total dissolved solids (TDS), volatile dissolved solids (VDS), total suspended solids (TSS), volatile suspended solids (VSS) were measured in all samples as described in CPPA standard H.1 (Canadian Pulp and Paper Association, 1993), with the exception of the mixed liquor TSS (MLTSS) and mixed liquor VSS (MLVSS). The MLTSS and MLVSS were measured as summarized in Table 4.5 since filtration of an adequate volume of sample using a Whatman 934-AH

was not possible. Prior to analysis, the permeate samples were preserved for up to a week at 4°C, while the influent and mixed liquor samples were analyzed within a few hours of their collection.

Table 4.5.   Summary of methods used for the determination of solids content in samples.

Solids type	Method used for determination
Total solids (TS) (all samples)	A known volume of the sample was oven-dried at 104°C in a porcelain dish.
Volatile Solids (VS) (all samples)	The dish used to determine the TS was then ignited at 550°C in a muffle furnace to determine the VS.
Total dissolved solids (TDS) (influent and permeate samples)	The sample was filtered using a Whatman 934-AH glass microfiber filter. A known volume of the filtered sample was oven-dried at 104°C in a porcelain dish.
Total dissolved solids (TDS) (mixed liquor samples)	As above, except the samples were centrifuged at 3000 rpm for 30 minutes before the filtering the supernatant.
Volatile dissolved solids (VDS) (all samples)	The dish used to determine the TDS was then ignited at 550°C in a muffle furnace to determine the VDS.
Total suspended solids (TSS) (influent samples)	A known volume of the sample was filtered using a Whatman 934-AH glass microfiber filter. After rinsing the filter with distilled water, the filter was placed on an aluminium planchet for support and was oven-dried at 104°C.
Volatile suspended solids (VSS) (influent samples)	The filter used to determine the TSS was then ignited at 550°C in a muffle furnace to determine the VSS.
Total suspended solids (TSS) (mixed liquor samples)	The TSS in the mixed liquor samples were evaluated by subtracting the TDS from the TS.
Volatile suspended solids (VSS) (mixed liquor samples)	The VSS for the mixed liquor samples were obtained by subtracting the VDS from the VS.

The suspended solids concentration in the permeate samples was verified regularly and was nil throughout the study, as the nominal pore size of the MBR ultrafiltration unit (0.08 μm) was smaller than the effective retention size of the Whatman 934-AH 1.5 μm glass microfiber filters used to determine the concentration of suspended solids. Therefore, the permeate TS being equal to the permeate TDS, only the TS and VS were measured regularly in the permeate.

4.3.7. Oxygen Uptake Rate

The oxygen uptake rate (OUR) of mixed liquor samples was measured weekly at the same temperature at which the sample was taken. The OUR and the specific OUR (SOUR) were measured immediately after collection of the sample from the MBR as follows:

1. One hundred and fifty mL of synthetic whitewater were added to a 300 mL biological oxygen demand (BOD) bottle already containing 150 mL of treated permeate. This solution was placed in 1 L plastic beaker containing water heated by a Haake (of Paramus, New Jersey) FJ circulator set at the same temperature at which the MBR was operating (40°C, 47.5°C or 55°C) and was aerated using a gentle stream of air bubbles. A magnetic stir bar was also placed in the BOD bottle and a magnetic stirrer was placed under the plastic beaker in order to provide mixing in the BOD bottle.

2. The aeration of the solution prepared in step 1 was ceased and a small volume of the solution contained in the BOD bottle was put aside in order to add a 15 mL sample of mixed liquor just taken from the MBR. The solution was thoroughly mixed with the stir bar and the BOD bottle level was topped up with the solution previously put aside.

3. A YSI 5720A self-stirring BOD bottle probe (obtained from YSI Inc. of Yellow Springs, Ohio) was fitted snugly over the BOD bottle. The probe was connected to a YSI model 54ARC DO meter.

4. After allowing the probe to adapt to the conditions, DO readings were taken every 20 seconds and entered directly in a spreadsheet application until the DO reached 2.0 mg O_2/L. The OUR was then evaluated by calculating the slope of the DO reduction over time and expressed in terms of mg O_2/L·min.

5. Following the measurement of the MLVSS concentration in a sample of mixed liquor taken at the same time as the 15 mL sample used for the OUR determination, the specific OUR, or SOUR, was expressed in terms of mg O_2/mg MLVSS·min using Equation 4-4.

$$SOUR = \frac{DO \text{ consumption rate (mg } O_2 \text{ / L} \cdot \text{ min)} \cdot 0.3 \text{ L}}{MLVSS \text{ concentration (g / L)} \cdot 15 \cdot 10^{-3} \text{ L}} \qquad \textbf{Equation 4-4}$$

Where 0.3 L is the DO bottle volume and $15 \cdot 10^{-3}$ is the mixed liquor volume added to the DO bottle for the OUR determination. The MLVSS concentration was measured from a second sample taken from the MBR.

4.3.8. Ammonia and Ortho-phosphate

The permeate samples were stored at 4°C for up to one week for soluble ammonia and ortho-phosphate analysis. A Lachat (of Milwaukee, Wisconsin) Quickchem® AE autoanalyzer was used to determine the residual concentration of these compounds in the permeate.

4.3.9. pH

The pH of the influent, mixed liquor and permeate was monitored weekly and measured within hours of sampling using a Beckman pH meter with automatic temperature compensation. The pH meter was calibrated using standard 4.0, 7.0 and 10.0 buffers.

4.3.10. Temperature

The mixed liquor temperature in the MBR was monitored several times daily using a YSI model 47 scanning tele-thermometer equipped with a submersible temperature probe.

4.3.11. Dissolved Oxygen

The dissolved oxygen concentration of the MBR mixed liquor was also monitored several times daily using a YSI model 54 ARC DO meter equipped with a model 5739 submersible probe.

4.3.12. Permeate Flow Rate

The flow rate of the permeate was monitored daily by measuring the time necessary to fill a graduated cylinder with permeate from either the recycle line or the drain line.

5. RESULTS AND DISCUSSION

In this section, a description of the data and results obtained during the characterization of the Zenon Permaflow-1 membrane and during the operation of the MBR are presented and discussed.

5.1. Synthetic Whitewater Characteristics

Since TMP newsprint mills with excess flows of 2 to 5 m^3/adt are not currently in operation, a synthetic whitewater containing RFA and solids concentrations judged acceptable was prepared using screw pressate and evaporator concentrate as described in Section 4.1.1 on page 41. The synthetic whitewater used during the MBR study had the characteristics given in Table 5.1. The whitewater varied slightly in composition, since it was made from different batches of screw pressate and evaporator

Table 5.1. Influent (synthetic whitewater) characteristics for the MBR study only. The average influent characteristics for the UF study are presented in Table 5.2.

Measurement	Number of data points	Units	Average	Standard Deviation	Minimum	Maximum
Total Solids	20	mg/L	3570	390	2330	4250
TSS	21	mg/L	250	70	150	370
VSS	21	mg/L	180	60	80	280
TDS	20	mg/L	3200	370	2360	4050
VDS	20	mg/L	1890	330	1390	2800
Total COD	21	mg O_2/L	3390	230	2650	3820
Dissolved COD	20	mg O_2/L	2670	280	1860	2990
DOC	20	mg/L	1060	110	750	1160
Colour	20	colour units	1000	280	1320	574
Cationic demand	21	μeq/L	410	30	350	470
Dissolved Ammonia	6	mg N/L	0.2	0.2	0.1	0.6
Dissolved ortho-P	6	mg P/L	0.7	0.2	0.5	1.2
Total RFA	21	mg/L as DHA	27.2	10.0	10.6	39.0
FA	21	mg/L as DHA	13.8	5.8	2.7	22.1
RA	21	mg/L as DHA	13.4	5.1	4.1	21.6

concentrate over the experimental period.

5.2. Initial Ultrafiltration Membrane Characterization Using Distilled Water

For future comparison purposes, the permeate flux of the Permaflow-1 ultrafiltration unit (PF-75) was measured over several hours with distilled water at a transmembrane pressure of 103 kPa (15 psi) and at a recirculation rate of 50 L/min (velocity in the membrane unit = 1.7 m/s). Due to the recirculation of the water through the progressive cavity pump, the temperature of the distilled water increased from an initial 24°C to reach a stable 42°C after about 5 hours. After 12.7 hours, the distilled water that had been recirculating was flushed out and replaced with fresh distilled water. The measured permeate flux immediately dropped (sharp dip in the "flux as measured curve" in Figure 5.1), since the fresh water temperature suddenly dropped to 24°C. However, no immediate drop in temperature-corrected flux actually resulted, since the permeate flux is dependent on the viscosity of the solution.

The measured permeate flux values were adjusted to 25°C as detailed in Equation 5-1 (from Zenon Environmental Inc., 1994).

$$\text{Corrected flux for } 25°C \ = \ \text{Flux at } T_x \ \cdot \ \left(\frac{\text{Viscosity at } T_x}{\text{Viscosity at } T_{25°c}} \right) \qquad \textbf{Equation 5-1}$$

The corrected permeate flux decreased slowly over time (Figure 5.1), from an initial value of 500 L/(m²·h) to a stabilized final value of 211 L/(m²·h). Once the flux was stabilized, the permeate flux was measured under various transmembrane pressures ranging from 3 kPa (0.5 psi) to 275 kPa (40 psi). These results are illustrated in Figure 5.2. In accordance with theory, the permeate flux of the distilled water increased almost linearly with transmembrane pressure (Cheryan, 1986). In order to minimize the heat generated by the continuous operation of the pump, the minimal manufacturer-recommended transmembrane pressure (69 kPa or 10 psi (Zenon Environmental Inc., 1994)) was chosen for the

ultrafiltration of the process water. The distilled water flux under these conditions, corrected to 25°C, was measured at 168 L/(m^2·h) (Figure 5.2).
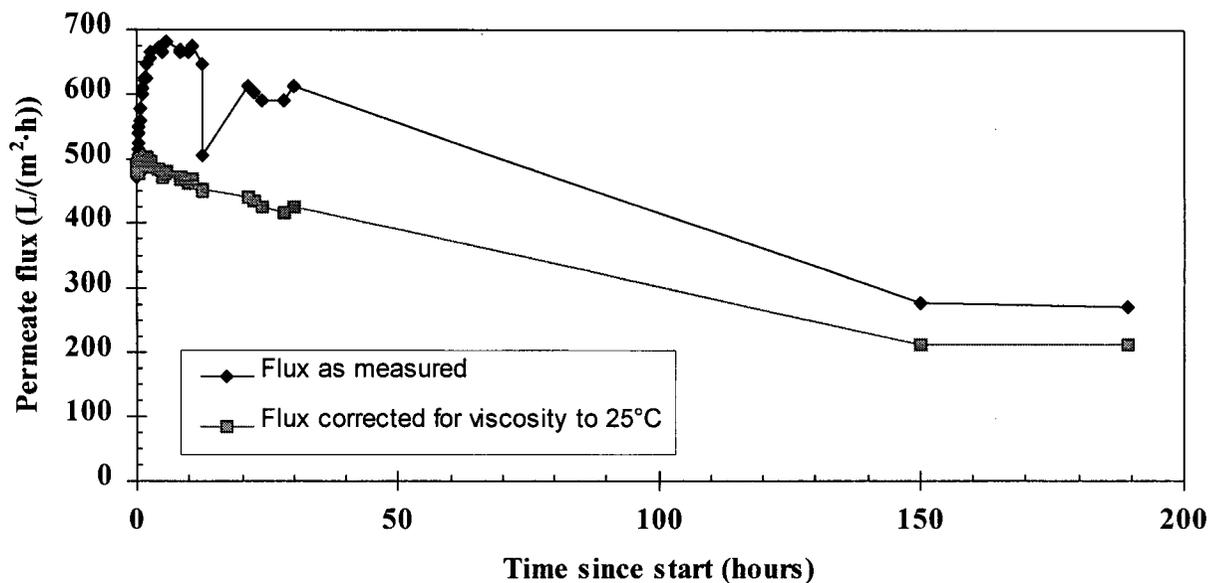
Figure 5.1. **Permeate flux during the distilled water run using the PF-75 unit under a transmembrane pressure of 103 kPa (15 psi) at a recirculation rate of 50 L/min.**
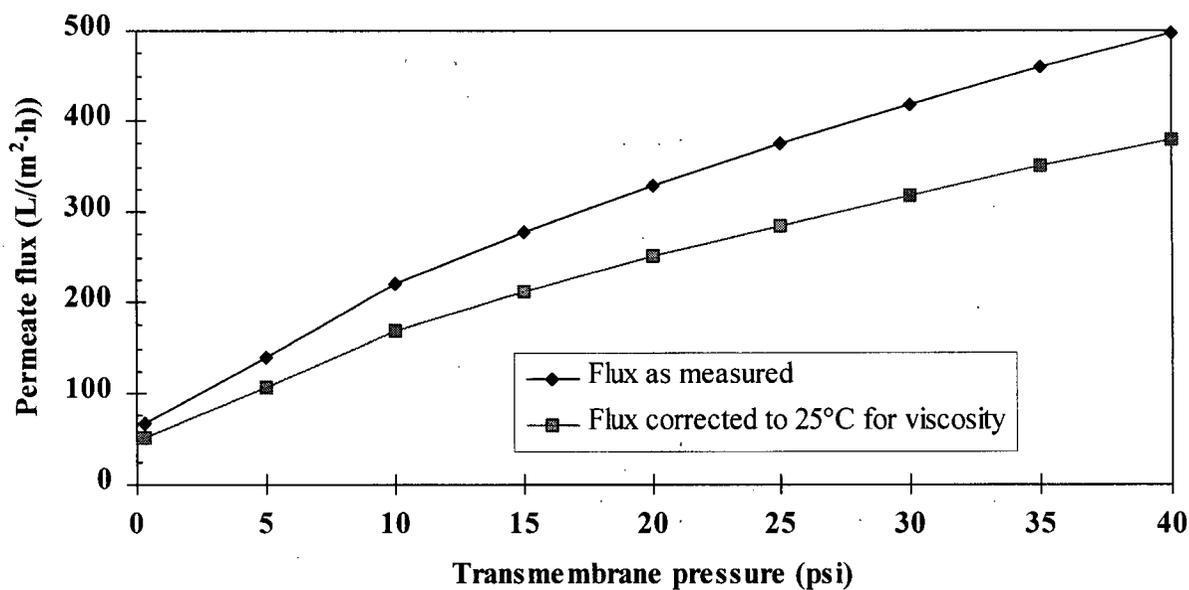
Figure 5.2. **Permeate flux vs. concentrate pressure using the PF-75 unit with a recirculation rate of 50 L/min.**

5.3. Ultrafiltration of the Process Water

In order to assess the efficiency of the ultrafiltration membrane unit without the presence of a mixed population of microorganisms, synthetic whitewater was ultrafiltered to a concentration factor (CF) of 37 by adding 40 L of whitewater per day for 13 days to the initial fourteen liters of whitewater present in the system. The concentration factor was calculated using Equation 4-1 on page 44. The average temperature of the concentrate was 37°C, due to heat generated by the recirculation pump. The flux over the experimental period, as well as the concentrations of dissolved and colloidal substances (DCS) in the permeate and the concentrate are presented in this section. The removal efficiencies associated with the DCS are also presented.

5.3.1. Summary of the Results and General Observations

During the operation of the membrane unit, both the concentrate and the permeate became noticeably darker as the concentration factor increased. At concentration factors greater than 12, the level control float switches in the reactor occasionally stuck due to the deposition of sticky pitch, thereby requiring frequent check-ups to ensure the proper operation of the float switches. At concentration factors greater than 18, pitch deposits were noticeable on the reactor walls and sticky "balls" of agglomerated pitch were present in the concentrate. These sticky pitch balls and deposits grew in size and numbers as the concentration factor increased. At the end of the run, some pitch deposits present on the reactor walls were several millimeters in thickness. The pitch deposits were greatest in areas were there seemed to be little turbulence. In other places, no pitch deposits were noticeable. Despite the high concentration of contaminants in the reactor, the permeate flux remained between 18 and 28 L/m^2·h throughout the experimental period.

The average feed concentration for the whitewater contaminants as well as their respective removal efficiencies measured during the process water run are presented in Table 5.2. The percent removal efficiencies for each contaminant usually decreased as the concentration factor increased, except

those for the solids, which were independent of the concentration factor, and for RFA, for which the removal efficiency increased as the concentration factor increased. The average percent removal efficiencies observed during the process water ultrafiltration study were low or nil for DCOD, DOC and colour, fair for TCOD and cationic demand, good for solids and RA and excellent for FA. These results, as well as the permeate flux during the study, are discussed below.

Table 5.2. **Summary of the removal efficiencies obtained during the process water run (transmembrane pressure = 69 kPa; recirculation rate = 50 L/min).**

Contaminant	Average influent concentration	Unit	Percent removal efficiency				
			Average	St. dev.	Min.	Max.	Relation of percent removal with CF
Total Solids	4670	mg/L	40%	2%	35%	46%	= with ↑CF
TSS	370	mg/L	100%	0%	100%	100%	= with ↑CF
TDS	4300	mg/L	35%	2%	29%	41%	= with ↑CF
TCOD	3300	mg O_2/L	23%	6%	10%	35%	↓ with ↑ CF
DCOD	2700	mg O_2/L	5%	7%	-11%	20%	↓ with ↑ CF
DOC	900	mg/L	0%	8%	-16%	17%	↓ with ↑ CF
Colour	900	colour units	5%	21%	-22%	54%	↓ with ↑ CF
Cationic demand	360	µeq/L	44%	25%	-1%	89%	↓ with ↑ CF
Total RFA	32	mg/L as DH	90%	11%	67%	100%	↑ with ↑ CF
FA	18	mg/L as DH	100%	0%	98%	100%	↑ with ↑ CF
RA	14	mg/L as DH	77%	24%	24%	100%	↑ with ↑ CF

The concentrations of the various process water contaminants present in the permeate and in the concentrate during the experimental period are represented in the following sections of this chapter. In many cases, the concentrations of the contaminants increased with the concentration factor in the beginning and then seemed to stabilize. This may have been due to two factors: (i) the contaminants may have deposited with the pitch on the surface of the reactor and equipment and (ii) the concentration of contaminants in the reactor became so high that concentrate samples taken from the reactor became significant in terms of mass relative to the influent input of these contaminants. Mass balances were therefore plotted for most contaminants.

5.3.2. Permeate Flux

The permeate flux as measured during the process water continuous run is illustrated on Figure 5.3. The flux corrected to 25°C is also shown, since the operating temperature varied from an initial value of 28°C to a maximum value of 40°C. The average temperature during the process water run was 37°C, and was usually within three degrees of that temperature. The flux was not adjusted for changes in viscosity linked to the build-up of solids in the permeate. After showing a sharp initial decline from 28 to 19 L/m²·h, the flux increased again to 28 L/m²·h again (at a concentration factor of 22) then declined to about 18 L/m²·h. The initial decline of the permeate flux is probably due to the formation of a gel layer (or cake) on the membrane, which may then have reached a critical thickness and started to slough off, creating an increase in the flux The second decline of the permeate flux may have been caused by the deposition of pitch on the membrane, when the concentration of dissolved and colloidal substances started to agglomerate and adhere to surfaces of the system.

At the end of the process water run, the membrane was rinsed and then cleaned using a solution
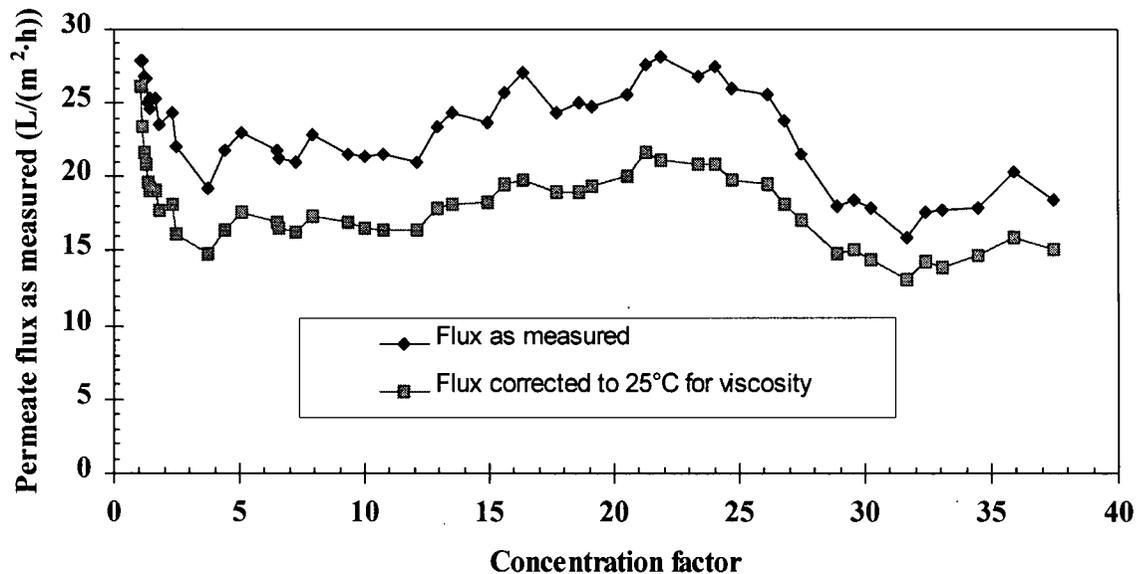
Figure 5.3. **Permeate flux rate as measured during the process water continuous run using the PF-75 unit under a transmembrane pressure of 69 kPa (10 psi) at a recirculation rate of 50 L/min.**

containing NaOH (to a pH of 10.5). The distilled water flux was then measured under a recirculation

rate of 50 L/min (velocity in the membrane unit = 1.7 m/s) and a concentrate pressure of 103 kPa (15

psi). The distilled water permeate flux after the cleaning procedure, corrected to 25°C, was 97 $L/m^2 \cdot h$.

This is much lower than the 212 $L/(m^2 \cdot h)$ measured before the process water run (Figure 5.2). The

membrane cleaning procedure was thus modified for future membrane cleaning to use a water-based

solution containing proprietary cleaner and sodium hypochlorite. This cleaning regime, described in

Section 4.2.2 on page 44, was highly successful, and could restore the membrane flux to the original

values presented in Figure 5.2.

