PARALLEL TREATMENT OF A MINIMUM EFFLUENT TMP-NEWSPRINT WHITEWATER BY AEROBIC MEMBRANE BIOLOGICAL TREATMENT AND ULTRAFILTRATION AT 55°C

by

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ABSTRACT

A lab scale membrane biological reactor (MBR) consisting of an aerobic biological reactor coupled to a lab scale ceramic ultrafiltration membrane (pore size 500 Angstroms) was operated in parallel with an ultrafiltration treatment system consisting of a non-inoculated mixing tank and the identical ultrafiltration membrane to treat a simulated minimum effluent TMP-newsprint whitewater at 55°C.

The MBR system was operated at hydraulic residence times (HRTs) of 1 day, 0.5 days and 0.33 days with a constant solids retention time (SRT) of 20 days, corresponding to water recovery fractions of 0.95, 0.975, and 0.983, while the UF system was operated at water recovery fractions of 0.9, 0.95, 0.983. The filters were operated at a flow through velocity of 4 m/s and a transmembrane pressure of 138 kPa (20 psi).

The MBR performed optimally at a water recovery fraction of 0.983, achieving removal of total and dissolved solids of 29% and 22%, and total and dissolved chemical oxygen demand of 48% and 34%. Removal of resin and fatty acids were 66% and 99% respectively, cationic demand removal was 48% and removal of UV-Lignin, 8%. The maximum flux through the filter was 162 L/(m^2•hr) and the time for a 20% loss of flux was 110 hours.

The UF system performed best at a water recovery fraction of 0.95, achieving lower removal of total solids (23%), dissolved solids (18%), total COD (31%), dissolved COD (4%) than the MBR. Removal of resin and fatty acids were 95% and 98% respectively, and removal of cationic demand was 74%. UV-Lignin was not removed at all by the UF system. Maximum flux through the filter was 162 L/(m^2•hr) and the time for a 20% loss of flux was 170 hours.

The reduced fouling potential and improved removal of certain contaminants coupled with the lower cost of operation and fewer operational upsets would suggest the ultrafiltration treatment system operated at a water recovery fraction of 0.95 (or volume reduction factor of 20) has higher potential for treating minimum effluent TMP-newsprint whitewater at 55°C than aerobic membrane biological treatment.

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LIST OF ABBREVIATIONS AND ACRONYMS

adt	Air-dried tonne
ASB	Aerated stabilization basin
AST	Activated Sludge Treatment
ATAD	Autothermal aerobic digester
BCTMP	Bleached chemi-thermomechanical pulp
BCOD	Biodegradable Chemical Oxygen Demand
BOD	Biochemical oxygen demand
BOD_5	Biological oxygen demand (5 day)
CD	Cationic demand
CF	Concentration factor
COD	Chemical oxygen demand
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
F/M	Food to microorganism
FA	Fatty acids
HRT	Hydraulic retention time
MBR	Membrane biological reactor
MF	Microfiltration
ML	Mixed liquor
MLSS	Mixed liquor suspended solids
MLTDS	Mixed liquor total dissolved solids
MLVSS	Mixed liquor volatile suspended solids
MST	Membrane sewage treatment
MVR	Mechanical vapour recompression
MW	Molecular weight
MWCO	Molecular weight cutoff
N	Nitrogen
NF	Nanofiltration
OUR	Oxygen uptake rate
P	Phosphorus
P	Pressure
PAPRICAN	Pulp and Paper Research Institute of Canada
psi	Pounds per square inch

PVSAK	Polyvinyl sulphuric acid potassium salt (K)
RA	Resin acids
RFA	Resin and fatty acids
rpm	Revolutions per minute
S_0	Influent COD or BOD concentration
SBR	Sequencing batch reactor
SOUR	Specific oxygen uptake rate
SRT	Solids retention time
T	Temperature
TBO	Toluidine blue O
TCOD	Total chemical oxygen demand
TDCS	Total dissolved and colloidal solids
TMP	Thermomechanical pulp
TS	Total solids
TSS	Total suspended solids
UASB	Upflow anaerobic sludge blanket
UBC	University of British Columbia
UF	Ultrafiltration
UV	Ultraviolet
VDS	Volatile dissolved solids
VFA	Volatile Fatty Acids
VRF	Volume reduction factor
VS	Volatile solids
VSS	Volatile suspended solids
Y	Water recovery fraction

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1. INTRODUCTION

1.1 Motivation for Research

Economic and environmental considerations in the pulp and paper industry have led to interest in and research into the minimization of fresh water use and progressive systems closure. Reduction of fresh water input to a mill system would incorporate such strategies such as pulp washing and countercurrent water recycling to maximize the degree of water reuse within a mill. With the reduction of fresh water into pulp and paper processing, however, will come an increase in the concentration of dissolved and colloidal contaminants in both the pulp and water streams, as well as an increase in operating temperatures. The increase in contaminant concentrations may negatively affect mill operation and paper quality. One strategy to minimize some of the problems associated with a high degree of closure and water reuse in a pulp and paper mill is the insertion of a treatment step (or "kidney") into the water recirculation system, for purging the water stream of such contaminants. The reduction of contaminants in the water stream will result in decreased contamination of the pulp stream and higher newsprint quality.

Thermo-mechanical pulping (TMP)-newsprint operations have historically used large volumes of water (as much as 200 m^3/adt) in the pulping and paper forming processes to purge the system of excess heat and contaminants. Newer mills use less water, in the range of 10-150 m^3/adt. With effluent flows in excess of 10 m^3/adt, "end of pipe" secondary (biological) treatment and disposal to the environment is the only economically viable option for liquid waste management. As TMP-newsprint operations use water reduction strategies to bring

fresh water excess flows into the range of 2-5 m^3/adt, other treatment options become economically viable (Wearing, 1992, 1993).

This thesis project was initiated as part of a long term examination of possible treatment options for the whitewater derived from a low water use (2-5 m^3/adt) integrated thermomechanical (TMP) newsprint mill. Treatment options investigated to date include: ultrafiltration of whitewater at 10-50 °C using plate and frame filters with molecular weight cutoffs (MWCOs) of 10 and 100 kDaltons (Elefsiniotis, 1994); biological treatment of whitewater using a sequencing batch reactor (SBR) in the range of 20-50 °C, and a retention time of 2 days (Johnson, 1995); ultrafiltration of SBR effluent with a plate and frame filter with MWCOs of 10 and 100 kDaltons in the range of 20-40 °C (Elefsiniotis *et al.*, 1995); and aerobic membrane biological treatment of whitewater at temperatures of 40-55 °C, and HRTs of 0.7-2.8 days (Tardif, 1996). This thesis focuses on a direct comparison of ultrafiltration (UF) and aerobic membrane bioreactor (MBR) treatment for the removal of dissolved and colloidal contaminants from a simulated minimum effluent TMP-newsprint whitewater. A comparison of these treatment systems (including those examined in this thesis) is presented in section 5.6.

1.2 Thesis Organization

This thesis is divided into six chapters. The first three chapters introduce the background information and the context for this research: an introduction; a background literature review and a discussion of the motivation for this particular research. Chapter 4 describes the methods and materials used in this research, and Chapter 5 presents the results and a

discussion of them. Chapter 6 summarizes some conclusions from this research and the entire research project.

2. BACKGROUND AND LITERATURE REVIEW

2.1 Systems Closure and Minimum Impact Technology in the Pulp and Paper Industry

"The ultimate goal of a closed cycle mill is to have minimal impact on the environment" (Johnson *et al.*, 1996).

Systems Closure or *closed cycle* refers to a form of pollution prevention control practiced by the pulp and paper industry in which liquid effluents are minimized by recycling them back into the process (Towers and Wearing, 1994).

The driving pressures behind closed cycle developments in the pulp and paper industry have been increasing public environmental expectations reflected both in regulation and the market place.

Relevant concerns surrounding the pulp and paper industry in particular include (Gleadow *et al.*, 1994):

- forest ecology - including concerns regarding sustainable forestry and protection of old growth forests and bio-diversity;
- emissions- toxicity and odors from air and water emissions from processing operations;
- waste reduction- paper recycling, and decreased consumption of water and energy use.

It has been suggested that minimization of the environmental impact of the pulp and paper industry will require an integrated approach - a combination of measures including: pollution control at the source (choice of species for pulp production, optimization of storage to

prevent pollution to the surrounding environment and transformation of wood based pollutants while in storage); appropriate choices regarding fillers and additives, in-plant changes to reduce fresh water requirements and allow for process water recycling (integration of biological and physical treatments on-line) and application of additional chemicals (for example, biocides) (Geller and Göttsching, 1982).

Regulation of the pulp and paper industry from an environmental perspective has undergone significant changes since the 1970's, when emissions controls were first implemented. The original wastewater discharge regulations were based almost entirely on the assimilative capacity of specific receiving water bodies (Edde, 1994), whereas recent amendments to wastewater discharge regulations and future legislation are aimed at prevention of degradation of sensitive environments and promotion of innovative solutions to pollution prevention, including closed cycle technologies (Dexter, 1996).

Production of paper from a closed cycle or zero-effluent mill offers a recyclable product (paper) produced from a renewable resource which directly addresses the issues of water use and toxicity. When combined with an air quality control program, solid waste minimization and appropriate forest management, it represents a significant step to address public concerns surrounding the environmental impacts of the pulp and paper industry (Gleadow *et al.*, 1994). Closed cycle technology is seen by many proponents as environmentally "benign" (Patrick *et al.*, 1994).

The challenge of closed cycle technology raises a number of issues, including technical and economic feasibility, and questions regarding the effects on the process operation and

maintenance, air quality and product quality (Johnson *et al.*, 1996). Closure of pulp and paper operations will clearly result in increased temperatures and contaminant concentrations, changes in pH and electrochemical properties and microbial populations in the process waters which may result in a variety of detrimental process and product effects (Kotila and Estes, 1994). Retrofitting of "open" pulp and paper mills to closed cycle operation would require a vast reduction in fresh water use, due to the fact that the costs associated with system closure are a direct function of the volume of process water to be recovered. Fresh water requirements for mechanical newsprint mills need to be reduced to the 2-5 m^3/adt range before the very high capital and operating costs associated with closure compare favorably to external biotreatment and disposal

Nonetheless, there is evidence to suggest that improved resource productivity (heat, fiber and chemical recovery) and decreased treatment costs may offset some of the major capital costs associated with closure (Dexter, 1996; Towers and Wearing, 1994).

There have been several attempts at closure and zero effluent technology in the pulp and paper industry. These have met with varying degrees of success, with 20 mills operating world wide (in 1996) as totally effluent free operations (Wiseman and Ogden, 1996).

The first commercial attempt at closed cycle technology in the pulp and paper industry was the Rapson-Reeve process. The Rapson-Reeve approach to closure of bleached kraft mills was first proposed by two University of Toronto researchers, Dr. W.H. Rapson and Dr. D.H. Reeve in 1967. The process proposed to eliminate all contaminated effluent and fresh water make-up by several modifications to the process: replacement of up to 70% of the chlorine in

the first stage bleaching process with chlorine dioxide; use of counter current washing; minimization of fresh water use in the bleach plant; recovery of salt from white liquor crystallization; provision of spill control; and use of a stripper to treat evaporator condensates. In 1973, Great Lakes Forest Products (now Avenor) proposed to use this process in a new bleached kraft mill in Thunder Bay, Ontario. In 1977, the construction was completed and bleach plant effluent recovery and salt removal from the kraft liquor recovery cycle commenced.

This process was never able to achieve full recycle of bleach plant effluents, and after repeated efforts to modify the process, it was abandoned in 1985. Failure of the process was attributed to a variety of causes (Hershmiller *et al.*, 1992):

- significant corrosion throughout the process - the operational lifetime of evaporators and boiler recovery tubes was judged to be about one quarter of that observed in similar equipment from an "open" operation;
- low steam economy in the white liquor evaporators, resulting in high energy costs;
- pitch build up and deposition preventing production of acceptable quality market pulp;
- scaling and solids precipitation in the first two evaporators of the salt recovery plant, and plugging of pipelines carrying alkaline bleach plant effluent as a result of $CaCO_3$ deposition;
- problems with recovery furnace operation and emissions control as a result of the high salt content in the black liquor;
- significant operating problems in the causticizing of green liquor;

- increased consumption (approximately 15%) of bleaching chemicals due to the reduced efficiency in pulp washing.

Several other attempts at zero effluent technologies were pursued following the failure of the Rapson-Reeve approach.

In 1991, the BCTMP (bleached chemi-thermomechanical pulp) mill owned and operated by Louisiana Pacific in Chetwynd, British Columbia attempted to operate a zero-effluent mill by implementation of a freeze crystallization process.

Freeze crystallization is a process most often associated with the concentration of fruit juices. As a mechanism for dehydration, it is preferable to evaporation, as the latent heat of crystallization is lower than the latent heat of vaporization, and as such, represents a significant savings in energy. In this application, process water from the pulping operation was first clarified by dissolved air flotation and then passed through a series of low temperature heat exchangers to crystallize off the pure water, leaving a contaminated concentrate. This concentrate was then recycled to the freeze process or incinerated.

This process failed to work as a result of the covering of the heat exchangers with huge sheets of ice and calcium carbonate deposits which completely inhibited heat transfer. This process was abandoned in 1993 and replaced with a mechanical vapor recompression (MVR) evaporation system which had been used successfully at the Millar Western BCTMP mill in Meadow Lake, Saskatchewan.

The zero-effluent operation at Meadow Lake was devised as a solution to a lack of locally available fresh water. The Millar Western mill is situated in a location with a ready supply of wood, electricity, natural gas and labor, but with a limited water supply, particularly in winter when the water supply is anoxic and the flow is extremely limited (Gleadow *et al.*, 1994).

BCTMP pulping is particularly amenable to closed cycle technology due to the low water use pulping (10 - 20 m^3/adt), the compatible effluent from pulping and bleaching operations, high yield and relatively new plants (Reid and Lozier, 1996).

At Meadow Lake, process water from the pulp mill is screened and treated in flotation clarifiers to remove suspended solids and then evaporated in large vapor recompression evaporators from 2% to 35% w/w solids. The TOPS from the evaporators is then stripped of volatile organics, while the MIDS is biologically stabilized and returned to the process water stream. The liquor from this process is incinerated in a recovery furnace. Suspended solids removed in the screening and flotation processes are passed through a sludge press and incinerated, or sent to landfill.

The Millar Western mill at Meadow Lake has instituted a number of in-mill changes to further minimize fresh water consumption, such as the use of 2% (solids content) water in chemical feed applications and to wash process equipment with a high degree of counter current washing (Reid and Lozier, 1996).

Still, there is a net loss of water from this operation, requiring a fresh water make-up of approximately 2 m^3/adt. Pulp quality does not appear to be compromised as a result of this

reduced fresh water consumption, though the energy requirement per tonne of pulp is significantly higher than from a traditional BCTMP pulping operation.

Current research in the area of pulp and paper mill closure is focused on separation technologies to purge trace contaminants which otherwise would accumulate to unacceptable levels in the process water (Wearing, 1993). There are a variety of options, physical, chemical and biological, to treat whitewater reviewed in later sections. A brief discussion of published technical and economic assessments is also presented.

"The challenge is to develop alternative process configurations in existing and new installations and to evaluate and verify their economic and technical performance" (Gleadow *et al.*, 1994)

2.2 Closure of Integrated TMP-Newsprint Mills

2.2.1 Integrated TMP-Newsprint Whitewater System

TMP, or thermomechanical pulping, is a type of mechanical pulping in which wood chips are steamed at atmospheric pressure, prior to refining in a disc refiner. Pulp may be processed in either one or two refiners, mixed with water in a latency chest to straighten the pulp fibers and then screened and cleaned.

In the case of an integrated TMP-newsprint mill, the cleaned pulp is thickened and then sent to a paper machine where it is processed and dried into sheets of finished paper. For

newsprint manufacture, TMP is mixed with a small percentage of kraft, or chemical pulp, prior to papermaking, to improve the quality of the paper

Large quantities of fresh water and steam are added to the wood fibers during the pulping and papermaking process, 50-200 m^3 of water/adt of pulp in older mills and 10-20 m^3 of water/adt pulp in newer mills. This water, when reclaimed in the mill, is then referred to as whitewater. Whitewater, also referred to as backwater, is the general term for any stock filler or process water containing fiber fines (Smook, 1990). "Rich" whitewater contains a high concentration of fiber fines (>0.02%), while "lean" whitewater contains a lower concentration of fiber fines (Smook, 1992).

2.2.2 Minimum Effluent TMP-Newsprint Whitewater

As a completely closed TMP-newsprint mill does not presently exist, the composition of the whitewater from such an operation is unknown. To date, several researchers have investigated the potential composition of a whitewater from a mill implementing water reduction/closure strategies.

Jarvinen *et al.* (1980) determined that the release of pollutants from TMP pulp occurred in two stages: carbohydrates dissolve at the refiner, while lignins and extractives dissolve in conjunction with pulping post-treatment. It has been found that the bulk of the biochemical oxygen demand found in TMP pulping whitewaters is released at the primary refiner. Closure of the whitewater system of an integrated TMP-newsprint mill and implementation of a countercurrent flow system, with all fresh water entering the mill at the paper machine would

result in a concentration gradient between the pulp and paper mill whitewaters, and a decreased dissolution of extractives and lignin in the pulp mill (Jarvinen *et al.*, 1980).

Pietschker (1996) assessed the impact of total water system closure on whitewater quality, chemical additive performance and microbial populations. Closing the whitewater system resulted in higher concentrations of suspended and dissolved solids, increased temperature and reduced dissolved oxygen in the whitewater. The increased temperatures and decreased oxygen levels resulted in a decreased concentration of aerobic bacteria, and a burgeoning of anaerobic microbiological activity (Pietschker, 1996).

Table 2-1 presents some published composition data for minimum effluent TMP newsprint whitewaters. All data presented in this table (with the exception of Lo *et al.*, 1994) were collected in pilot plant experimentation using the SCAN-M method of "hot disintegration" pulp washing.

Table 2-1: Composition of TMP-Newsprint Whitewater

Reference	Francis, 1996b	Jarvinen *et al.*, 1985	Francis, 1996b	Jarvinen *et al.*, 1985	Lo *et al.*, 1994
Water use (m^3/adt)	2	4.6	5	6.8	7
Temperature (°C)		50-60		50-60	
TDS (mg/L)	8510		4960		
RFA (mg/L)	71.94		50.4		15.4 - 13.6
Extractives (mg/L)	458	349	300	258	
TCOD (mg/l)		3720		3140	
BOD_5 (mg/L)		1400		1300	1050
Lignin (mg/L)	1880	823	2110	1075	

Table 2-1 indicates that the concentrations of all contaminants greatly increase with decreasing water consumption.

Table 2-2 presents data from three researchers who were investigating different treatment methods for a minimum effluent TMP-newsprint whitewater. The whitewaters were produced using three different methods: "hot disintegration" (Jahren and Rintala, 1996); a mixture of 10% evaporator concentrate, 80% 4th stage TMP cleaner rejects and 10% chip wash water (Lagacé *et al.*, 1996); and a mixture of 0.7% evaporator bottoms, 20% plug screw feeder pressate and tap water (Tardif, 1996). The whitewater used by Tardif had been used in two previous studies - Johnson (1995) and Elefsiniotis (1994).

Table 2-2: Composition of Manufactured TMP-Newsprint Whitewater

Reference	Jahren and Rintala, 1996	Lagacé *et al.*, 1996	Tardif, 1996
Water use (m^3/adt)		15	2-5
Temperature (°C)	62		
TDS (mg/L)		2400	3200
RFA (mg/L)			27.2
Extractives (mg/L)		170	
TCOD (mg/l)	2200		3390
BOD_5 (mg/L)	1100		1865
Lignin (mg/L)	630		

Clearly, there has been a wide variation in the accepted composition of simulated low water use TMP-newsprint whitewaters studied to date.

Table 2-3 presents data from two sewer profiles on the whitewater from the TMP-newsprint mill used in this thesis.

Table 2-3: TMP Whitewater from Howe Sound Pulp and Paper

Reference	Sim, 1993	Mawbray, 1995
Water use (m^3/adt)	20	20
Temperature (°C)	57	61.4 (68.6 - 35.1)
TSS (mg/L)	606	972 (2016 - 140)
BOD_5 (mg/L)	648	

2.3 Implications of TMP-Newsprint Closure

Although no fully closed TMP-newsprint mills exist at present, there is a body of literature examining the potential effects of closure on the composition of whitewater, the operating conditions within the mill and pulp and newsprint quality.

2.3.1 Whitewater Characteristics

2.3.1.1 Increased Temperature

Present TMP whitewater temperatures range from 57-62 °C (Sim, 1993; Mawbray, 1995; Jahren and Rintala, 1996). With closure, and the reuse of process water, will come an increase in the average temperature of this whitewater (Pietschker, 1996; Wearing, 1992; Järvinen *et al.*, 1985).

Increased operating temperatures may result in energy cost savings and production increases for energy limited systems (Kotila and Estes, 1994), but may also result in increased wear and maintenance costs for production equipment (Johnson *et al.*, 1996).

The negative impact of increased operating temperatures with closure would be most apparent in the biological waste treatment plant of a closed system. Flippin and Ekenfelder (1994) summarized these effects as: suppressed BOD removal, increased effluent solids concentrations and poorer sludge settleability, with the magnitude of these problems increasing at temperatures above 40 °C. Johnson (1995) observed very poor sludge settleability and poor removal of all contaminants of interest in a sequencing batch reactor treating simulated TMP-newsprint whitewater when operated at temperatures greater than 40°C. Liu *et al.* (1993b) examined the effect of temperature on the treatment of a CTMP effluent in an aerobic bioreactor over the range of 13-50 °C. They observed a moderate increase in removal of RFA, BOD_5, COD, TOC and total carbohydrates (measured as apparent glucose) as the temperature was raised from 13 °C to 20 °C, a slight drop in removal effectiveness of all contaminants as the temperature was raised from 20 °C to 40 °C, and a dramatic decrease in contaminant removal when the temperature was increased from 40 °C to 50 °C. The reduction in treatment performance above 40 °C was attributed to a lower mixed liquor suspended solids concentration and a decrease in dissolved oxygen concentrations (Liu *et al.*, 1993b).

Treatment of pulp and paper wastewater by anaerobic biological systems does not appear to be as highly affected by increases in temperature. Rintala *et. al* (1991) used an anaerobic treatment system at 55 °C and 65 °C to treat sulfate-rich pulp and paper wastewater and observed little appreciable difference in COD removal. Jahren and Rintala (1996) reported slightly lower removal of COD from a TMP whitewater at 70°C (55%) than at 55 °C (68%).

2.3.1.2 Increased Contaminant Concentrations

Clearly with process water recycle and fresh water input minimized, there will be an increase of all substances in a TMP-newsprint whitewater. The potential implications of increased concentrations of five particular contaminants are discussed here.

Pilot plant and simulation studies have demonstrated that the accumulation of contaminants in the whitewater circuits increases exponentially with system closure - these contaminants can result in a wide range of problems, often synergistic in nature (Noel *et al.*, 1992).

Dissolved, Colloidal, and Suspended Solids

An increase in dissolved and suspended solids concentrations can affect both the pulping and paper making processes, as well as the quality of the product.

Wearing (1992) indicated that increased concentrations of dissolved and colloidal substances (DCS) were a major concern in closure of mechanical newsprint operations, although lab scale and pilot plant experiments indicated that high concentrations of DCS can be tolerated.

Dissolved solids contain inorganic and organic species - primarily wood components dissolved in the refining process but also chemical additives. These include (but are not limited to) hemicellulose fragments, resin and fatty acids, extractives, cations (Na, K, Ca, Mg, Fe, Al), chloride ions and oxidized sulfur compounds (Asselman *et al.*, 1994). The presence and concentration of various dissolved components in the whitewater can be highly affected by process conditions and wood species (Lloyd *et al.*, 1996). Asselman *et al.* (1994) also reviewed a number of articles that investigated the impacts of dissolved solids on the

papermaking process. Effects included a reduction in the surface tension of the pulp, decreased retention aid efficiency and corrosion.

Suspended solids or "fines" potentially pose significant problems for mill closure. The major problems associated with increased fines concentration are: consumption of additives and the production of surface foam. Additives, particularly high molecular weight cationic bridging polymers, associate with suspended solids, which results in a reduction of their effective volume and a shielding of their effective charge. As a result, much larger quantities of cationic additives are required in paper making (this is discussed further under the heading "Cationic Demand"). High concentrations of suspended solids also result in the production of surface foam. This foam causes problems with housekeeping and safety, in addition to causing deposition on the product. Surface foam carries entrained air which can cause pump cavitation and drainage problems, (Barnett and Grier, 1996).

Organics

Increased organic concentrations and long incubation periods in the whitewater system will result in increased microbiological activity. As discussed under the heading "Solids", the increased operating temperatures and the resulting decrease in dissolved oxygen will cause a shift in bacterial populations towards microorganisms which are primarily anaerobic (Gudlauski, 1996).

Increased anaerobic bacteria levels will result in slime deposition, odor, under-deposit corrosion, toxic gases and fiber degradation. Two anaerobic species commonly found in papermaking systems - *Desulfovibrio* spp. and *Clostridium* spp, which would flourish under

closed conditions, produce volatile fatty acids and hydrogen sulfide which have strong distinct odors which can permeate both the mill atmosphere and the finished product (Gudlauski, 1996).

Resin and Fatty Acids (RFA)

Resin and fatty acids are members of a large group of compounds referred to as extractives, comprising 8% of the dissolved and colloidal substances in the whitewater from TMP processing (Voss, 1987). Resin and fatty acids are released at the first refiner of a two refiner pulping system and are present in the process water in dissolved, colloidal and particulate form (Peng and Roberts, 1996). With increased closure and process water reuse, resin and fatty acid concentrations in the process water will increase.

Resin acids (RA) are tricyclic, diterpenoid, carboxylic acids that are naturally found in the wood extractives fraction of softwoods. Resin acids are classified as either abietanes or pimaranes, differentiated by the substitutions at the C13 position. Resin acids are non-volatile, hydrophobic, and tend to be more soluble under alkaline conditions (at pH >7 the dissolution of resin acids increases dramatically (Voss, 1987; Bicho *et al.*, 1995). Ekman *et al.* (1990) showed that a greater fraction of resin and fatty acids were found in the whitewater at pH 8 than at pH 5 - 5.5.

Resin acids are the primary cause of toxicity in wastewaters from mechanical pulping. Leach and Thakore (1976) determined that 60 - 90% of the acute toxicity resulting from TMP wastewater could be attributed to resin acids. Resin acids are most toxic in their particulate and colloidal fractions (Hoel, 1995), with toxicity increasing markedly with decreasing pH

(Leach and Thakore, 1976). Dehydroabietic acid (DHA) is the most abundant resin acid in TMP pulp and paper wastewaters, and although it is the least degradable, it is also the least toxic. Abietic acid is the second most abundant resin acid in TMP wastewaters - it is both more degradable and more toxic than DHA (Patoine *et al.*, 1997).

Zender *et al.* (1994) examined the biotransformation pathways in resin acid degradation in an aerobic/ anaerobic treatment plant for wastewater from a kraft pulp and paper mill and found that resin acids could be broken down by hydrogenation, hydroxylation and decarboxylation. Resin acids are readily degradable in aerobic treatment plants (Liu *et al.*, 1993b), and are removed by bio-oxidation, adsorption onto sludge and air oxidation (Liu *et al.*, 1996). Resin acids have been shown to be problematic in anaerobic treatment plants - often causing inhibition of methanogens (Patoine *et al.*, 1997; Bicho *et al.*, 1995).