5.3.3. Chemical Oxygen Demand Removal

During the process water run, the PF-75 ultrafiltration unit removed an average of 23% of the

influent total COD. However, this included an average removal of only 5% of the influent dissolved

COD. This can be visualized on Figure 5.4, where the permeate DCOD concentrations, represented by

the carat symbols, are almost equal to the average influent DCOD concentration, represented by the long-
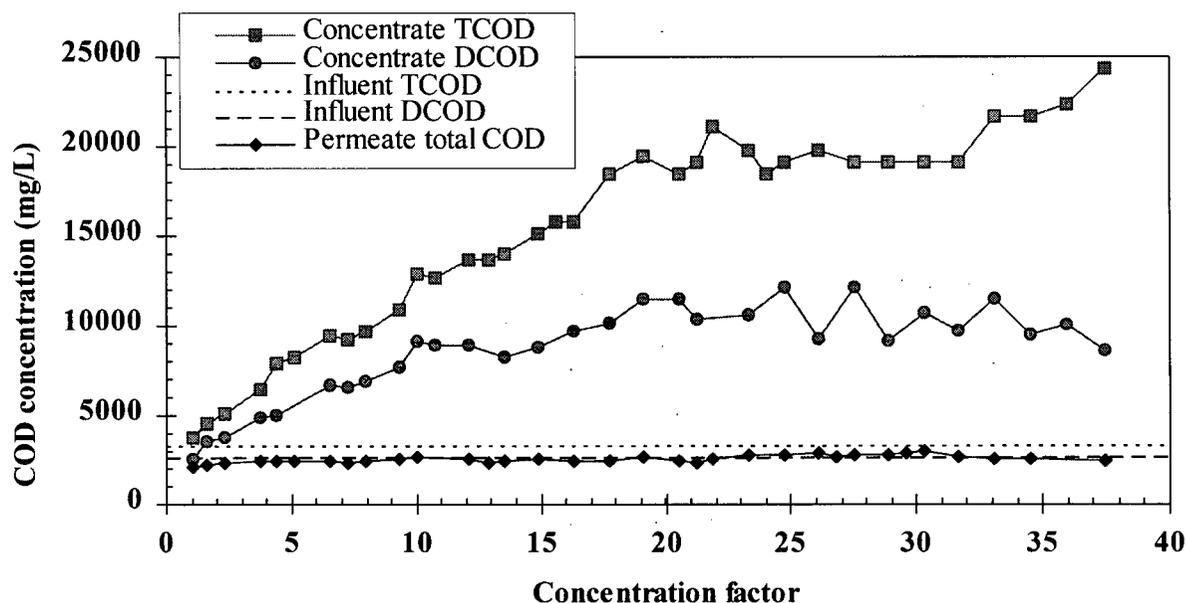
Figure 5.4. TCOD and DCOD concentrations in the permeate and the concentrate during the process water continuous run using the PF-75 unit under a transmembrane pressure of 69 kPa (10 psi) at a recirculation rate of 50 L/min.

dashed line. The removal efficiencies for both DCOD and TCOD generally decreased with an increase

in the concentration factor: at the higher concentration factors, the permeate actually contained higher

DCOD concentrations than the influent whitewater. This was never the case for TCOD: large colloids

were retained by the membrane and accumulated in the concentrate.

A mass balance was done to visualize which fractions of the TCOD and DCOD added to the

MBR system as influent were retained, taken out with reactor sampling or left with the effluent. It can

be seen from Figure 5.5 that most (an average of 77%) of the incoming TCOD was not retained and left

with the effluent). Some of the TCOD was taken out with reactor sampling and the rest was retained in

the UF concentrate. The small amount of TCOD that is unaccounted for may have deposited with the

pitch on the equipment.
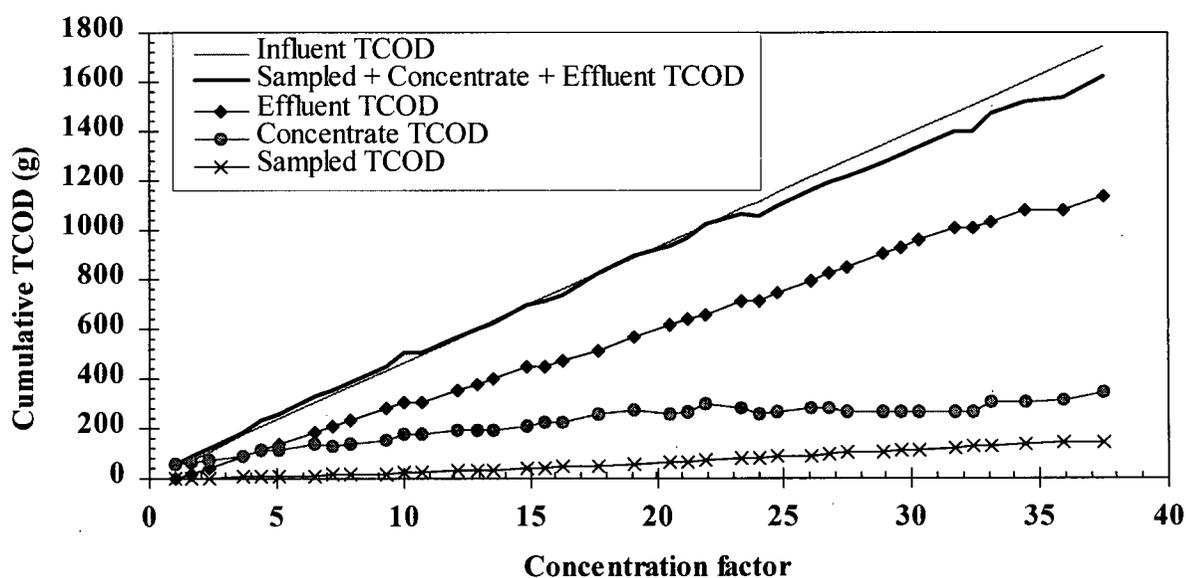
Figure 5.5. Cumulative TCOD mass added (Influent TCOD), removed (Effluent TCOD, Sampled TCOD) and retained (Concentrate TCOD) vs. Concentration Factor during the UF process water run.

The mass balance for DCOD (Figure 5.6) didn't leave any DCOD unaccounted for. Most of the

influent DCOD left with the permeate, while the rest was retained in the reactor concentrate or was

removed by reactor sampling. In summary, the PF-75 UF unit was only moderately effective at retaining

TCOD and removed little or no DCOD, especially at higher concentration factors.
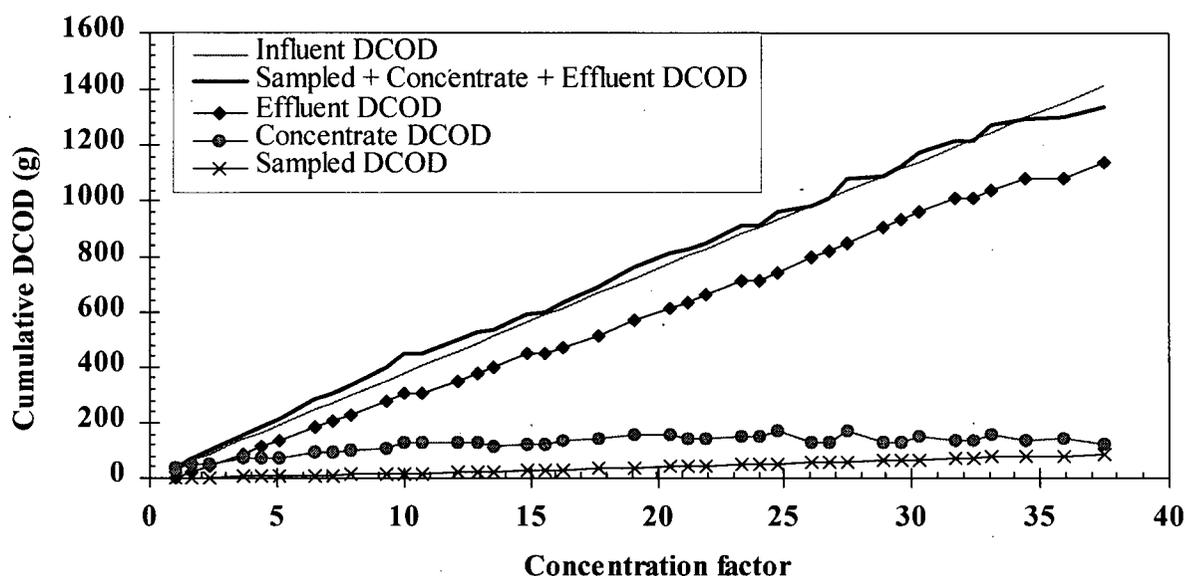
Figure 5.6. **Cumulative DCOD mass added (Influent DCOD), removed (Effluent DCOD, Sampled DCOD) and retained (Concentrate DCOD) vs. Concentration Factor during the UF process water run.**

5.3.4. Dissolved Organic Carbon Removal

The dissolved organic carbon removal efficiencies were similar to the DCOD removal efficiencies, ranging from -11% to 17%, for an average removal efficiency of 0%. As for the DCOD, the permeate DOC concentration was generally higher in the permeate than in the influent at higher concentration factors (Figure 5.7). The DOC accumulated in the reactor, but only slightly. As can be seen from Figure 5.8, most of the influent DOC left with the permeate. Little DOC deposited with pitch on the equipment, as the incoming and outgoing DOC mass plots closely match. In conclusion, the ultrafiltration of the synthetic whitewater, using the PF-75 unit, was ineffective at removing the DOC, especially at higher concentration factors.
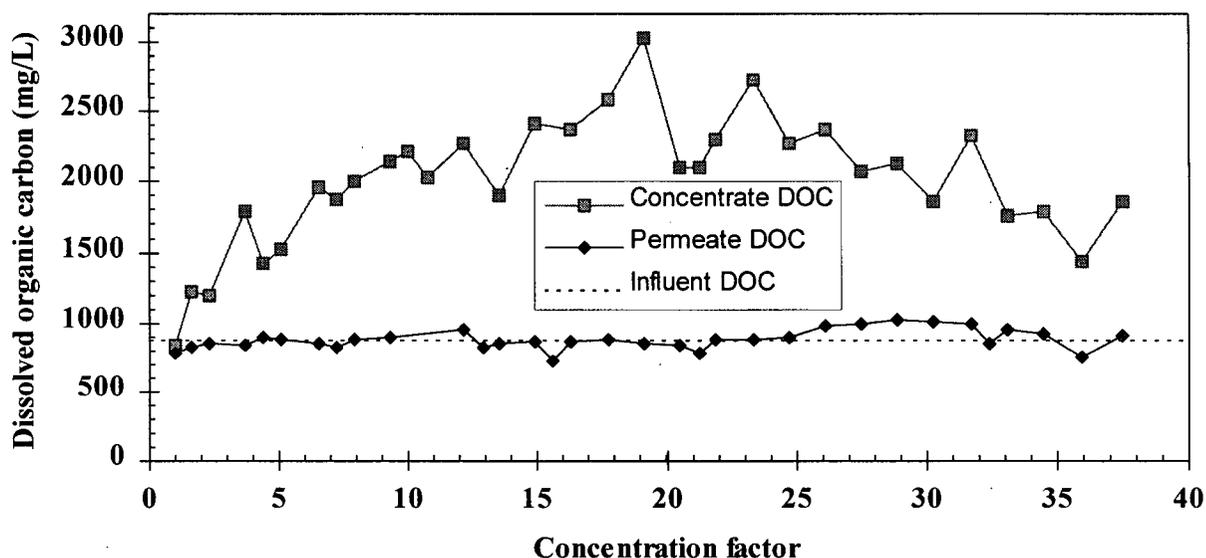
Figure 5.7. Dissolved organic carbon concentrations in the permeate and the concentrate during the process water continuous run using the PF-75 unit under a transmembrane pressure of 69 kPa (10 psi) at a recirculation rate of 50 L/min.
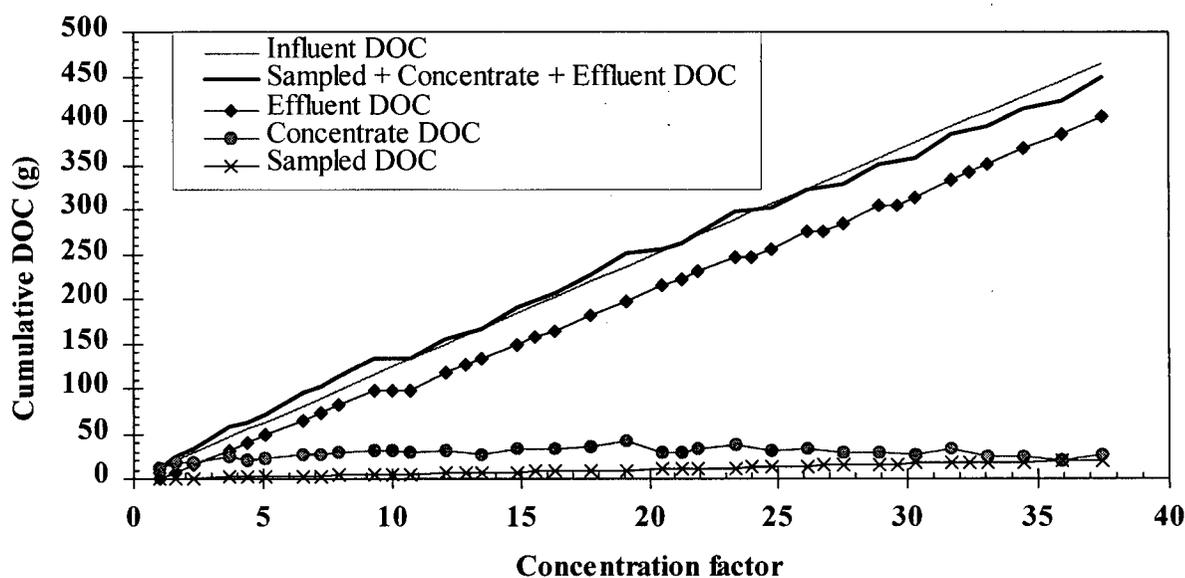
Figure 5.8. Cumulative DOC mass added (Influent DOC), removed (Effluent DOC, Sampled DOC) and retained (Concentrate DOC) vs. Concentration Factor during the UF process water run.

5.3.5. Colour Removal

The average colour removal during the process water run was only 5%. However, the removal efficiency was initially 54%, but it decreased to a low of -22% as the concentration factor increased.

Figure 5.9 shows the gradual increase in the amount of colour present in the permeate as the concentration factor increased. The concentrate colour tended to increase with the concentration factor, but seemed to stabilize. This may have been due to the fact that the permeate colour was higher than the influent colour for all of the samples taken after the concentration factor reached 21, probably because of the very high colour of the concentrate (19,000 to 24,000 units). Another possible explanation for the stabilization of the concentrate colour is that some of the colour causing compounds may have deposited with the pitch on the equipment. A mass balance could not be done for colour as for other contaminants, since the units used for measuring colour do not depend on the mass of the colour-causing compounds.
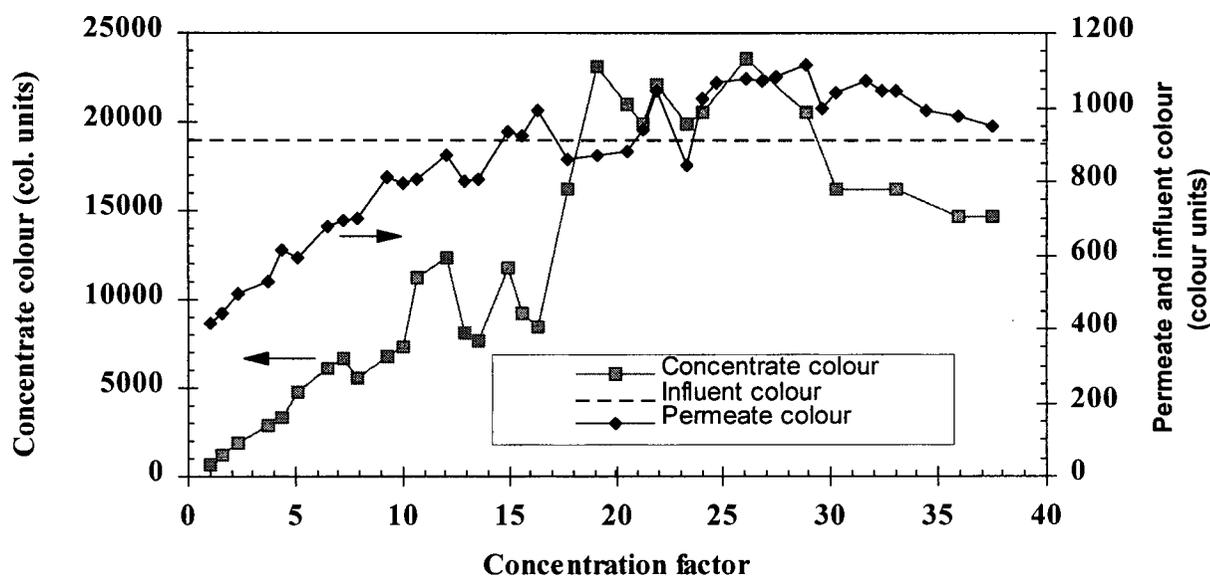

Figure 5.9. Colour in the permeate and concentrate during the process water continuous run using the PF-75 unit under a transmembrane pressure of 69 kPa (10 psi) at a recirculation rate of 50 L/min.

5.3.6. Solids Removal

The ultrafiltration of the process water during the run resulted in the complete removal of TSS and the consistent removal of 35% of the influent TDS (or 40% of the TS, the difference being the TSS). The solids concentration in the effluent seemed independent of the increase in the concentration factor (Figure 5.10). Even though the TS and TDS concentrations seem to stabilize at higher concentration factors, this is probably due to the deposition of some solids along with the pitch on the reactor walls and

equipment. This can be inferred from Figure 5.11 and Figure 5.12, which show a significant discrepancy

between the incoming and outgoing total solids and total dissolved solids.
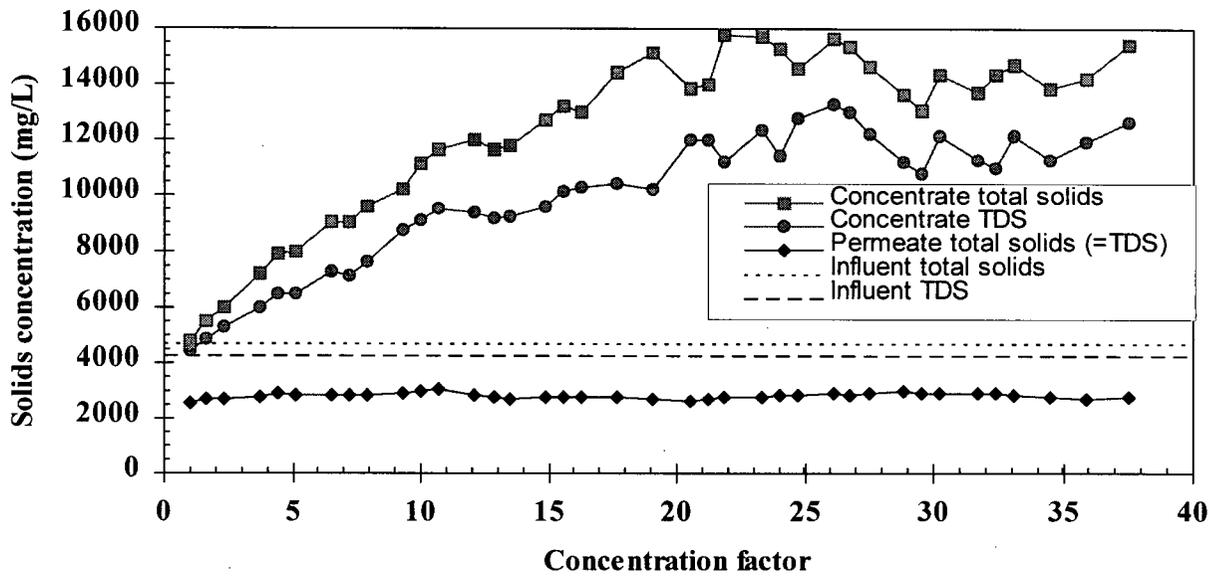
Figure 5.10. Solids concentrations during the process water continuous run using the PF-75 unit under a transmembrane pressure of 69 kPa (10 psi) at a recirculation rate of 50 L/min.
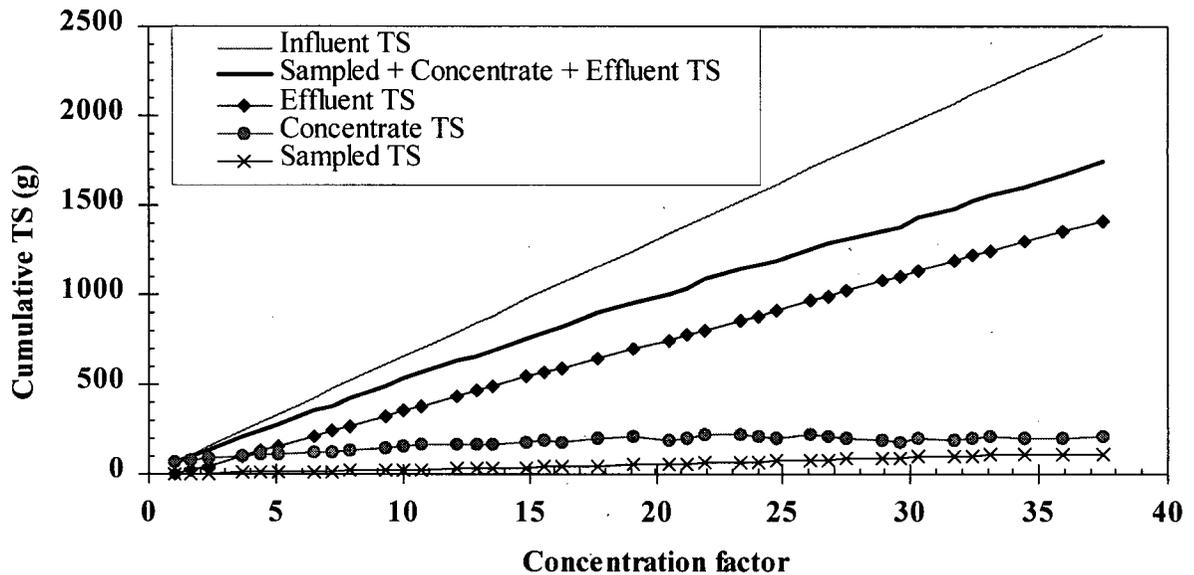

Figure 5.11. Cumulative total solids mass added (Influent TS), removed (Effluent TS, Sampled TS) and retained (Concentrate TS) vs. Concentration Factor during the UF process water run.
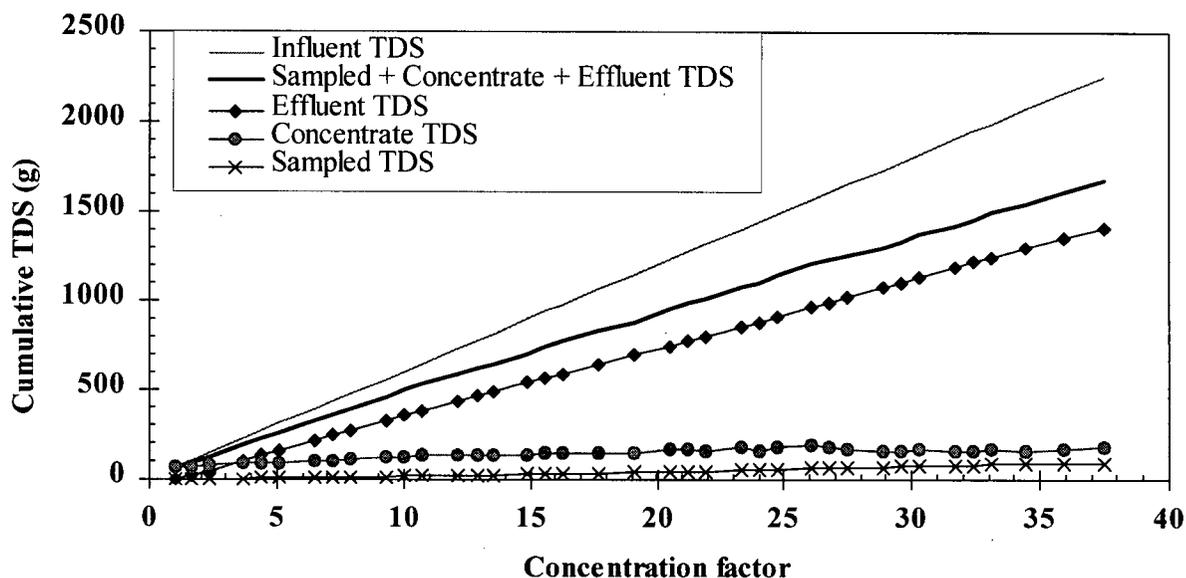
Figure 5.12. Cumulative total dissolved solids mass added (Influent TDS), removed (Effluent TDS, Sampled TDS) and retained (Concentrate TDS) vs. Concentration Factor during the UF process water run.