The resin acid content of wastewater streams in pulp and paper mills has been found to vary seasonally (Bicho *et al.*, 1985) perhaps as a function of changes in the wood furnish or possibly due to in-mill changes. Total resin acid content of the chip wash stream from a mill in the interior of British Columbia was found to be significantly higher (60%) in the winter months (December - February) than in the summer and fall (Bicho *et al.*, 1995).

Fatty acids (FA) are straight chain carboxylic acids having an even number of carbon atoms ranging from 12 - 24. In mechanical pulp suspensions, fatty acids exist primarily as "bound" esters rather than free fatty acids. Fatty acid removal in biological treatment systems is nearly 100% (Voss, 1987).

"Pitch" is a term used to describe colloidal deposits of free fatty acids (5-15%), esterified fatty acids (30-55%), glycerols (30-50%) and resin acids (2-40%) and their esters (Mouyal, 1996). Pitch is known to be highly problematic in papermaking, causing deposits on paper, wires and felts of the paper machine (Nguyen and Dreisbach, 1996) and slowing production by diminishing water drainage and decreasing paper strength, resulting in costly web breaks and shut-downs (Jacobs, 1995).

The presence of resin and fatty acids at high concentrations, can cause pitch to form as a thin layer on the surface of fines and fibers and as droplets freely suspended among the fibers in the process water (Jacobs, 1995).

Cationic Demand

Closing of the whitewater system will give rise to an increase in cationic demand (also referred to as "anionic trash" or detrimental substances) as these compounds are only partially adsorbed or not adsorbed at all onto solids in the paper stock, and as such, accumulate in the water circuit (Linhart *et al.*, 1987; Mikkonen and Eklund, 1996). This group of compounds is particularly prevalent in TMP pulping wastewaters and consists primarily of acid soluble lignin, Klason lignin, carbohydrates, uronic acids, fatty acids, resin acids, acetic acid, acetyl compounds, organic extractives and minerals (Alince, 1987). The "anionic" nature of this material is associated with the dissociation of carboxyl and sulfonic acid groups, and specifically adsorbed hydroxyl groups. These compounds form a relatively stable suspension, as the particles are prevented from settling by repulsive electrostatic forces (Nylund, 1993). The accumulation of cationic demand within the water system is limited by the solubility of each compound - at extremely high concentrations, some cationic demand will agglomerate

onto the active surfaces of solids materials - leading to paper deposits and runnability problems (Linhart *et al.*, 1987).

Control of cationic demand is of particular concern to papermakers concerned with the retention of fillers, fines and additives (Alince and Pikulik, 1991). Retention is an important control parameter to minimize fiber loss, to reduce deposits on paper forming equipment responsible for corrosion and, in a closed system, to maximize the quantities of BOD, COD and nutrients which leave with the paper stock - preventing microbial growth in the whitewater system (Foster and Rende, 1997). Retention aids, typically high molecular weight cationic polymers, are added to mechanical pulp suspensions to increase the retention of fines and fillers by adherence to the surface of the fiber particles and "bridging" between individual fibers (Mikkonen and Eklund, 1996).

Cationic demanding substances interact with these cationic polymers and reduce the effectiveness of these retention aids by three mechanisms: decreasing the effective volume of the polymer, shielding the effective cationic charge, and complexing with the polymer to form polyelectrolyte complexes (PEC) which are ineffective as retention aids (Barnett and Grier, 1996; Nylund, 1993; Jacobs, 1995). Figure 2-1 shows the change in effective volume of the polymer with increased salt concentration, an indication of the decreased effectiveness of cationic polymers with high contaminant concentrations.

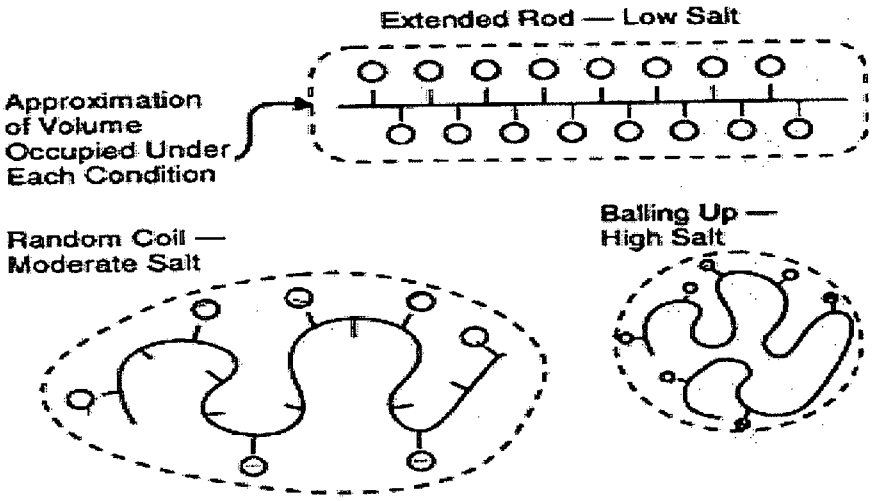

Figure 2-1: Configuration of a Linear Cationic Polymer (taken from Pietschker (1996))

The degree to which cationic demand limits the effectiveness of retention aids is a function of a number of factors including pH and salt concentration (Foster and Rende, 1997; Mikkonen and Eklund, 1996; Nylund, 1993), the effective charge of the polymer (Linhart *et al.*, 1987), type of polymer, concentration of suspended colloidal and particulate matter (Sundberg, 1995) and ionic strength of the whitewater (Alince and Pikulik, 1991; Penniman, 1995).

Linhart *et al.* (1987) identified some actions which can be taken to minimize the effect of cationic demand on retention aid systems: correct selection of raw materials; improvement of the water circuit; purification of fresh water and whitewater; removal of detrimental substances with the paper stock by use of fixing agents and choosing a suitable combination of cationic retention aids.

UV-Lignin

UV-lignin, so-called for the fact that it comprises the majority (>70%) of all material in pulping effluents which absorbs light in the ultraviolet region, is the second most abundant component of wood. Lignin is the glue, or cement which binds the cellulose and hemicellulose fibers together to give wood its structural rigidity. Lignin is a high molecular weight, complex, three dimensional aromatic polymer composed of three phenyl propane monomers. Lignin is only soluble in water when it has been broken down into smaller fragments. (Voss, 1987).

Due to its inherently insoluble nature, lignin is associated with the "colloidal" fraction of whitewater, consisting of high and low molecular weight lignosaccharides adsorbed onto colloidal resin particles (Jacobs, 1995).

Lignin, when in high concentrations, such as in closed whitewater systems is a major component of pitch (refer to "Resin and Fatty Acids") and a primary culprit in the neutralization of cationic polymers used as retention aids.

2.3.2 Corrosion

Increased temperatures and high concentrations of dissolved solids, and gases, enhanced biological activity and failure to provide adequate cleaning and flow result in substantially increased rates of corrosion in closed mill systems (Bowers, 1983).

Hubbe and Bowers (1978) examined 30 northern European mills which were closed or partially closed, and found that lower pH (below 5) and high alum concentrations resulted in

corrosion of mild steel and brass, for all grades of paper production. A number of authors (Robinson, 1982; Thompson and Garner, 1996) have documented increased corrosion of 304 stainless steel, although corrosion of 316 SS was very uncommon. Corrosion of 304 SS appears to be of three types (Robinson, 1982)) heat affected zone (HAZ) pitting on welded coupons; ii) pitting of guillotined edges and iii) pitting on plain surfaces - initiated by a scratch of other surface defect. Corrosion by galvanic action may be enhanced when mixed metals are installed with new process equipment (Bowers, 1983).

Increased concentrations of "critical" ions - thiosulfate ($S_2O_3^{2-}$), sulphate (SO_4^{2-}) and chloride (Cl^-) have been shown to cause increased pitting, increased propagation rates in crevice corrosion and increased cracking in austenitic steel (Thompson and Garner, 1996). Sodium hydrosulphite, a common bleaching agent in mechanical pulping, dissociates by the following reaction to produce sodium thiosulfate:

$$H_2O + 2Na_2S_2O_4 \rightarrow Na_2S_2O_3 + 2NaHSO_3$$

A number of other whitewater characteristics have been shown to influence the rate and degree of corrosion of process machinery including: pH (the production of sodium thiosulfate drops off rapidly above pH 5); concentration of organic acids and microbiological activity (Bowers, 1983).

Corrosion in closed systems can be minimized by reducing the concentration of Cl^- in the whitewater; restricting the use of sodium hydrosulfite, increasing the pH of pulp stock prior to bleaching, and replacement of 304 SS piping with 316 SS.

2.3.3 Product Quality

Decreased fresh water usage in the manufacture of TMP-newsprint would result in increased concentrations of certain key contaminants (e.g. lignin, extractives and carbohydrates) which could negatively impact the quality of the finished product.

A number of investigations, presented here in chronological order, have examined the effects of whitewater closure on TMP pulp and newsprint. Heller *et* al (1979) operated a pilot scale paper machine under complete whitewater recycle conditions and found problems with brightness reversion, color, sizing and first pass retention. Increased conductivity, extractives and sulfate concentrations have been shown to have a detrimental effect on electrochemical mechanisms required for drainage, retention, and sizing and decreased physical strength of the newsprint (Wenzl, 1981). Wenzl also observed that increased anaerobic microbiological activity in the whitewater system resulted in production of H_2S, and acetic, propionic, butyric, and lactic acids resulting in strong putrefactive odors in the finished product. Järvinen *et al.* (1985) found that increased lignin, carbohydrate and extractive concentrations resulted in lowered brightness and slightly decreased tensile strength but that opacity and light scattering properties of the newsprint increased with whitewater closure. No change in the printing properties of newsprint produced under closed conditions was observed (Järvinen *et al.*, 1985).

Wearing *et al.* (1985a) performed an extensive series of experiments examining the effect of closure on newsprint properties. Increased concentrations of lignin, extractives,

polysaccharides and other surface active components were found to change the hydrophobic/hydrophilic balance of the fiber and effluent, resulting in decreased interfiber hydrogen bonding and strength and a reduced effectiveness of brightening agents. Wet web tensile strength and dry strength properties were impaired as a result of lower surface tension forces, reduced fiber/fiber interaction, decreased bonded area and decreased bond strength. Handsheet drainage time was found to be unaffected by the increased concentrations of dissolved and colloidal substances, while the optical properties of the handsheets appeared to be slightly affected by the increase. Of all contaminants, fatty acids were identified as the most detrimental due to their high surface activity (Wearing *et al.*, 1985a).

It has been determined that increased concentrations of colloidal particles (0.1 - 1 μm), composed primarily of extractives, decreased the tensile strength of newsprint (Francis, 1996a).

2.4 Closure Alternatives

2.4.1 Fresh Water Use Minimization

The primary step in the closure of integrated pulp and paper mills will be a reduction of fresh water usage from current values of 10-150 m^3/adt, to 2-5 m^3/adt, such that novel treatment alternatives become economically viable (Wearing, 1992; Robinson, 1982). In addition to increased closure opportunities, reduction of fresh water usage results in other savings including reduced effluent treatment costs, lower energy costs, higher recovery of fiber, reduced water treatment costs, and compliance with effluent regulations.

The fresh water requirement of a particular mechanical newsprint mill is determined by the quantity of contaminants released from the wood into the water stream during pretreatment, refining and bleaching, the type of paper being produced and the age of the mill. The concentration of contaminants in the water stream is a function of the type and extent of pretreatment, the presence or absence of interstage or pulp washing, the bleaching conditions, and the maximum allowable BOD in the effluent (conventional treatment systems should not have greater than 600 - 700 mg/L BOD) (Reside, 1994).

Whitewater management strategies are based on two main principles (Noel *et al.*, 1992): where possible, whitewater should be used to replace fresh water; and water streams must be segregated based on water quality (i.e. rich or cloudy whitewater should be kept separate from lean or clear whitewater). A high degree of whitewater closure can be achieved by replacing fresh water additions by recirculated whitewater of a suitable quality. The choice of which whitewater streams can be reused is primarily a function of the quality of the whitewater. Water use reduction in mechanical pulp and paper mills is often limited by the stringent water qualities perceived as being necessary for certain pieces of critical mill equipment, such as paper machine showers (Reside, 1994).

Simulation models can be used to estimate the degree of water reduction possible for a particular mill and the possible locations for water reuse in mechanical pulp and paper mills. Jantunen (1993) applied the RAMI dynamic simulation of mass and energy balances to an integrated pulp and paper mill and determined that replacement of fresh water with paper machine whitewater in pulp washing and the wood room could reduce fresh water consumption from over 20 m^3/adt to 6.9 m^3/adt.

Noel *et al.* (1992) used the PAPMOD steady state simulation package developed by Paprican to investigate water use reduction in a Canadian TMP-newsprint mill. For this particular mill, they identified four practical changes the mill could implement to limit fresh water requirements: i) recirculation of water from the paper machine section (following filtration to remove long fibers); ii) improvement of the cleaner circuit to increase fiber recovery from the rejects; iii) reuse of screw press whitewater and other highly contaminated streams as dilution for a high consistency streams; and iv) increased use of whitewater on paper machine showers along with the installation of self cleaning shower heads to prevent clogging.

Potential opportunities for the reduction of fresh water requirements have been investigated by a number of authors. Noel *et al.* (1992) suggested that the fresh water minimization would require mill wide control and management of whitewater inventories - allowing for fluctuations in individual chest levels and tank sizing capable of handling exceptional needs like paper breaks. Ropponen (1979) concurred that fresh water requirements could be minimized by controlling the number of chaotic events like accidental overflows which disrupt the water and fiber balance in a mill and by decreasing the volume of water leaving with rejects. Reside (1994) identified a number of streams with the potential for fresh water replacement within the mill, namely: saveall whitewater, cloudy/rich whitewater, paper machine rejects, press section whitewater, vacuum pump seal water, cooling water returns, evaporator distillates and dryer vapor. In addition, reduction of the pulp mill purge rate, an increase of the consistency of the final pulp press, recovery of heat, paper machine reject thickening, and use of clear whitewater for hoses, cleanup and showers could result in major savings in terms of fresh water requirements and as a result, effluent production.

2.4.2 Pulp Washing

As was briefly mentioned in the previous section, pulp washing is one means of reducing the fresh water requirements of an integrated TMP-newsprint mill.

Over 90% of the BOD, COD, extractives and trace inorganics (Na, K and SiO_2) found in TMP pulping effluents are derived from the dissolution of cellulosic substances during the mechanical defibration process (Breck and Wong, 1983). In a mill where the pulp is not washed, these contaminants are carried into the whitewater system and then distributed throughout the mill. Breck and Wong (1983) showed in laboratory experiments, that the overall effluent production of a TMP-newsprint mill could be reduced to 10-15 m^3/adt when pulp washing and pressing was incorporated, with some portion of the press filtrate being recycled into the whitewater system.

Henzel (1984) demonstrated the removal of 75% of the BOD load in the final effluent by washing the pulp prior to paper making in Consolidated's Fort Madison corrugated pulp and paper mill. By washing the pulp and removing a high proportion of the contaminants from the process with a relatively small volume of water, the volume of mill effluent can be reduced allowing for partial closure.

Wearing *et. al.* (1985b) examined two pulp washing arrangements (counter current and interstage washing) which would remove some contaminants from the pulp without increasing the final effluent volume and compared the mass and energy balances with a fully operational

integrated mill, using the GEMS dynamic simulator. It was found that the washing of pulp with recycled filtrate decreased the dissolution of wood components - that is, contaminants were more likely to remain bound to the fiber when washed with filtrate rather than fresh water. In a countercurrent washing arrangement, where fresh water is added at the paper machine, this may result in redissolution of contaminants in the paper machine section.

In addition, it was determined that an integrated TMP-newsprint mill instituting interstage washing could reduce effluent volume from 10 m^3/adt to 1.7 m^3/adt, as compared to 3.7 m^3/adt for a mill using a countercurrent whitewater arrangement, with pulp washing following the secondary refiner. However, interstage washing requires substantially higher capital costs and mill modification. Most mills have already instituted some degree of countercurrent flows, and pulp washing could be amalgamated with latency removal (Wearing *et al.*, 1985b).

2.4.3 Mechanical Vapor Recompression (MVR) Evaporation

The most successful technology used for mill closure to date is mechanical vapor recompression (MVR) evaporation. This technology is currently employed in the two zero effluent mills in Canada, and is described in detail in section 2.1.

2.4.4 Physical Chemical Treatment

Lagacé *et al.* (1993, 1996) examined the possibility of treating a low flow integrated TMP-newsprint whitewater using a lime addition and clarification in an attempt to improve the quality of the whitewater for recycle into the mill. This was proposed as a low cost alternative

for whitewater treatment, eliminating the need for expensive, maintenance-intensive equipment and high operating costs.

A whitewater was prepared to mimic a mill using 15 m^3 fresh water/adt by combining 80% TMP cleaner rejects with 10% contaminated condensates from heat recovery and 10% chip wash water. Lagacé *et al.* (1993) found that they could remove 91% of extractives, 24% of the TOC, 43% of the color and 36% or the turbidity with an optimal dosage of 800 mg/L KH_2PO_4, 200 mg/L MgO and 1000 mg/L CaO. The addition of lime, however, resulted in increased dissolved concentrations of calcium and phosphate (628% and 1300% respectively). This may limit the reuse potential for this whitewater as the scaling potential would be significant.

In a second paper published by Lagacé *at al.* (1996), they cited the optimal dose of chemicals to be 500 mg/L KH_2PO_4, 300 mg/L MgO and 1000 mg/L CaO for removal of over 90% of the extractives and 60% of the color from whitewater. Again, the hardness of the treated effluent was very high, and the dissolved solids increased by 50%. They proposed a whitewater treatment scheme for recycle to include a physical-chemical treatment step followed by biological treatment step to remove smaller organic contaminants and then an ion exchange step to remove sodium from the effluent. This would suggest that physical-chemical treatment alone would be insufficient for treatment of whitewater for recycle to the mill, but it may provide an inexpensive option for removal of some contaminants.

2.4.5 Aerobic Biological Treatment

Conventional aerobic biological treatment or secondary treatment for pulp and paper mill effluents usually consists of an aerated lagoon, activated sludge treatment system (AST), or a sequencing batch reactor (SBR). The treatment process includes a primary treatment step, where the wastewater is settled in a primary clarification tank, an aerobic biological treatment step and a secondary clarifier where the biomass is settled from the treated effluent. Secondary biological treatment is the current "end-of-pipe" technology used to reduce organic material, suspended solids and toxic constituent concentrations to within effluent limitation guidelines.

The installation of secondary treatment systems for TMP-newsprint effluents was a result of the implementation of strict discharge limitations and guidelines promulgated to protect aquatic ecosystems. TMP-newsprint effluents have low pH (4.6 - 6.1), low alkalinity, low acidity and high concentrations of organic materials, dissolved and colloidal solids and toxic extractives such as resin acids, that are not removed by primary treatment alone (Thurley, 1983; Huster *et al.*, 1991). TMP whitewaters are toxic to fish, and anaerobic treatment alone is insufficient to completely detoxify these effluents (Lo *et al.*, 1994).

Thurley (1983), Servizi and Gordon (1986), Liver *et al.* (1993) and Lo *et al.* (1994) have published results from activated sludge (AST) pilot scale and mill scale plants treating TMP and CTMP effluents. Earlier studies (Thurley, 1983; Servizi and Gordon, 1986) suggested that long retention times (5-7 days) were required to remove sufficient levels of BOD_5 and to detoxify effluents, but more recent studies (Liver *et al.*, 1993a; Lo *et al.*, 1994) have shown that shorter retention times (8-24 hours) will remove up to 96% of the BOD_5 and 100% of the

influent resin acids can be removed from the influent stream. Degradation of organic components follows first order kinetics (Lo *et al.*, 1994) and requires careful control of biological parameters such as F/M ratio, sludge age and loading rate to optimize removal and prevent sludge bulking (Liver *et al.*, 1993).

Conventional aerobic systems are relatively simple to operate and are capable of treating TMP effluent sufficiently for discharge into the environment under current legislation. However, aerobic biological treatment requires high capital (large storage tanks, and control equipment) and operational (nutrient addition, cooling, pH neutralization, aeration, sludge disposal) costs and is susceptible to system upsets. Drastic changes in effluent composition, as a result of a spill or break can disrupt aerobic biological systems and may result in incomplete treatment or "toxicity breakthrough" (Roy-Arcand *et al.*, 1996). At temperatures greater than 40 °C, problems with biomass decay and sludge settling can also occur (Johnson, 1995; Liu *et al.*, 1993a).

Roy-Arcand *et al.* (1996) investigated the use of ozonation in conjunction with an aerobic biological system to treat high strength TMP wastewaters. They examined the pretreatment of the high strength components of the wastewater stream (e.g. wood room and chip wash wastewaters) with ozone prior to biological treatment and found an improved removal of contaminants.

Johnson and Hall (1995) examined the treatment of a simulated, low effluent, integrated TMP-newsprint whitewater with a sequencing batch reactor at temperatures of 20, 30, 40, 45 and 50 °C. They reported removal of COD from 76-65%, removal of dissolved and colloidal

solids (32-25%) and high removal of fatty (92-95%) and resin acids (99 - 100%) below 40 °C. Above 40 °C, fatty acid removal was 95-96% but removal of all other contaminants significantly decreased. The lowered contaminant removal efficiencies were observed concurrent to lower reactor biomass concentrations and reduced substrate utilization rates and growth yields.

2.4.6 Recycle of Secondary Effluent

Wearing (1992) suggested that one option for mill closure is the reuse of secondary treated effluent (possibly following a tertiary polishing step) in mill operations. A number of North American pulp and paper operations reuse treated sewage or treated mill wastewater mixed with treated linerboard effluent as the mill water source (Dorica *et al.*, 1996).

Dorica *et al.* (1996) examined a TMP-newsprint wastewater treated by a full scale primary treatment system (including coagulation and flocculation) followed by a pilot scale air activated sludge system, for reuse within a mill. The treatment system was capable of removing 95% of the influent BOD_5, 91% of the COD, 94% of the total suspended solids (TSS), 87% of the color and 99% of the resin and fatty acids. Even with high treatment efficiencies, the concentrations of COD, TSS and color in the treated effluent were still 80-120% higher than the surface water used in the mill. Concentrations of certain metals and ionic species - aluminum, calcium, silicate, chloride and sulfate - were also slightly higher in the treated effluent. Mixing of the treated effluent with surface water in various proportions also yielded interesting results. Residual ionic species in higher concentrations in the treated effluent responded in a straight line dilution, but a synergistic removal (9-30%) was observed

with COD, potassium, aluminum, iron and manganese. With this information, they attempted some steady state modeling of replacement of the mill fresh water supply with a mixture of a 1:1 fresh water:treated effluent and found that the expected steady state concentrations of most contaminants would be in the range presently encountered in pulp and paper operations.

2.4.7 Anaerobic Biological Treatment

Anaerobic biological treatment is similar to aerobic biological treatment, in that it may consist of primary clarification followed by a biological (in this case anaerobic) step and, often, secondary clarification. Anaerobic biological treatment has a number of advantages over aerobic biological treatment (Jurgensen *et al.*, 1985) including reduced capital and operational costs, an ability to treat high strength wastes and methane production to offset power costs. Anaerobic systems can tolerate higher organic loading rates than aerobic systems as they are not limited by oxygen transfer (Ince *et al.*, 1993).

Anaerobic treatment has seen some application as an internal "kidney" to purge contaminants from closed cycle waste paper mills (Huster *et al.*, 1991; Barascud *et al.*, 1992, 1993; Habets *et al.*, 1996). Huster *et al.* (1991) discussed the idea of an installation of an anaerobic treatment step into the whitewater circuit of a plant processing waste paper to prevent the build up of impurities in the water circuit and deposits on the product. Barascud *et al.* (1992) built a lab scale upflow anaerobic sludge blanket (UASB) to treat whitewater from a recycled paper mill and were able to remove 75% of the COD from the high strength wastewater (10,000 mg/L) stream. A pilot scale application of this same technology was only able to remove (64 - 42%) of the influent COD, but resulted in reduced cationic demand and

improved sheet forming characteristics and strength properties of the paper when used in paper forming experiments.

Habets *et al.* (1996) documented the installation of a pilot scale treatment system with an aerobic "polishing" step to removed dissolved and colloidal solids, volatile fatty acids, secondary stickies and anionic trash at the Zulpich Papier recycled paper mill in Cologne, Germany. The anaerobic stage was able to degrade carbohydrates, VFA's and sulphates to produce methane and hydrogen sulphide for low energy consumption and a low biomass growth. However, the degradation was incomplete and produced odorous byproducts which could contaminate the final product. The aerobic polishing step was able to convert the remaining organics to carbonate and remove calcium hardness in the form of a calcium carbonate precipitate, and remove the odor causing compounds.

Schnell *et. al.* (1990) examined the effluent management system at the Spruce Falls Power and Paper Co. in Kapuskasing, Ontario and found that a pilot scale high rate anaerobic treatment system installed at the mill was incapable of completely detoxifying the effluent and removing sufficient quantities of BOD_5 to meet effluent discharge requirements. In this case also, an aerobic treatment step was added to remove the residual BOD_5 and resin acids.

Rintala and Lepistö (1992) examined the feasibility of treating a TMP whitewater for reuse within the mill by batch anaerobic treatment at 35, 55 and 65 °C and UASB treatment at 55 and 70 °C. The TMP effluent was treatable at all temperatures - 65-75% of the influent COD was removed in the UASB at 55 °C and 60% of the COD was removed in the 70 °C reactor.

They found that carbohydrates accounted for 40-50% of the COD removal and that methane was produced from 57-85% of the metabolized COD.

Low molecular weight and monomeric lignins and fatty acids are easily degraded in anaerobic treatment systems, while resin acids and high molecular weight lignin usually comprise the recalcitrant fraction of COD. Anaerobically treated effluent is darker in color, likely due to the increase in chromophoric phenolic groups produced in the breakdown of polymeric lignin (Rintala and Lepistö, 1992; Sierra-Alvarez *et al.*, 1990).

The quality of the anaerobically treated effluent may be negatively impacted by the high decay rate of thermophilic bacteria - Rintala and Lepistö (1991) found that some portion of the COD in the treated effluent was a result of bacterial lysis.

Jahren and Rintala (1996) studied the closure of a TMP whitewater circuit by the insertion of a UASB at 55 and 70 °C. They built a treatment system in which the whitewater was passed through a UASB and was then cycled through a "hot disintegration" process (to mimic pulp washing) and then returned to the UASB. They found that the UASB was able to remove all COD, carbohydrate and UV-Lignin that was dissolved in the hot disintegration step and that the system was stable following two recirculations. The study did not examine the influence of the UASB effluent on product quality, although the pulp washed with the effluent from the UASB was reported to be discolored and less cohesive.

2.4.8 Ultrafiltration

Membrane separation processes remove contaminants from a feed stream based on steric exclusion and/or interaction of the solute and solvent with the membrane surface. Nonporous membranes remove unwanted contaminants by molecular interactions with the membrane surface, while porous membranes transfer the bulk fluid through the membrane leaving the contaminants behind (Pfromm, 1996). Classification of porous membranes is based on the molecular weight cutoff (MWCO) and pore size of the rejecting surface - microfiltration (MF) has a pore size of 1000-10000 Å, ultrafiltration (UF) has a pore size of 10 Å, and reverse osmosis (RO) has a pore size of 1 Å. Nanofiltration (NF) lies between ultrafiltration and reverse osmosis (Bryant and Sierka, 1993).

Membrane filtration is generally operated under "cross flow" conditions in which membranes are configured in a tubular arrangement and the liquid to be clarified is pumped axially through the membrane tube under pressure. The pressure forces the permeate (primarily solute and some fraction of dissolved materials) to pass through the membrane while larger solutes and solids are retained in the feed stream. Some rejected material accumulates at the membrane surface as a "gel layer", imparting an additional resistance to permeation in a process referred to as concentration polarization. The thickness of this layer is controlled by the axial flow of fluid through the membrane tube which creates a shear stress field parallel to the membrane surface retarding the accumulation of a thick filter cake. Under steady state conditions, the convective transport controlling the accumulation of a gel layer, and the shear force dispersion, balance each other (Upton *et al.*, 1997). The rate at which permeate is produced per unit area of membrane is referred to as the flux (J), and can be modeled by the following equation:

$$J = \frac{\Delta P}{\eta \times \Sigma(R_m + R_p + R_c)}$$

where:

ΔP = transmembrane pressure

η = dynamic viscosity

R_m = resistance associated with the membrane

R_p = resistance associated with pore plugging

R_c = resistance associated with cake fouling of the membrane surface

The two major disadvantages of membrane treatment are the high energy requirement to produce permeate and the loss of flux resulting from membrane compaction and fouling of the membrane surface (Sierka *et al.*, 1994).

Ultrafiltration is able to remove most suspended and colloidal materials, including microbial matter from the feed stream at relatively high fluxes (Deitrich, 1995). Ultrafiltration compares favorably, in terms of capital and operational costs, to other closed cycle technologies (mechanical vapor recompression and freeze crystallization) at fluxes greater than 140 L/(m^2 hr) (Paleologou *et al.*, 1994).

Treatment of wastewaters by membrane filtration technology results in a treated filtrate or permeate and some volume of concentrate which still requires disposal following treatment. This concentrate can be burned in an incinerator or used in the manufacture of such products as adhesives (Dorica, 1986).

The original membranes used in filtration technology were constructed from organic polymers, but more recently, inorganic (ceramic) membranes have been introduced into use. Ceramic membranes are generally superior to organic membranes in thermal, mechanical and structural stability, chemical and microbiological resistance and ease of cleaning and regeneration. Ceramic membranes are constructed from inert mineral materials (such as zirconia or alumina) and generally consist of a porous, mechanically strong supports a few millimeters thick, upon which is superimposed a thin layer of a selective membrane (a few microns thick) with one or more intermediate layers sandwiched between the membrane and support (Hseih, 1988). Figure 2-2 shows a scanning electron micrograph of an alumina membrane and support.

Ceramic membranes generally have a sharply defined pore size, a high tolerance to extreme pH, to oxidizing and reducing environments, and radiation. They can easily be cleaned by removing single units from a module. They can also withstand temperatures of up to 350 °C and pressures of up to 15 bar (Pejot and Pelayo, 1993).

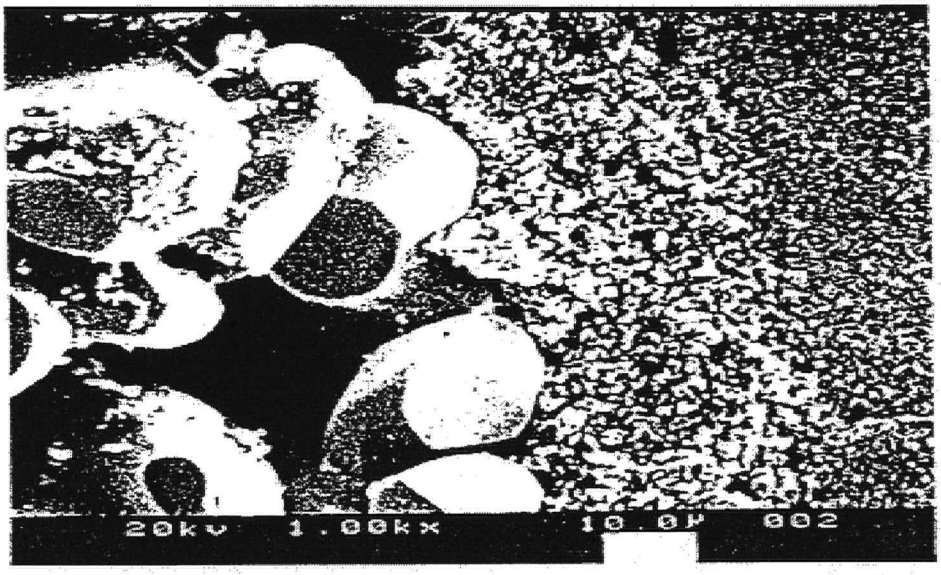

Figure 2-2: Scanning Electron Micrograph of Alumina Ultrafiltration Membrane (Hseih, 1988)

In ultrafiltration applications, fouling is primarily attributed to the deposition of colloidal material on the membrane surface. Rejected colloidal materials deposited on the membrane surface can be transported back into the bulk fluid by Brownian motion, by shear induced lift or by electrostatic repulsion. Diffusivity resulting from Brownian motion increases with decreasing particle size (<0.01 μm), while diffusivity as a result of shear induced lift increases with particle size (>10 μm) such that colloidal particles in the range of 0.01 - 10 μm are most likely to cause the fouling of ultrafiltration membranes (Ramamurthy *et al.*, 1995).

The nature and extent of fouling is influenced by the chemical nature of the membrane, the solution to be filtered and membrane/solute interactions. Proteins, salt, and lipids can adsorb onto the membrane surface and/or precipitate into the pores resulting in increased resistances, and decreased flux. Physical factors, such as temperature, flow rate, pH and pressure also affect the rate and extent of fouling (Cheryan, 1986).

Table 2-4: Comparison of UF studies on Pulp and Paper Effluents

Study	Operating Conditions	Performance
Dorica et al. (1985)	Membrane: Tubular Cross Flow	Flux: 198 L/(m^2•hr)
	MWCO: 20 kDaltons	Removal Efficiencies:
	Pressure: 1 MPa	% RFA = 100%
	Temperature: 75 °C	
	VRF 20	
Elefsiniotis et al. (1995)	Membrane: tangential flow	Flux: 48 L/(m^2•hr)
	MWCO: 10 kDaltons	Removal Efficiencies:
	Pressure: 240 kPa	% Total Solids = 21
	Temperature: 40 °C	% Dissolved COD = 35
	VRF 10	% RA = 25
		% FA = 94
Elefsiniotis et al. (1995)	Membrane: tangential flow	Flux: 72 L/(m^2•hr)
	MWCO: 100 kDaltons	Removal Efficiencies:
	Pressure: 240 kPa	% Total Solids = 13
	Temperature: 40 °C	% Dissolved COD = 20
	VRF 10	% RA = 45
		% FA = 100
Ekengren et al. (1993)	Membrane: Tubular cross-flow	Flux: 100 L/(m^2•hr)
	(negative charge)	Removal Efficiencies:
	Pressure: 750 kPa	% COD = 58
	Velocity - 3 m/s	% AOX = 63
		% RA = 55
		% FA = 75
Ekengren et al. (1991)	Membrane: Tubular cross-flow	Flux: 135 L/(m^2•hr)
	(negative charge)	Removal Efficiencies:
	Pressure: 750 kPa	% COD = 60-80
	Velocity - 4.5 m/s	% AOX = 60-9

Table 2-5: continuing (Table 2-4)

Study	Operating Conditions	Performance
Jönsson and Wimmerstedt (1985)	Membrane: Tubular cross-flow MWCO: 60 kDaltons Velocity - 4 m/s VRF: 10	Flux: 150 L/(m^2•hr) Removal Efficiencies: % COD = 50
Pejot and Pelayo (1993)	Membrane: Tubular cross-flow Pressure: 400 kPa Velocity - 4 m/s VRF: 15	Flux: 100 L/(m^2•hr) Removal Efficiencies: % COD = 75 % Total Solids = 32
Manttari et al. (1997)	Membrane: flat sheet cross flow MWCO: 8 kDaltons Pressure: 1.5 MPa Temperature: 40 °C Velocity = 3 m/s	Flux: 15 L/(m^2•hr) Removal Efficiencies: % COD = 56 % UV_{280} = 67
Nuortila-Jokinen et al. (1994)	Membrane: ceramic tubular cross flow MWCO: 10 kDaltons Pressure: 101 kPa Temperature: 25 °C VRF = 1.8	Flux: 54 L/(m^2•hr) Removal Efficiencies: % Cationic demand =72 % UV_{400} = 62
Nuortila-Jokinen et al. (1995)	Membrane: tubular cross flow MWCO: 8 kDaltons Pressure: 200 kPa Temperature: 41 °C Velocity = 2 m/s	Flux: 51-62 L/(m^2•hr) Removal Efficiencies: % COD = 20-8 % Dissolved Solids = 12-2 % Cationic demand =72-77 % UV_{280} = 24-7 % UV_{400} = 62

Ultrafiltration has been used in the pulp and paper industry for effluent treatment, concentration of dilute streams and fractionation (Jönsson and Wimmerstedt, 1985). Zaidi and Buisson (1991) published a comprehensive historical review of the use of membrane technology in the pulp and paper sector, noting the renewed interest in membrane treatment in the 1990's as a result of the increasing pressure on industry to reduce the discharge of toxic organics (with the long term expectation of eliminating discharges) and the improved manufacturing technology for membranes and membrane systems allowing for the production of membranes which are customized to suit specific requirements. Table 2-4 presents a comparison of UF treatment studies for pulp and paper effluents.

Ultrafiltration is a physical treatment technology to separate contaminants from a wastewater stream based on steric exclusion and membrane interactions which has seen extensive application and research in the pulp and paper sector as a result of its simplicity of operation and lower cost than some biological operations at higher temperatures.

2.4.9 Membrane Bioreactor (MBR)

The membrane biological reactor (MBR) is a wastewater treatment technology which is a modification of the activated sludge process, whereby the solid-liquid separation step is performed by an ultrafilter rather than a secondary clarifier. Activated sludge treatment systems often experience incomplete sedimentation or problems with sludge bulking, such that long HRTs, low biomass concentrations and tertiary polishing may be required to keep the quality of the final effluent high (Ilias and Schimmel, 1995).

The biological step of the MBR treatment system converts soluble organic contaminants into insoluble biomass, which can then be filtered out using the ultrafilter (Drummond *et al.*, 1992). The effectiveness of the solid-liquid separation is primarily a result of interactions between the membrane and the solute and solvent, in addition to steric (size exclusion) and electrochemical (Van der Waals) effects (Dufresne *et al.*, 1996).

Membrane bioreactor technology was conceptualized at the University of California at Los Angeles in 1959 when Sourijan and Loeb developed an asymmetric thin skin cellulose acetate membrane (Mishra *et al.*, 1994). By the mid-1960's Dorr-Oliver began to explore the technology of membrane ultrafiltration and in 1969 they oversaw the development of the membrane sewage treatment system (MST) (Budd and Okey, 1969). The MST consisted of a suspended growth aerobic biological reactor, from which effluent was drawn and passed through a membrane loop. The first large scale application of this technology was a pilot plant in the mid 1960's in Greenwich, CT. By the mid 1970's, Thetford systems developed a similar municipal sewage treatment plant, the "Cycle-Let" system. To date, there are over 80 Cycle-Let systems for aerobic and anoxic treatment of municipal wastewater. By the 1980's there were many versions of conventional MBR systems, both aerobic and anaerobic, available for the treatment of industrial wastewater. The major supplier of these systems in North America is Zenon Municipal Systems, with other versions in operation in Japan, Germany, South Africa and France including MEMBIO, Zenogem (part of Zenon) and ADUF treating a variety of municipal and industrial wastewaters (Janson and Mishra, 1993; Ross and Strohwald, 1994).

Membrane biological treatment offers a number of advantages over conventional biological treatment - smaller land space requirements, improved effluent quality (including complete pathogen removal (Aya, 1994)), operation at high biomass concentrations since all biomass is retained within the system, complete independence of hydraulic residence time (HRT) and solids retention time (SRT), reduced sludge production and reduced chemical costs (Zaloum *et al.*, 1996; Hare *et al.*, 1990).

The performance of any biological treatment system is dictated by the overall metabolic activity, which can be controlled by two parameters: A. active biomass concentration and B. biomass specific activity. A membrane bioreactor is able to operate under high concentrations of biomass, allowing for compact treatment systems capable of high organic loading rates. Lubbecke *et al.* (1995) examined the influence of high biomass concentrations (up to 40 g/L) on the biological response and the operating conditions in a membrane bioreactor. Loading was held constant over the course of the experiment, with the feed rate increasing with higher biomass concentrations. At biomass concentrations greater than 22 g/L they observed a wider distribution of floc size and a greater mean size. Above 30 g/L there was a drop in the flux across the membrane as a result of increased kinematic viscosity. In addition, the rate at which BOD_5 could be consumed (specific substrate utilization rate) dropped slightly (less than 0.5%) at high biomass concentrations.

One of the first commercial applications of membrane bioreactor technology was a pilot scale aerobic suspended growth reactor coupled with an ultrafiltration system for the treatment of oily wastewater from the automotive manufacturing industry. The system exhibited almost complete removal of BOD_5 and suspended solids, and COD removal ranging from 90.3% to

96.8% under a range of operating conditions (HRT = 1.8-3.4 days, SRT = 50-100 days) (Hare *et al.*, 1990). The manufacturing facility compared the cost effectiveness of three wastewater management options: ultrafiltration (which was the current treatment system), MBR treatment and physical-chemical treatment. It was determined that although ultrafiltration was the least expensive option, they would build a full scale MBR system in anticipation of additional imminent restrictions on wastewater discharges. Two full scale treatment systems were built at automobile manufacturing facilities in Ohio. The Mansfield, Ohio plant is treating 151 m^3 of wastewater a day containing (on average) 5643 mg/L COD, removing 100% of the BOD_5 and TSS and 97% of the COD (Knoblock *et al.*, 1994).

Zaloum *et al.* (1994) published the results from an MBR system treating wastewater from the metal transformation industry. The MBR system was capable of removing over 95% of the BOD_5 (as compared to only 60% removal by UF) and was able to detoxify the final effluent.

The use of MBR technology in the pulp and paper industry is still being examined at the pilot scale stage. Table 2-6 presents a comparison of some studies of MBR treatment of pulp and paper effluents.

One of the major design parameters in membrane biological treatment is the maximum attainable flux through the filter. As discussed in section 2.4.8, flux is defined as the volume of effluent passing through an area of the filter per unit time and is controlled by a variety of resistances.

Table 2-6: Comparison of MBR studies on Pulp and Paper Effluents

Study	Operating Conditions	Performance
Dufresne et al. (1996)	Membrane: Hollow Fiber	Flux: 30 L/(m^2•hr)
	MWCO: 0.1 μm	Removal Efficiencies:
	Pressure: 13.5 kPa (vacuum)	% COD = 80
	Temperature: 35 °C	% Total Solids = 36
	VRF 15	% Dissolved Solids = 32
Nuortila-Jokinen et al. (1996)	Membrane: cross flow flat sheet (neg. charge)	Flux: 38 L/(m^2•hr)
		20% loss of flux = 2 hours
	Pressure: 800 kPa	Removal Efficiencies:
	Velocity = 2.8 m/s	% COD = 77.9
Tardif (1996)	Membrane: tubular cross flow	Flux: 15 L/(m^2•hr)
	MWCO: 0.08 μm	Removal Efficiencies:
	Pressure: 79 kPa	% COD = 81
	Temperature: 55 °C	% Dissolved COD = 78
	VRF 37	% Total Solids = 43
		% Dissolved Solids = 38
		% RFA = 100
		% Cationic Demand = 53
Bohman et al. (1991)	Membrane: tubular cross-flow	Removal Efficiencies:
	MWCO: 8 kDaltons	% COD = 69-74
	Pressure: 1000 kPa (vacuum)	% BOD_7 = 69-74
		% AOX = 56-60

In the case of filtration of biosolids, flux is controlled by transmembrane pressure, viscosity and the resistances across the membrane surface (Magara and Itoh, 1991). The fouling resistance associated with cake fouling (R_c) is the predominant resistance in the filtration of biosolids, and the factors affecting it and its development have been the subject of extensive study.

Magara and Itoh (1991) found that the development of the cake layer was a function of the suspended solids concentration, and that the thickness of the cake layer was determined by fluid shear stress and operating pressure. They observed a decrease in flux with high concentrations of suspended solids.

Physiochemical models used to estimate flux when filtering a solution of abiotic particles have been found to underestimate the cross-flow microfiltration flux of colloidal particles (Shimizu *et al.*, 1993). Dufresne *et al.* (1996) suggested that the decrease in flux across membranes used in membrane biological systems is attributable to those substances with a molecular weight of more than 500,000. This is in direct contradiction to the published work of Shimizu *et al.* (1993) who found that the formation of the cake layer was controlled by the shear induced back transport of particles (controlled by lift velocity) which, in the filtration of a fluid with different size particles, is controlled by the smallest particles.

Temperature has also been shown to influence the flux across an ultrafiltration membrane. Chiemchaisri and Yamamoto (1994) found that flux decreased with decreasing temperature (from 25 -5 °C), as a result of the increase in kinematic viscosity.

The rate and extent of fouling of the ultrafilter in a membrane biological system is another important design consideration. Fouling by biosolids has been investigated by a number of authors.

Fane *et al* (1994) showed that in some cases the accumulation of only one layer of bacteria along the surface of the membrane is sufficient to reduce the flux by one or two orders of magnitude. Biomass particulates are colloidal and adhesive, and biofluids are adsorptive and tend to aggregate such that the fouling potential of biological suspensions is very high. They observed that the filtration of bacteria which form an extracellular (EC) matrix causes the void spaces in the filter to become filled with EC matrix which can impart the bulk of the hydraulic resistance across a filter. The extent of fouling and the difficulty of cleaning appear to be functions of the ionic concentration of the filtrate and the transmembrane pressure. To minimize fouling when filtering biological material, low to modest pressures should be used, and the filter should be an isoporous membrane of high porosity.

Shimizu *et al* (1994) observed that the shear stress applied by cross flow pumping used in the filtration process broke bacterial cells and induced the discharge of granulated matter such as glycogen and cell wall fragments. These particles were found to increase the mean specific filtration resistance, and to reduce the flux as a result of the increased cake fouling. They also reported that the steady state flux in a mixture of different size particles (such as a shear broken cell suspension) was controlled by the lift velocity of the smallest particle.

Choo and Lee (1996) examined the fouling in a membrane coupled anaerobic bioreactor (MCAB) and found that the external fouling was closely related to two factors: migration of cells to the surface of the membrane and inorganic precipitation. They found that 16% of the biomass in the reactor was associated with the membrane surface as a result of the shear stresses associated with mechanical pumping, the flow of permeate across the cell surface forcing cells to move and anchor to the membrane surface and the ideal growth conditions at

the membrane surface with a constant permeation of nutrients and substrate through the attached layer. The inorganic precipitate struvite ($MgNH_4PO_4 \cdot 6H_2O$) was found to harden the cake layer at the membrane surface and prevent sloughing of the foulant.

2.5 Technical and-Economic Assessments of Closure Options

Several authors have published economic and technical comparisons of closure options in an attempt to identify the most feasible technology to achieve zero effluent. Jantunen (1993) used the RAMI dynamic mass and energy balance simulator to compare the capital and operating costs for open and closed greenfield newsprint mills. The proposed technologies for the closed mill included a combination of evaporation, ultrafiltration and reverse osmosis to treat 6.9 m^3/adt water internally, while the open mill treated this same effluent in an external biological treatment plant. It was determined that there were no major differences in capital or operating costs between the open and closed greenfield mill. However, using this same model, the author concluded that the closure of an existing newsprint mill is unlikely to be profitable.

The lowest cost and optimal performance closed cycle configuration would be specific to each particular mill, requiring some combination of in-mill and ex-mill measures to achieve zero discharge. Gerbasi *et al.* (1993) examined three options for closing a TMP-newsprint mill producing 550 adt newsprint/day. The authors determined the capital and operating costs for the treatment of 20 m^3/adt, 10 m^3/adt and 5 m^3/adt of effluent by three systems: biological-membrane treatment (including anaerobic, aerobic, ultrafiltration and reverse osmosis unit operations); freeze crystallization and mechanical vapor recompression evaporation. These

costs were then compared with the capital and operating cost of a conventional end-of-pipe biological treatment plant with discharge to the environment. They determined that the costs associated with any of the closed cycle technologies were significantly higher than the cost for treating the effluent in a conventional secondary treatment plant, and the difference between these costs increased as the volume of effluent to be treated was increased. Of the three closed cycle technologies, they determined that evaporation is the least costly and most proven technology available for systems closure at this time. Suitable technologies for system closure must be insensitive to effluent flow rates, should treat the effluent only to the degree required and be able to be implemented in stages.

A techno-economic assessment for the closure of an older integrated-newsprint mill was developed to determine the relative costs of reducing effluent flows to 10 m^3/adt, 5 m^3/adt and 2 m^3/adt and then treating the effluent by evaporation (Francis *et al.*, 1995). These costs were compared to the costs of constructing and operating a biological (secondary) treatment plant and discharging the effluent. Effluent volumes were minimized by a number of measures: counter current water recycling, paper machine furnish thickening, ultrafiltration of whitewater for shower water and broke system sizing. Unlike the results reported by Gerbasi *et al.* (1993), this study found that effluent reduction and system closure had a higher capital cost but a lower operating cost than biotreatment and discharge, and that amortized over time, system closure was a more economically viable treatment option.

Braker *et al* (1996) examined four strategies for effluent reduction in a fully integrated TMP-newsprint mill: partial closure without effluent segregation, total closure without effluent segregation, partial closure with effluent segregation and total closure with effluent

segregation. With the use of a simulation model, they determined the operating concentrations of dissolved solids and the relative pay-back periods for each of the options.

Results from the model indicated that the biological system currently treating the effluent would require some modifications to assimilate the increased concentrations of contaminants present in the wastewater and that under total system closure scenarios, the concentration of dissolved solids could increase to values in excess of 13,000 mg/L, which could result in decreased product quality and increased corrosion of the system. Evaluation of all the options determined that partial closure without segregation of the process and non-process streams was the simplest option to implement, with a quick pay-back period, but that partial closure with segregation of process and non-process streams would ultimately be the best option to minimize biological treatment costs.

Wiseman and Ogden (1996) evaluated the costs for six options of zero effluent pulp and paper processing: physical treatment (clarification); physical treatment followed by biological treatment; physical treatment, biological treatment and membrane filtration; physical treatment and membrane filtration; mechanical vapor recompression evaporation and freeze crystallization. The authors noted that zero effluent would first require a major reduction in the volume of effluent to be treated, by means of such water reduction techniques as the use of mechanical seals, clarified whitewater for cleaning, savealls for fiber recovery, and the segregation of water streams. The conversion to a closed cycle system would require a major capital investment and the incurring of significant operating cost. It was determined that physical treatment alone, although being the least expensive option, would not produce sufficiently clean water for reuse. Membrane treatment was determined to be less expensive

(lower capital and operating costs) than MVR evaporation or freeze crystallization, but was thought to be of limited practical application as a result of its susceptibility to chemical fouling and attack.

Tardif and Hall (1997) examined ultrafiltration (UF), sequencing batch reactor (SBR), filtration of SBR effluent and MBR treatment of a minimum effluent integrated TMP-newsprint whitewater for reuse within the mill. They determined that the most effective removal of the contaminants of interest (resin and fatty acids, total dissolved solids, dissolved COD and dissolved organic carbon) was by the sequencing batch reactor followed by ultrafiltration. However, this treatment was only effective up to temperatures of 40 °C, such that it was not appropriate for high temperature applications. For high temperature treatment of this effluent, the MBR was judged to be the most suitable process for treating the whitewater. It was found that the MBR was stable under a range of operating conditions, and was able to remove 100% of the influent RFA, 84-72% of the dissolved COD and 18-37% of the dissolved solids. The MBR was shown to be a superior technology to the SBR for this application. The MBR allowed for total retention of solids, complete control of the sludge retention time, produced less sludge requiring disposal and was a more robust and compact treatment system.

2.6 Summary and Conclusions

A review of the current literature on systems closure in integrated TMP-newsprint mills yielded the following conclusions.

- Systems closure or closed cycle technology is a form of pollution prevention in which liquid effluents are minimized by recycling them back into the process. System closure in the pulp and paper industry is of interest due to increased public environmental expectations and increasingly stringent legislation.
- TMP-newsprint operations use large quantities of water; older mills in the range of 50-200 m^3/adt and newer mills in the range of 10-20 m^3/adt.
- Closure of pulp and paper mills will first require a drastic reduction in the volume of effluent requiring treatment, into the range of 2-5 m^3/adt.
- Closure of whitewater systems will result in a variety of effects, including: increased temperature (up to 70 °C), decreased oxygen levels and increased concentrations of various contaminants (solids - both suspended and dissolved, organics, resin and fatty acids, cationic demand and UV lignin), corrosion of piping and equipment and reduced product quality. Complete closure of TMP-newsprint mills will require management of contaminants at a levels at which runnability and product quality are not compromised.
- There are a number of alternatives available to close the water system in a TMP-newsprint mill - reduction of fresh water use and implementation of pulp washing as well as various treatment alternatives: mechanical vapor recompression evaporation, physical-chemical treatment, biological treatment (aerobic and anaerobic), recycle of secondary treated effluent, ultrafiltration and membrane biological treatment, most of which are still being investigated at a lab scale. Viable treatment alternatives must be able to withstand changes in effluent supply and quality, be able to treat effluent only to the level required and be able to be implemented in a staged fashion.

- Techno-economic assessments have been performed on some of the treatment technologies, with evaporation appearing to be the most viable treatment alternative presently available.
- Two promising alternatives for system closure which have not been demonstrated at pilot or full scale to date are ultrafiltration and membrane biological treatment. A direct comparison of these two treatment alternatives would provide valuable information about the treatment effectiveness and system capacity before pilot scale testing.

3. OBJECTIVES FOR THE RESEARCH

The hypothesis stated at the onset of this research was as follows: "*There will be an appreciable difference between the treatment capabilities of an aerobic membrane bioreactor and an ultrafiltration system for the treatment of a minimum effluent integrated TMP-newsprint whitewater when operated under identical conditions*".

As discussed in Chapter 1, this research project was part of an investigation into possible treatment options for a minimum effluent integrated TMP-newsprint whitewater for direct reuse within the mill. Related research completed prior to this thesis was as follows: Johnson (1995) examined the biological treatment of minimum effluent integrated TMP-newsprint whitewater by a sequencing batch reactor (SBR) at temperatures from 20 to 50 °C and an HRT of 2 days; Elefsiniotis (1994) investigated the treatment of this same whitewater by ultrafiltration at temperatures ranging from 10 to 50 °C using two plate and frame filters (operated in batch mode) with differing membrane pore sizes (10 and 100 kDaltons); Elefsiniotis *et al.* (1995) then considered the treatment of minimum effluent whitewater by SBR and UF in series, by filtering SBR effluent using the plate and frame 10 and 100 kDalton UF filters. Tardif (1996) considered the treatment of a similar minimum effluent whitewater by aerobic membrane biological reactor (MBR) at temperatures from 40 to 55 °C and HRTs of 0.7-2.8 days, with a ultrafilter of a MWCO of 75 kDaltons. The investigations into treatment options at that point had rendered several key conclusions (Tardif and Hall, 1996).

- Aerobic biological treatment of a minimum effluent integrated TMP-newsprint whitewater in a sequencing batch reactor (SBR) at temperatures between 20 and 40 °C resulted in removal of 40% to 100% of all contaminants of interest.