5.3.7. Cationic Demand Removal

The cationic demand removal during the process water run was good, averaging 44%. However, the removal efficiency was dependent on the concentration factor: the initial and highest removal efficiency observed was 89%, while the lowest removal efficiency was -1%. The variability in the results (Figure 5.13) is due to the difficulty of observing the titration end-point during the cationic demand determination of samples with significant colour.

The cumulative mass plots of the incoming and outgoing cationic demand (Figure 5.14) are closely matched until a concentration factor of 20. This is when pitch deposits were starting to be noticeable on the walls of the concentrate tank and sticky balls of agglomerated pitch could be observed in the concentrate. A significant part of the anionic trash retained in the UF concentrate may therefore have deposited with the pitch on the equipment or was centrifuged out with the sticky pitch balls during the centrifugation of the cationic demand samples. This was expected since part of the pitch-causing dissolved and colloidal substances contribute to the cationic demand of the TMP whitewater. The

deposition of pitch on the equipment or the pitch balls centrifuged out of the concentrate samples prior

to the cationic demand analysis would therefore decrease the measured concentrate cationic demand.
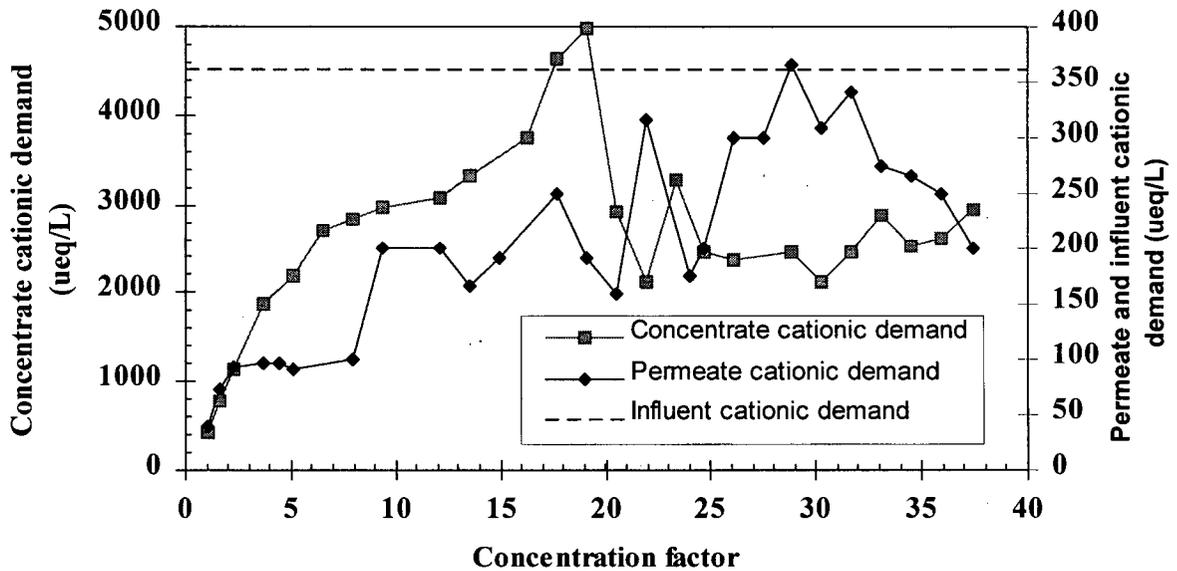
Figure 5.13. Cationic demand of the permeate and the concentrate during the process water continuous run using the PF-75 unit under a transmembrane pressure of 69 kPa (10 psi) at a recirculation rate of 50 L/min.
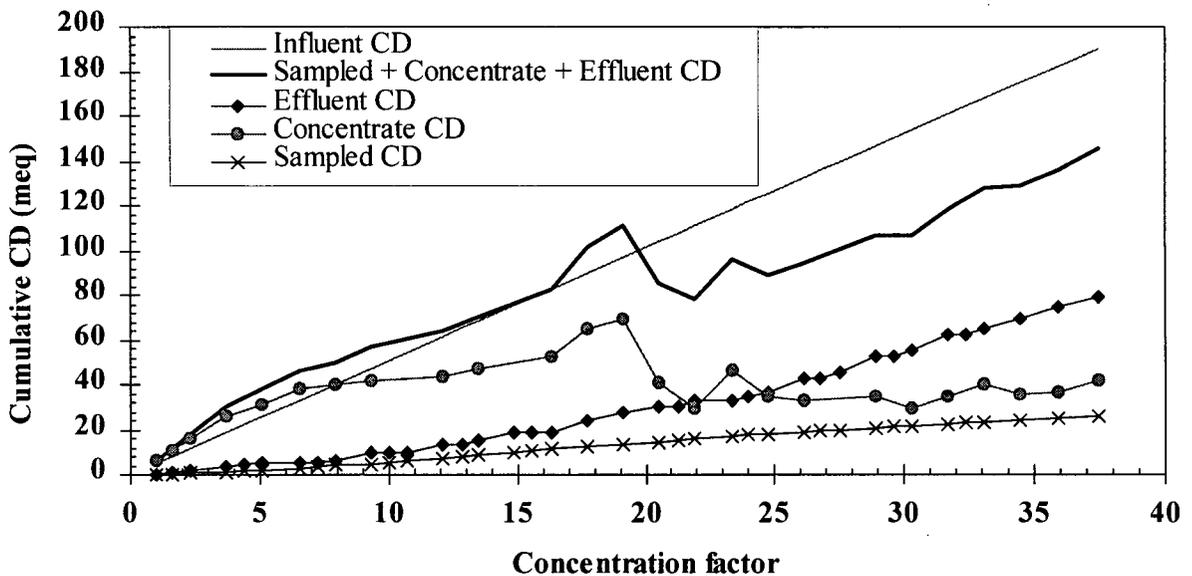

Figure 5.14. Cumulative cationic demand added (Influent CD), removed (Effluent CD, Sampled CD) and retained (Concentrate CD) vs. Concentration Factor during the UF process water run.

5.3.8. Resin and Fatty Acids Removal

The removal of resin acids during the ultrafiltration of the process water was initially poor (24% removal), but improved with increasing concentration factors (Figure 5.15, Figure 5.16), reaching 100% by the end of the run. The fatty acids removal efficiency was excellent throughout the run, ranging from 98% to 100%. The RA and FA accumulated in the concentrate as the concentration factor increased, however, the concentrate RA and FA concentrations seemed to plateau (Figure 5.15). However, this may have been due to (i) the deposition of pitch on the equipment during the study, (ii) an incomplete extraction of the RFA during the analysis of the samples when the RA and FA were agglomerated in sticky pitch balls in the concentrate samples and, (iii) the abiotic breakdown of the RA and FA due to air oxidation during the recirculation of the concentrate. This can be inferred from Figure 5.17, Figure 5.18 and Figure 5.19, from which it can be seen that there is an important discrepancy between the incoming and outgoing RFA. This is especially true for the FA, for which the cumulative mass balance doesn't close by an order of magnitude. However, the mass of RFA unaccounted for represents only about 12 g of material, an important fraction of which may have been deposited on the equipment, judging from the amount of pitch deposited on some parts of the concentrate tank walls. The pitch deposited on the equipment was sometimes several millimeters thick. A significant fraction of the RA and FA unaccounted for in the mass balance plots may have also been degraded by air oxidation. Air bubbles were drawn into the system during the ultrafiltration of the process water, and, as a result, aerating the UF concentrate. Liu et al. (1993a) have shown that about 20% of the RFA were removed after aerating 96 hours a concentrated CTMP effluent with an initial RFA concentration of 44 mg/L. Elefsiniotis (1994) has also shown that an important part (10 to 70%) of the influent RFA from a synthetic whitewater may have been removed by air oxidation, depending on the operating temperature (20 to 50°C). However, it is possible that RFA may also have been deposited on the equipment in that study.
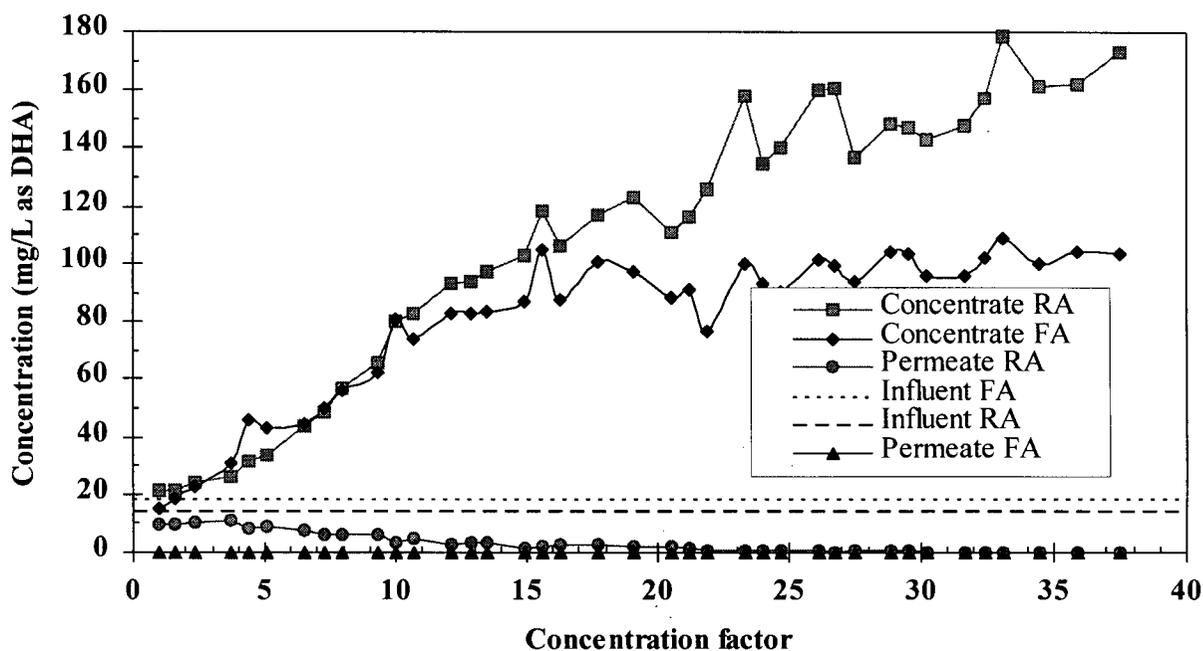
Figure 5.15. Resin acids and fatty acids concentrations during the process water continuous run using the PF-75 unit under a transmembrane pressure of 69 kPa (10 psi) at a recirculation rate of 50 L/min.

The FA removal was consistent throughout the study, but the RA removal efficiency increased as the concentration factor increased (Figure 5.16). This may have been caused by the agglomeration of RA onto larger colloids or pitch "sticky balls" which were rejected by the UF membrane. The formation of a gel layer on the surface of the membrane may also have played a role in the improvement of the rejection of RA with an increase in the concentration factor.
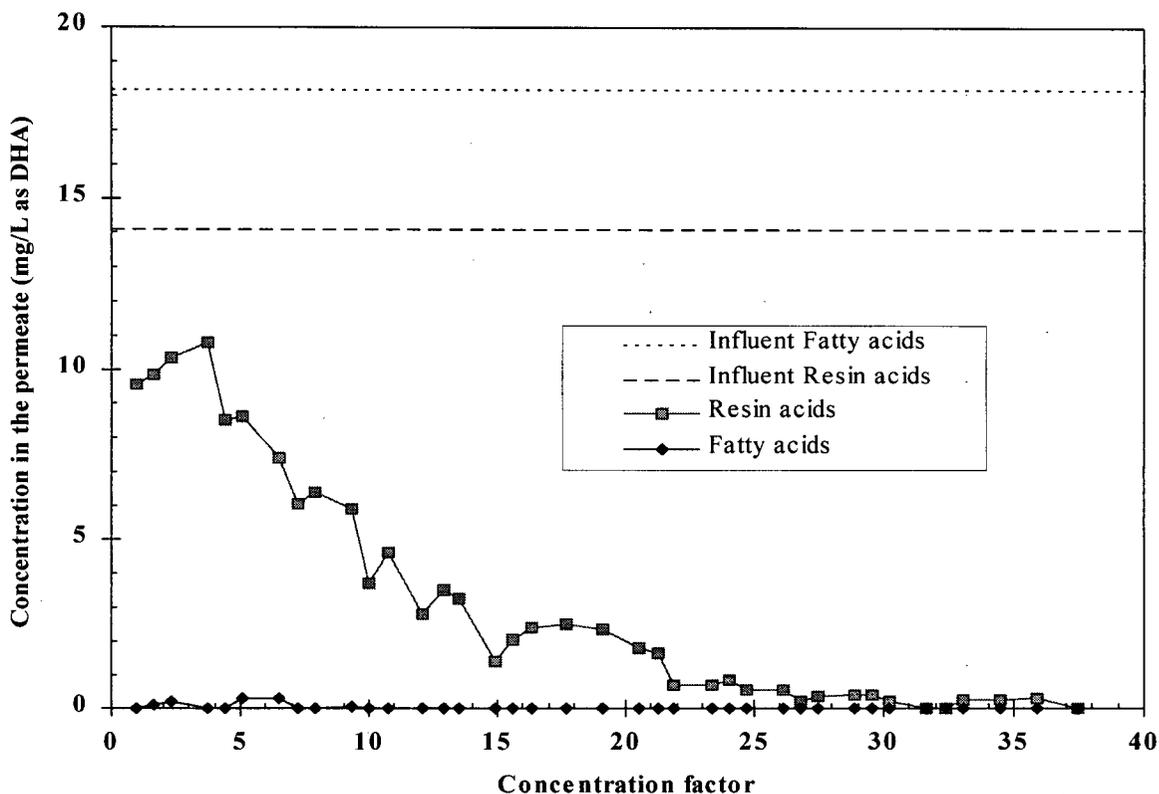
Figure 5.16. RA and FA concentrations in the permeate during the process water continuous run using the PF-75 unit under a transmembrane pressure of 69 kPa at a recirculation rate of 50 L/min. (Different scale than Figure 5.15).
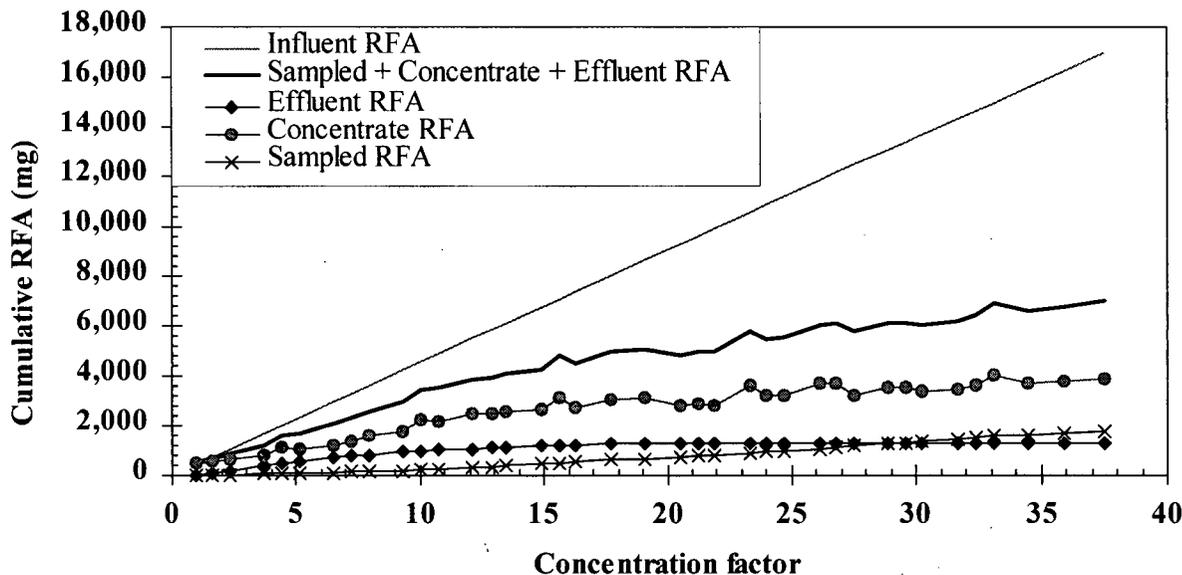
Figure 5.17. Cumulative RFA mass added (Influent RFA), removed (Effluent RFA, Sampled RFA) and retained (Concentrate RFA) vs. Concentration Factor during the UF process water run.
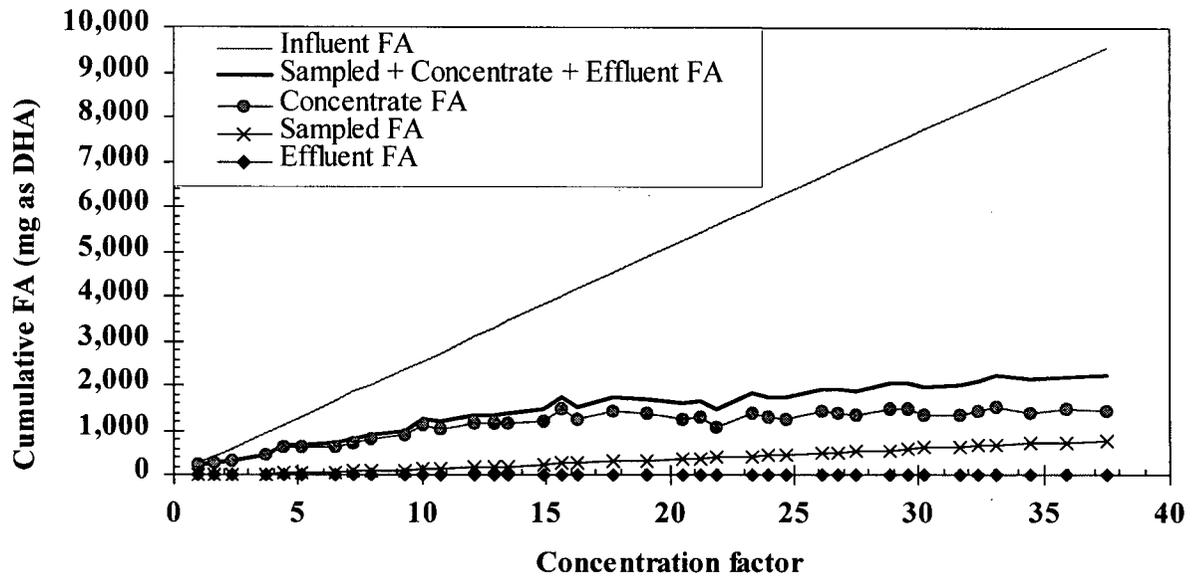
Figure 5.18. Cumulative FA mass added (Influent FA), removed (Effluent FA, Sampled FA) and retained (Concentrate FA) vs. Concentration Factor during the UF process water run.
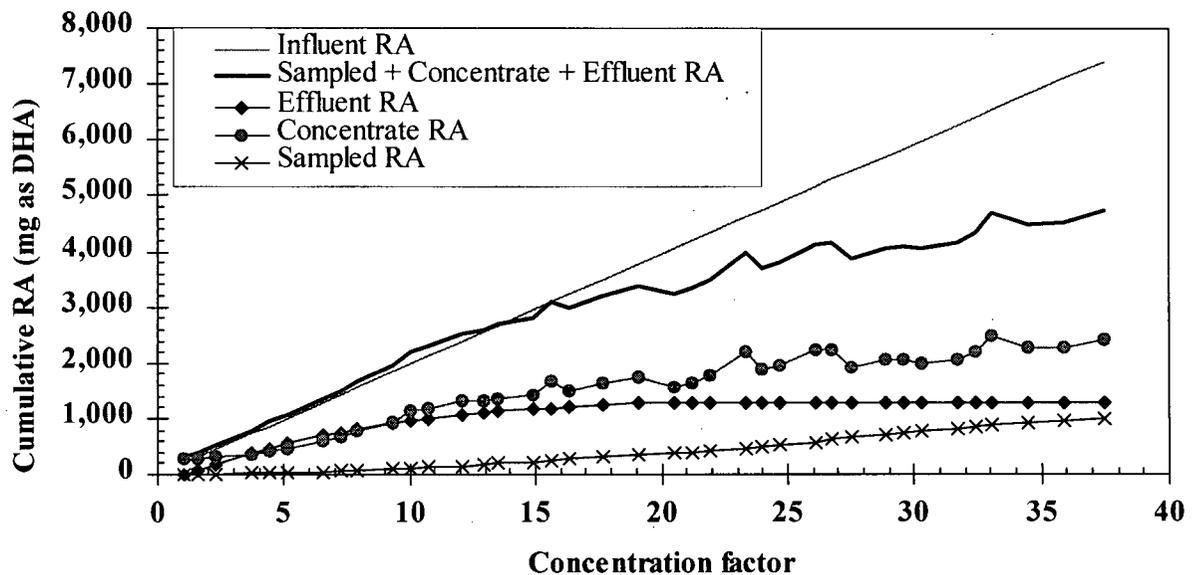
Figure 5.19. Cumulative RA mass added (Influent RA), removed (Effluent RA, Sampled RA) and retained (Concentrate RA) vs. Concentration Factor during the UF process water run.

5.3.9. Comparison with Another Ultrafiltration Study

The efficiency of the ultrafiltration of the process water may be compared to a recent study conducted by Elefsiniotis *et al.* (1995). That study was carried out using the same whitewater composition but involved the use of cassette-type UF membranes, which are similar in design to the plate

and frame modules described in Table 2.1 on page 24, except that a set number of UF membranes are stacked into a pre-fabricated cassette. One or more cassettes can be stacked in a UF unit. The ultrafiltration unit used in that study was a Minisette acrylic cell tangential flow unit obtained from Filtron Technology Corporation of Northborough, MA, USA. The UF membranes were made of polyethersulfone (negatively charged) with a molecular weight cut-offs of either 10 or 100 kDaltons. The operating temperatures for that study ranged from 20 to 60°C and the whitewater was ultrafiltered to a concentration factor of 10. In order to facilitate the comparison between the two studies, the average concentrations and removal efficiencies obtained during the ultrafiltration of the whitewater using the PF-75 unit were calculated for concentration factors ranging from 1 to 10. These results were then compared to the average results obtained with the results from the study involving the use of the cassette-type UF units, at an operating temperature of 40°C (Figure 5.20).
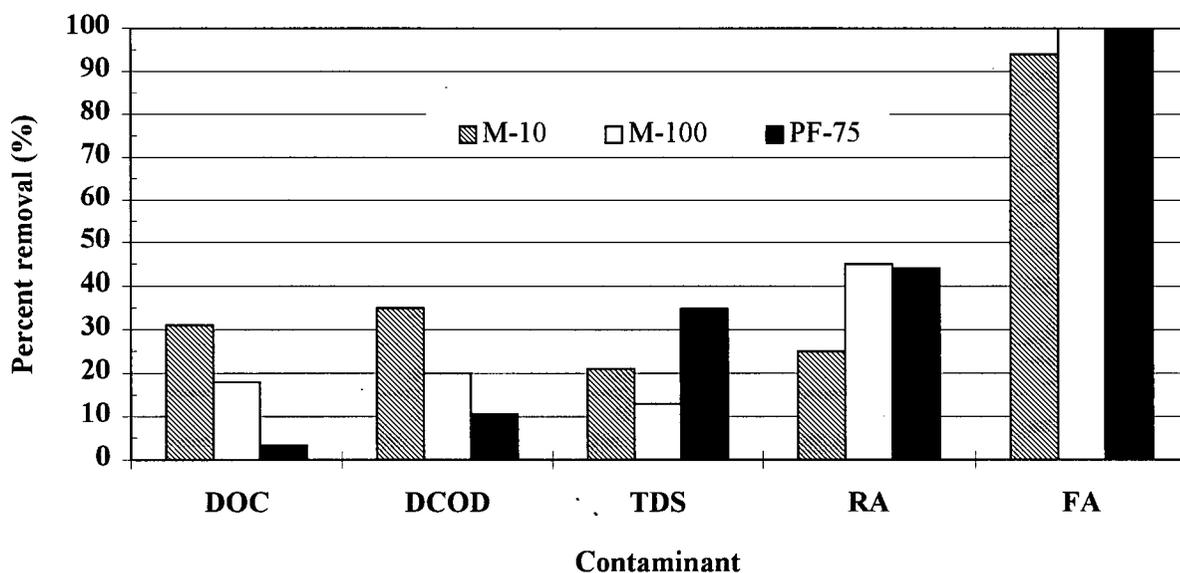
Figure 5.20. Average removal efficiency for whitewater contaminants using a Minisette 10 kDaltons (M-10) unit, a Minisette 100 kDaltons (M-100) unit and the Permaflow-1 75 kDaltons (PF-75) unit at operating temperatures of approximately 40°C to a concentration factor of 10.

The removal efficiencies using the different membrane units were similar for RA and FA. The different removal efficiencies for RA and FA between the Minisette cassette unit with a MWCO of 10

kDaltons (M-10) and the Minisette cassette unit with a MWCO of 100 kDaltons (M-100) are due to differences in the influent concentration. In contrast, the removal efficiencies for DOC, DCOD and TDS were significantly different in the two different studies. For the cassette membranes, the M-10 unit was more efficient at removing these contaminants than the M-100 unit because of the lower nominal molecular weight cut-off. The PF-75 unit was significantly less effective at removing the dissolved organic matter than the cassette units, despite its intermediary nominal molecular weight cut-off (75 kDaltons), but more efficient at removing dissolved solids. Since the ultrafiltration units are made by different manufacturers, it is reasonable to expect different rejection characteristics from the Minisette and the PF-75 units. However, it is surprising that the dissolved solids were removed more effectively using the PF-75 unit while other contaminant removal efficiencies were very low.

The permeate fluxes for the same experiments are given in Table 5.3. The average permeate flux for the experiment involving the PF-75 membrane was the lowest measured. However, this was expected, as tubular ultrafiltration usually generates lower fluxes but offers the possibility of filtering solutions containing solids which may clog other types of membrane. In addition, the average concentrate pressure used for the experiment involving the use of the PF-75 was half that of the one used for the experiments involving the use of Minisette membranes. Moreover, the feed recirculation rate of 50 L/min for the PF-75 experiment was much lower than the 90-130 L/min recommended by the manufacturer (Zenon Environmental Inc., 1994).

Table 5.3. **Average permeate flux measured during the experiments involving a Minisette 10 kDaltons (M-10) unit, a Minisette 100 kDaltons (M-100) unit and the Permaflow-1 75 kDaltons (PF-75) unit at operating temperatures of approximately 40°C to a concentration factor of 10.**

UF unit	Unit type	Molecular Weight Cut-Off	Concentrate pressure	Average permeate flux
M-100	cassette	100 kDaltons	138 kPa (20 psi)	109 L/(m^2·h)
M-10	cassette	10 kDaltons	138 kPa (20 psi)	69 L/(m^2·h)
PF-75	tubular	75 kDaltons	69 kPa (10 psi)	24 L/(m^2·h)

5.3.10. Ultrafiltration Studies of Recirculated Mechanical Newsprint Whitewater - Conclusions

From the ultrafiltration studies conducted at the UBC Pulp and Paper Centre, it appears that ultrafiltration of recirculated mechanical newsprint whitewater up to a concentration factor of 10 can be moderately effective at removing DOC, DCOD, TDS and RA, with measured removal efficiencies of up to 30-40% This is in accordance with results from another study involving the use of a 100 kDaltons membrane to ultrafilter paper machine clear whitewater (Nuortila-Jokinen et al., 1995). Reported removal efficiencies were low for TDS (3 to 10%) and COD (8 to 20%). The same authors reported that nanofiltration (MWCO 400 Daltons) was much more effective at removing TDS (65 to 90% removal efficiencies) and COD (60 to 75%).

The ultrafiltration membranes used for the studies conducted at the UBC Pulp and Paper Centre were effective at removing FA, but ultrafiltration to high concentration factors (>15) resulted in sticky pitch deposits on the concentrate tank walls and equipment. During the study using the PF-75 unit, 54% of the colour was initially removed (at a concentration factor of 1), but removal efficiencies were low (about 10%) at a concentration factor of 10. The increase in the concentration factor had the same effect on the removal efficiency of the cationic demand: the initial removal efficiency of the cationic demand was 89% (at a concentration factor of 1) but a removal efficiency of about 50% at a concentration factor of 10.

In conclusion, the ultrafiltration of mechanical newsprint whitewater is only moderately effective in removing most contaminants. MWCO alone is not a useful criterion for assessing the separation/fractionation ability of a membrane to separate the whitewater contaminants, since the PF-75 (MWCO = 75 kDaltons) was more effective than the M-10 (MWCO = 10k Daltons) at rejecting the dissolved solids. Zaidi et al.(1991) also arrived to this conclusion during their study of 13 different membranes potentially suitable for the treatment of pulp mill effluents.

5.4. MBR Operating Parameters over the Experimental Period

In this section, different operating parameters of the aerobic membrane bioreactor are presented over the experimental period, such as the MLVSS, the specific oxygen uptake rate, the permeate flux, the pH and the temperature.

5.4.1. MLVSS Levels and Specific Oxygen Uptake Rate Levels

The biomass concentration in the MBR, expressed as the mixed liquor volatile suspended solids (MLVSS), is given in Figure 5.21. The MLVSS concentration varied from a minimum of 1.9 g/L (Run 1) to a maximum 9.5 g/L (Run 3). Run 3 and Run 5 had the highest average MLVSS levels, while Runs 1 and 2 had the highest specific activity, also illustrated in Figure 5.21 as the specific oxygen uptake rate (SOUR). SOUR values for Runs 1 and 2 ranged from 2.15 to 2.42 and 0.92 to 2.08 respectively (with the exception of the SOUR for day 117, measured after a 9-day period with no nutrient additions to the MBR). Comparatively, SOUR values ranged from 0.35 to 1.26 for Runs 3, 4 and 5. This suggests a higher average biomass specific activity at 40°C than at 47.5°C and 55°C.

A decrease in the MLVSS concentration in Run 4 resulted from a series of significant losses of mixed liquor due to the formation of cracks in some PVC fittings between days 190 and 192. These events may also explain the lower removal efficiencies of certain contaminants during Run 4 (presented below). Wasting of the mixed liquor was interrupted for several days after these events to allow the MLVSS concentration to increase.

The precise control of the MLVSS wasting, and thus the organism specific growth rate, is one of the interesting advantages of the MBR. No solids can be lost in the effluent due to poor sludge settleability. The start-up of the MBR was also facilitated by this fact, as all biomass was retained.

The MLVSS concentrations in the MBR reactor (1.9 g/L to 9.5 g/L) were higher than typical values reported for the conventional activated sludge process (1.2 to 3 g/L) (Metcalf & Eddy Inc., 1991), since no biomass was lost with the effluent and the SRT used (25 days) was long. Higher MLVSS

concentrations than conventional activated sludge processes are typically reported for MBRs. Knoblock *et al.* (1994) reported MLVSS concentrations of 4 to 15 g/L in their pilot scale MBR designed to treat oily wastewater. MLVSS concentrations in one full scale plant to treat oily wastewater were reported to range from 19 to 29 g/L (Mishra *et al.*, 1994). MLSS concentrations in MBR systems can be as high as 40 g/L (Bemberis *et al.*, 1971; Lübbecke *et al.*, 1995).
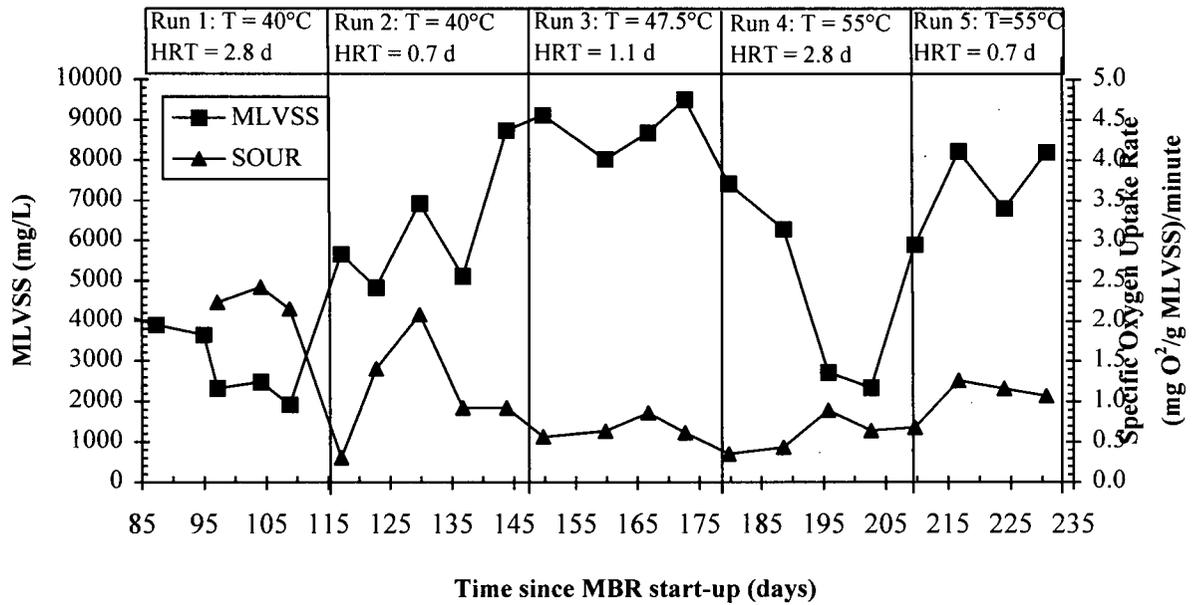
Figure 5.21. Biomass concentration (as MLVSS) and specific oxygen uptake rate (SOUR) in the reactor over time in the MBR.

5.4.2. Permeate Flux

An important aspect for the design of a full scale MBR system is the total membrane area required. The area required can be calculated from:

$$\text{Membrane Area} = \frac{\text{Effluent Flow Rate (volume / time)}}{\text{Membrane Flux (volume / area} \cdot \text{time)}}$$

Equation 5-2

The membrane flux depends on factors such as the mixed liquor TSS, the recirculation rate (or cross-flow velocity), temperature, transmembrane pressure, surface concentration polarization and surface fouling (Hare *et al.*, 1990). Concentration polarization occurs when rejected solutes form a

viscous gel layer, acting as a secondary membrane, which may in turn increase rejection of lower molecular weight compounds but decrease the permeate flux. Fouling occurs as a result of the clogging of the ultrafiltration membrane pores by crystallization and precipitation.

The performance of the ultrafiltration membrane used in this study is illustrated in Figure 5.22. This flux is not corrected for temperature, and is presented as measured, because the variations in the MLVSS and dissolved and colloidal substances concentrations in the mixed liquor prevent the comparison of the fluxes between the runs. The permeate flux, initially measured at 40 $L/m^2 \cdot h$ on the first day of the MBR operation (mixed liquor temperature = 22°C, TMP = 79 kPa), decreased over time. However, this was partly reversible by cleaning the membrane. Whole flakes of the gel, cake-like, layer which had formed on the membrane surface during the operation of the MBR were removed during the cleaning. Each membrane cleaning event is represented by a bold line on Figure 5.22. The membrane flux increased with higher operating temperatures, as can be seen at the transition period between Run 2 (40°C) and Run 3 (47.5°C) as well as between Run 3 and Run 4 (55°C). In addition, the MBR permeate flow rates following membrane cleaning were higher with higher temperatures.

In one case, the MBR was capable of operating for up to 55 days without cleaning (during Runs 2 and 3). This is longer than typical values reported in the literature: Lübbecke *et al.* (1995) cleaned their MBR UF membrane every 24 days, which they reported to be a very long interval between cleaning events. More frequent cleanings were necessary during Run 5 because of rapid fouling of the membrane. However, the permeate flow rate seemed to stabilize at the end of Run 5 before the final shutdown of the MBR.

It is highly likely that less frequent cleaning intervals, better permeate flow rates and better flux restoration after cleaning could have been achieved if a pump capable of generating higher recirculation rates (90 to 130 L/min) had been available for this study. However, permeate flux optimization was not a primary goal for this study.

The membrane flux was successfully restored after completing the cleaning procedure described

in Section 4.2.2 on page 44. At the end of the MBR study, the tap water flux adjusted for T = 25°C,

measured at a transmembrane pressure of 69 kPa (10 psi) and a recirculation rate of 50 L/min after

cleaning the membrane, was 165 $L/(m^2 \cdot h)$. This value is only slightly lower than the stable distilled

water flux of 168 $L//(m^2 \cdot h)$ measured before using the PF-75 to ultrafilter process water (Figure 5.2).

Hence, the membrane cleaning procedure was highly successful at restoring the original permeate flux.
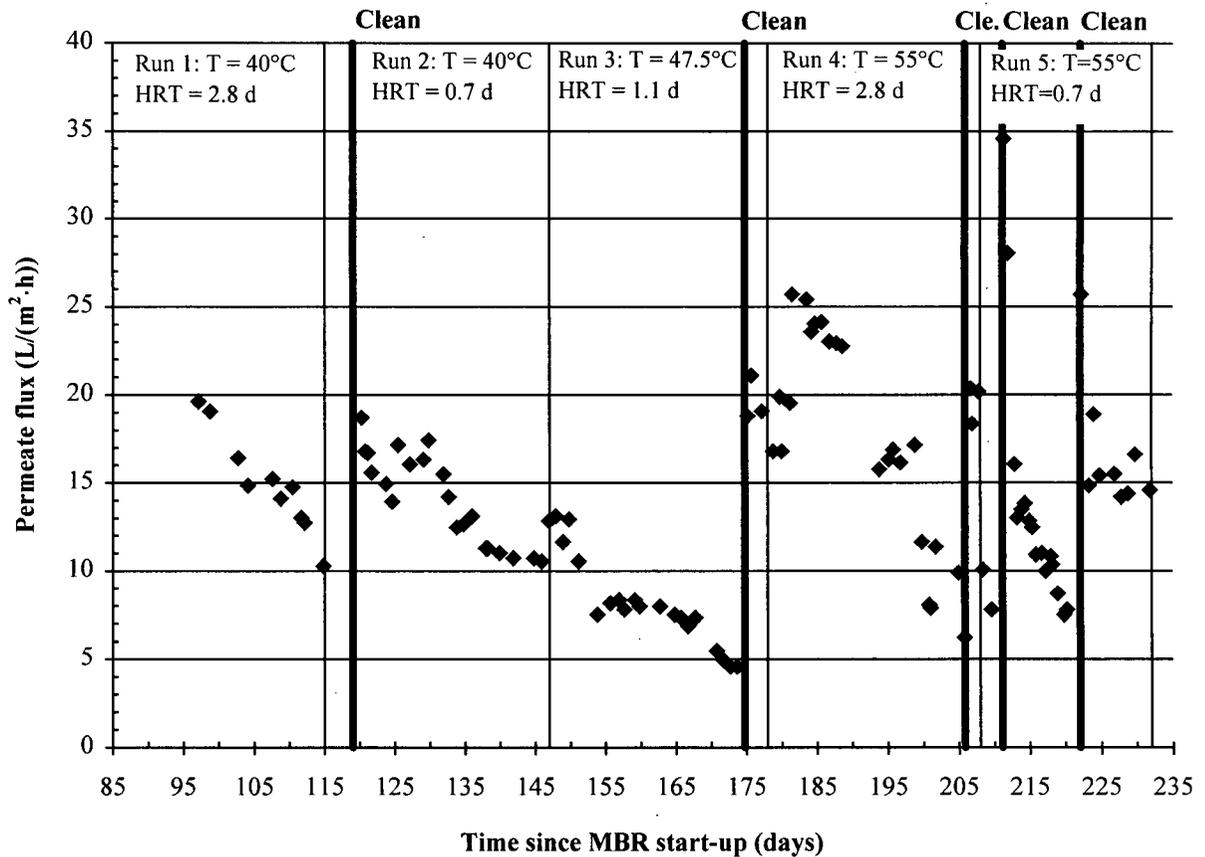
Figure 5.22. Permeate flux during MBR runs.

5.4.3. Temperature

Maintaining a constant operating temperature in the MBR was difficult, due to variations in the

ambient temperature, the addition of heat to the MBR system through the recirculation pump (or loss of

heat when to the pump shut down due to operational difficulties). Although the temperature variations

were usually within three degrees Celsius of the planned operating temperature (Figure 5.23), some difficulties led to variations in the MBR operating temperature of up to 10°C from the planned operating temperature for short periods of time. These important temperature variations, which were due to the recirculation pump shut-down or to an increase in the average concentrate pressure due to an incorrect setting of the ultrafiltration pressure-control valve, did not have any serious effects on the efficiency of the system to treat the whitewater. This suggests that the MBR is capable of tolerating significant variations in the operating temperature without serious repercussions.
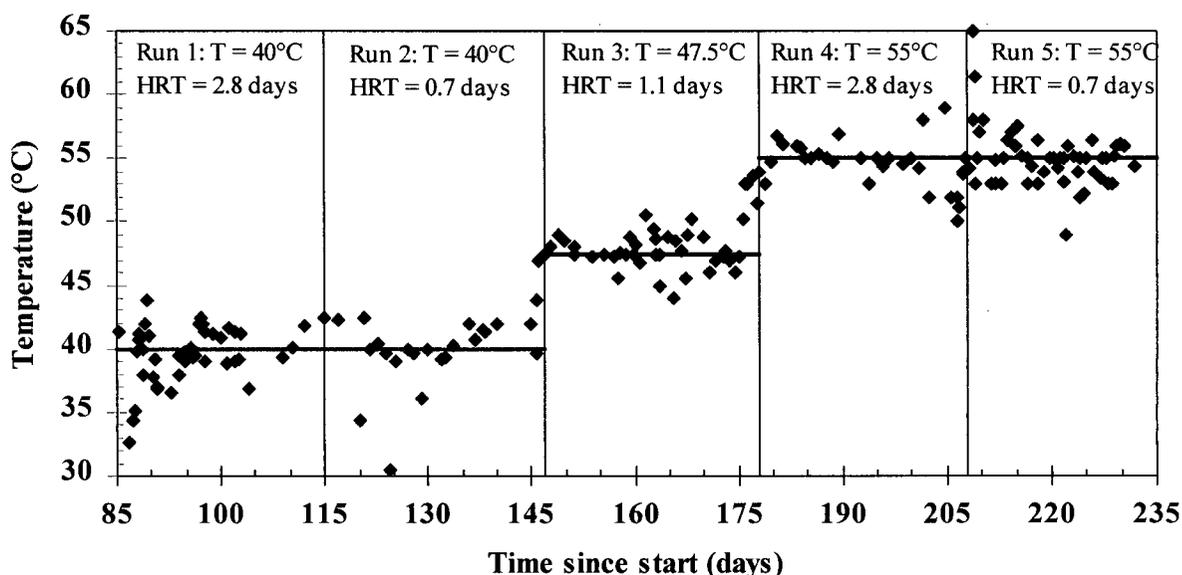
Figure 5.23. Temperature of the MBR mixed liquor over the experimental period. Important variations from the planned operating temperature are related to problems in the operation of the recirculation pump.

5.4.4. pH

No attempt was made to control the mixed liquor pH during the MBR operation. It usually was within 1 unit of the influent pH, with the exception of Run 4, when unplanned mixed liquor losses where experienced and the MLVSS concentration dipped to a low of approximately 2500 mg/L from 7500 mg/L (Figure 5.24). However, the mixed liquor pH soon returned to near its average value of 8.0 units.
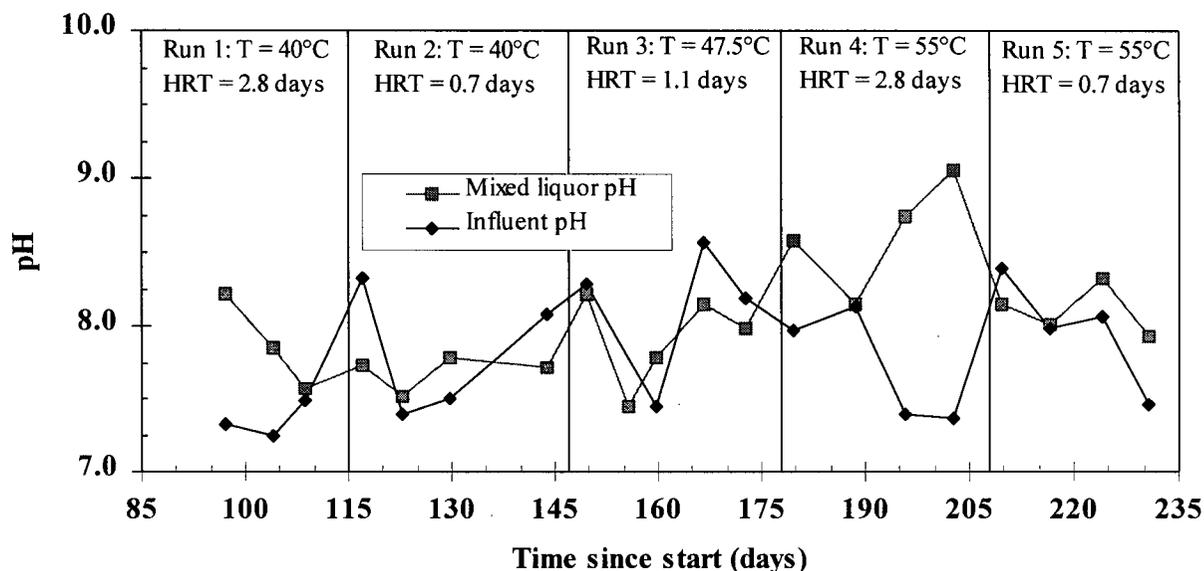
Figure 5.24. MBR mixed liquor and influent pH over the experimental period. The average pH value of the mixed liquor over the experimental period was 8.0 units.