- At temperatures greater than 40 °C, treatment of the whitewater in the SBR resulted in poor contaminant removal efficiencies as a result of low biomass concentrations, poor sludge growth and poor sludge settleability.
- Ultrafiltration of the whitewater was unaffected by temperature, but yielded poor removal of most key contaminants of interest (with the exception of fatty acids).
- The sequential combination of SBR+UF resulted in significant removals of all contaminants considered, but was not feasible at temperatures greater than 40 °C (due to the poor settleability of the sludge), and resulted in the production of significant volumes of waste sludge and/or concentrate from both treatment systems.
- MBR treatment resulted in removal of 35% - 100% of all contaminants of interest (with the exception of color) under the full range of operating conditions considered: temperatures from 40 to 55 °C and HRTs of 0.7-2.8 days and produced minimal waste sludge.
- Flux through the MBR ultrafilter with a MWCO of 75 kDaltons was very low - (8-13 L/m^2 hr), a full order of magnitude lower than the flux through the UF membranes with MWCOs of 10 and 100 kDaltons used by Elefsiniotis (1994).

There were a number of unanswered questions remaining following these investigations:

1. What would the composition of a minimum effluent integrated TMP-newsprint whitewater be, and how could that be most closely simulated using existing pulp and paper mill wastewaters?
2. Does an MBR offer sufficient advantages over ultrafiltration to offset the additional costs associated with biological treatment (such as: aeration, temperature regulation, and

nutrient addition) and the potential for process instabilities under dynamic operating conditions?

3. What is the minimum hydraulic retention time in the MBR to adequately degrade the organic matter in the whitewater?
4. What is the effect of volume reduction factor (VRF) on the performance of the ultrafiltration membrane in the MBR and UF treatment systems?

It was thought that operation of an MBR and a UF system in parallel, (using identical membranes, under a range of operating conditions) treating a simulated minimum effluent TMP-newsprint whitewater could answer these questions.

Ultrafiltration membranes typically operate in the range of VRF = 3 to VRF = 15, while aerobic membrane biological systems operate at HRT's of 3 days to several hours. It was desirable that the range of operating conditions examined in this experiment would include the optimum range for each system. A minimum hydraulic residence time of 8 hours was chosen to comply with the experimental constraints of whitewater supply and to minimize whitewater storage time prior to use.

The approach chosen for this project attempted to address a number research objectives:

1. To compile a thorough review of any information in the literature pertaining to TMP, newsprint and integrated TMP-newsprint whitewaters and determine:
    - the most likely concentrations of key contaminants in a TMP-newsprint whitewater in a mill with excess flows of 2-5 m^3/adt, and

- the most reasonable approximation of that whitewater using existing pulp and paper wastewater streams.

2. To operate a lab scale ultrafiltration system and an aerobic membrane bioreactor in a manner that allowed for a comparison their treatment capabilities, maximum flux, fouling potential, and retentate characteristics.
3. To determine the effects of varying the hydraulic retention time (to a minimum of 8 hours) on the biokinetics of the MBR.
4. To investigate the behavior of an ultrafiltration system operated in a continuous fashion under varying volume reduction factors.
5. To compare the treatment capabilities and flux through the MBR and UF treatment systems when operated in parallel.

4. EXPERIMENTAL METHODS AND APPARATUS

In this section, descriptions of all materials and experimental methods used in this investigation are presented. Section 4.1 describes the apparatus used, Section 4.2 the materials, and Section 4.3 the methods. Section 4.4 gives a brief description and explanation of the experimental design used in this study

4.1 Experimental Apparatus

4.1.1 Membrane Biological Reactor System

A schematic of the system, which consisted of an aerobic biological reactor and ultrafiltration unit, is shown in Figure 4-1. All process piping was PFA (Teflon) except for the membrane module which was constructed from alpha alumina.

4.1.1.1 Aerobic Reactor

The aerobic reactor was constructed from clear polyacrylate tubing with a diameter of 25.4 cm (10") and a length of 29.6 cm. This reactor was surrounded by a second piece of tubing also 29.6 cm in length and 30.4 cm (12") which acted as a water jacket for temperature control. Ports were located in the lid of the reactor for feeding of wastewater and nutrients, and wasting of sludge. A thermocouple, aeration unit, three level controllers and a condenser, to prevent water vapor loss due to evaporation, were mounted on the lid of the reactor. Mixed liquor was pumped from the aerobic reactor to an ultrafiltration unit using a progressing cavity Moyno 500 pump, model number 33304-04 from Cole Parmer, Inc. The pump was powered by a 3/4 hp motor fitted with a variable speed controller. Liquid level in the reactor was 10 L for runs 1 and 2, and 5 L for run 3.

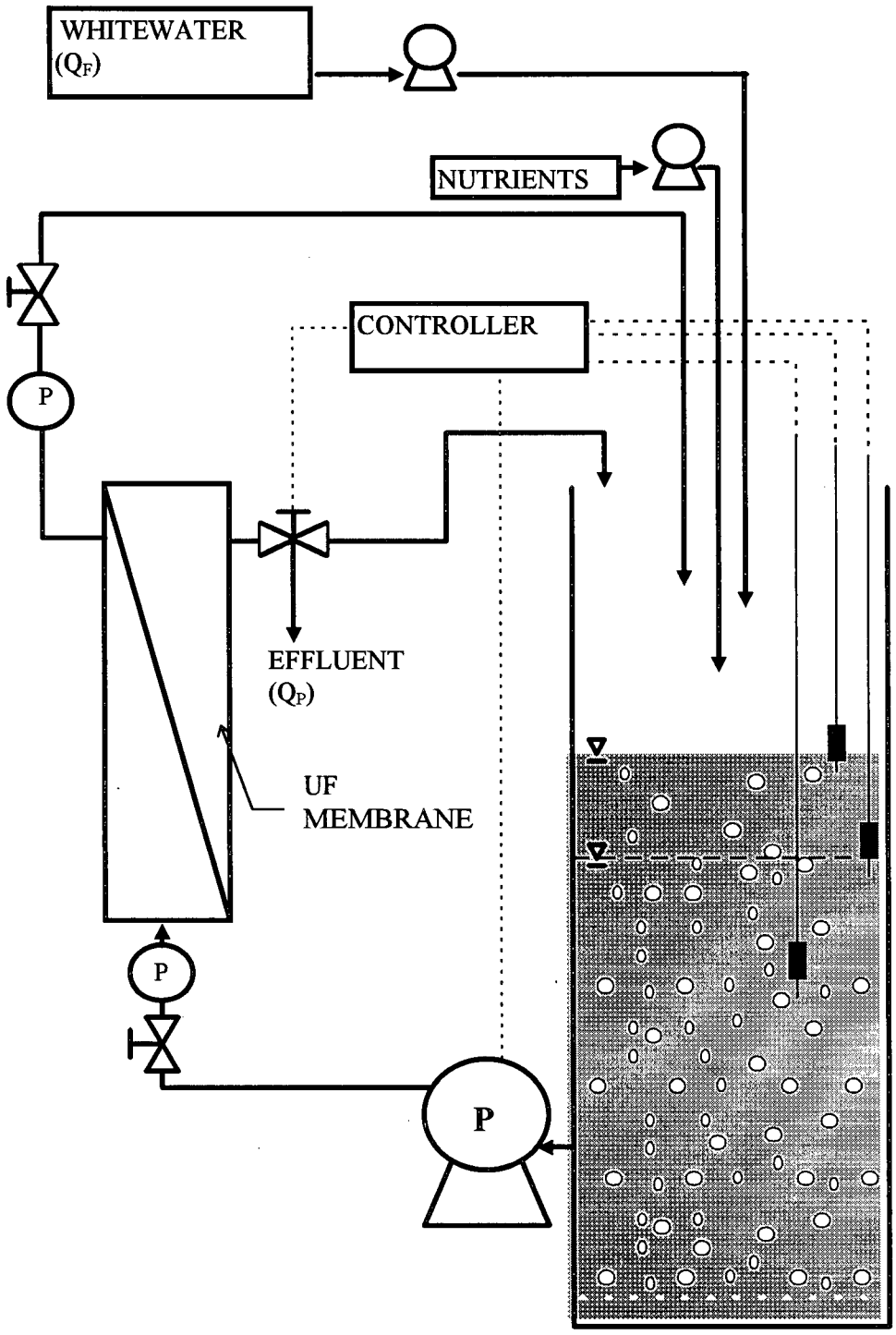

Figure 4-1: Aerobic Membrane Biological Reactor

4.1.1.2 Ultrafiltration Unit

The ultrafiltration membrane chosen for this experiment was a ceramic membrane with a pore size of 500 Angstroms, small enough to filter bacteria from solution. A pilot scale Membralox™ ceramic filter distributed by the United States Filter Corporation of Warrendale, PA was chosen for this experiment on the basis of its small size, its chemically inert nature, and ease of cleaning. The ultrafiltration unit consisted of a porous ceramic filter element sealed in stainless steel housing fitted with Viton gaskets. The ceramic membrane was constructed of alpha alumina (99.9% pure) supported by sub-layers of ceramic material through which the permeate flowed to two outlets on the side of the housing. One of the permeate ports was capped, such that permeate flowed from a single port. A diagram showing the unit and fittings is presented in Figure 4-2. The unit was removed from the system by disconnecting the 3/8" NPT fittings at each end of the filter.

The nominal pore size of the ceramic membranes was 0.05 μm. The filter unit was 250 mm in length with a channel inside diameter of 7 mm. The membrane provided a total surface area of 0.0055 m^2. The expected flow rate from the permeate port was 5 to 250 mL/min, corresponding to a flux of 50 to 2500 L/m^2 hr. The characteristics of the membrane, as provided by the manufacturer are presented in Table 4-1.

Pressure gauges were installed at the membrane inlet and outlet to enable measurement of the pressure drop through the tube and the transmembrane pressure. These glycerine filled gauges manufactured by WIKA, were able monitor pressures from 0 to 413 kPa (0 to 60 psi) and were fitted with chemical seals to prevent clogging of the gauges by particulate matter. The inlet pressure was maintained at approximately 138 kPa (20 psig). The flow rate through

the system was 10 L/min., resulting in liquid flow through velocities of approximately 4 m/s. Adjustments in pressure and flow rate were made by manipulating the pump speed and a plug valve on the concentrate line.

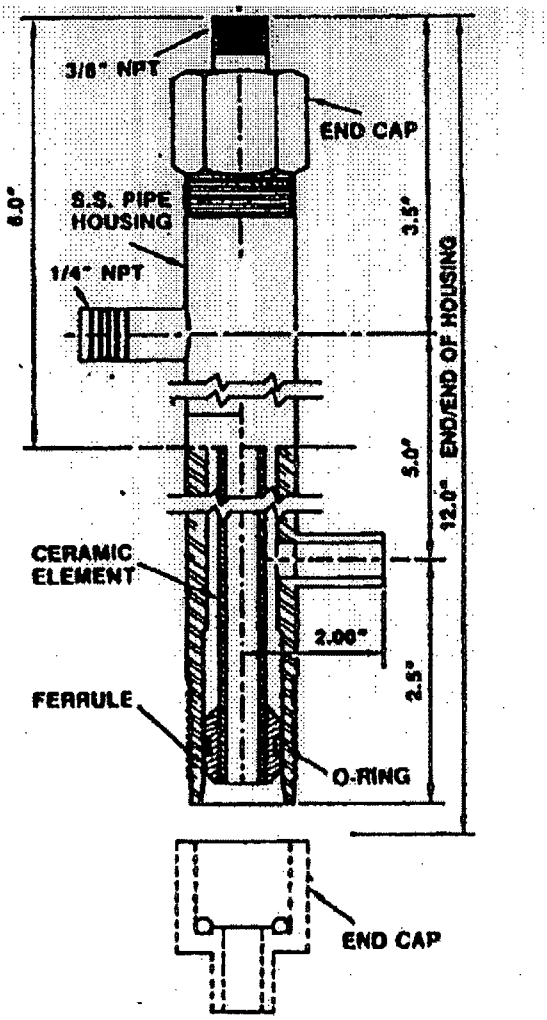

Figure 4-2: IT-70 Alpha Alumina Membralox Membrane (Membralox, 1996)

Table 4-1: Specifications and Operating limits of the Membralox 1T1-70 Ultrafiltration Membrane (Membralox, 1996)

Model	Membralox Ceramic Filter 1T1-70
Material of construction	99.9% alpha alumina
Housing Material	316 L stainless steel
Nominal Pore Size	0.05 μm
Configuration	single 7 mm internal diameter tube
Nominal Membrane Surface Area	0.0055 m^2
Maximum Operating Pressure	1030 kPa (150 psig)
Recommended Operating Pressure	140 - 200 kPa (20-30 psig)
Temperature Operating Range	0 - 300 °C
pH Operating Range	0 - 14
Recommended velocity	2 - 4 m/s
Suggested Flux (tap water)	5 - 250 mL/min.

4.1.1.3 Feeding and Wastage of the Reactor

A feed solution consisting of simulated, concentrated whitewater from a TMP mill was fed to the reactor using a variable speed Masterflex peristaltic pump and speed controller. A nutrient solution containing nitrogen from ammonium nitrate, and phosphorus from NaH_2PO_4, was fed to the reactor using a second Masterflex pump and controller. Volumetric flow rates delivered by the pumps were controlled by the speed of the pump motor. This was measured daily by means of a large graduated cylinder and timer and was adjusted as necessary.

Pumping of feed and nutrient solutions was activated once an hour by a Chrontrol timer to approximate a continuous feed. The composition of the feed and nutrient solutions are described in Sections 4.2.1 and 4.2.2 respectively.

Biomass was manually wasted from the reactor once daily to maintain a sludge retention time of 20 days.

4.1.1.4 Instrumentation

Temperature in the bioreactor was maintained at a constant 55 °C by a water jacket surrounding the bioreactor. Water was circulated from a 62 °C water bath using a centrifugal pump at a rate of approximately 40 L/min., which resulted in a mixed liquor temperature of 55 °C. The internal temperature of the reactor was measured using a YSI thermocouple suspended from the lid into the reactor contents.

Three level controllers were installed in the reactor to control the working liquid volume and to prevent over flow from the system or burn out of the recirculation pump in the event of a mechanical or system failure. One controller activated a three way solenoid valve which recycled permeate to the reactor when flux from the filter exceeded the feed rate to the reactor. This allowed for control of the hydraulic residence time through the feed rate. A second controller interrupted feeding to the reactor when a high level float switch was activated, and a third controller switched off power to the recirculation pump when the low level float was activated.

4.1.2 Ultrafiltration System

The system, consisting of a non-inoculated mixing tank and ultrafiltration unit, was identical to the membrane bioreactor system depicted in Figure 4-1, though the dimensions varied slightly. Total system volume was approximately 10 L, for run 2 and 5 L for runs 3, 4 and 5.

4.1.2.1 Mixing Tank

The mixing tank was constructed from clear polyacrylate tubing with a diameter of 20.3 cm (8") and a length of 52.8 cm. The mixing tank was surrounded by a second piece of tubing also 52.8 cm in length and 25.4 cm (10") in diameter which acted as a water jacket for temperature control. As in the membrane bioreactor, ports were located in the lid of the reactor for feeding and wastage, in addition to supporting the thermocouple and level controllers. Nutrients and aeration were not provided to the mixing tank. Concentrate was pumped from the mixing tank to an ultrafiltration unit using a progressive cavity Moyno 500 pump, model number 33304-04 from Cole Parmer, Inc. The pump was powered by a 3/4 hp motor fitted with a variable speed controller. The ultrafiltration unit, feeding and wasting system, and instrumentation were configured in the same manner as in the bioreactor.

4.1.3 Membrane Cleaning System

A schematic of the membrane cleaning system is shown in Figure 4-3.

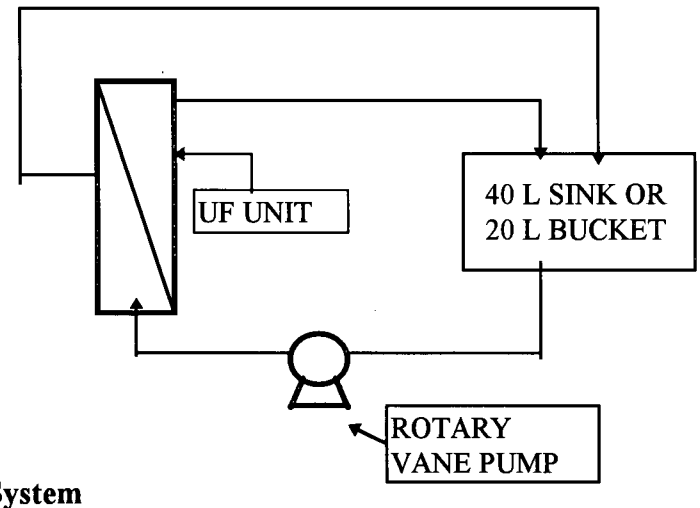

Figure 4-3: Cleaning System

The circuit consisted of a 40 L sink basin, two 20 L buckets containing stock solutions of acid and caustic and a rotary vane pump. Permeate flow rate was measured by collecting permeate as it was filtered into a graduated cylinder.

4.2 Materials

4.2.1 Wastewater Feed

The influent to the bioreactor and ultrafiltration system consisted of a simulated thermomechanical-newsprint whitewater with a composition that was based on whitewater characteristics predicted for a low water use or zero-effluent integrated newsprint mill, as presented in Section 2.2.2. The formulation of the feed was similar to that used by Johnson (1995) and Tardif (1996) and was derived in consultation with Wearing, Francis, and Reside.

The simulated closed mill integrated TMP whitewater was prepared by combining 125 mL of 35% w/w evaporator bottoms with 2.5 L of plug screw feeder pressate and 22.375 L of clear TMP whitewater to a total volume of 25 L. In order to remove suspended fiber, the effluent was passed through a 0.4 mm mesh screen. Simulated whitewater was made up approximately every four weeks and stored in carboys at 4 °C. Some fiber settled in the storage carboys, but the feed was mixed again prior to feeding.

Plug screw feeder pressate and clear TMP whitewater were collected from the Howe Sound Pulp and Paper thermomechanical pulp mill, where TMP pulp is manufactured from a 55% spruce, 45% hemlock balsam composite (hembal) furnish. Average collection temperatures were 85 °C for the plug screw feeder pressate and 65 °C for the clear whitewater. Evaporator

bottoms (35% w/w) from the zero-effluent Millar Western BCTMP mill in Meadow Lake, Saskatchewan, were stored at 4 °C until use.

4.2.2 Nutrient Solution

A nutrient solution was added to the aerobic reactor to provide nitrogen and phosphorus sources for cell metabolism and growth. The nutrient solution consisted of 110 g of NH_4NO_3 and 117 g of H_3PO_4 dissolved in 2 L of water. Nutrients were added separately from the feed solution in excess of the COD:N:P ratio of 200:5:1.

4.2.3 Biomass

The aerobic sludge used to seed shake flasks was collected from a variety of sources to provide a mixed microbial culture. Biomass sources were selected in an attempt to enrich for a thermophilic population that was able to degrade and metabolize typical constituents of the simulated thermomechanical pulping whitewater. Sludge was collected from the 47 °C auto-thermal aerobic digester (ATAD) at the Whistler municipal sewage treatment plant, in Whistler , B.C. and was mixed with mixed liquor (37 °C) from the treatment facility at Howe Sound Pulp and Paper, in Port Mellon, B.C., settled sludge from a bench scale municipal sewage treatment study at the University of British Columbia (UBC) at 22 °C and sludge (53 °C) from a bench scale kraft ATAD unit operating at the Pulp and Paper Center at UBC.

The biomass was re-seeded periodically with sludge from the bench scale kraft ATAD, and was cultured in a shake flask incubator as described in Section 4.3.1.

4.3 Experimental Methods

In this section, the techniques used for biomass acclimation, membrane cleaning, sampling and analytical methods will be described.

4.3.1 Biomass Acclimation

Seed biomass for the bioreactor was acclimated in a shake flask incubator. Organisms were cultured in six 1 L Erlenmeyer shake flasks at a constant temperature of 55 °C and agitated at a rate of 80 rpm. The shake flasks were removed from the incubator and biomass was wasted and wastewater and nutrients were fed at a rate corresponding to a three day hydraulic residence time. Biomass was acclimatized for two months in this fashion, after which it was transferred to the aerobic bioreactor operated in a batch mode for two weeks. For an additional 6 weeks prior to beginning the experimental period, the reactor was operated in a continuous fashion to further acclimatize the biomass.

4.3.2 Membrane Cleaning

Prior to removal of the membrane from the system for cleaning, the pressure on the membrane was relieved and biomass or concentrate was removed by opening the plug valves on either end of the filtration unit. The recirculation pump was shut off, the filter apparatus drained and valves closed, and the membrane module, gauges and valves were disconnected from the system. The membrane module, valves and gauges were then connected to the cleaning system and the permeate port was capped. The membrane was first rinsed with water for approximately 10 minutes. A 200-300 mg/L free chlorine solution made up from 130 mL of

5% NaOCl in 20 L water was then circulated through the system for 10 minutes at ambient temperature. The ultrafiltration unit was then drained and a 20 L stock solution of 2% NaOH solution was circulated for 20-30 minutes, first with permeate ports closed, and then at a transmembrane pressure of 5-10 psi for an additional 15-20 minutes. Following that, the spaces on both sides of the membrane were drained and the filter was rinsed with tap water for approximately 10 minutes, until the pH was close to neutral. The permeate ports were then closed, and the membrane was rinsed with a 1% HNO_3 solution for 15-20 minutes. The permeate ports were then opened at a transmembrane pressure of 10 psi for 10-20 minutes. The filter was then drained and water rinsed to neutral pH before being returned to the system. The clean water flux was then measured to confirm that the cleaning was complete. The cleaning process took approximately six hours to complete.

4.3.3 Sampling and Sample Preparation

All liquid samples were collected in washed and distilled water-rinsed Nalgene containers. Samples of whitewater influent, and permeate were collected daily from each system and were analyzed for total, dissolved and suspended solids, total and dissolved chemical oxygen demand (COD), resin and fatty acids (RFA), cationic demand and UV lignin. Samples (2 mL) for RFA analysis were preserved with 1 mL of a 50% methanol, 50% 2N NaOH solution and frozen in fired glass test tubes until extracted and analyzed. Samples of mixing tank concentrate and sludge were also collected daily and analyzed for total, suspended and volatile suspended solids.

Grab samples of the reactor and mixing tank contents were taken from the wastage line and analyzed for total and dissolved COD, and resin and fatty acids

4.3.4 Quality Assurance/ Quality Control (QA/QC)

All samples were analyzed in-house, following the analytical methods outlined below. Standards, blanks and in some cases, duplicates were analyzed as part of a quality control program. Further details are given in section 4.3.5. Percent removal data for each contaminant, for each water recovery fraction, are presented with 90% confidence intervals to indicate the variability of each data set.

4.3.5 Analytical Methods and Equipment

4.3.5.1 Solids Analysis

Samples were analyzed for total solids (TS), total dissolved and colloidal solids (TDCS), and total suspended solids (TSS) as described in Standard Methods for Water and Wastewater Testing (APHA *et al.*, 1989) immediately following collection.

Mixed liquor samples from the membrane bioreactor (MBR) and concentrate samples from the mixing tank were analyzed for total, suspended and volatile suspended solids content using a slightly modified method, as filtration of an adequate volume of sample using a Whatman 934-AH was not possible. Mixed liquor and concentrate samples were centrifuged at 3000 rpm for 30 minutes and a known volume of supernatant was filtered and dried at 104 °C to determine dissolved solids content. Volatile suspended solids from mixed liquor samples were calculated by difference. Table 4-2 outlines the methods used for solids analysis used in this study.

Table 4-2: Analysis of Solids

Solids type	Experimental Method
Total solids	A known volume of sample was oven-dried to a constant weight at 104 °C.
Volatile Solids (mixed liquor and concentrate samples only)	Sample from total solids determination was fired to a constant weight at 550 °C.
Total dissolved and colloidal solids (influent and permeate samples)	A known volume of sample was filtered with a Whatman 934-AH glass microfibre filter and oven dried to a constant weight at 104 °C.
Total dissolved and colloidal solids (mixed liquor and concentrate samples)	40 mL of sample was centrifuged for 30 minutes at 3000 rpm. A known volume of sample was filtered using a Whatman 934 AH glass microfibre filter and oven dried to a constant weight at 104 °C.
Volatile dissolved and colloidal solids (mixed liquor and concentrate samples only)	Sample from total dissolved and colloidal solids determination was fired to a constant weight at 550 °C.
Total suspended solids (influent and permeate)	A known volume of the sample was filtered using a Whatman 934-AH glass microfibre filter. Filter was then dried to a constant weight at 104 °C.
Total suspended solids (mixed liquor and concentrate samples)	Total suspended solids in the mixed liquor and concentrate samples were evaluated by subtracting the total dissolved solids form the total solids.
Volatile suspended solids (mixed liquor and concentrate samples)	The volatile suspended solids for the mixed liquor and concentrate samples were obtained by subtracting the volatile dissolved solids from the volatile solids.

4.3.5.2 Chemical Oxygen Demand

Influent samples were diluted 1:10, and UF and MBR permeate samples were diluted 1:5, with distilled water prior to analysis for total COD (TCOD). Samples analyzed for dissolved COD were filtered prior to dilution using Whatman 934-AH 1.5 μm microfibre filters. Permeate samples were not filtered and DCOD was assumed to be equivalent to the TCOD as the nominal pore size of the ultrafiltration unit (0.05 μm) was smaller than the pore size of the

glass microfibre filters (such that all the particulates would be removed). Diluted samples (2 mL) were added to COD vials containing a mixture of 1.6 mL of COD digestion reagent and 2.4 mL of acid reagent (APHA *et al.*, 1989). The vials were preserved at 4 °C until analysis. Samples were prepared and analyzed using the closed reflux colorimetric procedure (standard method 5220D) adopted by the American Public Health Association (APHA *et al.*, 1989). Chloride ions were found to be present in all samples, such that the standard method addition of mercuric chloride was required. Following digestion in a Hach COD reactor the absorbance of the samples and standards was measured at 600 nm using a Hach DR-2000 spectrophotometer.

4.3.5.3 Resin and Fatty Acid Analysis

Permeate and influent was sampled daily for resin and fatty acid (RFA) analysis. RFA concentrations were determined using a method adapted from Voss and Rapsomatiotis (1985) by the Pulp and Paper Research Institute of Canada (1988), and which was further modified in-house. Two mL of sample were placed in a fired glass test tube and 1 mL of a solution of 50% methanol and 50% 2N NaOH was added prior to freezing and storage Frozen sample tubes were then thawed immediately prior to extraction and were analyzed for resin and fatty acid content.

Grab samples of the mixed liquor from the membrane bioreactor and concentrate from the ultrafiltration unit were collected once per run. Samples were centrifuged at 3000 rpm for 30 minutes. The supernatant was retained as one sample, and the pellet, containing the particulates, was resuspended in distilled water to a volume equal to the original sample

volume of mixed liquor and kept as a second sample. This allowed for the determination of the resin and fatty acids in solution and bound to the solids. Samples were preserved and analyzed in the same manner as for the influent and permeate samples.

Each sample was neutralized with 2N HCl to between pH 9-11, after which an internal extraction standard of heptadecanoic acid was added. Samples were then extracted twice with equal volumes of methyl-t-butyl-ether. The solvent extracts were concentrated by allowing the methyl-t-butyl-ether to evaporate under nitrogen gas. An internal methylation standard (methyl heneicosanoate and tricosanoic acid) was then added and dried again under vacuum. Methylation of the resin and fatty acids was then carried by addition of 250 μL of a solution of diazomethane gas in methanol/methyl tert-butyl ether. The samples were then transferred to 100 μL glass inserts in 3 mL teflon-lined glass vials prior to analysis.

Derivitized RFAs were analyzed using a Hewlett-Packard 5880A gas chromatograph with 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) and detected using a flame ionization detector (FID). The carrier gas was helium at a linear velocity of 20 cm/s at 290 °C. The flame ionization detector (FID) makeup gas was composed of helium, hydrogen and purified air (flows of 20, 30 and 400 mL/min., respectively). The temperature regime used is detailed in Table 4-3. The method detection limit was approximately 0.1 mg/L.