5.5. Removal of Contaminants During the MBR Operation

5.5.1. Summary of the MBR Performance

The average contaminant percent removal efficiency is given in this section for each one of the five runs of the MBR for each contaminant.

The Figure 5.25 shows the average removal of RA, FA, COD, dissolved COD, DOC and cationic demand for the different MBR operating conditions. The average removal efficiencies were determined using Equation 5-3.

$$\text{Average removal (\%)} = \left(1 - \frac{\text{Average permeate concentration}}{\text{Average influent concentration}}\right) \bullet 100\%$$

Equation 5-3

The MBR was very effective for controlling RA and FA, removing an average of over 99.8% of FA and 99% of the RA present in the influent whitewater. The MBR was also effective at reducing both the influent TCOD, for which average removal efficiencies ranged from 78% (Run 4) to 89% (Run 1) and the DCOD, for which removal efficiencies ranged from 72% (Run 4) to 84% (Run 1). The DOC

average removal efficiency ranged from 67% (Run 4) to 86% (Run 1). The cationic demand removal efficiency varied with the runs, ranging from 48% for Run 3 to 88% for Run 1.

The Figure 5.26 shows the average removal for different fractions of solids. The MBR removed all influent total suspended solids (TSS) since the pore size of the ultrafiltration unit of 0.08 µm is much smaller than 1.5 µm pore size of the glass microfiber filters used for the suspended solids determination. This retention of suspended solids and, in some cases, large molecules, is an inherent advantage of the MBR system over conventional biological treatment methods. The average removals of the volatile fraction of the total solids and of the total dissolved solids, or volatile solids (VS), and volatile dissolved solids (VDS) were good, ranging from 68% (Run 2) to 79% (Run 1) for VS and from 65% (Run 2) to 74% (Run 1) for VDS. The removal of the total solids (TS) and the total dissolved solids (TDS) were moderate, ranging from 24% (Run 4) to 42% (Run 5) for TS and from 18% (Run 4) to 37% (Run 5) for TDS. This moderate removal of TDS and TS could be improved by the use of an ultrafiltration membrane of a lower nominal pore size.

Slightly lower removal efficiencies obtained during Run 4 may be due to the many operational difficulties experienced during this run.

The MBR system was ineffective at removing colour from the influent whitewater (Figure 5.27). The MBR in fact added colour during three of the runs. This may have been due to the fact that the colour of the MBR concentrate was much higher than the influent colour (more details are given in Section 5.5.4, page 95). The best colour removal achieved was 9% (Run 5), while the worst removal was -26% (Run 3). Again, the use of an ultrafiltration membrane of a smaller nominal pore size could improve colour removal.

Overall, the MBR treatment was very stable over the temperature range and for the various hydraulic retention times used in this study, as similar removal efficiencies of the contaminants were observed for all runs (Figure 5.26, Figure 5.25). Average removal rates for the duration of the five runs

were as follows: 100% for FA, 99.2% for RA, 82% for TCOD, 78% for DCOD, 76% for DOC, 64% for the cationic demand, 36% for TS, 27% for TDS and -5% for colour.
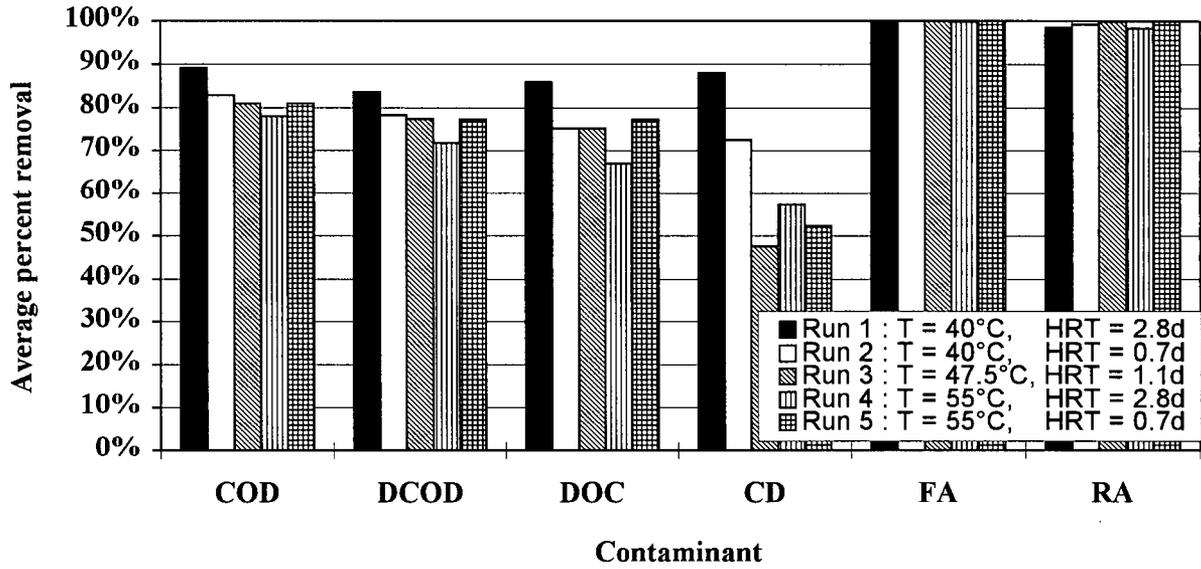
Figure 5.25. Average TCOD, DCOD, DOC, CD, FA and RA removal efficiencies for the different MBR runs.
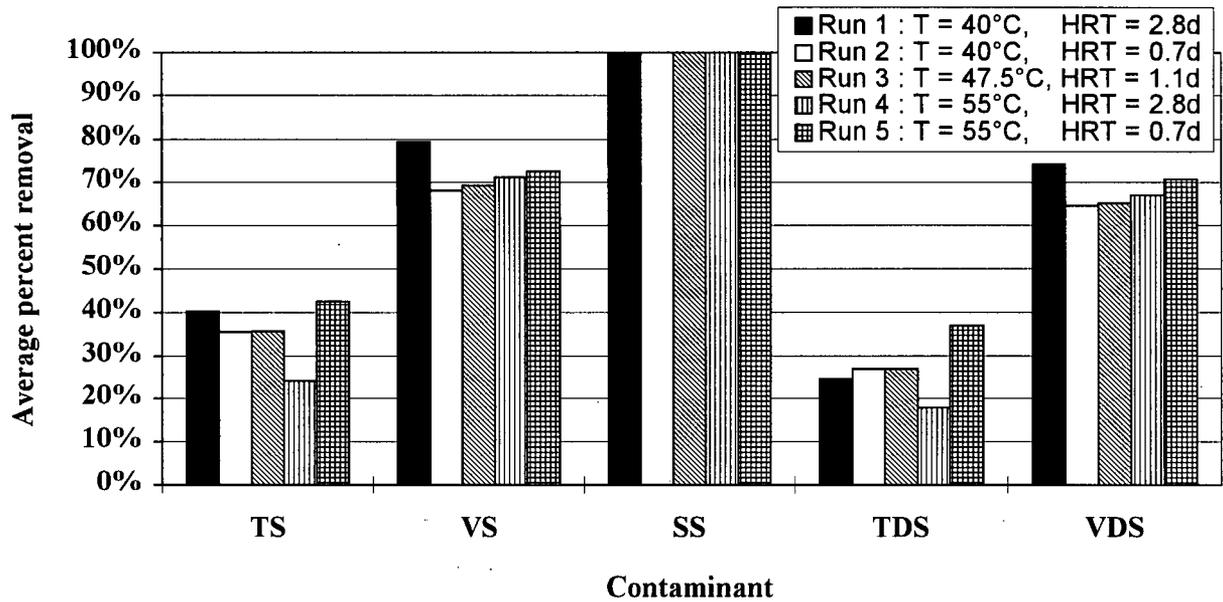
Figure 5.26. Average solids removal efficiencies for the different MBR runs.
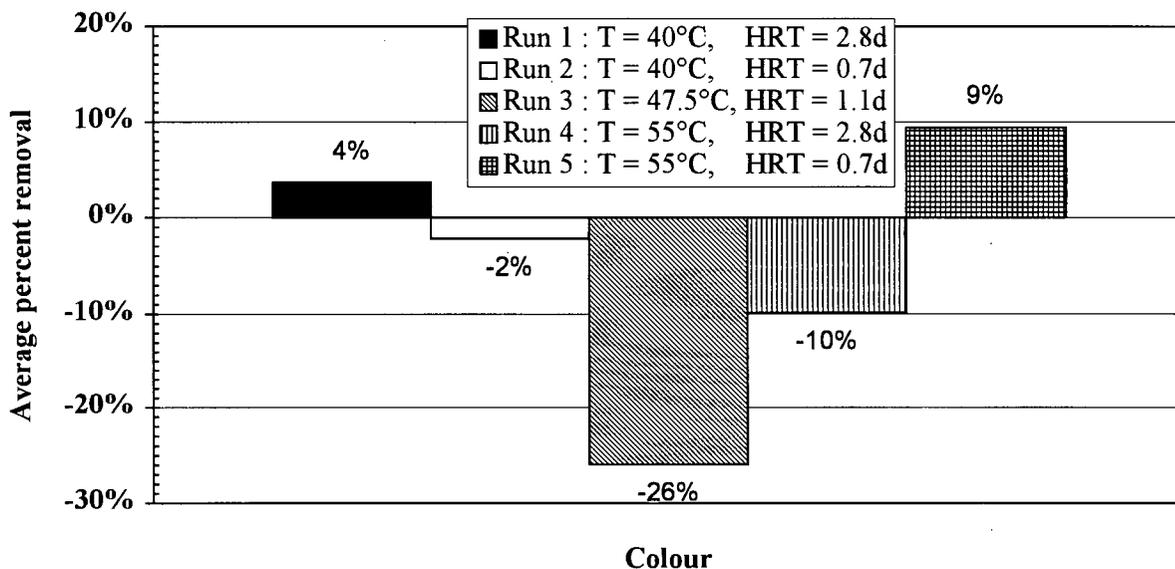
Figure 5.27. Average colour removal efficiencies for the different MBR runs.

5.5.2. Chemical Oxygen Demand

Although some variations in the permeate TCOD concentrations can be seen in Figure 5.28, these values were on average 82% lower than the influent TCOD and 78% lower than the influent DCOD (the permeate TCOD and DCOD are the same, because the ultrafiltration retains all filterable material). The concentrate DCOD did not increase appreciably over the experimental period (Figure 5.29), as it did during the ultrafiltration experiment, indicating that the microorganisms present in the mixed liquor mineralized the dissolved organic matter.

A peak in the concentrate DCOD at day 117 was due to the lack of nutrients (N and P) in the mixed liquor due to the lack of nutrients from day 108 to day 117, as detailed in Section 4.2.4 on page 50. The DCOD quickly dropped when the addition of nutrients was resumed, even though the HRT was lowered.
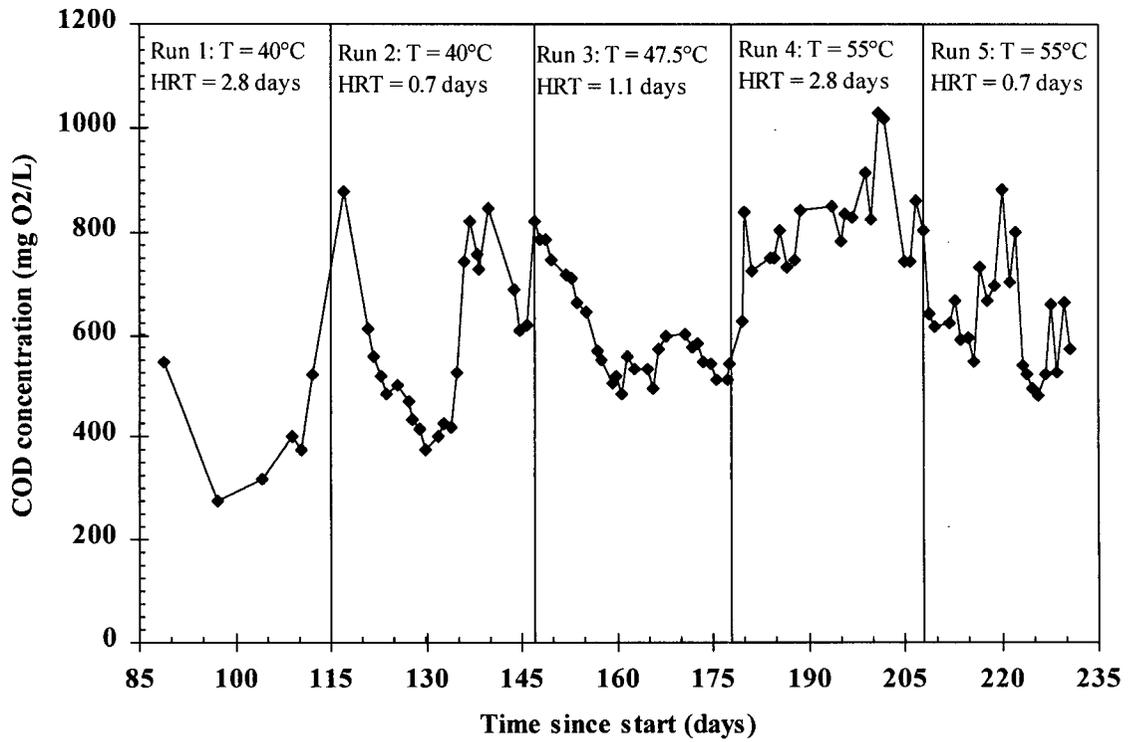
Figure 5.28. TCOD concentrations in the MBR permeate over the experimental period.
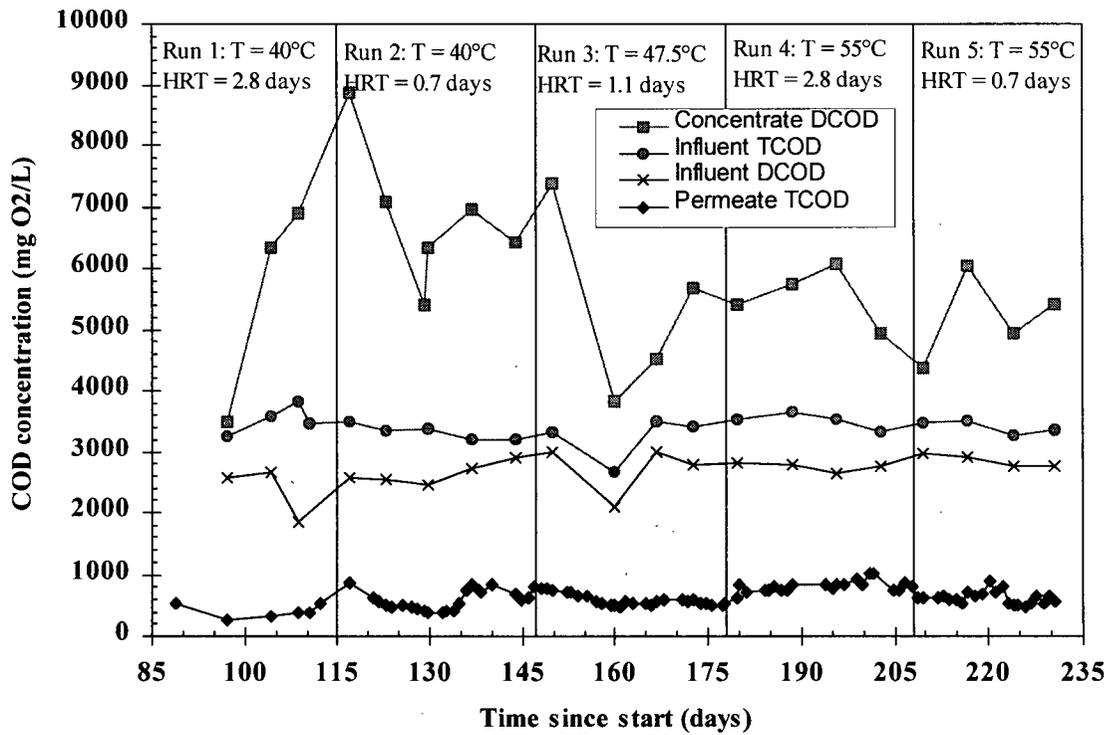
Figure 5.29. TCOD and DCOD in the MBR concentrate, influent and permeate over the experimental period (different scale than Figure 5.28)

5.5.3. Dissolved Organic Carbon

Trends for the dissolved organic carbon concentrations in the concentrate and permeate were

similar to those observed with DCOD (Figure 5.30, Figure 5.31). Permeate DOC concentrations were on

average 76% lower than the influent DOC concentrations. DOC did not accumulate in the reactor, as the
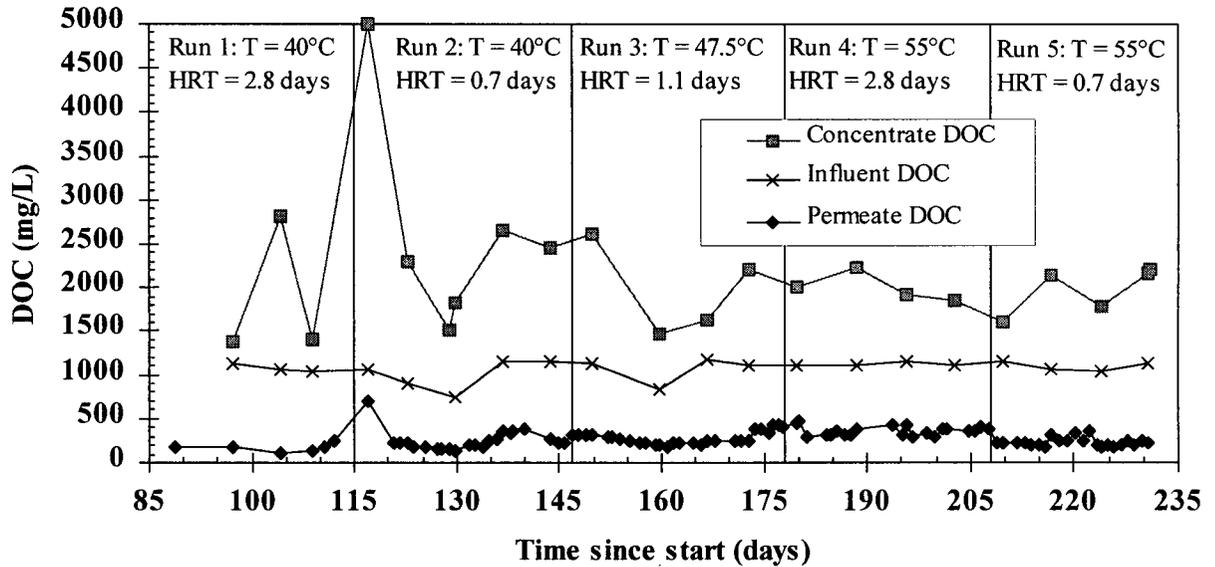
Figure 5.30. DOC concentrations in the MBR concentrate, influent and permeate over the experimental period.
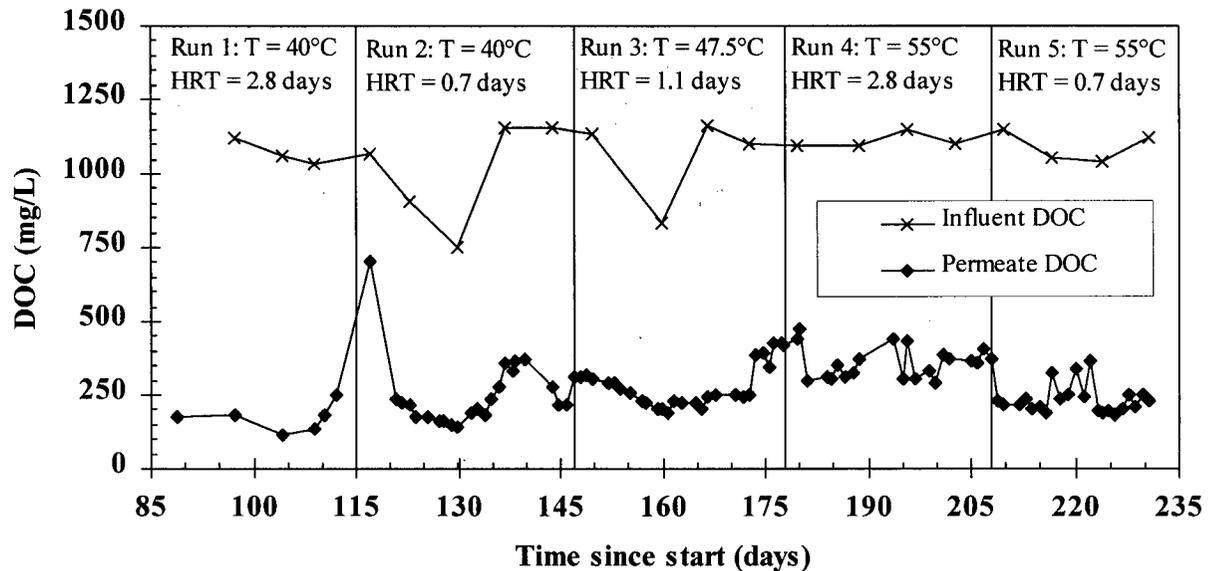
Figure 5.31. DOC concentrations in the influent and the MBR permeate over the experimental period (different scale than Figure 5.30).

concentrate DOC concentrations were usually only about twice the influent DOC concentrations. One

notable exception is following the lack of nutrient addition from day 108 to 117, when the DOC reached

5000 mg/L. However, the concentrate DOC quickly dropped when the nutrient additions were resumed.