Table 4-4 summarizes the resin and fatty acids measured in the samples analyzed. Resin and fatty acid concentration values reported are in mg/L as dehydroabietic acid (DHA), as DHA was used as the methylation standard. This approach has been used by Voss and

Rapsomatiotis (1985). Palustric and levopimaric acid concentrations were recorded as a pair as their peaks could not be separated.

Table 4-3: Temperature Program for Gas Chromatographic Analysis of Samples for Resin and Fatty Acids

Time (min)	Temperature(°C)	Rate of Change (°C/min)
1.00	150	stable
23.75	increasing	4 °C/ min
3.00	265	stable
5.00	290	stable

Table 4-4: Resin and Fatty Acids Quantified in this Study

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

4.3.5.4 Cationic Demand

The cationic demand of influent and permeate samples was determined upon collection using a method developed by the Pulp and Paper Research Institute of Canada (Kwong, 1994). Samples were centrifuged and a cationic polymer, 1,5-dimethyl 1-1,5 diazaundecamethylene polymethylobromide (DDPM) was added to the supernatant. The excess cationic polymer in the sample was titrated with an anionic polymer, polyvinyl sulfuric acid potassium salt (PVSAK), using toluidine blue O (TBO) as a color indicator.

A summary of the method is as follows.

1. A solution of 0.1 % toluidine blue O was prepared by dissolving 0.100 g of TBO in deionized water in a 100 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 with deionized water in a 1.0 L volumetric flask. This titration solution was used to standardize the PVSAK solution as detailed below, based on an equivalent weight of 187.11 and an average equivalent weight to cationic charge ratio of 200 for the DDPM.

3. A stock solution of approximately 0.002 N of PVSAK was prepared by slowly adding approximately 0.1622 g of PVSAK (obtained from ACROS) in 1.0 L of warmed deionized water. This solution was continuously warmed and stirred with a magnetic stir bar to enhance dissolution. An approximate 0.001 N solution was made up by dilution of this solution by 50% with deionized water. Standardization of the solution was carried out as follows:

a) A blank titration was carried out to determine the cationic demand of distilled deionized water. A 100 mL aliquot of deionized water was added to a 250 mL beaker and 3 drops of the 0.1 % TBO solution were added. The solution was mixed with a magnetic stirrer for 1 minute and then titrated with the PVSAK solution until a pink end point was reached. This volume ($V_{water\ blank}$) was then used for the calculations below.

b) The PVSAK solution was then standardized: 10.00 mL of 0.001 N DDPM solution 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

approximate 0.001 N PVSAK solution until the pink end point. This volume corresponds to $V_{PVSAK\ blank}$ in Equation 4.1.

$$N_{PVASK} = \frac{N_{DDPM} \times V_{DDPM}}{V_{PVASK} - V_{PVASK\ blank}} \qquad (4.1)$$

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 consumed for titrating 100 mL of deionized water containing three drops of TBO.

Process samples were centrifuged at 3000 rpm for 30 minutes and 20 mL of supernatant from each sample was diluted to 200 mL using a volumetric flask. One hundred mL of the diluted sample were then placed in a 250 mL beaker and 3 drops of 0.1 % TBO and 10.00 mL of 0.001 N DDPM standard were added. The samples were then mixed for one minute and titrated with the PVSAK titration solution until a pink end point was reached. This volume (V_{PVSAK}) was recorded. The cationic demand of the sample could then be calculated using Equation 4.2. 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 Equation 4.2.

$$\text{Cationic Demand} = \frac{N_{PVASK} \times (V_{PVASK} - V_{PVAK\,blank}) \times 2 \times 10^5}{V_{sample}} \qquad (4.2)$$

where:

N_{PVSAK} = Normality of the PVSAK solution (as determined from Equation 4.1)

$V_{PVSAK\ blank}$ = Volume of PVSAK consumed titrating 10.0 mL of DDPM in a deionized water blank

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

V_{sample} = Actual volume of sample (10.00 mL)

4.3.5.5 UV - Lignin

Influent and permeate samples were analyzed for UV lignin daily. Four mL of each sample were acidified with 3 drops of concentrated sulfuric acid and after mixing, were allowed to react and settle. Samples were then filtered using a Whatman 934 AH glass microfibre filter and 1 mL of the filtrate was diluted 200 times with distilled water. Diluted sample was then placed in a 1 cm glass cuvette and absorbance at 205 nm was measured against a standard of distilled water using a Hach spectrophotometer.

UV- Lignin concentrations were determined as follows:

$$\text{UV - Lignin (g / L)} = \text{Absorbance (@ 205 nm)} \times \text{Dilution} \qquad (4.3)$$

4.3.6 pH

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

4.3.7 Temperature

The mixed liquor temperature in the ultrafiltration system and in the membrane bioreactor was measured constantly and recorded daily using a YSI model 47 scanning tele-thermometer equipped with a submersible thermocouple.

4.3.8 Dissolved Oxygen

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

4.3.9 Permeate Flow Rate

The flow rate of the permeate from both systems was monitored daily by collecting permeate in a graduated cylinder and determining the volume filtered as a function of time.

4.3.10 Statistical Analyses

All percent removal data were analyzed for standard deviation and confidence intervals. The 90% confidence intervals are plotted on each graph to indicate the variability of the data presented.

4.4 Experimental Design and Operating Parameters

4.4.1 Water Recovery Fraction

Water recovery fraction (Y) was the key process design parameter varied in this experimental work. Water recovery fraction corresponds to the ratio of the permeate flow rate (Q_P) to feed flow rate (Q_F), and can be related to the volume reduction factor (VRF) as depicted in Equation 4.4.

$$Y = \frac{Q_P}{Q_F} = \frac{Q_F - Q_W}{Q_F} = 1 - \frac{1}{VRF} \qquad (4.4)$$

where:

Y = water recovery fraction; Q_P/Q_F

Q_P = flow rate of permeate, standardized flux (L/day)

Q_F = feed rate (L/day)

Q_W = wastage rate (L/day)

VRF = volume reduction factor

Volume reduction factor (VRF) is a means of expressing the degree to which the ultrafiltration unit has reduced the volume of the raw influent stream. For a batch system, this corresponds to the ratio of the original volume to be filtered (V_o) to the final, retained filtered volume (V). In a system run in a continuous fashion, this can be expressed as the ratio of feed flow rate (Q_F) to the wastage rate (Q_W).

Assuming a constant volume of retentate in the mixing tank, this can also be related to the sludge retention time (SRT) and the hydraulic residence time (HRT) (Equation 4.5).

$$VRF = \frac{Q_F}{Q_W} = \frac{(V / HRT)}{(V / SRT)} = \frac{SRT}{HRT} \qquad (4.5)$$

where:

HRT = hydraulic residence time; V/Q_F (days)

SRT = solids retention time; V/Q_W (days)

V = volume in reactor (L)

As discussed in the previous section, this study examined the effect of water recovery fraction on permeate flux and the removal efficiencies of certain key contaminants of interest from a low water flow TMP-newsprint whitewater in a membrane bioreactor and an ultrafiltration system.

Figure 4-4 and Figure 4-5 illustrate the experimental design used in this study. There were a total of five experimental runs - one on the membrane bioreactor alone, two with the membrane bioreactor and the ultrafiltration system running in parallel and two with the ultrafiltration system running alone.

Experimental runs one, two and three ran for approximately three weeks, with sampling almost daily. Run 3 was cut short for the ultrafiltration system (13 days versus 23 for the

MBR) as it was inoperable at the high volume reduction factor of 60. Run 4 (a duplication of run 2 for the ultrafiltration system) ran for 10 days with samples being taken (on average) every two days, and run 5 was approximately two weeks in length, with samples being taken every other day. Table 4.5 details the experimental program with respect to run duration, number of samples taken, solids retention time (SRT), hydraulic residence time (HRT), water recovery fraction and volume reduction factor. Runs were chosen to be approximately one solids residence time (SRT) - approximately 20 days (with the exception of run 4) , while the transitions were a minimum of 1.5 SRT (30 days). Transitions between runs were initiated the day following the last day of a run, such that the system was allowed approximately 30 days to acclimatize. Table 4-4 and 4-5 present the runs in chronological order, with run 1 beginning at day 0.

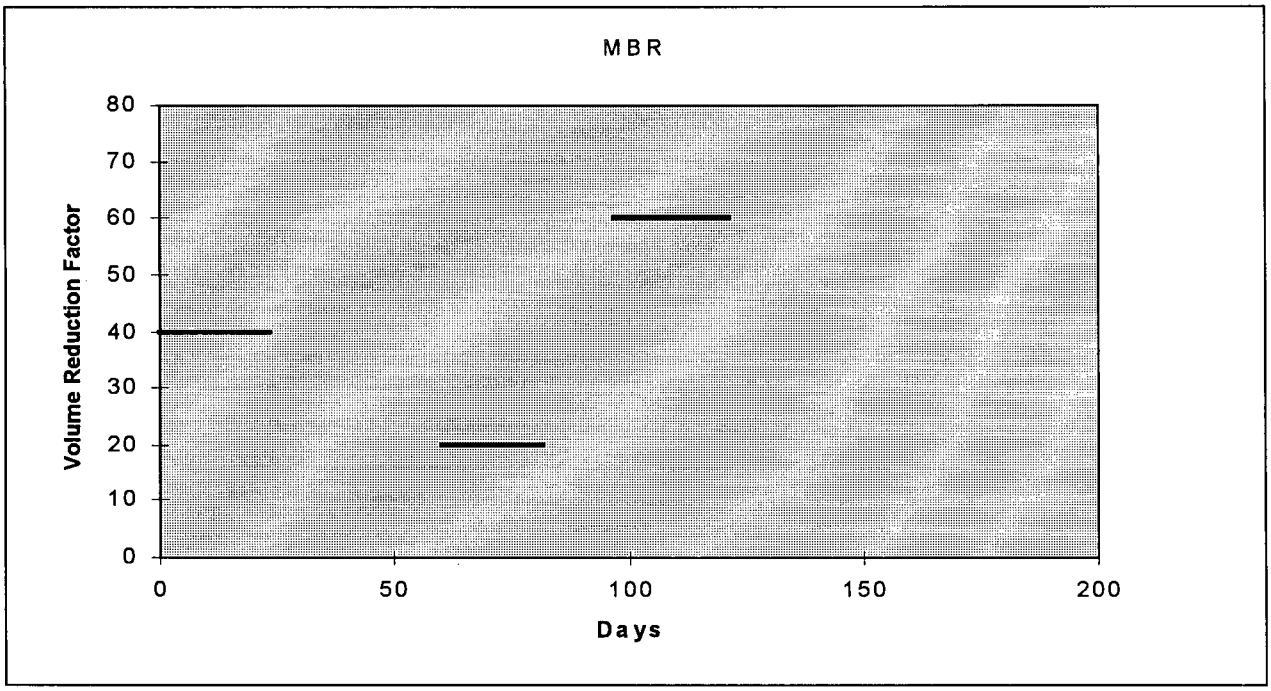

Figure 4-4: Experimental Program to investigate the application of an aerobic membrane biological reactor to treat low water use integrated TMP-newsprint whitewater.

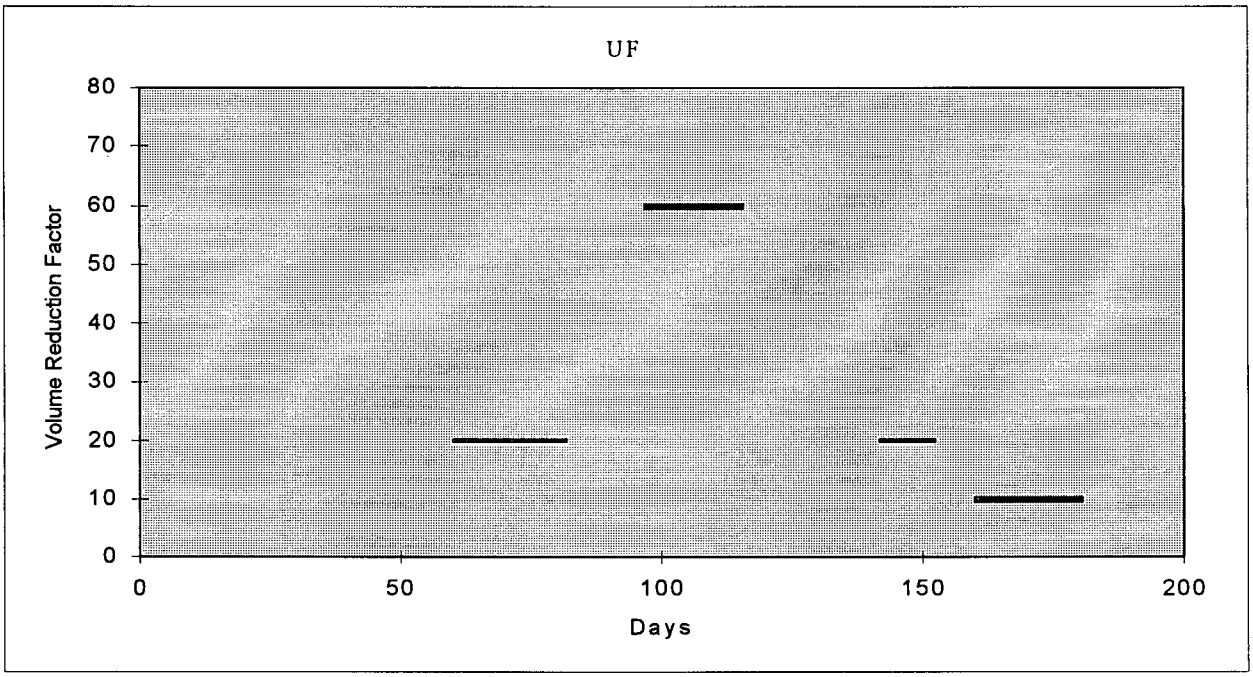

Figure 4-5: Experimental Program to investigate the application of an ultrafiltration system to treat low water use integrated TMP-newsprint whitewater.

Table 4-5: Experimental design and operational parameters

Run	Operational System(s)	Water Recovery Fraction (Y)	Volume Reduction Factor (VRF)	Duration (days)	Number of samples	HRT (days)	SRT (days)
1	MBR	0.95	40	25	17	0.5	20
2	MBR UF	0.90	20	20	18	1	20
3	MBR UF	0.983	60	23 13	17 12	0.333	20
4	UF	0.90	20	7	7	1	20
5	UF	0.9	10	10	10	1	10

4.4.1.1 Hydraulic Residence Time (HRT)

The hydraulic residence times in the membrane bioreactor and the ultrafiltration system were varied in conjunction with the solids retention time to control the water recovery fraction of

each system as outlined in Table 4-5. Hydraulic residence times were varied between 0.333 days and 0.75 days in the MBR and 0.333 days and 1 day in the UF system.

Hydraulic residence time was controlled using wastewater feed rate (Q_F). For run one this corresponded to a feed rate of 20 L/day, and for run two a feed rate of 10 L/day. The total system volume for runs one and two was 10 L. For run three, the feed rate was 15 L/day, and for runs four and five, the feed rate was 5 L/day. For runs 3, 4 and 5 the total system volume was reduced to 5 L., to reduce operational demands on the system.

4.4.1.2 Solids Retention Time (SRT)

Solids retention time in each reactor was controlled by the wastage rate (Q_W) under steady state conditions. Table 4.5 indicates the SRT for each experimental run. For experimental runs one and two, corresponding to water recovery fractions of 0.95 and 0.90, the wastage rate, Q_W, was set at 500 mL/day, corresponding to a solids retention time of 20 days. For the runs three and four (water recovery fractions of 0.983 and 0.90) Q_w was set at 250 mL/day, corresponding to a SRT of 20 days for each run (volume of the reactor for those runs was lowered to 5 L). For run 5 Q_w was set at 500 mL/day, corresponding to a solids retention time of 10 days.

4.4.2 Temperature

Internal bioreactor and mixing tank temperatures were maintained at 55 °C for the duration of the study.

4.4.3 Transmembrane Pressure and Velocity

The transmembrane pressure on the ultrafiltration units on each system was maintained at 138 kPa (20 psi) and volumetric flow through the filters was controlled at 10 L/min. corresponding to a crossflow velocity through the filters of 4 m/s. Daily adjustments to the pump motor speed and the plug valve on the return line maintained these settings.

4.4.4 Nutrients

Nitrogen and phosphorus additions to the MBR were made in excess of a COD:N:P ratio of 200:5:1 to provide sufficient nutrients for cell metabolism and growth.

5. RESULTS AND DISCUSSION

In this section, the data and results obtained during the whitewater characterization and the operation of the ultrafiltration and membrane bioreactor treatment systems are presented and discussed.

5.1 Whitewater Characteristics

Due to the fact that closed or partially closed integrated TMP-newsprint mills do not exist at present, a simulated whitewater representative of a low water use process was developed for use in this research. The simulated whitewater was prepared to emulate contaminant concentrations for an integrated TMP newsprint mill with a total fresh water consumption of 2 - 5 m^3/adt (Wearing *et al.*, 1985b). Several authors have performed experiments to determine the composition of such a whitewater (Järvinen *et al.*, 1985; Lagacé *et al.*, 1996; Francis, 1996b). In general, closure or partial closure of an integrated TMP whitewater system would result in an increase in suspended solids, dissolved and colloidal solids, lignin and temperature, and a decrease in dissolved oxygen (Pietschker, 1996).

The whitewater used in this present research was prepared by augmenting a whitewater from a coastal TMP mill, derived from a 45% hembal (hemlock balsam composite) and 55% spruce furnish, with plug screw feeder pressate from the same mill and 35% w/w evaporator bottoms from a closed BCTMP mill as described in section 4.2.3. The characteristics of this whitewater following screening through a 4 mm mesh screen, are given in Table 5-1. The composition of the whitewater varied over the course of the experiment as a result of the varying composition of the feed stocks and natural variation in the source materials. Whitewater was collected from a saveall, in which solids were able to settle from the

whitewater. Depending on the time of collection, and the degree of settling which had occurred in the saveall, the composition of the whitewater was variable.

Table 5-1: Composition of Synthetic Whitewater

Contaminant	Mean	Standard Deviation
pH	5.67	
Total Solids (mg/L)	5125	446
Dissolved Solids (mg/L)	4640	270
Suspended Solids (mg/L)	488	312
TCOD (mg/L)	5420	915
Dissolved COD (mg/L)	4140	500
Resin Acids (mg/L)	23.4	
Fatty Acids (mg/L)	43.4	
Cationic Demand (mg/L)	0.077	0.014
UV Lignin (g/L)	1.05	0.09

5.2 System Characterization

5.2.1 Initial Membrane Flux

The initial permeate flux of the 500 Angstrom Membralox T1-70 filter was measured by filtering tap water through the membrane at a transmembrane pressure of 138 kPa (20 psi) and a recirculation rate of 10 L/min. This corresponded to a velocity across the membrane surface of 4 m/s at an operating temperature of 55°C. The tap water flux prior to "conditioning" (first use) was determined to be 1300 L/(m^2•hr), decreasing to 550 L/(m^2•hr) following several weeks of operation prior to commencement of the experimental period.

5.3 Comparison of MBR and UF System Performance

5.3.1 Operating Parameters

Two operational parameters which were independently controlled for this experiment were temperature and transmembrane pressure. Both of these parameters can greatly influence the performance of the biological and filtration systems and were held as constant as possible.

The transmembrane pressure in each of the reactors is presented in Figure 5-1 and Figure 5-2. The two systems were operated under similar and stable conditions at 138 kPa (20 psi). Variations in the transmembrane pressure were controlled by adjusting the outlet valve for the ceramic membrane. The drop in transmembrane pressure in the MBR from days 42 - 53 was due to operational difficulties which required that the pressure be lowered for that period of time.

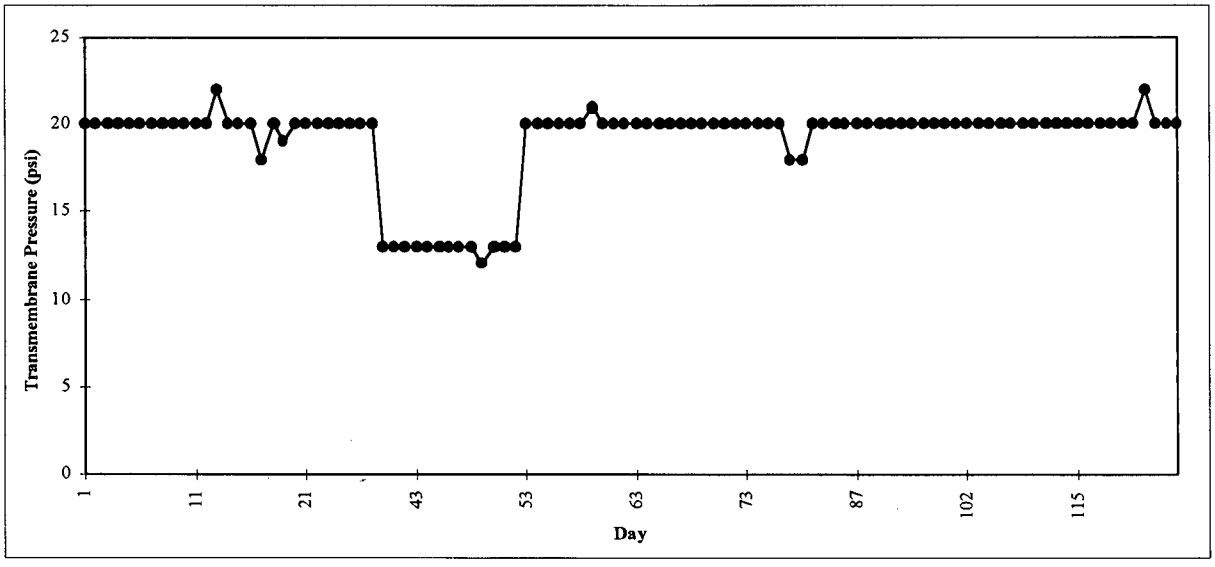

Figure 5-1: Transmembrane Pressure in the Membrane Bioreactor System

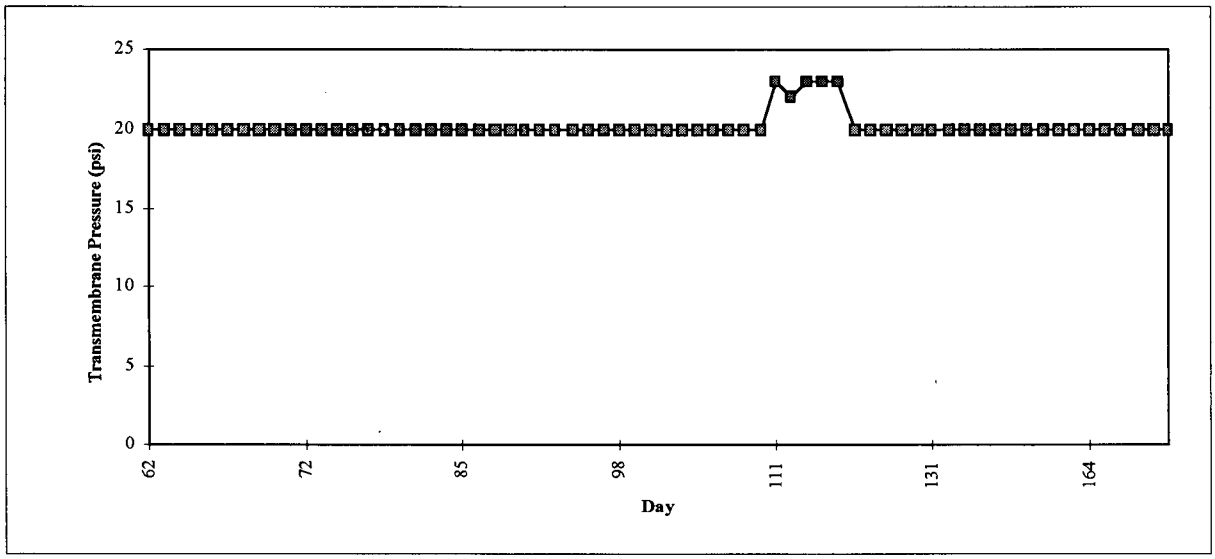

Figure 5-2: Transmembrane Pressure in the Ultrafiltration System

Temperature in each of the reactors over the experimental period is plotted in Figure 5-3 and Figure 5-4. Periods of low operating temperature were a consequence of occasional operating difficulties resulting in a temperature decline in the water bath or a stopping or slowing of one or both of the positive displacement recirculation pumps.

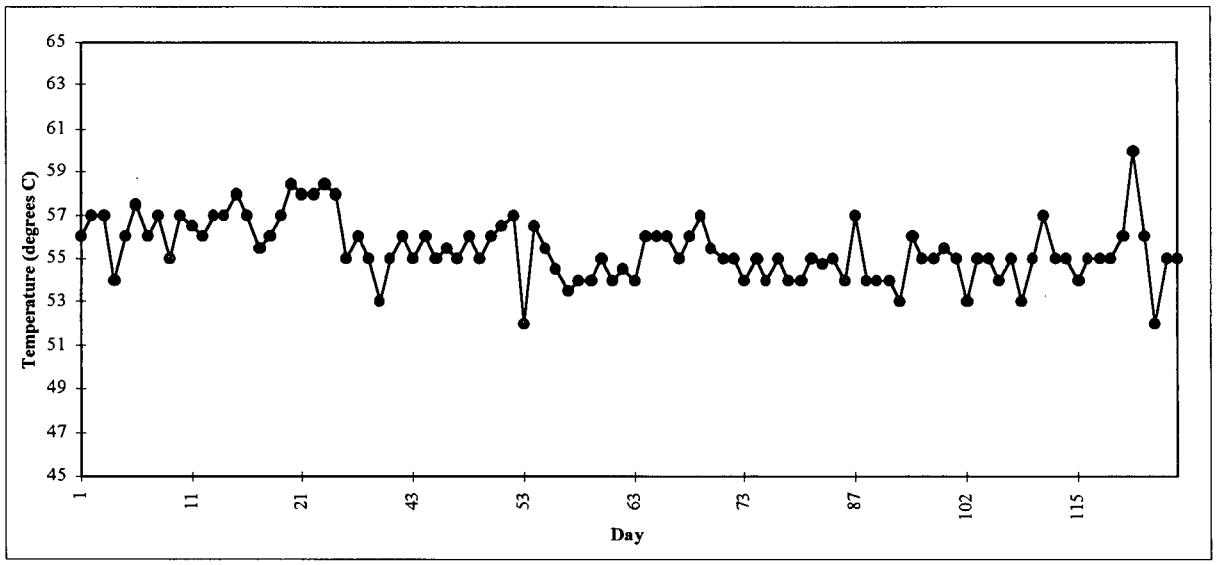

Figure 5-3: Operating Temperature in the Membrane Bioreactor System

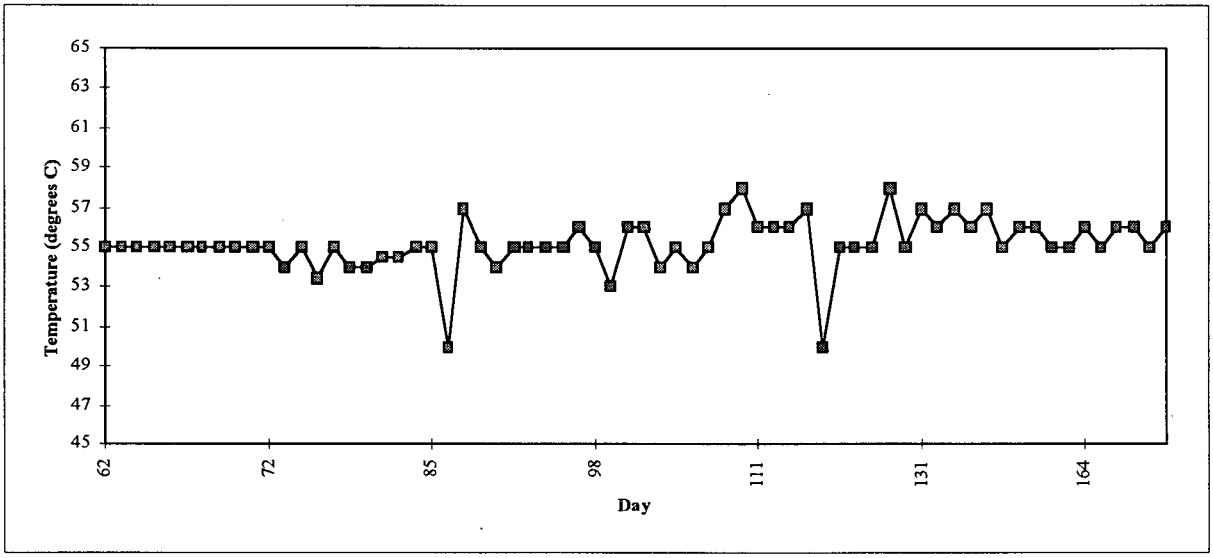

Figure 5-4: Operating Temperature in the Ultrafiltration System

5.3.2 Contaminant Removal

In this section the concentrations of each contaminant in the influent (both total and dissolved, where applicable), and the effluents of the MBR and UF treatment systems over each experimental period are presented along with the statistical mean percent removal, with 90% confidence interval bars for each contaminant of interest at the different water recovery fractions.

5.3.2.1 Solids

Figure 5-5 and Figure 5-6 present the solids concentrations over the course of the experimental period. Influent Total and Influent Dissolved refer to solids concentrations in the influent, while MBR and UF refer to the solids concentration in each of the permeates.

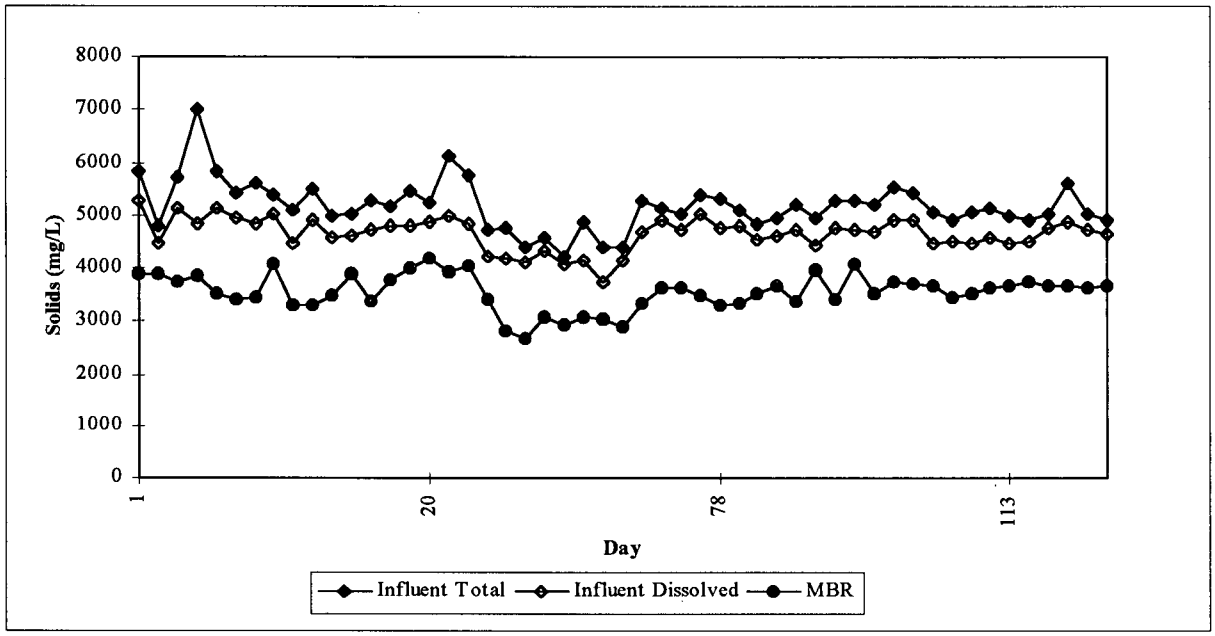

Figure 5-5 :Solids Concentration in the Membrane Bioreactor System as a Function of Time

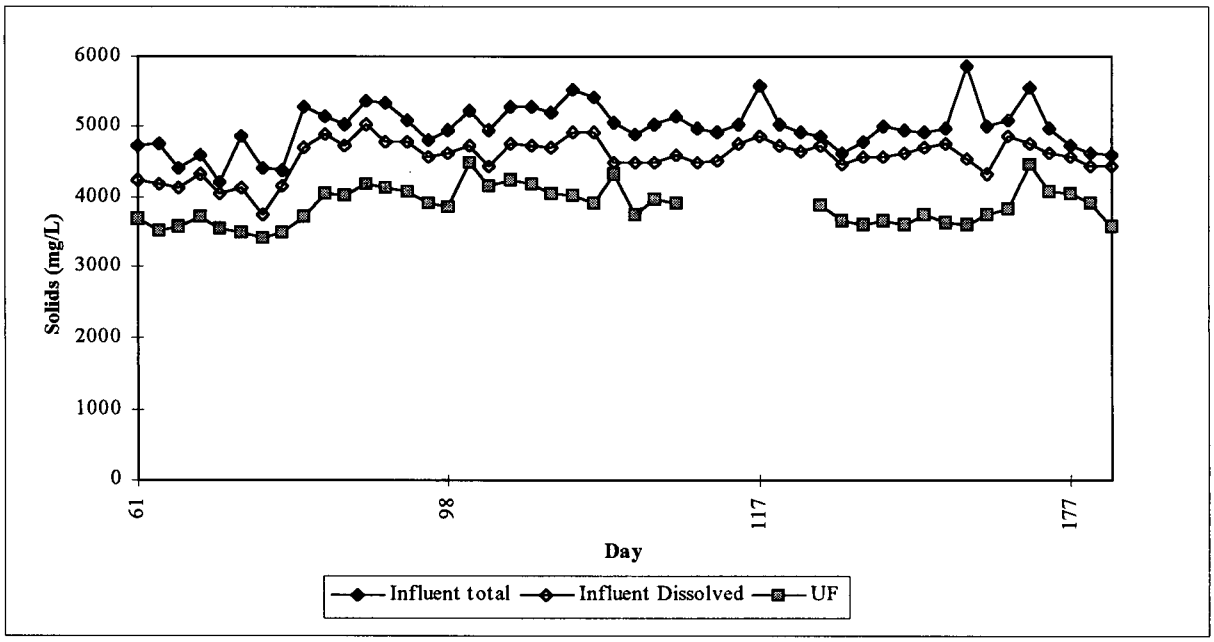

Figure 5-6: Solids Concentration in the Ultrafiltration System as a function of Time

The concentration of solids in the influent and each of the effluents was highly variable, suggesting that the degree to which the treatment systems were able to remove solids was

partly a function of the influent solids concentration, particularly in the case of the MBR system.

Figure 5-7, Figure 5-8, Figure 5-9 and Figure 5-10 show the average performance of each system for the removal of total and dissolved solids respectively.

Removal of total solids in the membrane bioreactor was between 34% and 29% (Figure 5-7) and decreased with increasing water recovery fraction, while removal of total solids in the ultrafiltration treatment system (Figure 5-8) was poor and remained relatively insensitive to the experimental conditions. These results suggest that capability of the ultrafiltration system for removal of total solids was not greatly affected by volume reduction factor, and was more likely a function of membrane pore size.

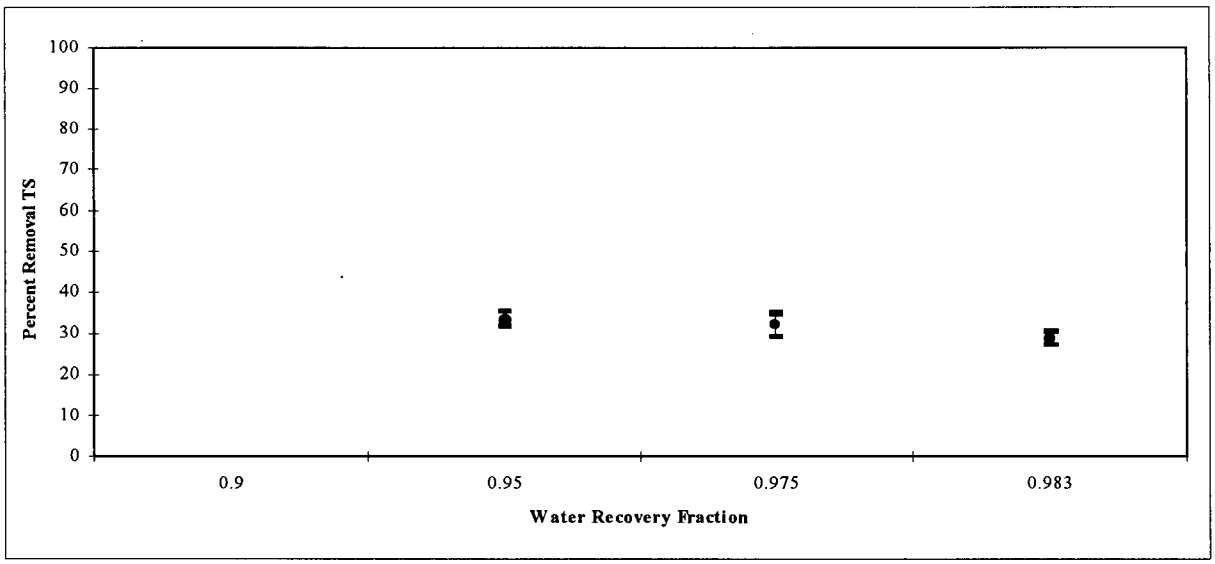

Figure 5-7: Total Solids Removal in the Membrane Bioreactor System as a Function of Water Recovery Fraction

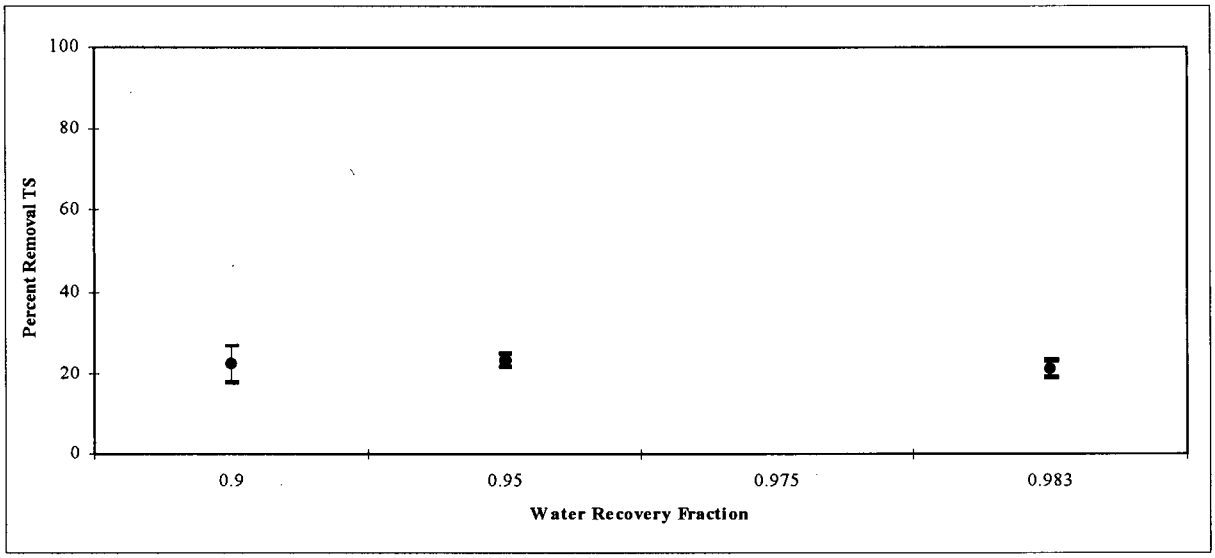

Figure 5-8: Total Solids Removal in the Ultrafiltration System as a Function of Water Recovery Fraction

In each system, the removal of suspended solids was 100%, as the pore size of the ceramic membrane (500 Angstroms) was smaller than the filter pore size (1450 Angstroms) used in the determination of suspended solids. Removal of dissolved solids was poor in both treatment systems, although as in the case of total solids removal, there was a decline in removal efficiency in the membrane biological reactor with increasing water recovery fraction (shorter HRT).

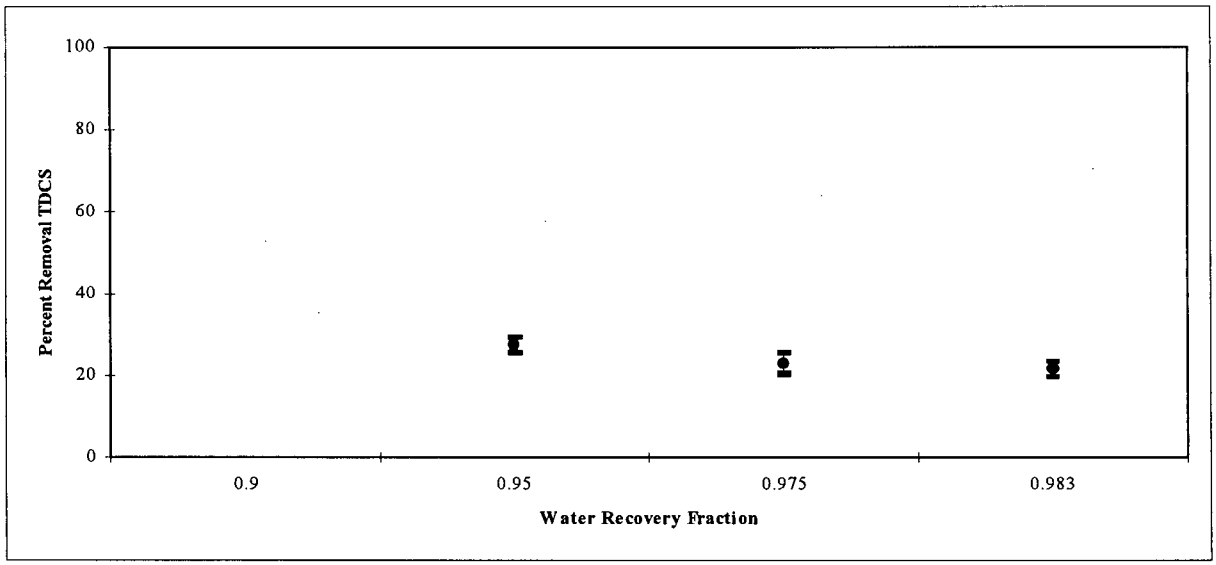

Figure 5-9: Dissolved Solids Removal in the Membrane Bioreactor System as a Function of Water Recovery Fraction

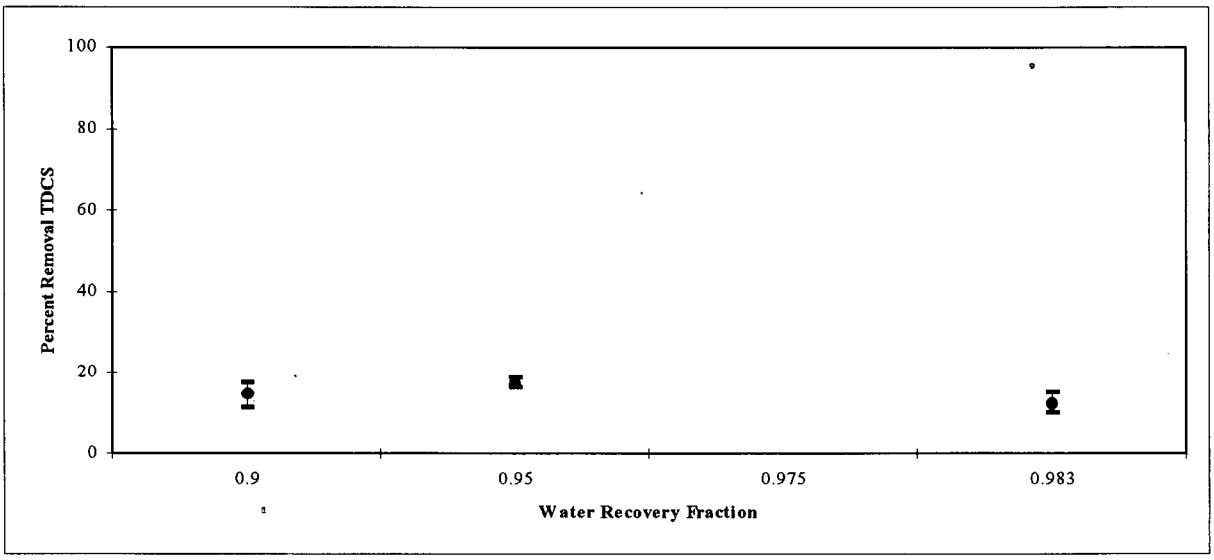

Figure 5-10: Dissolved Solids Removal in the Ultrafiltration System as a Function of Water Recovery Fraction

5.3.2.2 Chemical Oxygen Demand

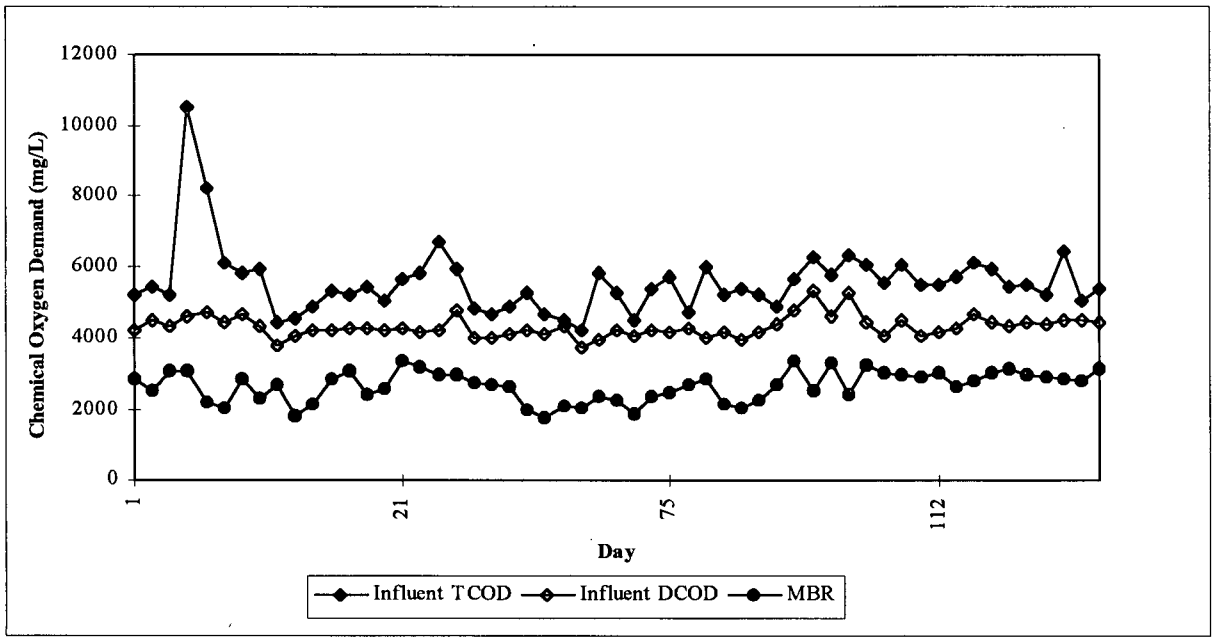

Figure 5-11: Chemical Oxygen Demand (COD) Concentration in the Membrane Bioreactor System as a Function of Time

Figure 5-11 and Figure 5-12 show the variation in chemical oxygen demand in the influent (total and dissolved) and in the permeate of the MBR and UF. As was the case with solids,

the concentrations of total and dissolved chemical oxygen demand in the influent were highly variable. In the case of the permeate from each of the treatment systems, however, the concentration of chemical oxygen demand in the effluent samples appeared to be more consistent than in the case of solids.

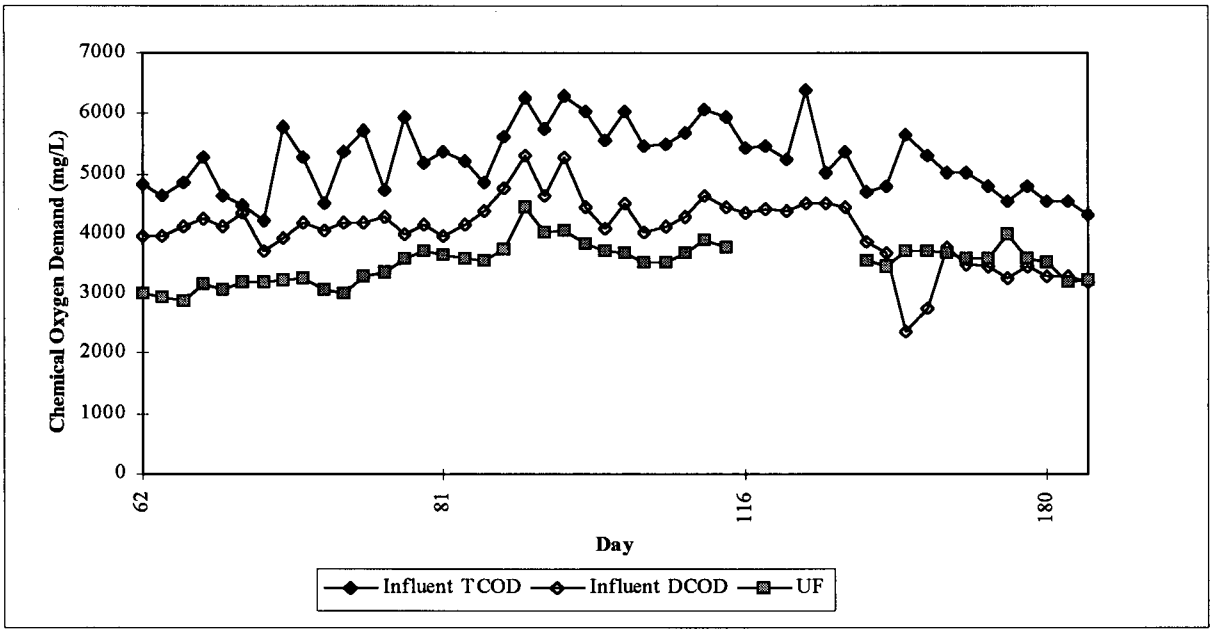

Figure 5-12: Chemical Oxygen Demand (COD) Concentrations in the Ultrafiltration System as a Function of Time

Removal of total chemical oxygen demand (Figure 5-13) by the membrane biological reactor ranged from 54% to 48%, and the removal efficiencies in the system decreased with increasing water recovery fraction. This corresponds to a decreased removal of total chemical oxygen demand with decreased hydraulic residence time (from one day to eight hours). Improved removals of COD (95 - 99%) by aerobic membrane bioreactor systems treating other industrial (car manufacturing; metal transformation; dairy production) wastewaters have been reported by a number of authors (Hare *et al.*, 1990; Zaloum *et al.*, 1994; Zaloum *et al.*, 1996)

as well as complete (99.9%) removal of COD from a municipal wastewater by aerobic membrane biological treatment (Trouve *et al.*, 1994).

Lower removal efficiencies for COD in the present research may be attributed to the large non-degradable COD fraction in this stream (refer to section 5.4.2), the short retention times of the treatment system and the large pore size of the membrane relative to organic macromolecules.

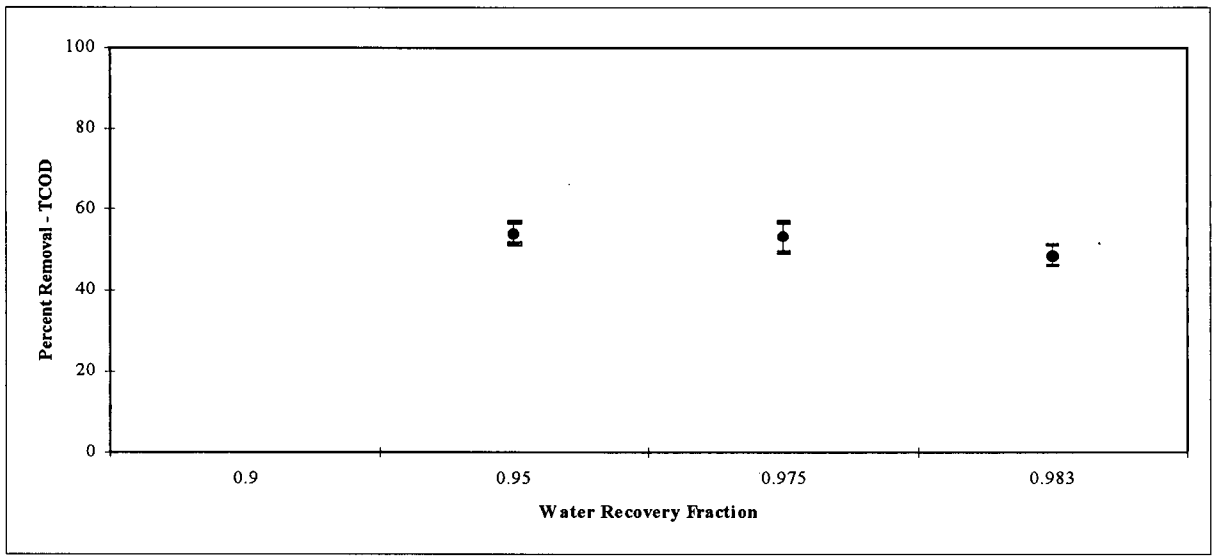

Figure 5-13: Total Chemical Oxygen Demand (TCOD) Removal in the Membrane Bioreactor System as a Function of Water Recovery Fraction

In the ultrafiltration system, the removal of chemical oxygen demand ranged from 36% to 23%. In the case of the UF system, however, removal efficiency appeared to increase with increasing water recovery fraction (Figure 5-14). One possible explanation for this result is an increased thickness of the gel layer with increased concentration of the retentate (i.e. under increased water recovery fractions). The thickness of the gel layer on the membrane surface would result in an increased selectivity of the membrane and an improved removal of insoluble

contaminants. Another possible explanation for the increased removal of total chemical oxygen demand at higher water recovery fractions, would be the precipitation of some components of total chemical oxygen demand in the retentate at higher water recovery fractions.