5.5.4. Colour

The MBR was ineffective at removing colour from the influent (Figure 5.32). In fact, the MBR

permeate usually contained more colour than the influent. The degradation and oxidation of organic

matter and the concentration of solids in the reactor probably produced this additional colour. The

colour of the concentrate was much higher than the permeate colour (Figure 5.33), indicating the

effectiveness of the gel layer at rejecting colour bodies. This conclusion may be reached because the

nominal pore size of the membrane filter used for the filtration of the sample for colour determination is

the same as the PF-75 UF membrane nominal pore size. Hence, it is reasonable to assume that the gel

layer formed at the MBR UF membrane is responsible for much of the rejection of the colour present in

the concentrate. The increase in the influent colour from 575 colour units to 1000 colour units on day

136 is due to the use of a new batch of evaporator concentrate in the preparation of the influent synthetic

whitewater.
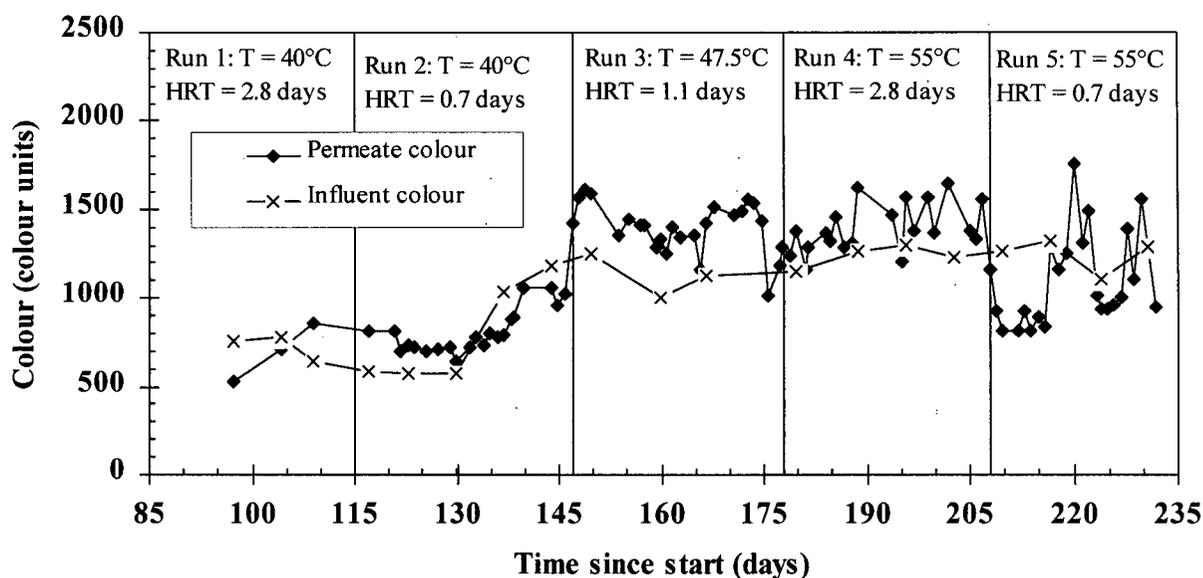
Figure 5.32. Colour of the MBR permeate and influent over the experimental period.
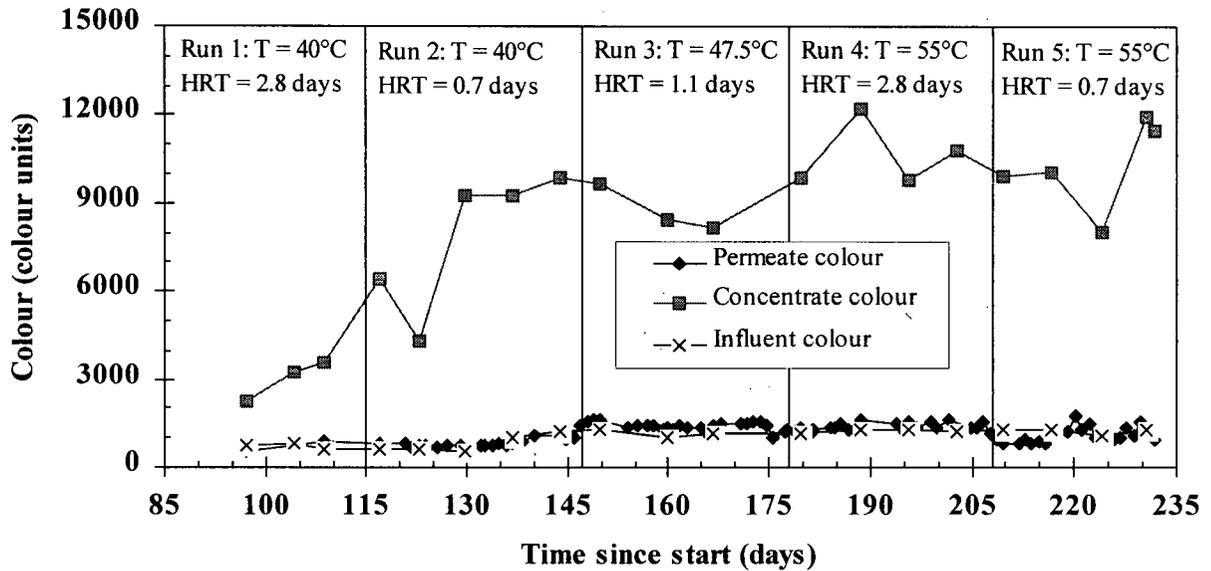
Figure 5.33. Colour for the MBR concentrate, permeate and influent over the experimental period (different scale than Figure 5.32).

5.5.5. Solids

The MBR treatment of the synthetic whitewater resulted in moderate solids removal (Figure 5.34, Figure 5.35). On average, 36% of TS were removed, including an average removal of 24% of the TDS. Some of the solids accumulated in the reactor. It is difficult to evaluate if some of these solids were destroyed in the reactor, as the concentrate total solids concentrations also include the MLVSS concentrations, which fluctuate with the biomass present in the reactor. Nevertheless, it appears that some of the influent solids may have been destroyed in the reactor. This can be inferred from the higher concentrate TDS concentrations in the MBR reactor when operating conditions were changed, i.e. at the beginning of Runs 2, 3 and 4. The concentrate TDS sharply increased at the beginning of these runs, probably because the biomass was adapting to the new operating conditions and couldn't degrade the volatile fraction of the TDS as well as usual. The concentrate TDS concentrations decreased when the microorganisms adapted to the new conditions, which seemed to indicate that the microorganisms were then adapted to the new operating conditions.
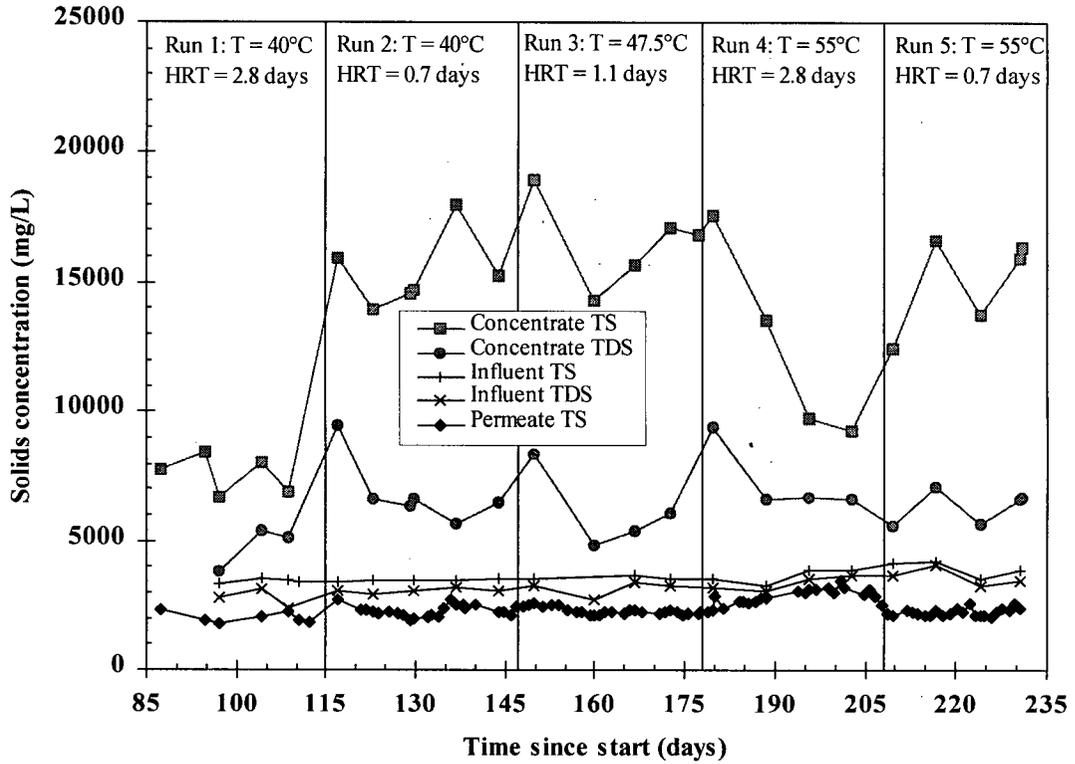
Figure 5.34. Solids concentration in the MBR concentrate, permeate and influent over the experimental period.
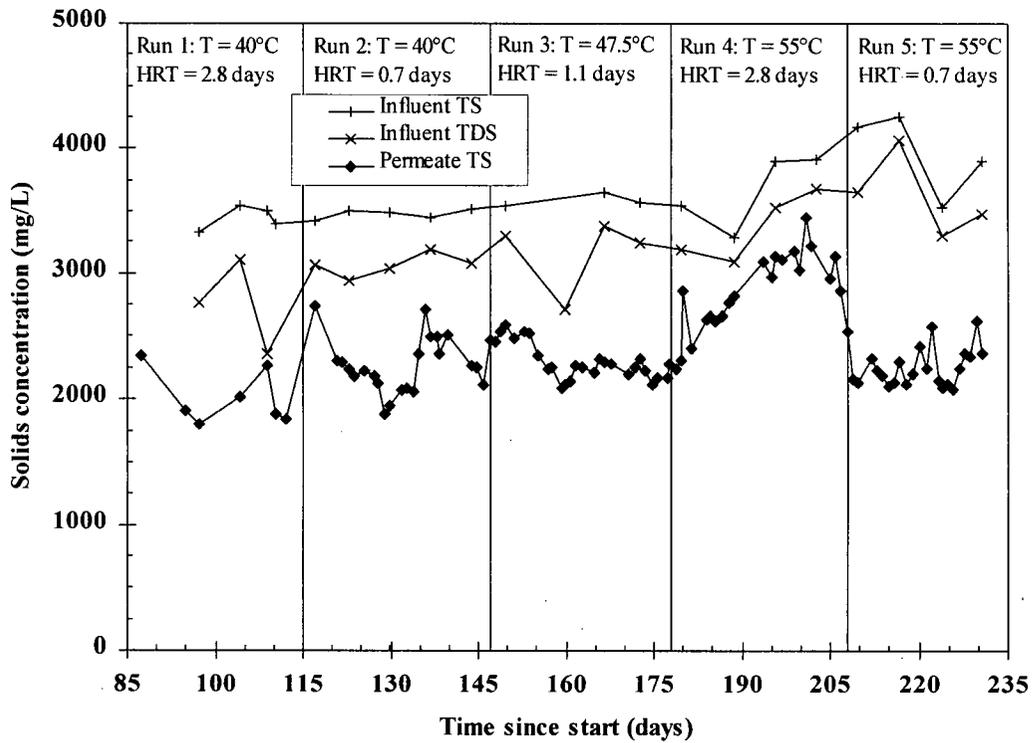
Figure 5.35. Solids concentration in the MBR permeate and influent over the experimental period (different scale than Figure 5.34)

5.5.6. Cationic Demand

The MBR was moderately successful at removing the influent cationic demand (CD), removing an average of 64% of the CD over the experimental period. Fluctuations in the permeate cationic demand, illustrated in Figure 5.36, are due to the imprecise nature of the CD determination, which involved a titration with an end-point that was difficult to determine. High cationic demand concentrations in the reactor (Figure 5.37) seem to be due to the presence of higher concentrations of TDS in the reactor.
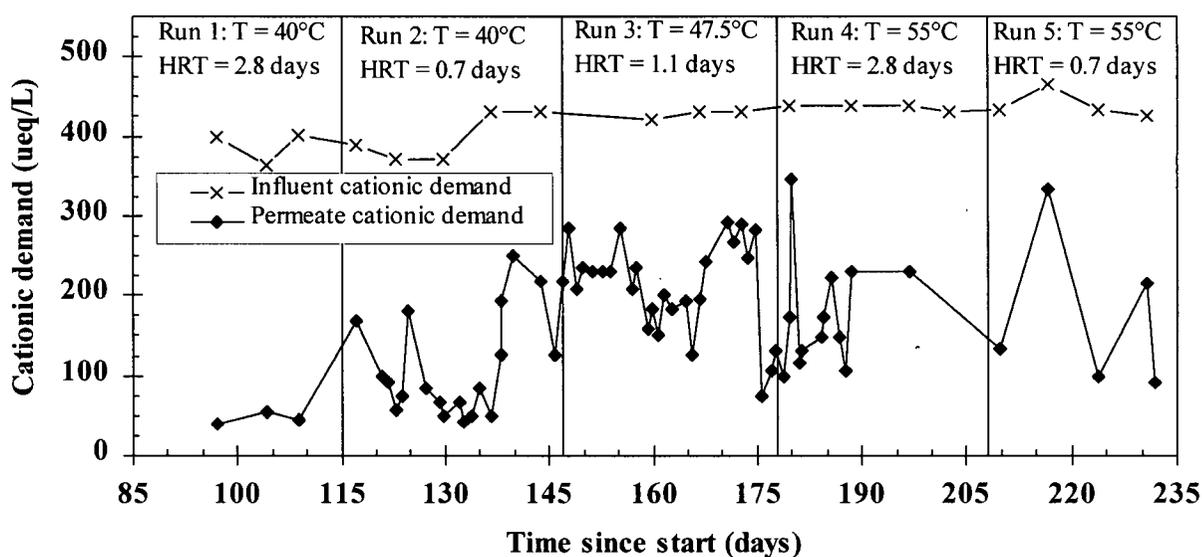
Figure 5.36. Cationic demand of the MBR permeate and influent over the experimental period

Cationic demand in thermo-mechanical whitewater is thought to be caused mainly by the release of galacturonic-acid rich hemicelluloses (polygalacturonic acids) during peroxide bleaching of the pulp (Thornton *et al.*, 1993). These compounds should have been easily biodegraded by the MBR during biological treatment, as they are complex carbohydrates which can be utilized as growth substrates by a variety of bacteria, yeasts and filamentous fungi (Pilnik and Rombouts, 1981). The cationic demand removal efficiencies measured during the MBR treatment of the whitewater were thus lower than expected. However, the compounds causing cationic demand in the synthetic whitewater used in this
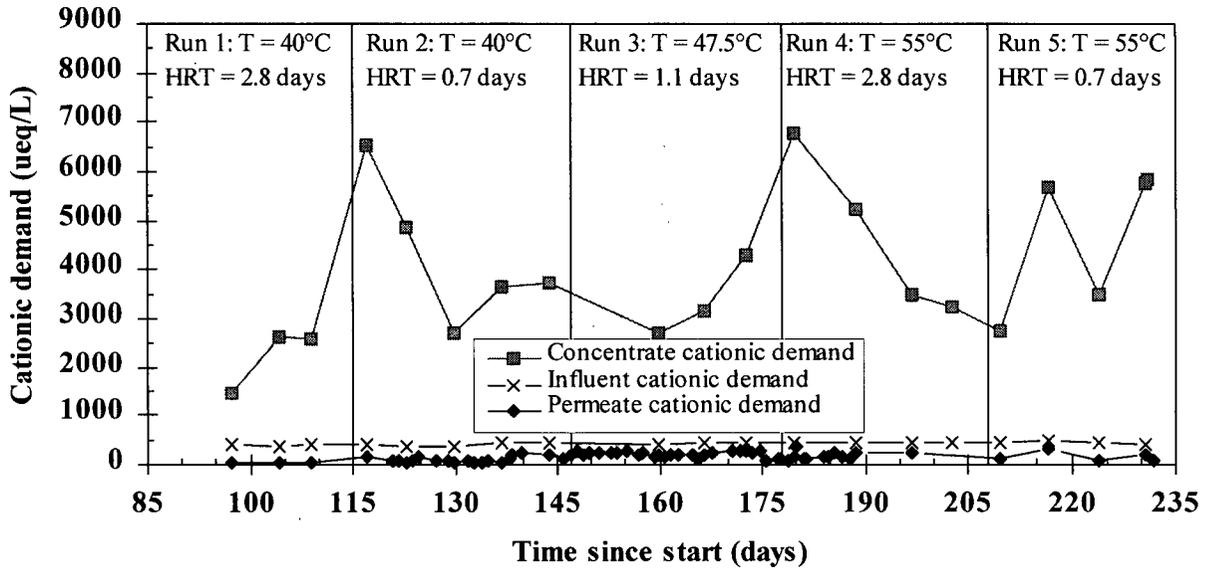
Figure 5.37. **Cationic demand of the MBR concentrate, permeate and influent over the experimental period (different scale than Figure 5.36).**

experiment may not have been of the same origin as the material commonly referred to as "anionic trash" in actual thermo-mechanical newsprint whitewater.

The cationic demand of the concentrate samples seemed to correlate to the MBR concentrate TDS (MLTDS) concentrations (Figure 5.38). This may be due to the fact that most of the dissolved
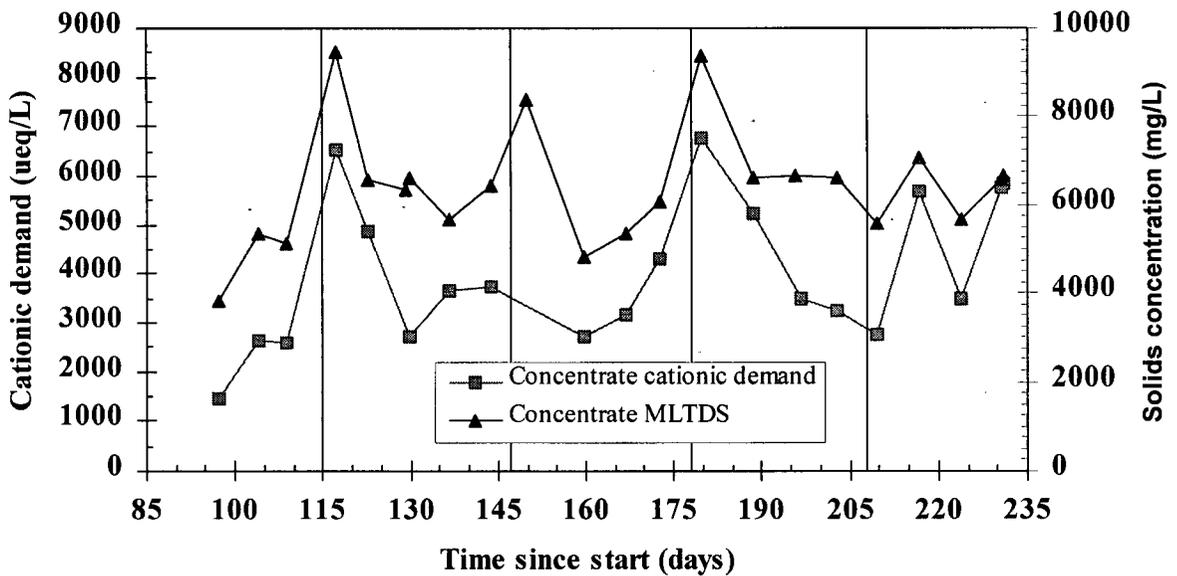
Figure 5.38. **The concentrate cationic demand seemed correlated to the MLTDS concentration.**

solids added to the synthetic whitewater may be anionic in nature because they originated from the evaporator concentrate obtained from the Millar-Western zero-effluent BCTMP mill located Meadow Lake, Saskatchewan, Canada. According to David Reside of NLK Consultants (1996), much of the material present in these evaporator bottoms should be anionic, because of the bleaching operations of the Meadow Lake mill.

5.5.7. Resin and Fatty Acids

The MBR was very efficient at removing the influent FA (Figure 5.39): of 96 permeate samples analyzed over the experimental period, only 4 samples were found to contain fatty acids at concentrations above the method detection limit of 0.1 mg/L. These isolated incidents are documented in Table 5.4. For each one of these cases, only one fatty acid, usually linoleic acid, was detected at concentrations of less than 0.25 mg/L. In addition, these events could be linked to a specific cause, usually a significant loss of solids from the mixed liquor, or a change in the influent composition which may have had toxic effects on the mixed liquor microorganism population. So, in essence, the fatty acids were totally removed from the influent whitewater after MBR treatment.

Table 5.4.   Permeate samples with FA concentrations superior to the method detection limit.

Date	Day #	Run #	FA detected	Concentration	Probable cause
March 31, 1995	140	2	linoleic acid	0.15 mg/L	New evaporator concentrate used for preparing influent may have affected the biomass population.
May 11, 1995	181	4	linoleic acid	0.23 mg/L	Mixed liquor loss on day 181
May 24, 1995	194	4	palmitic acid	0.21 mg/L	Mixed liquor loss on day 190
May 26, 1995	196	4	linoleic acid	0.22 mg/L	Mixed liquor loss on day 190

The MBR was also very efficient at removing the influent RA, as can be seen from Figure 5.39. However, some dehydroabietic acid was detected 19 times out of 97 permeate samples. Apart from the

three cases listed in Table 5.5 below, no other resin acids were detected in the permeate. Dehydroabietic acid concentrations in the permeate were always below 0.75 mg/L, except for two cases documented in Table 5.5.

Table 5.5. **Permeate samples with RA concentrations above the method detection limit (dehydroabietic acid excluded)**

Date	Day #	Run #	RA detected	Concentration	Probable cause
April 25, 1995	165	3	abietic acid	0.29 mg/L	No special probable cause.
May 31, 1995	201	4	pimaric acid	0.12 mg/L	Pump shut-down on days 198 and 200 due to a defective level control (note dehydroabietic acid concentration in permeate = 1.60 mg/L)
June 1, 1995	202	4	pimaric acid	0.24 mg/L	Same as above (note dehydroabietic acid concentration in permeate = 2.88 mg/L)
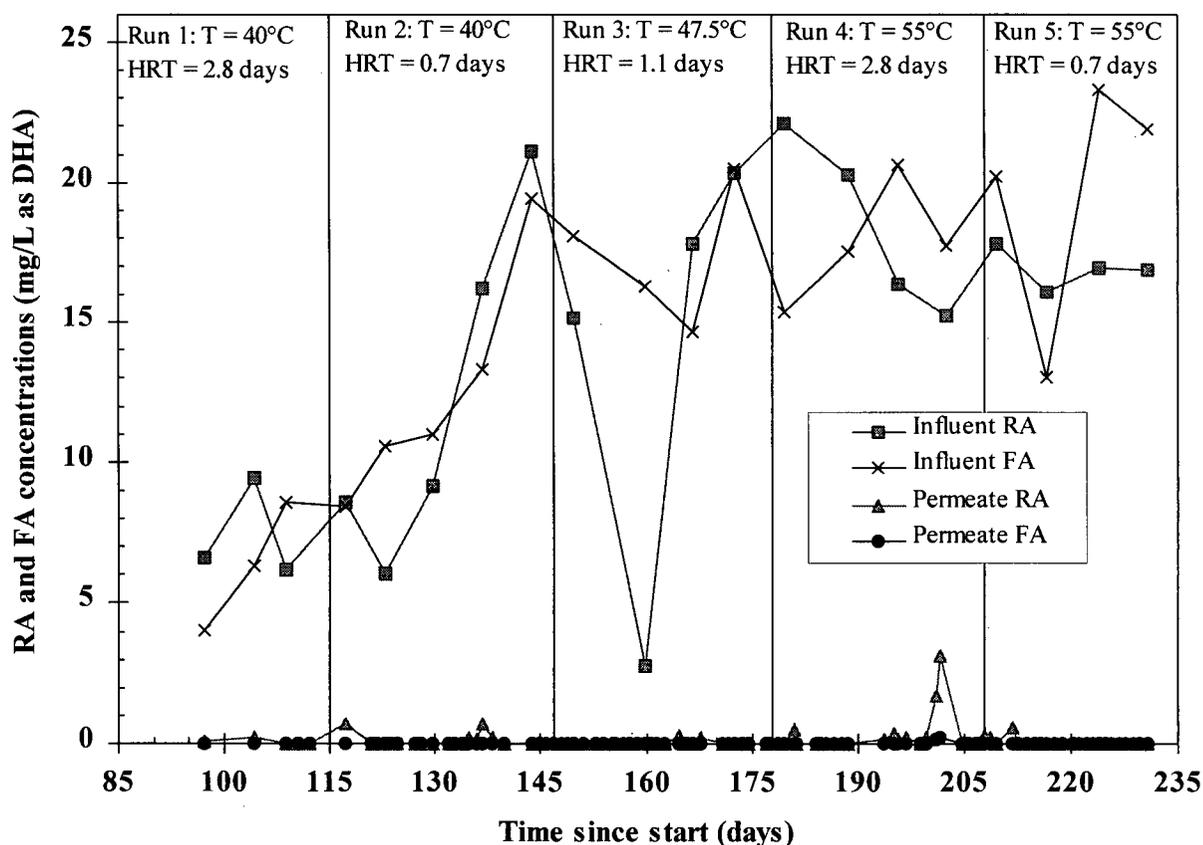
Figure 5.39. RA and FA concentrations in the MBR permeate and influent over the experimental period.