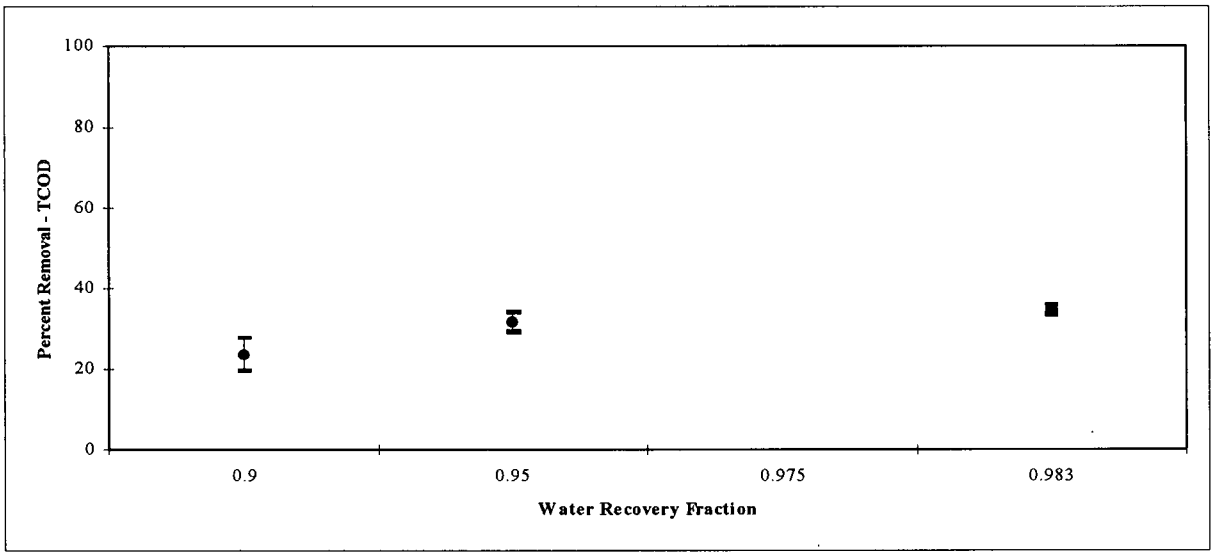

Figure 5-14: Total Chemical Oxygen Demand (TCOD) Removal in the Ultrafiltration System as a Function of Water recovery Fraction

Nuortila-Jokinen *et al.* (1995) reported that they observed improved percent removals of COD with increasing concentration of COD in the retentate (as in the case of increasing water recovery fractions) when treating a papermill whitewater by ultrafiltration.

Removal of dissolved chemical oxygen demand (Figure 5-15) ranged from 45-25% in the MBR, and -6 - 18% in the UF system (Figure 5-16). It is possible that in the case of the UF system, some insoluble COD was being converted into dissolved COD through of anaerobic biodegradation at a water recovery fraction of 0.9, the final experimental run, leading to an apparent increase in dissolved COD over the experimental period.

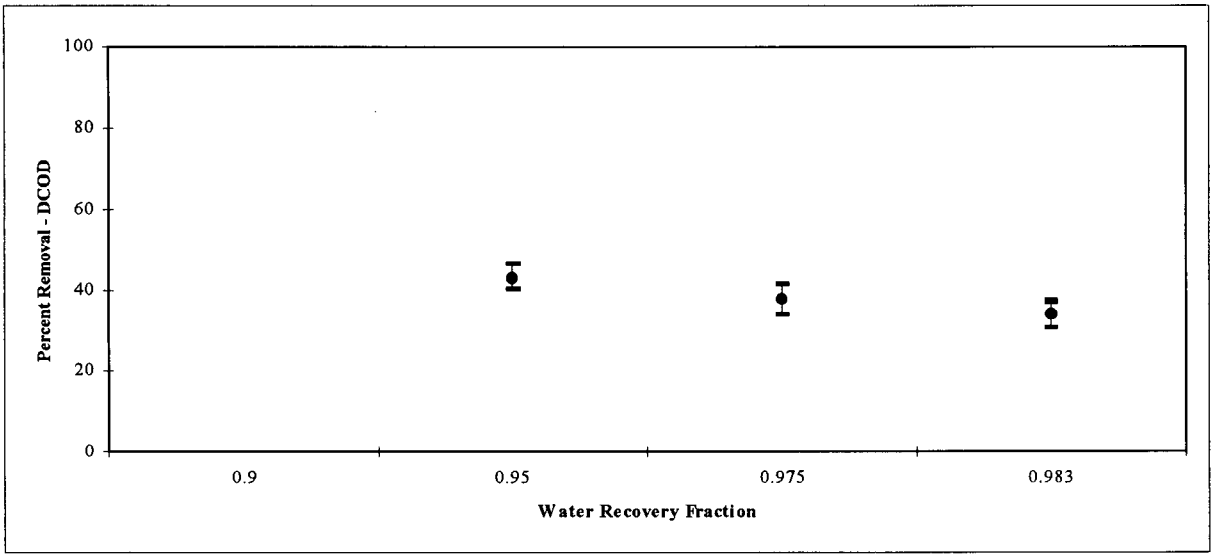

Figure 5-15: Dissolved Chemical Oxygen Demand (DCOD) Removal in the Membrane Bioreactor System as a Function of Water Recovery Fraction

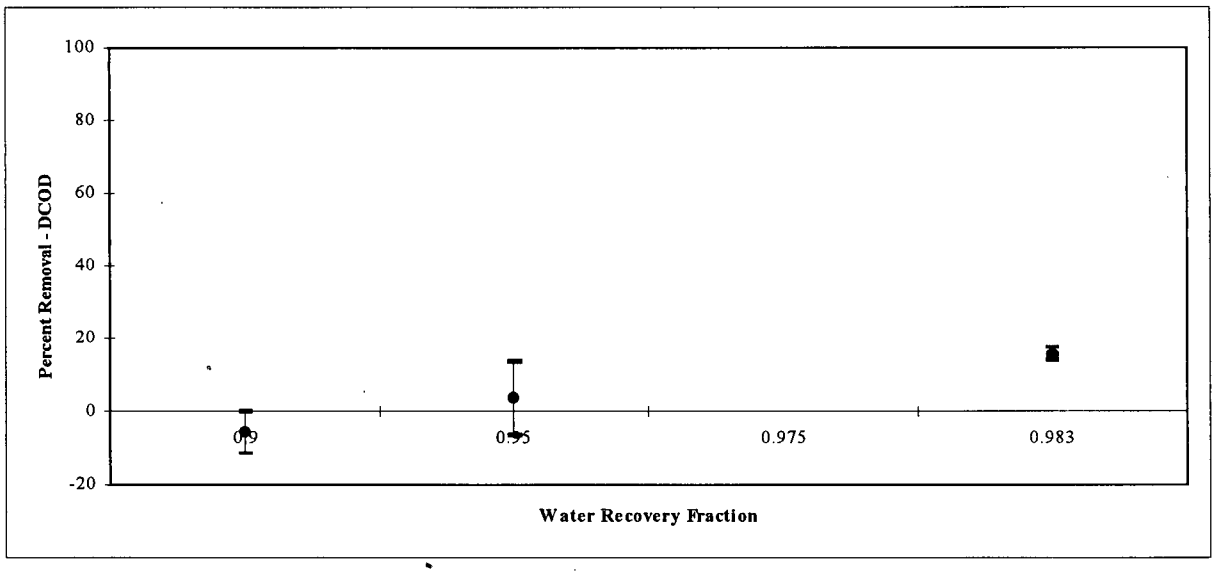

Figure 5-16: Dissolved Chemical Oxygen Demand (DCOD) Removal in the Ultrafiltration System as a Function of Water Recovery Fraction

5.3.2.3 Resin and Fatty Acids

Figure 5-17 shows the concentration of resin acids in the influent and MBR and UF permeates, while Figure 5-18 shows fatty acid concentrations.. The concentrations of resin

and fatty acids in the influent were very high for run 1, at which time only the membrane bioreactor was operational. Following run 1, the concentrations of both resin and fatty acids decreased (presumably as a result of the changing composition of furnish in the TMP-newsprint mill), and remained relatively stable for the remainder of the experiment.

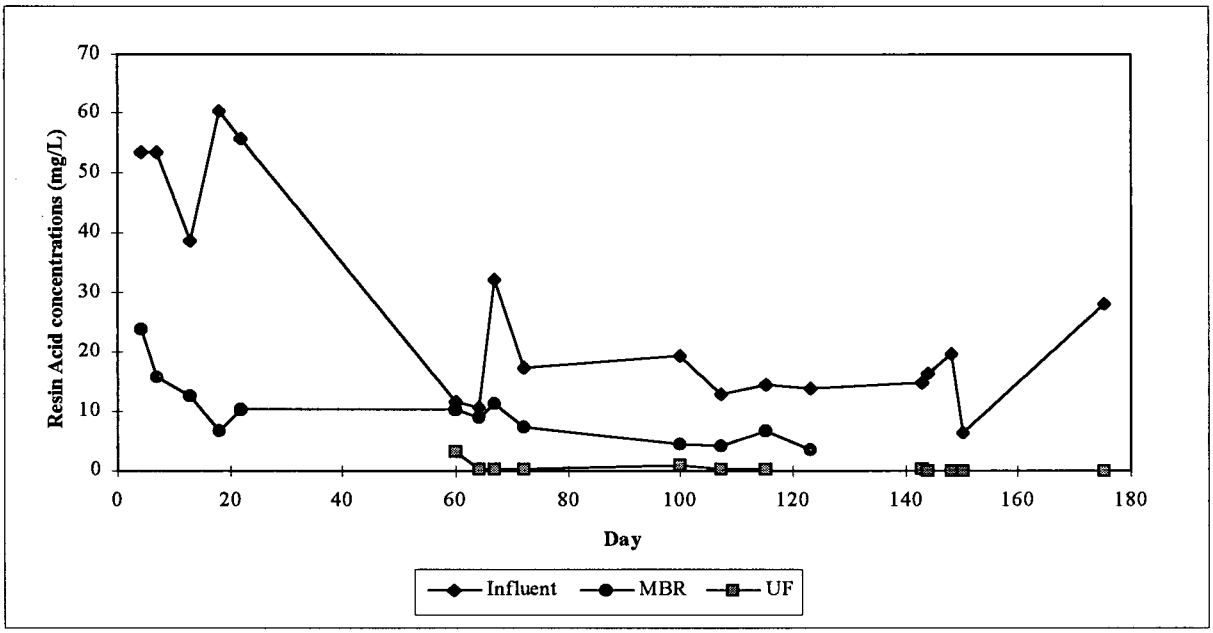

Figure 5-17: Resin Acid Concentration

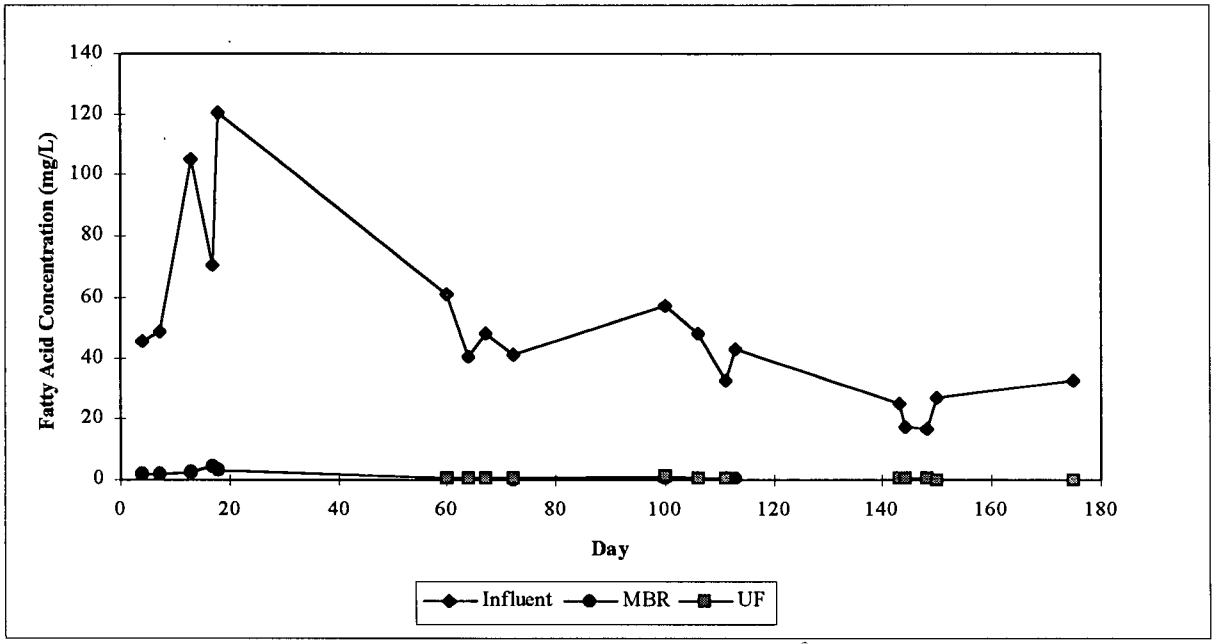

Figure 5-18: Fatty Acid Concentration

Figure 5-19 and Figure 5-20 illustrate the removal of resin acids by each of the treatment systems. The ultrafiltration system demonstrated superior removal of these compounds in all experimental runs, with removal efficiencies ranging from 99- 93%. The most complete removal of resin acids occurred at the lowest water recovery fraction, 0.9. Zaidi and Buisson (1991) found that resin acids existed as calcium salts in the retentate of UF systems, and as such may be rejected both by steric exclusion (as a result of being adsorbed onto suspended solids) and solute/membrane interaction.

The removal of resin acids by the MBR ranged from 52 - 76%, with the removal of resin acids being most pronounced at the highest water recovery fraction. The difference between the two systems may be explained on the basis of the different pH's in each of the operating systems. The pH in the ultrafiltration system was in the range of 5.2 - 5.5 while the pH of the MBR system was in the range of 6.8 - 7.5.

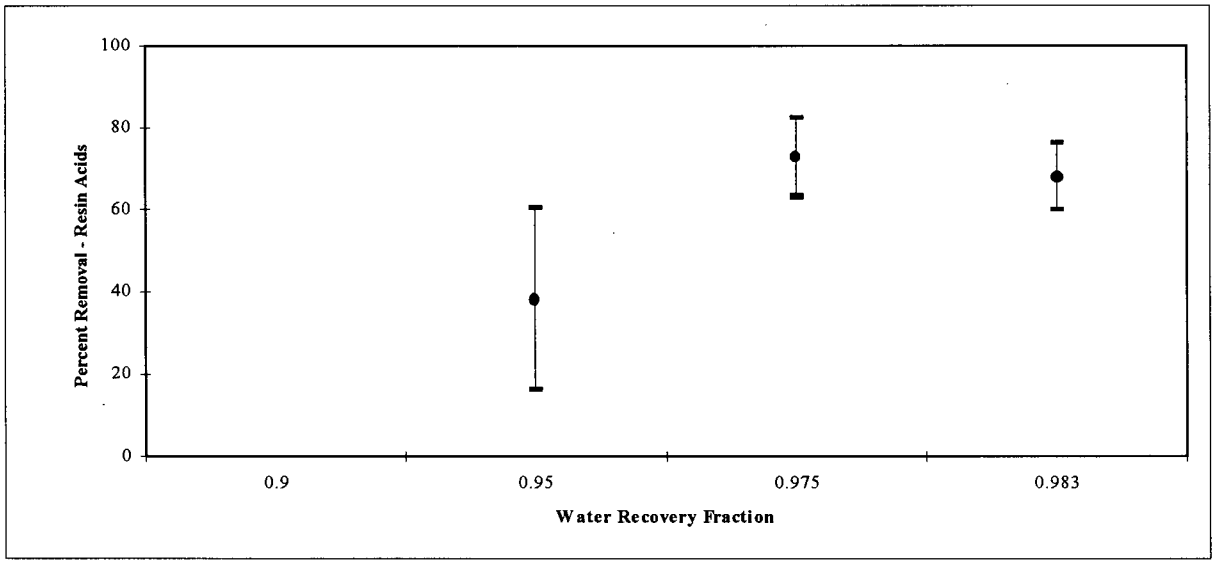

Figure 5-19: Resin Acid Removal in the Membrane Bioreactor System as a Function of Water Recovery Fraction

The solubility of most resin acids is at a maximum at pH's greater than 7, such that in the pH range of the MBR, a substantial portion of the resin acids would have been soluble and therefore able to pass through the membrane (unlike the colloidal resin acids retained in the UF system). Removal of resin and fatty acids from solution is facilitated by the agglomeration of colloidal resin and fatty acids onto larger macromolecules, (or onto each other) to form pitch deposits. These pitch deposits are filterable from solution, though the individual resin and fatty acid molecules are able to pass through a 500 Angstrom filter (Zaidi and Buisson, 1991).

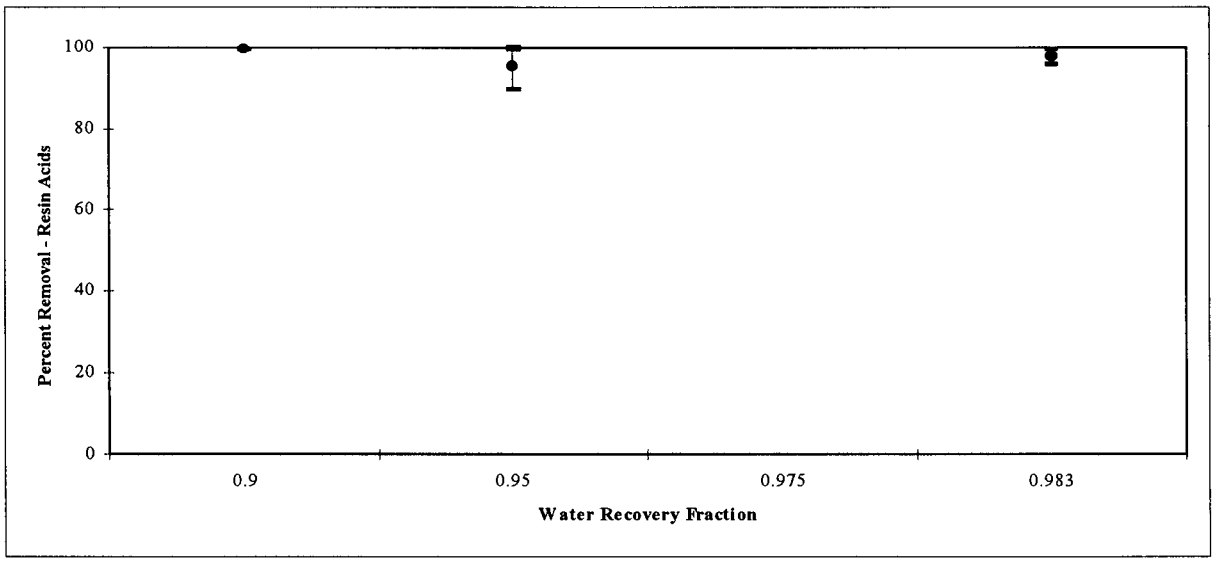

Figure 5-20: Resin Acid Removal in the Ultrafiltration System as a Function of Water Recovery Fraction

Fatty acids molecules are considered to be among the most detrimental, as they are more readily able to form larger, filterable pitch deposits (Welkener *et al.*, 1993). This would account for the near complete removal of fatty acids in both treatment systems (Figure 5-21 and Figure 5-22).

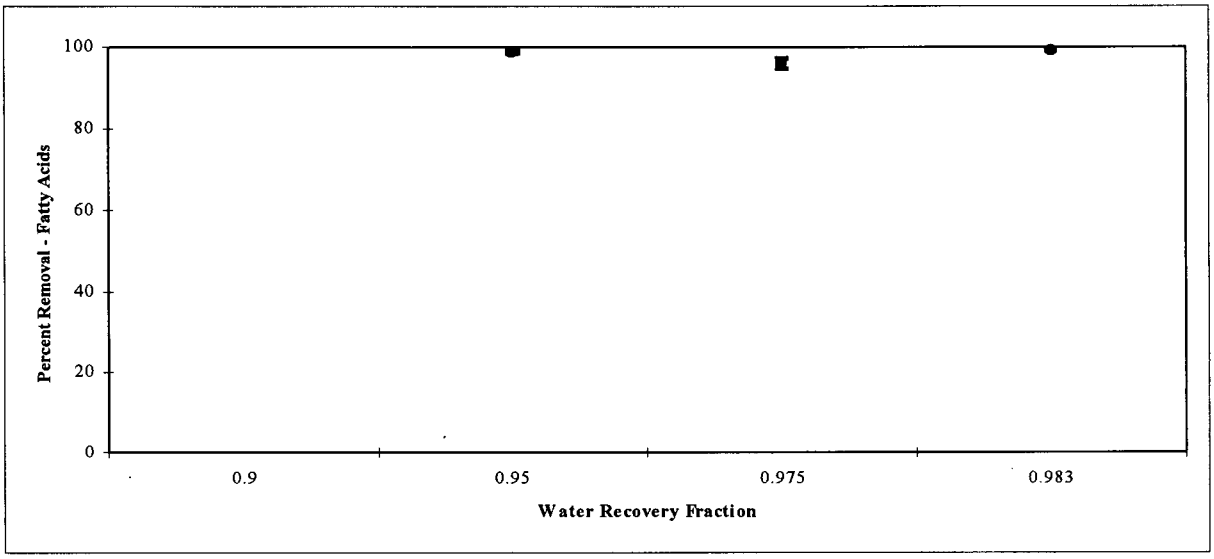

Figure 5-21: Fatty Acid Removal in the Membrane Bioreactor System as a Function of Water Recovery Fraction

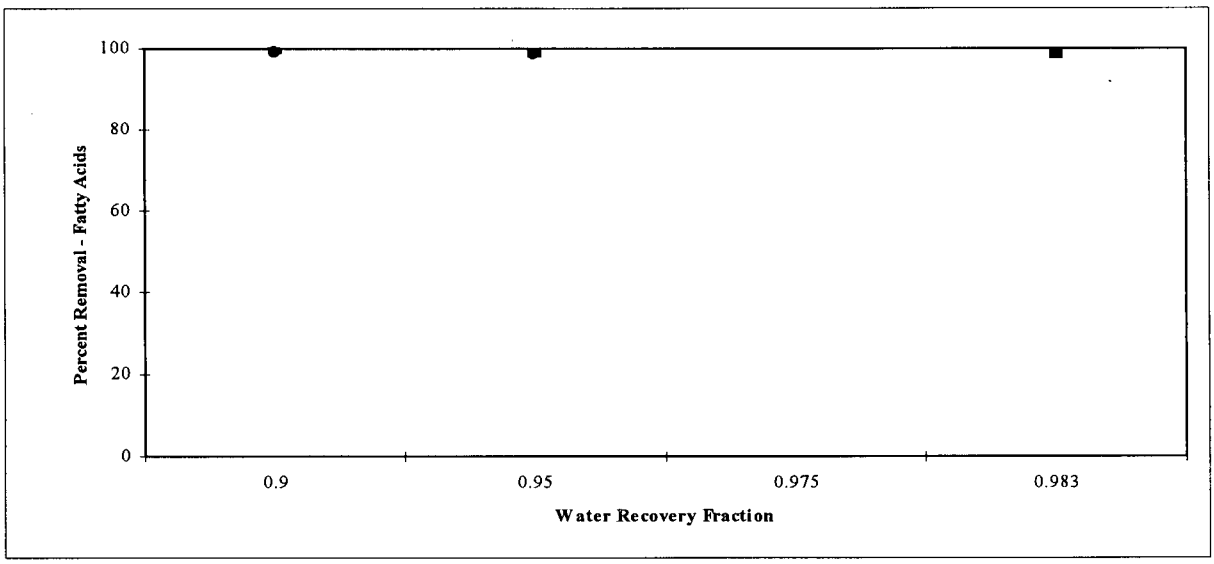

Figure 5-22: Fatty Acid Removal in the Ultrafiltration System as a Function of Water Recovery Fraction

Removal of resin and fatty acids from the influent stream may also have been a result of the formation of a colloidal "gel layer" of RFAs along the surface of the membrane. This surface layer would promote filtration of RFAs from solution by two mechanisms: one, the gel layer

would serve as a more selective membrane surface through which agglomerated resin and fatty acids were unable to pass, and two, the gel layer may have induced an electrostatic repulsion which prevented the permeation of agglomerated and individual molecules of resin and fatty acids, and their salts into the effluent stream.

In the UF system at low water recovery fractions, the flux was relatively high and the rate of fouling was low (sections 5.3.3.1 and 5.3.3.2) such that cleaning was required only infrequently. The long period of time between cleanings would have allowed for a full development of a gel layer. At higher water recovery fractions, the rate of permeation was considerably lower, and the rate of fouling increased, such that cleaning frequencies were also higher. This frequent cleaning would have prevented the formation of a membrane surface layer of resin and fatty acids, and allowed for the permeation of a greater fraction of RFAs.

Removal of resin acids in the membrane biological reactor was considerably poorer than in the UF system, and was most likely attributable to the difference in system pH, as discussed earlier. Unlike the UF system, resin acid removal appeared to improve in the MBR with increasing water recovery fraction. This suggests that there may have been some biologically-mediated interactions involved in the removal of resin acids in the MBR, such as adsorption of resin acids onto the surface of biological solids (Hall and Liver, 1996) or biological degradation of resin acids (Liu *et al.*, 1993b). In the MBR system, the rate of fouling of the membrane was lower with increasing water recovery fraction (section 5.3.3.2) and as such, required less frequent cleanings, possibly allowing for a build up of a gel layer of resinous materials on the membrane over time.

5.3.2.4 Cationic Demand

Figure 5-23 and Figure 5-24 present the concentrations of cationic demand in the influent, MBR and UF permeate streams over the course of the experimental period.

Cationic demand removal efficiencies are plotted in Figure 5-25 and Figure 5-26. The ultrafiltration system was very effective at removing cationic demand from the influent stream, with efficiencies ranging from 85 - 67%. In general, the effectiveness of the UF system decreased with increasing water recovery fraction.

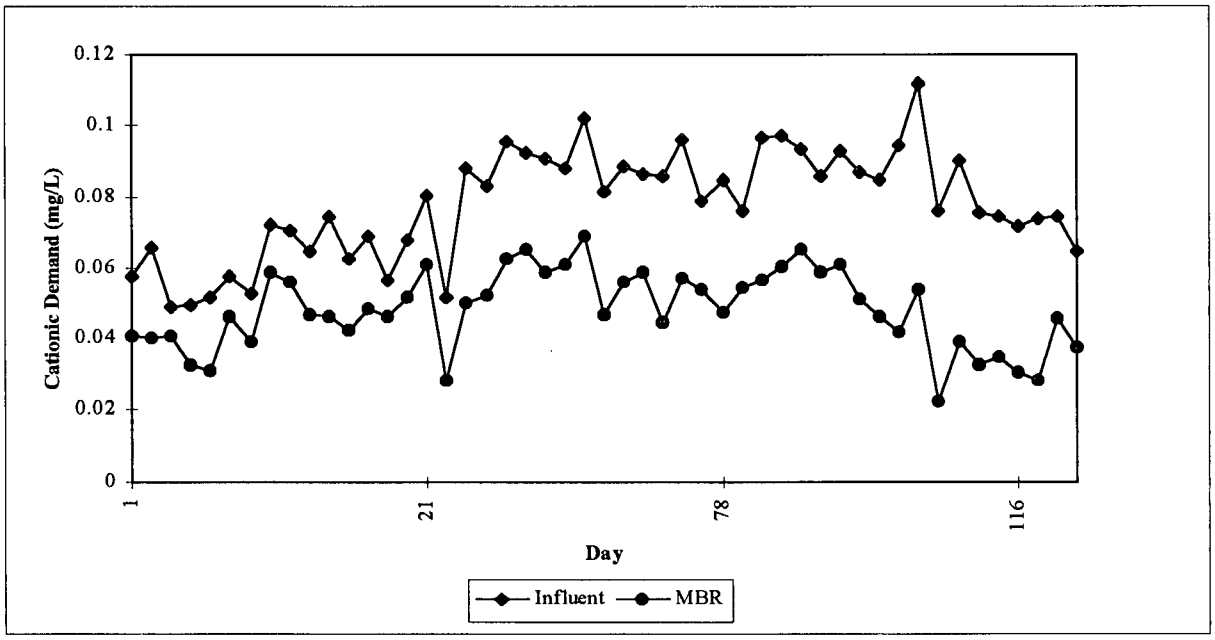

Figure 5-23: Cationic Demand Concentration in the Membrane bioreactor System as a Function of Time

Cationic demand removal efficiencies in the membrane bioreactor were not as high, ranging from 29 - 48 %. Unlike the ultrafiltration system, the MBR system appeared to exhibit improved removal of cationic demand with increasing water recovery fraction.