The RA and FA bound to the concentrate suspended solids or dissolved in the concentrate are shown in Figure 5.40. The results are expressed in mg of FA (or RA) per L of concentrate. The sum of the dissolved RA and the RA bound to the suspended solids would give the total concentration of RFA present in the concentrate.

Most of the RA and FA present in the concentrate were bound to the concentrate suspended solids. The data points with high concentrations of RA or FA dissolved in the concentrate are thought to be due to a poor centrifugation of the concentrate sample, since some samples with high concentrations of RA and FA had almost no dissolved RA or FA (day 145) while others with relatively low concentrations of RA or FA bound to the suspended solids had high concentrations of dissolved RA or FA (day 117). The fact that RA or FA did not accumulate in the concentrate (the RA and FA concentrations were usually much lower than the influent RA and FA concentrations) suggests that the RFA were biodegraded in the reactor. This is supported by Liu *et al.* (1993a), who have shown that bio-oxidation is the major removal mechanism of RFA in aerobic biological treatment of CTMP effluent. These researchers have also shown that sludge adsorption plays a very important role in removing the RFA: over 70% of the RFA present in a CTMP effluent was adsorbed by static sludge adsorption in less than 30 minutes. The destruction of the RFA in the MBR by the biosolids eliminated the problems of pitch deposition observed when using ultrafiltration alone to treat the synthetic whitewater (Section 5.3.1). No pitch deposits or sticky balls of agglomerated pitch were observed during the MBR treatment of the synthetic whitewater.

In the MBR treatment of the synthetic whitewater, the adsorption of the RFA to the sludge also seems to have played an important role in the successful removal of virtually all influent RFA. Since the influent RFA probably quickly bound to the sludge and the sludge was retained by the ultrafiltration membrane and returned to the reactor, RFA were only occasionally detected in the permeate. When MBR operational difficulties led to a reduction in the bio-oxidation of RFA, it appears that the MBR

sludge still adsorbed most of the RFA (Figure 5.40, Figure 5.41), to bio-oxidize the adsorbed RFA when the biomass population recovered from the shock caused by the operational difficulty.

From Figure 5.41, it appears that the biomass population could bio-oxidize FA more quickly at 47.5°C and 55°C than at 40°C, since the proportion of FA present in the biomass was lower at the higher temperatures. The biomass seemed to be able to bio-oxidize the RA well at all operating temperatures, but seemed sensitive to operational incidents: the proportion of RA present in the sludge peaked on day 145, shortly after the composition of the influent was altered on day 134 (use of a new batch of evaporator concentrate) and the loss of solids on day 136. Similarly, the proportion of RA present in the sludge peaked on day 203, following the pump shut-down incidents of days 198 and 200.
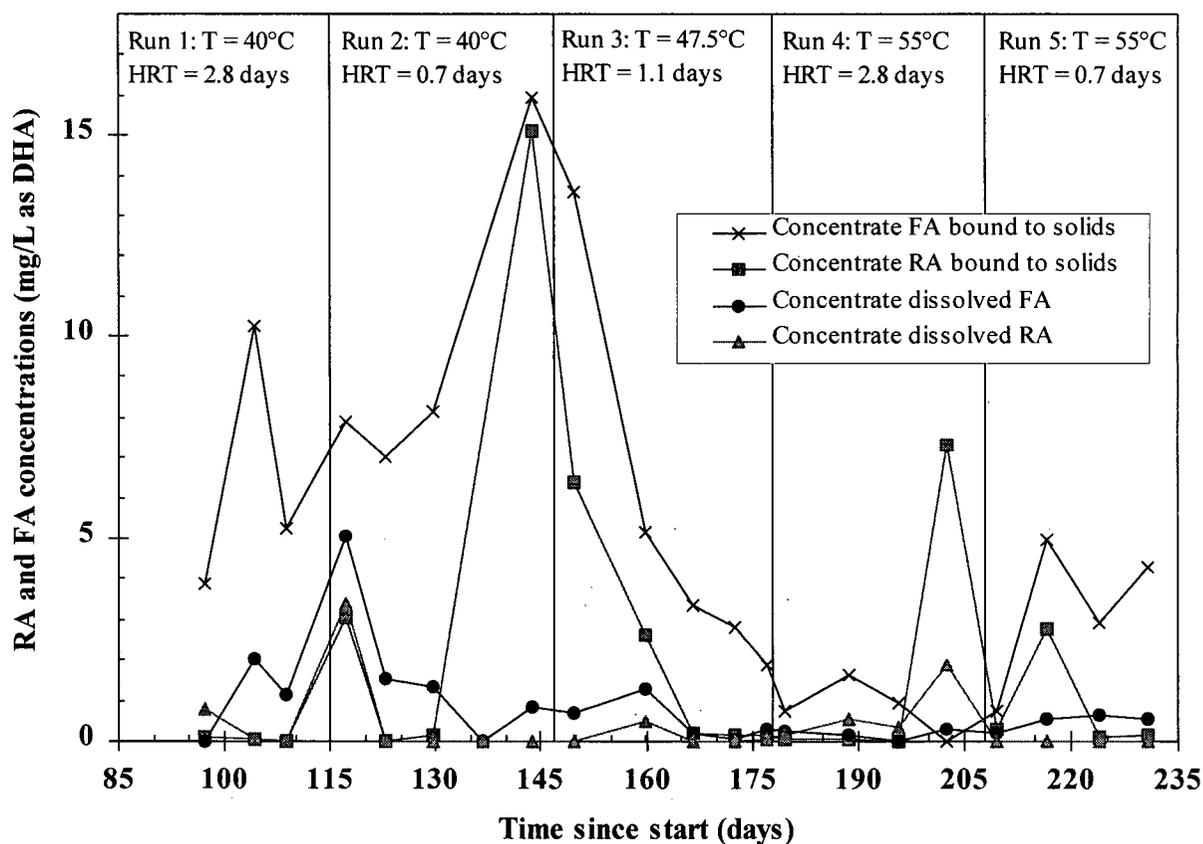
Figure 5.40. RA and FA bound to the MBR concentrate solids and RA and FA dissolved in the concentrate over the experimental period.
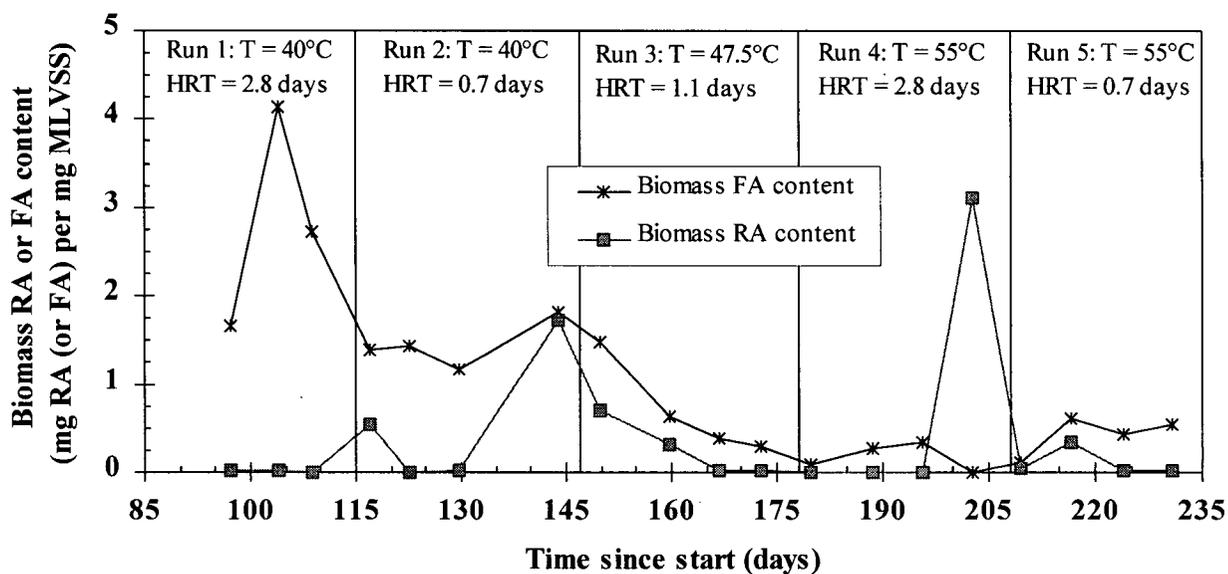
Figure 5.41. MBR biomass RA and FA content per mg of MLVSS over the experimental period.

5.6. Summary of the Effects of HRT and Temperature on the MBR Treatment Efficiency

During the MBR study, the use of different operating temperatures (40, 47.5 and 55°C) and the use of different HRTs (0.7, 1.1 and 2.8 days) over the experimental period produced little effect on the removal efficiency of the process (Figures 5.25, 5.26, 5.27). The treatment efficiency was similar for all runs, but somewhat better for Run 1 (T = 40°C and HRT = 2.8 days). Slightly higher biomass activity, as measured with the SOUR, was found at 40°C than at 47.5°C or 55°C. However, the MLVSS concentrations were generally higher at 47.5°C and 55°C than at 40°C. One interesting advantage of the MBR is that sludge bulking, which is often an important problem for conventional aerobic sludge processes, was not a concern for the MBR at any operating temperature, as no settling is required for solids-liquid separation. Higher maximum membrane fluxes were reached at 55°C, but the membrane had to be cleaned more often. The MBR sludge was capable of tolerating sudden variations in the operating temperature (up to 10°C) without significant repercussions on the treatment efficiency. The change in HRT from Run 1 to Run 2 (T= 40°C) and from Run 4 to Run 5 (T= 55°C), which in both cases was lowered from 2.8 d to 0.7 d, did not produce important variations in the removal efficiencies of the

various contaminants. Although contaminant removal efficiencies declined slightly when the HRT was lowered from 2.8 to 0.7 d from Run 1 to Run 2, the removal efficiencies for most contaminants improved slightly when the HRT was lowered from 2.8 to 0.7 d from Run 4 to Run 5. It is therefore likely that the MBR could operate successfully, with similar removal efficiencies, at hydraulic retention times lower than the 0.7 d to 2.8 d range used in this study.

5.7. MBR Biokinetics

In this section, the specific substrate utilization rates (U) and the food to mass (F/M) ratio as well as the observed growth yield (Y_{obs}) are presented for the different MBR runs and are compared with that of the activated sludge process.

5.7.1. Food to Microorganism Ratios

The food to microorganism ratio, a parameter commonly used for the design and control of the activated sludge process, is defined by Equation 5-4 for the activated sludge process (Metcalf and Eddy, 1991, p. 532). Since the MBR can be considered a modification of the activated sludge process where no solids are lost in the effluent, due to the ultrafiltration step, the same equation can be used for calculating the F/M ratio for the MBR process. The average F/M ratios, presented in Table 5.6, were calculated for TCOD and DCOD for the different MBR runs by using the average influent substrate concentrations and average MLVSS concentrations for each MBR run.

$$F/M = \frac{S_o}{\theta X}$$

Equation 5-4

where S_o = influent COD or BOD concentration (mg/L)

F/M = food to microorganism ratio, d^{-1}

θ = HRT (d)

X = concentration of MLVSS in the MBR (mg/L)

Table 5.6.   Average F/M ratios for TCOD and DCOD for the different MBR runs.

Run #	Temperature	HRT	$F_{(TCOD)}/M$	$F_{(DCOD)}/M$
1	40°C	2.8 d	0.44 d^{-1}	0.30 d^{-1}
2	40°C	0.7 d	0.74 d^{-1}	0.59 d^{-1}
3	47.5°C	1.1 d	0.33 d^{-1}	0.28 d^{-1}
4	55°C	2.8 d	0.27 d^{-1}	0.21 d^{-1}
5	55°C	0.7 d	0.65 d^{-1}	0.54 d^{-1}

The average MBR F/M ratios presented in Table 5.6 can be compared to values reported in the literature (Table 5.7). Since F/M ratios given in the literature are often presented for $S_o = BOD_5$, the average MBR F/M ratios for $S_o = BOD_5$ was approximated by using Equation 5-5, since the BOD_5 of the influent synthetic whitewater used in the MBR study was approximately half of the TCOD (Johnson, 1995).

$$F_{(BOD_5)} / M = 0.5 \times F_{(TCOD)} / M \qquad \text{Equation 5-5}$$

Also presented in Table 5.7 are the volumetric loading rates for the MBR, calculated according to Equation 5-6, where the average influent BOD_5 (S_o) was approximated to half of the average influent TCOD (average influent TCOD = 3390 mg/L (from Table 5.1)) for the same reason given above.

$$\text{Volumetric loading rate} = \frac{S_o \cdot Q_{influent}}{\text{Operating Volume}} = \frac{S_o}{HRT} \qquad \text{Equation 5-6}$$

The F/M ratios and volumetric loading rates for the MBR were typical of complete mix activated sludge and were similar to those reported for the SBR treatment of the same synthetic whitewater (Johnson, 1995).

Table 5.7. **Comparison of the average MBR F/M ratios and volumetric loading rates (for S_o = BOD_5) with other values reported in the literature.**

Process	F/M $\left(\dfrac{\text{mg BOD5}}{\text{mg MLVSS} \cdot \text{d}} \right)$	Volumetric loading rate $(\text{kg BOD}_5 / \text{m}^3 \cdot \text{d})$
MBR	**0.1 - 0.4**	**0.6, 1.6 and 2.4**
SBR (T =20 to 45°C) (Johnson, 1995)	0.1 - 0.2	0.9
Activated sludge *complete mix* (Metcalf and Eddy, 1991)	0.2 - 0.6	0.8 - 1.9

5.7.2. Specific substrate utilization rates

The specific utilization rates (U) were calculated several times per experimental run for various substrates by using Equation 5-7, the same equation used for the activated sludge process (Metcalf and Eddy, 1991, p. 533). The average specific utilization rates for TCOD, DCOD, TDS and DOC are presented in Table 5.8 and Table 5.9.

$$U = \frac{S_o - S}{\theta X}$$

Equation 5-7

where S_o = influent substrate concentration (mg/L)

S = effluent substrate concentration (mg/L)

U = specific substrate utilization rate (mg S / (mg MLVSS $\cdot$ d))

θ = HRT (d)

X = concentration of MLVSS in the MBR (mg/L)

Table 5.8.   **Specific utilization rates (U) for the substrates TCOD and DCOD for the different MBR runs. S_R = substrate removed.**

Run #	U [mg S_R / (mg MLVSS · d)]									
	TCOD					DCOD				
	Avg	SD	Min	Max	n	Avg	SD	Min	Max	n
1	0.52	0.10	0.46	0.64	3	0.32	0.04	0.27	0.35	3
2	0.64	0.15	0.41	0.83	5	0.47	0.09	0.36	0.59	5
3	0.26	0.03	0.24	0.30	4	0.21	0.03	0.18	0.25	4
4	0.22	0.12	0.14	0.35	3	0.15	0.07	0.10	0.24	3
5	0.56	0.09	0.48	0.69	4	0.45	0.09	0.38	0.56	4

The specific utilization rates for the various substrates were at their lowest during the MBR runs 3 and 4. This may be due to the various operational problems experienced during these runs, or to a biomass population adaptation as the temperature was increased from 40°C to 47.5°C just before Run 3 and from 47.5°C to 55°C just before Run 4. The highest specific utilization rates were observed during Runs 1, 2 and 5, indicating that the MBR biomass was most efficient at utilizing the substrate at temperatures of 40°C or 55°C. The high specific utilization rates measured during Runs 2 and 5 may also have been caused by the higher loading rates (lower HRT) used for these runs.

Table 5.9.   **Specific utilization rates (U) for the substrates TDS and DOC for the different MBR runs. S_R = substrate removed.**

Run #	U [mg S_R / (mg MLVSS · d)]									
	TDS					DOC				
	Avg	SD	Min	Max	n	Avg	SD	Min	Max	n
1	0.11	0.08	0.02	0.16	3	0.15	0.02	0.14	0.17	3
2	0.17	0.06	0.08	0.22	5	0.16	0.05	0.09	0.22	5
3	0.08	0.02	0.07	0.11	4	0.08	0.01	0.07	0.09	4
4	0.04	0.02	0.02	0.05	3	0.06	0.03	0.03	0.09	3
5	0.28	0.07	0.20	0.37	4	0.17	0.04	0.13	0.23	4

The specific utilization rates for TCOD are compared to typical design values in Table 5.10, where the MBR U_{BOD5} was approximated conservatively by using Equation 5-8. This can be done since

(i) the BOD_5 of the influent synthetic whitewater used in the MBR study was approximately half of the TCOD and (ii) the BOD_5 removal efficiency should be higher than for TCOD.

$$U_{BOD_5} = 0.5 \cdot U_{TCOD}$$

<div align="right">**Equation 5-8**</div>

Table 5.10. **Comparison of the average MBR specific substrate utilization rates for BOD₅ with values for the SBR treatment of the same whitewater and the activated sludge treatment of pulp mill effluent (Johnson, 1995).**

Biotreatment system	U_{BOD5} [mg BOD₅ / (mg MLVSS · d)]
MBR	**0.1 - 0.3**
SBR₂₀°C	0.1 - 0.2
Activated sludge	0.2 - 0.4

The specific substrate utilization rate was found to be similar to values reported for the treatment of the same synthetic whitewater and for the activated sludge treatment of pulp mill effluent.

5.7.3. Sludge production: observed net growth yield

The observed net growth yield is a valuable coefficient which enables the operator of a biological treatment process to assess the net cumulative mass of sludge produced per net cumulative mass of substrate consumed over a reasonably long period of time. It differs from the specific utilization rate by taking into account the material added to the reactor, the material wasted and the material present in the effluent.

The observed net growth yield (Y_{obs}) is particularly useful to determine the ratio of the mass of sludge produced per mass of substrate actually destroyed (mineralized). It is desirable to obtain a low Y_{obs}, in order to minimize the solid waste produced during the treatment process. The observed growth yield for the various substrates were calculated using Equation 5-9 and are presented in Table 5.11.

$$Y_{obs} = \frac{\text{Mass of VSS formed during a run}}{\text{Mass of substrate removed during a run}} \qquad \textbf{Equation 5-9}$$

where Mass of MLVSS formed = (Mass of VSS wasted or sampled from the reactor - Mass of influent VSS) (Note: the accumulation of the VSS in the reactor during a run was negligible)

Mass of substrate removed = (Mass of influent substrate - Mass of permeate substrate - Mass of substrate wasted or sampled from the reactor)

Table 5.11. Biomass growth yields for the different MBR runs.

Run #	T (°C)	HRT (d)	Y_{obs} for TCOD (g VSS/g TCOD)	Y_{obs} for DCOD (g VSS/g DCOD)	Y_{obs} for DOC (g VSS/g DOC)
1	40	2.8	0.02	0.04	0.08
2	40	0.7	-0.02	-0.02	-0.06
3	47.5	1.1	0.14	0.14	0.36
4	55	2.8	0.34	0.31	0.80
5	55	0.7	0.02	0.02	0.06

Except for Run 4, during which several operational problems were experienced, the MBR produced little sludge during the MBR treatment of the synthetic whitewater: the observed net yield coefficients were low compared to those of conventional activated sludge processes but typical of those obtained in other MBR studies (Table 5.12). The low net yield values observed during this study can be attributed to the relatively long operating SRT of 25 days. The low sludge production of the MBR process is often cited as one of the advantages of the MBR over other treatment processes (Janson and Mishra, 1993; Trouve *et al.*, 1994; Lübbecke *et al.*, 1995). Little sludge is left to be disposed of in comparison to high rate aerobic treatment processes for which the biomass is usually in a log-growth phase.

Table 5.12. Comparison of the observed net growth yield with other treatment processes.

Treatment process	Y_{obs}	Reference
MBR (this study: mechanical newsprint whitewater, HRT = 0.7 to 2.8 d, SRT = 25 d))	**-0.02 - 0.3 g VSS/g COD**	**this study**
MBR (oily industrial wastewater, HRT = 1.9 to 3.8 d, SRT = 50 to 100d)	0.02 - 0.07 g VSS/g COD	(Hare *et al.*, 1990)
Pressurized MBR (vegetable canning wastewater, HRT = 6 d, SRT = 16 d)	0.09 g VSS/g COD	(Krauth and Staab, 1993)
MBR (municipal wastewater, HRT=1 d, SRT = 25 d)	0.3 g VSS/g COD	(Trouve *et al.*, 1994)
MBR (concentrated synthetic wastewater, HRT < 1 d, SRT 1.5 - 8 d)	0.2 - 0.3 g VSS/g BOD_5	(Lübbecke *et al.*, 1995)
conventional activated sludge (domestic wastewater)	0.4 - 0.8 g VSS/g BOD_5	(Metcalf & Eddy Inc., 1991)
Anaerobic treatment of domestic wastewater	0.04 - 0.1 g VSS/g BOD_5	(Metcalf & Eddy Inc., 1991)

5.7.4. MBR Biokinetics: Summary

In summary, the MBR was operated at F/M ratios similar to that of the complete-mix activated sludge process and was found to have specific substrate (BOD_5) utilization rates similar to that of activated sludge treatment of pulp mill effluent. However, the observed net growth yield coefficient was significantly lower than that of the activated sludge process, due to the long solids retention time used in this study. Low observed net growth yield coefficients are typical of aerobic MBR processes and are often cited as one of the advantages of the MBR process over other treatment processes.

5.8. Comparison: UF, MBR and SBR

In this section, the chronology of the long-term research project aiming at comparing various treatment processes to remove contaminants from recirculated whitewater expected of a TMP newsprint mill with excess flows of 2 to 5 m^3/adt is discussed. The average removal efficiencies and average membrane flux of the various processes that were studied so far are also compared and discussed.

5.8.1. Chronology of the Study

This research project was initially intended to compare biological treatment to ultrafiltration for the removal of dissolved and colloidal substances (DCS) from recirculated mechanical newsprint whitewater. It became clear, as discussed below, that ultrafiltration, used alone to treat the whitewater, could not completely remove the influent resin and fatty acids, the most troublesome of the DCS, and could only remove a fraction of the dissolved COD. Biological (SBR) treatment, however, could remove significantly more DCOD and RFA, but only at temperatures of up to 40°C. In addition, batch ultrafiltration of the SBR-treated whitewater significantly enhanced the removal of the target contaminants. However, poor sludge settleability at 45 and 50°C in the SBR, resulting in poor contaminant removal efficiencies, suggested a different approach might be better for treating recirculated whitewater at temperatures above 40°C, while still combining ultrafiltration and biological treatment. The membrane biological reactor, a process incorporating the advantages of biological treatment and membrane filtration in which the sludge is filtered, was thus studied for treating the recirculated whitewater at temperatures ranging from 40 to 55°C. In order to appreciate the effectiveness of the biosolids in the MBR process, a MBR test run with no biosolids was conducted with the PF-75 ultrafiltration membrane. It is important to note that MBR operating conditions were not intended to yield a high membrane flux.

5.8.2. Summary of the Results Obtained for the Different Treatment Processes

A summary of selected results for the different processes is presented in Table 5.13. For each experiment, variable conditions (Temperature (T), hydraulic retention time (HRT), type (M for Minisette or PF for Permaflow) and pore size of the ultrafiltration membrane used) are given. Results presented include the average removal of RA, FA, TDS, DOC, and dissolved COD. For the SBR and MBR experiments, average MLVSS concentrations in the reactor. For the experiments involving ultrafiltration (UF, SBR + UF, and MBR), the average membrane flux is also given.

RA and FA removal. Ultrafiltration of the whitewater using the Minisette membrane resulted in poor removals of RA (26 to 45%, depending on the membrane pore size) but good removal of FA (79 to 100% removed). The ultrafiltration involving the use of the Permaflow tubular membrane yielded similar results. SBR treatment at 20 to 40°C yielded excellent removals of both RA and FA (92 to 100%). However, the SBR treatment used at temperatures of 45 and 50°C resulted in poor RA removals (29 to 59%) but good FA removals (>95%). The MBR was the most effective treatment for both RA and FA, removing on average, 98 to 100% of those contaminants at temperatures ranging from 40 to 55°C.

Table 5.13. Summary of the average removal efficiencies and average membrane fluxes obtained for the different processes used to treat the synthetic recirculated mechanical newsprint whitewater.

Treatment type	T	HRT d	Membrane-pore size	MLVSS	RA removal	FA removal	TDS removal	DOC removal	DCOD removal	Membrane flux
	°C	(CF)	kDaltons	mg/L	%	%	%	%	%	$L/(m^2 \cdot h)$
UF	20	(10)	M-10		26	94	24	35	37	55
UF	30	(10)	M-10		38	94	21	34	42	59
UF	40	(10)	M-10		25	94	21	31	35	69
UF	50	(10)	M-10		32	79	26	33	35	71
UF	20	(10)	M-100		37	99	11	16	25	65
UF	30	(10)	M-100		44	100	6	16	22	88
UF	40	(10)	M-100		45	100	13	18	20	109
UF	50	(10)	M-100		41	90	9	15	20	128
SBR	20	2	-	5100	99	92	28	73	69	
SBR	30	2	-	5500	100	96	34	74	76	
SBR	40	2	-	4700	100	96	30	64	59	
SBR	45	2	-	3800	59	95	11	34	63	
SBR	50	2	-	1900	29	97	2	12	9	
SBR+UF	20		M-10		100	>92	46	89	92	69
SBR+UF	30		M-10		>99	>96	46	93	94	104
SBR+UF	20		M-100		100	>92	43	83	86	93
SBR+UF	30		M-100		>99	>96	42	86	89	128
SBR+UF	40		M-100		100	>96	44	85	84	153
UF	37	(10)	PF-75		37	99	36	4	13	24
UF	37	(52)	PF-75		77	100	35	0	5	23
MBR	40	2.8	PF-75	2900	98	100	25	86	84	16
MBR	40	0.7	PF-75	6500	99	100	27	75	78	14
MBR	47.5	1.1	PF-75	8800	100	100	27	75	77	8
MBR	55	2.8	PF-75	4700	98	100	18	67	72	18
MBR	55	0.7	PF-75	7500	100	100	37	77	77	13

The excellent RA and FA removals obtained with the MBR were thought to be due to the complete retention of suspended solids by using ultrafiltration as the solids-liquid separation step. A recent study (Hall and Liver, 1996) has shown that RA are quickly adsorbed to aerobic biomass. Other researchers (Liu *et al.*, 1993a) have also shown that sludge adsorption is a very important pathway to remove RFA during activated sludge treatment of CTMP effluents. Since the ultrafiltration unit used in the MBR process retained all the mixed liquor suspended solids, any RFA adsorbed to the sludge were also retained, providing increased contact time for bio-oxidation of these compounds. The destruction of these compounds during the MBR treatment represents an interesting advantage of using such a process over ultrafiltration alone for the treatment of whitewater at high temperatures, a process which only concentrates contaminants.

DCOD and DOC removal. The best removals for DCOD were achieved by using the SBR+UF treatment: 84 to 94% of the influent DCOD was removed using this 2-step process. DCOD removals using the MBR were also good, ranging from 72 to 84%. The SBR alone removed 59 to 69% of the DCOD at temperatures ranging from 20 to 45°C, but only 9% at 50°C. UF treatment of the whitewater resulted in generally low DCOD removals, ranging from 35 to 42% with the M-10 kDaltons membrane and from 20 to 25% with the M-100 kDaltons membrane. Even lower DCOD removal efficiencies were obtained using the PF-75 kDaltons membrane. DOC removals were similar to DCOD removals for all processes.

TDS removal. The best removals for TDS were obtained by treating the whitewater using the sequential SBR+UF process, with average removal efficiencies ranging from 42 to 46%. This is only slightly higher than the removals obtained with the SBR alone at temperatures ranging from 20 to 40°C, which range from 28 to 34%. However, the SBR could only remove an average of 2 to 11% of the TDS at temperatures of 45 and 50°C. The MBR was effective at removing TDS at higher temperatures, with average TDS removals ranging from 18 to 37%. The UF treatment of the whitewater resulted in TDS

removals of 35% with the PF-75 kDaltons membrane, 21 to 26% with the M-10 kDaltons membrane but only 6 to 13% with the M-100 kDaltons membrane.

5.8.3. Effects of Temperature and HRT on the Treatment Performance of the Various Processes

UF. The temperature used had little effect on contaminant removal during the UF experiments. However, higher operating temperatures did result in an increase of the permeate flux.

SBR. The operating temperature had little impact on the average removal of the contaminants for temperatures ranging from 20 to 40°C (Table 5.13). However, poor sludge settling and low biomass growth rates at 45 and 50°C resulted in low contaminant removals at these temperatures, with the exception of FA.

SBR+UF. The SBR+UF sequential treatment was only studied for temperatures ranging from 20 to 40°C. For this range, the operating temperature had little effect on the removal of contaminants. However, increased operating temperatures did result in an increase in the permeate flux rate.

MBR. The MBR operating temperature and HRT had little effect on the removal of the contaminants: the treatment efficiency was similar for all experimental runs, but somewhat better for T=40°C and HRT = 2.8 d (Table 5.13).

5.8.4. Advantages of Integrating the Membrane to the Biological Treatment for Solids-Liquid Separation

As illustrated in Figure 5.42, the use of ultrafiltration alone resulted in the lowest observed removal efficiencies for DCOD, RA and FA at 40°C. Biological (SBR) treatment was capable of achieving higher removal efficiencies for these contaminants, while ultrafiltration combined with biological treatment, either in a sequential process (SBR+UF) or in an integrated one (MBR) resulted in the highest contaminant removal efficiencies. For the treatment of whitewater at temperatures above 45°C, the MBR would be the preferable treatment option for removing dissolved and colloidal

from recirculated TMP newsprint whitewater: the poor sludge settleability experienced in the SBR at 45 and 50°C would preclude the satisfactory operation of a sequential SBR+UF treatment at such temperatures.
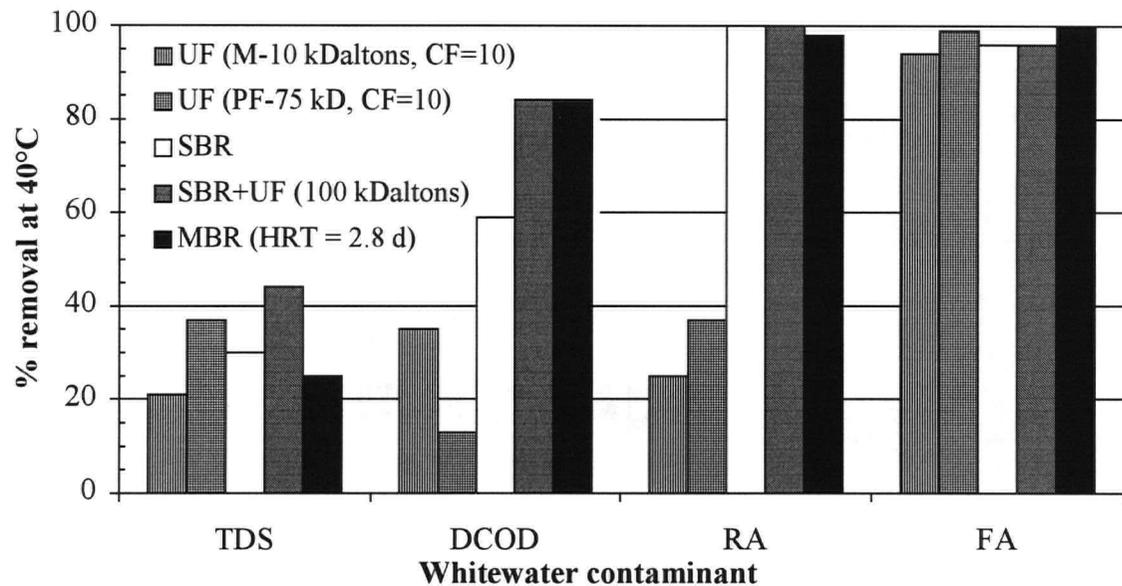
Figure 5.42. Average contaminant removal efficiencies for the various treatment processes at an operating temperature of 40°C.

The MBR also offered many advantages over the use of sequential SBR+UF treatment. These are listed below:

1. The retention of all biomass and suspended solids facilitated the control of the SRT in the MBR.

2. Since adsorption of the RA and FA to the sludge is important, the retention and recycling of the biosolids back to the reactor of the MBR maximized the opportunity of bio-oxidation of these compounds.

3. For the SBR+UF treatment, the SBR effluent was treated in batches using UF by concentrating it to a certain volume reduction factor. This still leaves a concentrated effluent to be disposed of, in addition to the excess sludge produced by the SBR. In comparison, excess sludge is the only waste produced by the MBR process.

4. The MBR was found to be a much more robust treatment process than the SBR at temperatures above 40°C, as the operation of the MBR was stable throughout the study, despite occasional power shortages, unplanned losses of biomass or temperature variations.

5. The MBR is a compact process, as no clarifier or holding tank for further batch treatment of the effluent is necessary. This could allow the treatment system to be located physically close to the whitewater system in a newsprint mill.

For the reasons given above, the MBR appears to be an effective, closed-cycle, technology to purge undesirable dissolved and colloidal substances from recirculated mechanical newsprint whitewater. The ultrafiltration as a solids-liquid separation step greatly improves conventional biological treatment of the whitewater by retaining all suspended solids and bacteria. Conversely, the biological treatment component of the MBR is effective at destroying contaminants and allows for continuous operation of the process without the problems of disposing of large volumes of ultrafiltration concentrate. Only little mixed liquor wastage from the reactor is necessary.

However, more research is necessary before the implementation of such a treatment process in a pilot scale operation. Now that it has been demonstrated that the MBR can treat recirculated whitewater effectively at high temperatures (40 to 55°C), future research in this area is necessary to make this technology attractive as a closed-cycle technology to mill operators and technical consultants. Firstly, higher permeate fluxes and lower HRTs than the ones measured during this study must be achieved (flux optimization was not one of the goals of this study). Secondly, the MBR process should be studied under extreme and transient conditions, since the recirculated whitewater in an actual mill situation might vary in composition and temperature. Thirdly, a different MBR configuration than the one used for this study, such as the one where a membrane is immersed directly in the biological reactor and suction is used to produce permeate (Dufresne *et al.*, 1996), might reduce the space requirements and energy costs associated with pumping for the filtration. The use of such a configuration could be studied for the

treatment of recirculated newsprint whitewater. Fourth, the use of different membrane materials and MWCO should be investigated to determine the best type of membrane for use in an MBR. Lastly, the use of reverse osmosis to treat part of the MBR effluent should be studied, since the MBR treatment of recirculated whitewater alone does not remove ionic material such as aqueous salts and metal ions which accumulate in recirculated whitewater and cause detrimental effects in the paper machine and equipment.

6. CONCLUSIONS AND RECOMMENDATIONS

This research investigated the performance of a lab scale MBR to treat a synthetic recirculated mechanical newsprint whitewater at operating temperatures of 40, 47.5 or 55°C, HRTs of 0.7, 1.1 or 2.8 days and SRT of 25 days. The removal efficiencies of RFA, COD, TOC, colour, cationic demand and solids were investigated, with a particular emphasis on RFA, which are among the most detrimental substances which accumulate in recirculated whitewater. The performance of ultrafiltration at removing the same contaminants using the same tubular ultrafiltration unit with a MWCO of 75 kDaltons which was used in the MBR study was also investigated.

6.1. MBR Treatment: Conclusions

From this research, the following conclusions were reached for the MBR treatment of recirculated newsprint whitewater:

1. The MBR was found to be a stable and robust form of biological treatment. It achieved very similar removal efficiencies for all operating temperatures and HRTs. It was particularly effective at removing fatty acids (100% average removal), resin acids (average removal $\geq$ 98%), TCOD (82% average removal), dissolved COD (78% average removal) and dissolved organic carbon (76% average removal). The reduction of the whitewater cationic demand was good (64% average removal). The average removal efficiencies for TS (36%) and TDS (27%) were fair, while the MBR was ineffective at removing colour (-5% average removal efficiency).

2. The MBR produced a clear effluent, free of any suspended solids. This is important as an internal whitewater treatment process to be used in a closed mill should not introduce microorganisms in the whitewater system. In addition, sludge bulking, which is often an important problem for conventional aerobic biological treatment processes at high temperatures, was not an concern for the MBR. Finally, the SRT could easily be controlled, as no solids were lost in the effluent.

3. Because no solids were lost with the effluent, the MBR SRT could be maintained at relatively long 25 days. The biomass growth yield coefficients were consequently low when compared to the conventional activated sludge process. This is a substantial benefit, since the excess amount of sludge to be disposed of is kept to a minimum.

4. RFA were successfully degraded in the reactor, as no accumulation of RFA could be detected in the reactor. It has been determined from the literature that RA and FA quickly adsorb to aerobic sludge. This was thought to contribute to the excellent RFA removal efficiency, as all biomass was retained by the MBR UF membrane.

5. The MBR was operated as long as 55 days without membrane cleaning. Membrane cleaning using a proprietary caustic cleaning agent could successfully restore the pure water flux to close to initial levels.

6. The MBR measured permeate fluxes were low, ranging from 5 to 35 L/m^2·h. However, permeate flux optimization was not a goal for this study: due to pump limitations, the transmembrane pressure (79 kPa or 11.5 psi) was kept at a minimum throughout the MBR study. Similarly, the recirculation rate of 50 L/min (velocity = 1.7 m/s) used was lower than the manufacturer-recommended range of 90 to 130 L/min.

6.2. Ultrafiltration: Conclusions

From this research, the following conclusions were reached for the UF treatment of recirculated newsprint whitewater using the PF-75 tubular ultrafiltration unit (MWCO = 75 kDaltons):

1. The ultrafiltration whitewater at concentration factors greater than 15 resulted in the deposition of pitch on the concentrate tank walls and equipment. Deposits were sometimes several millimeters in thickness.

2. The ultrafiltration was very effective at removing FA (>98%). The RA removal efficiency was initially poor (24%), but it improved as the concentration factor increased, reaching 100% by the end of the study. This improvement in the rejection of resin acids was thought to be due to the adsorption of the RA on suspended solids, which were rejected by the membrane. The formation of a gel layer on the surface of the membrane also might have improved the rejection of the RA at the higher concentration factors. Most of the incoming FA and an important fraction of the RA were thought to be deposited on the equipment with the pitch.

3. The average removal efficiencies observed during the UF study to a concentration factor of 37 were low or nil for DCOD, DOC and colour (0 to 5%), fair for TCOD (23%) and cationic demand (44%), and good for TS (40%) and TDS (35%). Suspended solids were completely rejected by the membrane. Solids removal efficiencies were consistent throughout the study. For DCOD, DOC, colour and cationic demand, some permeate samples were found to have higher concentrations in the permeate than in the influent whitewater (at high concentration factors).

4. The UF measured permeate fluxes were low. They ranged from 18 to 28 L/m^2·h. However, permeate flux optimization was not a goal for this study: due to pump limitations, the transmembrane pressure (69 kPa or 10 psi) was kept at a minimum throughout the MBR study. Similarly, the recirculation rate of 50 L/min (velocity = 1.7 m/s) used was lower than the manufacturer-recommended range of 90 to 130 L/min.

6.3. Most Appropriate Whitewater Treatment Technology

Different alternatives have so far been studied at the UBC Pulp and Paper Centre for the treatment of recirculated newsprint whitewater: (i) ultrafiltration, (ii) sequencing batch reactor (SBR) treatment, (iii) SBR treatment followed by ultrafiltration of the effluent, and (iv) MBR treatment. Of the alternatives studied so far, the MBR treatment was found to be the most suitable for treatment of

recirculated mechanical newsprint whitewater at the typically high whitewater temperatures (>50°C) measured in closed mills.

Ultrafiltration was found to be only moderately effective at removing most target contaminants. In addition, since the concentration factor must be limited to prevent pitch deposition during batch ultrafiltration and to maintain acceptable removal efficiencies, large volumes of concentrate must still be disposed of. Aerobic biological treatment was effective at removing contaminants, but only up to 40°C. Above this temperature, low biomass growth and, more importantly, poor sludge settleability resulted in poor contaminant removal efficiencies. The use of ultrafiltration to polish the SBR effluent, which was very effective at temperatures of 40°C and lower, is no longer a possibility at temperatures above 40°C, since the biological component of this combined process is not viable.

The integration of the MBR in the biological process as a solids-liquid separation step solved the settling problems and low biomass growth experienced during the SBR study, while providing excellent removal efficiencies for RFA, TCOD, DCOD and DOC, and good removal efficiencies for TS and TDS. The use of reverse osmosis could be used as a polishing step to treat a fraction of the MBR effluent, in order to purge ionic species and to remove colour-causing compounds from the recirculated whitewater.

6.4. Recommendations: Areas of Possible Future Research

Before the MBR process is used to treat recirculated mechanical newsprint whitewater at a pilot scale, more research is necessary. The following are possible areas of future research regarding the use of MBR technology as an internal treatment process in closed mechanical newsprint mills.

1. The use of higher transmembrane pressures and recirculation rates may have resulted in significantly higher permeate fluxes during this study. Investigating the effects of using higher pressures and velocities over the membrane area on membrane flux would provide data necessary to estimate the membrane area necessary for a full scale MBR.

2. A study to determine the lowest possible hydraulic retention times while still maintaining removal efficiencies similar to those obtained during this study would be of interest to adequately size a full scale MBR reactor.

3. Comparing different MBR configurations (i.e. the configuration detailed in this study or the configuration for which the membranes are immersed in the biological reactor and a vacuum pump is used to draw the permeate) in terms of treatment performance, energy requirements and space requirements would help determine which is the most suitable for the treatment of recirculated TMP newsprint whitewater.

4. Comparing different membrane materials and MWCO could be useful to determine the most suitable membrane for use in an MBR to be used to treat recirculated TMP newsprint whitewater.

5. Investigating the treatment efficiency of an MBR with reverse osmosis as an additional polishing step could help determine how large a fraction of the MBR effluent should be treated to remove the undesirable ionic substances which accumulate in recirculated mechanical newsprint whitewater and some of the other contaminants which are not completely removed using an MBR.

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APPENDIX 1: EXPERIMENTAL DATA

Files containing the experimental data as well as most of the graphs presented in the thesis are included on a single 1.44 megabytes IBM-PC formatted disk. The disk is attached at the end of this document (for the UBC Main Library copy, the disk can be requested from the Special Collections Division). These files are relevant to those who may want to consult or refer to the data used to generate the graphs and tables presented in this thesis, or to those who wish to include particular graphs in a future article or paper without having to photocopy or scan them.

Two files are included on the attached disk. Both were prepared using Microsoft Excel version 5.0c. On both of these files, the experimental data can be found on the "DATA" sheet. Most of the other sheets are graphs of the plotted data.

The first file, "MBRDATA.XLS" contains the data for the MBR study, as well as most of the graphs included in the thesis which concern the MBR. Some graphs were created directly in the thesis document (created with Microsoft Word (version 6.0c) for Windows 3.1), including the figures in Section 4, Figure 5.21 and Figure 5.22, and are therefore not in the file "MBRDATA.XLS". The data found on the "CUMDATA" sheet was used to calculate the observed net growth yield coefficient as described in 5.7.3 on page 109.

The second file, "UFDATA.XLS" includes the data and the graphs for the process water UF and the distilled water UF experiments. The data for the process water UF experiment can be found on the "DATA" sheet. *For the influent samples only*, Lines 10 and 11 give the measured concentration of contaminants, while the Lines 12 to 62 (for the same influent columns) list the percentage removal efficiencies calculated using Equation A-1.

$$\% \text{ removal efficiency } = 1 - \left(\frac{\text{permeate concentration}}{\text{average influent concentration}} \right) \cdot 100\% \qquad \text{\textbf{Equation A-1}}$$

Average concentrations for the process water experiment are given on Line 64, while average % removal data is presented on Line 68. The flux data for the distilled water run is presented starting at Line 72. Graph sheets to the left of the "DATA" sheet are for the process water and the distilled water experiments, while graph sheets to the right of the "DATA" sheet (all with a "C" prefix) consist of the cumulative plots for the UF process water experiment.

For both the "MBRDATA.XLS" and "UFDATA.XLS" files, after having copied the file to a new name, graphs can be created on new sheets by selecting any existing graph sheet and selecting "MOVE or COPY SHEET" from the Microsoft Excel "EDIT" menu: select "create a copy" and press OK. The copied sheet will have the same name as the original one, but with a number in brackets at the end of the name. This new graph can then be modified by double clicking any item, including the data series: new data to be plotted can be selected directly from the data menu using the mouse and the name of the data series can be modified to modify the legend.