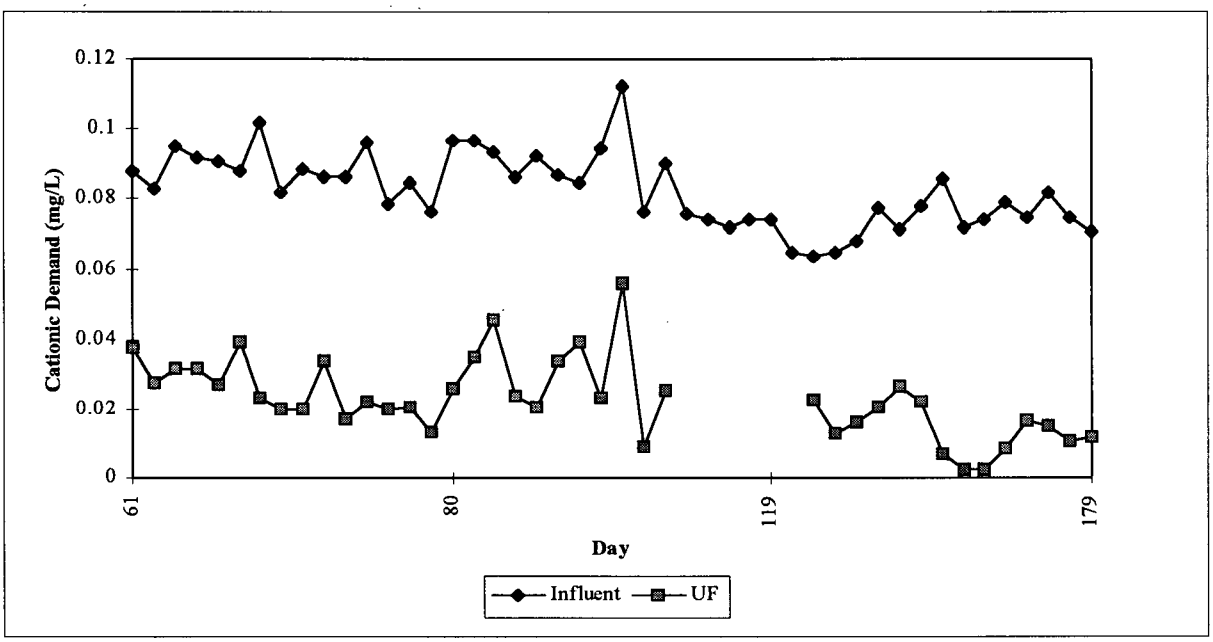

Figure 5-24: Cationic Demand Concentrations in the Ultrafiltration System as a Function of Time

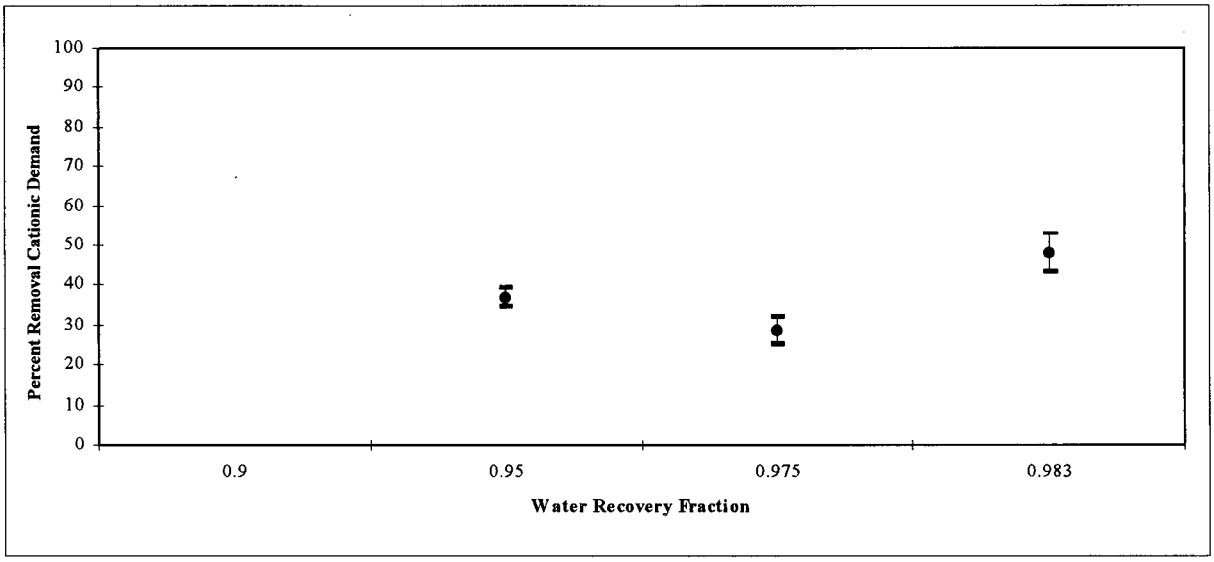

Figure 5-25: Cationic Demand Removal for the Membrane Bioreactor System as a Function of Water Recovery Fraction

Cationic demand, or "anionic trash" is composed primarily of small, negatively charged polysaccharides (Reside, 1996), which, in the case of the MBR may have actually been produced during hydrolysis of larger polysaccharides, or during cell lysis (Chaize and Huyard,

1991). The increased removal of cationic demand in the MBR at a water recovery fraction of 0.983 would likely have been a result of the shorter hydraulic residence time resulting in lower overall biological degradation and hydrolysis.

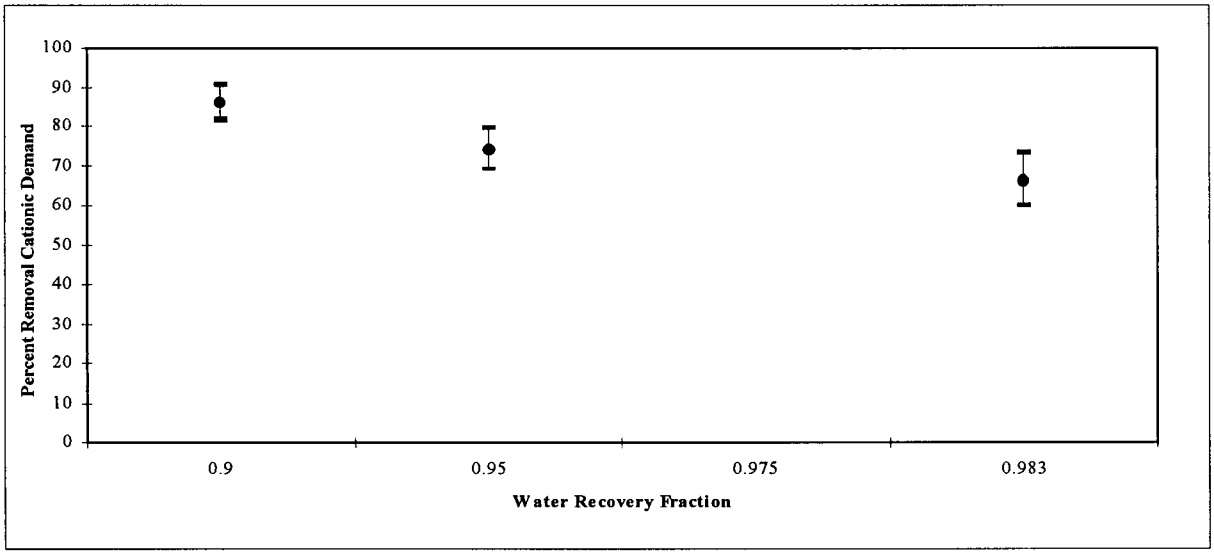

Figure 5-26: Cationic Demand in the Ultrafiltration System as a Function of Water Recovery Fraction

5.3.2.5 UV-lignin

The concentrations of UV-lignin in both the influent and the permeates from the MBR and UF treatment systems appeared to be highly variable over the course of the entire experimental period (Figure 5-27 and Figure 5-28). This may have resulted from variations in wood furnish as evidenced by high variation in the concentrations of total and dissolved solids, and COD.

Removal efficiencies for UV-lignin (205 nm) are presented in Figure 5-29 and Figure 5-30. UV-lignin concentration was determined by a procedure involving the acidification, filtration and dilution of samples, and measurement of the absorbance at 205 nm. In the samples from the UF system, UV-lignin was not removed at any water recovery fraction, and UV-lignin

appeared to increase in UF-treated whitewater at water recovery fractions of 0.9 and 0.983. This increase may be a result of absorbance by other components in the UF-treated effluent.

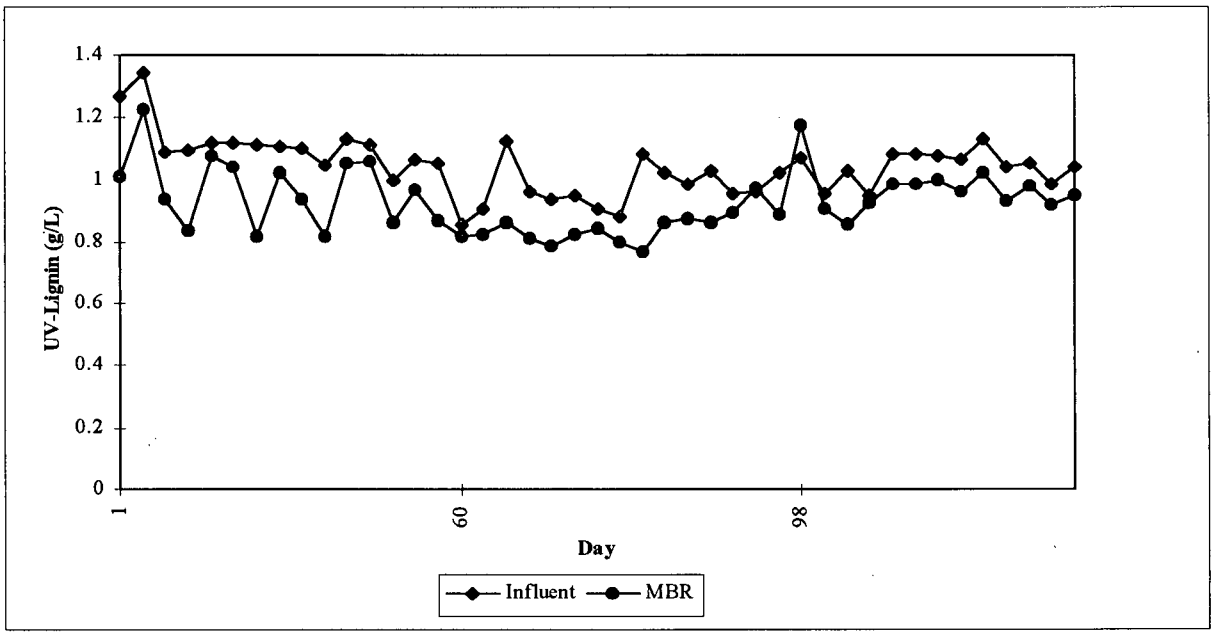

Figure 5-27: UV-Lignin Concentration in the Membrane Bioreactor System as a Function of Time

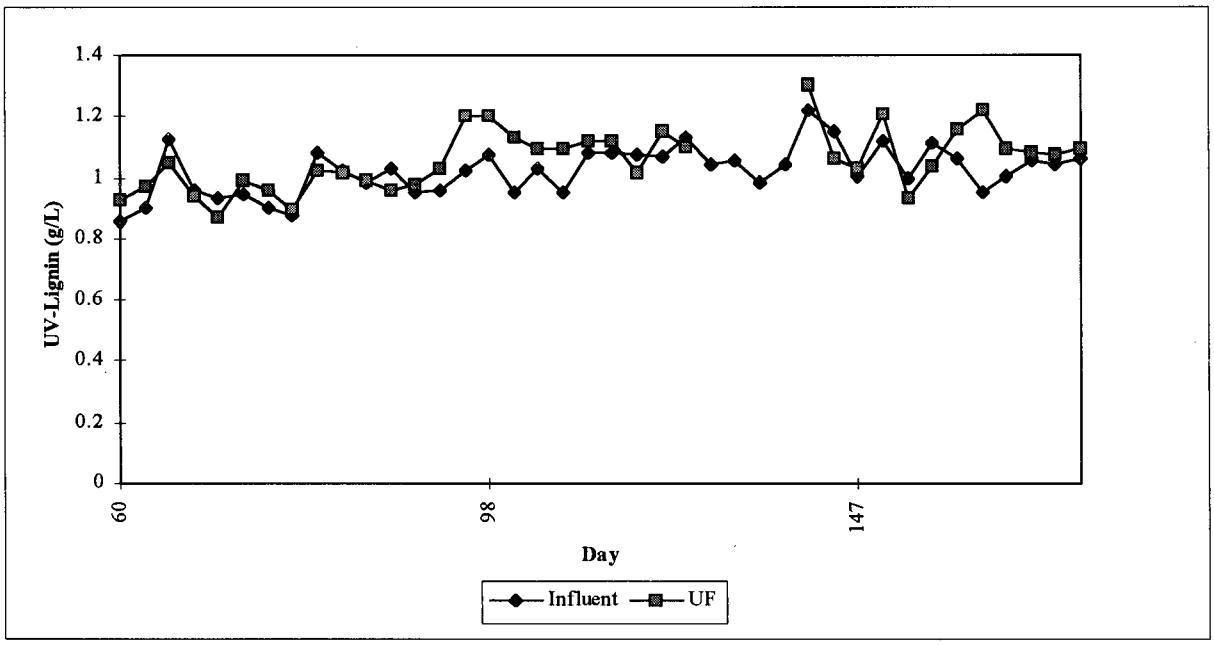

Figure 5-28: UV-Lignin Concentration in the Ultrafiltration System as a Function of Time

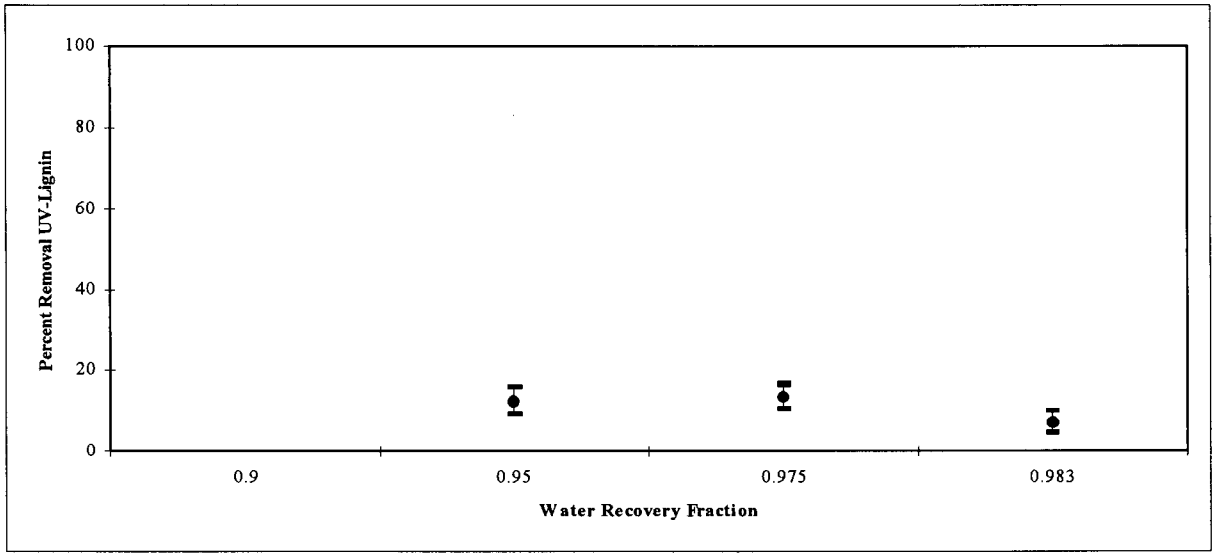

Figure 5-29: UV-lignin Removal in the Membrane Bioreactor System as a Function of Water Recovery Fraction

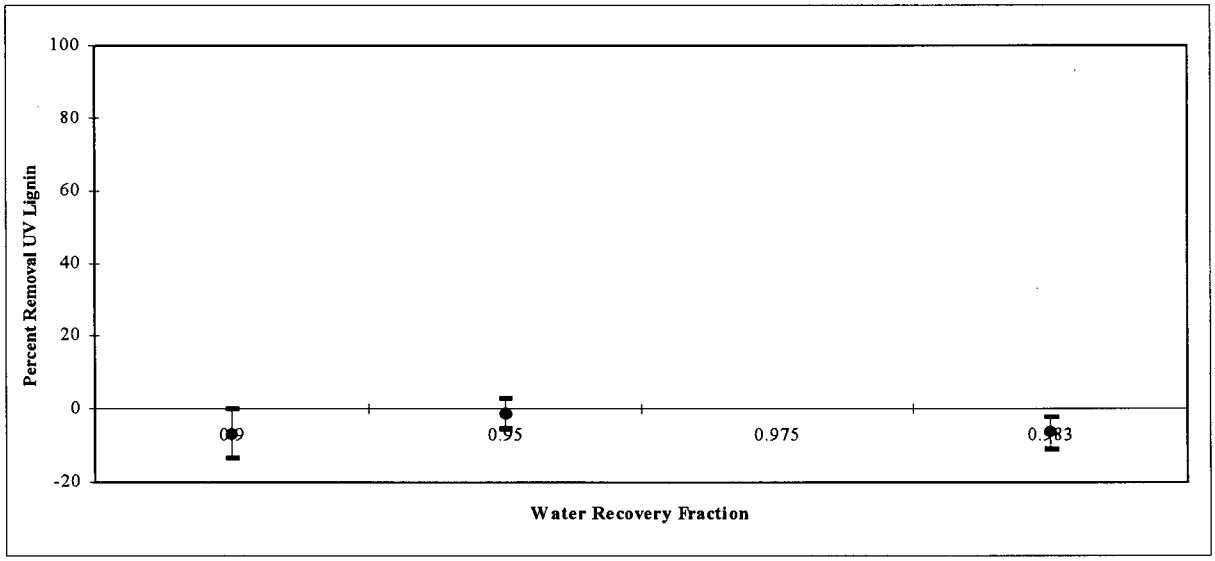

Figure 5-30: UV-lignin Removal in the Ultrafiltration System as a Function of Water Recovery Fraction

A small amount of UV-lignin was removed in the whitewater treated by the MBR system, ranging from 8 - 12%. Improved removal efficiencies were observed at lower water recovery fractions (longer hydraulic residence times). Dufresne *et al.* (1996) demonstrated an accumulation of lignin in the reactor contents of an MBR system operating in parallel to an

activated sludge system, which did not exhibit a similar accumulation. These results indicate poor biodegradability of lignin in an aerobic MBR.

5.3.3 Permeate Flux

As discussed in chapter two, a variety of factors control the flux through an ultrafiltration membrane. Figure 5-31 presents the flux through each of the membranes used in this experiment over the course of the entire experimental period.

5.3.3.1 Maximum Flux

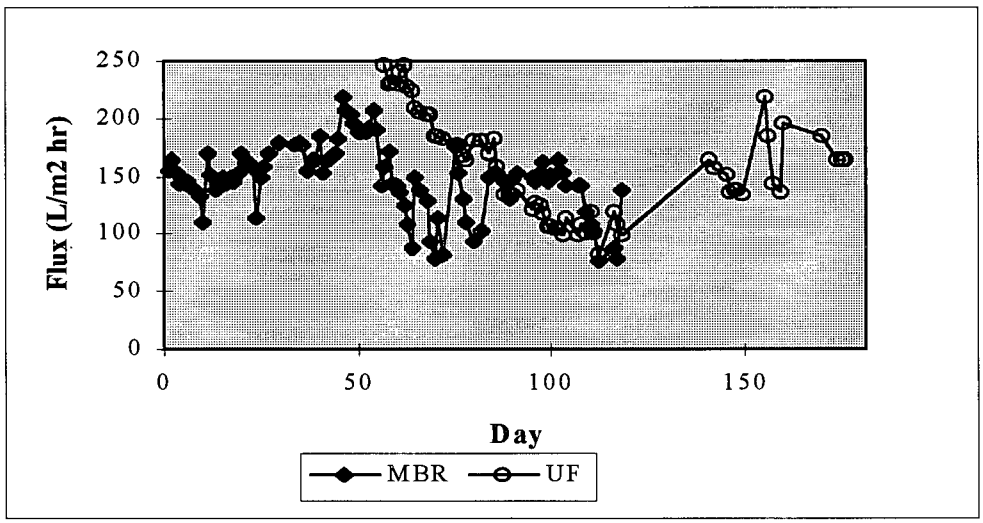

Figure 5-31: Permeate Flux in the Membrane Bioreactor and the Ultrafiltration System over the Experimental Period

Maximum attainable flux and the rate of loss of flux are two important parameters in the determination of the feasibility of an ultrafiltration system. Paleologou *et. al* (1994) suggested that a flux of at least 140 L/(m^2•hr) must be maintained to make ultrafiltration a viable economic alternative to vapor recompression evaporation or freeze crystallization for treatment of pulp and paper effluents for reuse within the mill. Maximum flux and loss of flux

are a function of properties of both the filter and the solution (solute and solvent)being filtered. The contributing properties of the filter include pore size, pore size distribution and the electrostatic nature of the surface of the membrane (Dufresne *et al.*, 1996). In addition, UF operational parameters such as the velocity through the membrane and transmembrane pressure are important. The contributing properties of the solution include viscosity, molecular size and distribution, pH, temperature, mineral salt, protein and lipid content (Cheryan, 1986).

Figure 5-32 is a plot of the maximum flux recorded in the MBR and UF treatment systems at each of the experimentally imposed water recovery fractions. The maximum flux was always observed immediately following cleaning of the filter, presumably due to the unclogging of the filter pores during the cleaning process. Cleaning was performed as necessary and varied between once per run and five times per run.

During periods of acclimatization between runs, each of the systems at times exhibited fluxes higher than those reported in Figure 5-32, but those were not observed under experimental conditions.

Maximal flux was attained in the ultrafiltration system under conditions of low loading (low water recovery fraction) and declined sharply with increasing water recovery fraction. Reported fluxes for ultrafiltration applications of mechanical newsprint whitewaters are in the range of 54 -62 L/(m^2•hr) (Nyström *et al.*, 1992; Nuortila-Jokinen *et al.*, 1995; Nuortila-Jokinen *et al.*, 1993b). The higher fluxes found in this present research may be a result of the

larger pore size (500 Angstroms), narrow pore size distribution and low fouling potential for ceramic membranes.

Ekengren *et al.* (1993), in their examination of the ultrafiltration of bleach plant effluents, reported that the maximum attainable flux through a particular filter decreased with increasing volume reduction fraction, and that the rate of decrease increased with increasing volume reduction factor, similar to the findings in the present study.

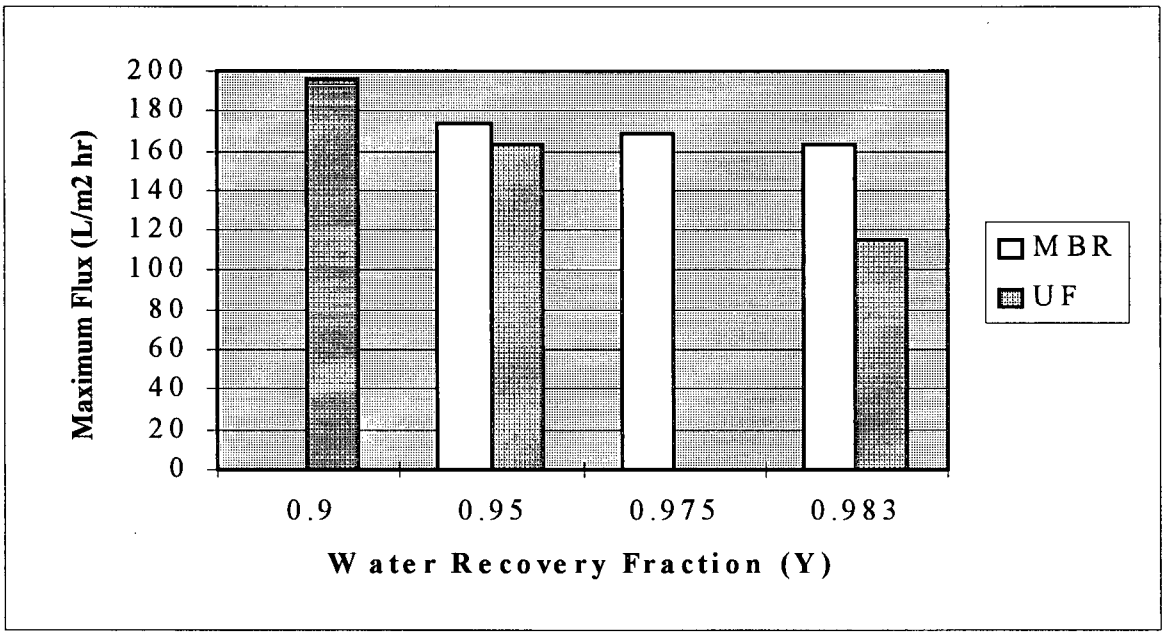

Figure 5-32: Maximum Flux

Flux in the MBR also decreased with increasing water recovery fraction, but not to the same degree. The build up of pitch and other resinous materials may have been responsible for the sharp decline in flux in the ultrafiltration system, as was apparent from a visual observation of the reactor contents, while in the MBR the decline in flux was more likely attributable to the increase in suspended solids (as is apparent in Figure 5-5), primarily of biological origin

(Magara and Itoh, 1991) and the deposition of hydrolysis products and inorganic precipitates as detailed in Chapter 2.

5.3.3.2 Rate of Fouling

Membrane flux is associated with three resistances: R_m - the intrinsic resistance associated with a particular membrane; R_p - the plugging of membrane pores and adsorption of effluent components onto the walls of the membrane, responsible for the initial decrease in flux (Ramamurthy *et al.*, 1995) and; R_c - the resistance associated with the accumulation of material on the surface of the membrane due to concentration polarization and consolidation of an accumulated cake, also referred to as "fouling". Choo and Lee (1996) determined that for the treatment of an alcohol distillery wastewater by a membrane coupled anaerobic bioreactor (MCAB) these contributed 0.5%, 16.6% and 82.8% to the loss of flux, respectively. Similar findings have been reported by a number of authors - that is, flux is limited almost exclusively by R_c (Shimizu *et al.*, 1993). Fouling of an ultrafiltration membrane is primarily attributable to the accumulation of colloidal particles in the size range of 0.1 - 1 μm (Ramamurthy *et al.*, 1995). Deposition of these colloidal particles is controlled by several factors including cross flow velocity (the velocity of the retentate across the surface of the membrane) (Pejot and Pelayo, 1993), concentration of nutrients in solution (Choo and Lee, 1996) and presence of larger macromolecules in solution (Upton *et al.*, 1997).

Figure 5-33 indicates the operating time over which a 20% loss of flux occurred in each of the experimental runs. Cleaning was performed as required to maintain sufficient flux through the system. The "set point" flux was different for each experimental run, and was determined by the hydraulic residence time in the reactor. A 20% reduction of the original (post cleaning)

maximal flux was chosen as a reference point to demonstrate differences in the rate of filter fouling in each treatment system, an arbitrary reference point which has been used by other authors (Pejot and Pelayo, 1993, Ramamurthy *et al.*, 1995).

In the ultrafiltration system studied here, fouling was most likely controlled by the concentration of colloidal particles in the liquid being filtered - as the concentration of colloidal materials in the retentate increased (as with increasing water recovery fraction) the rate of fouling sharply increased.

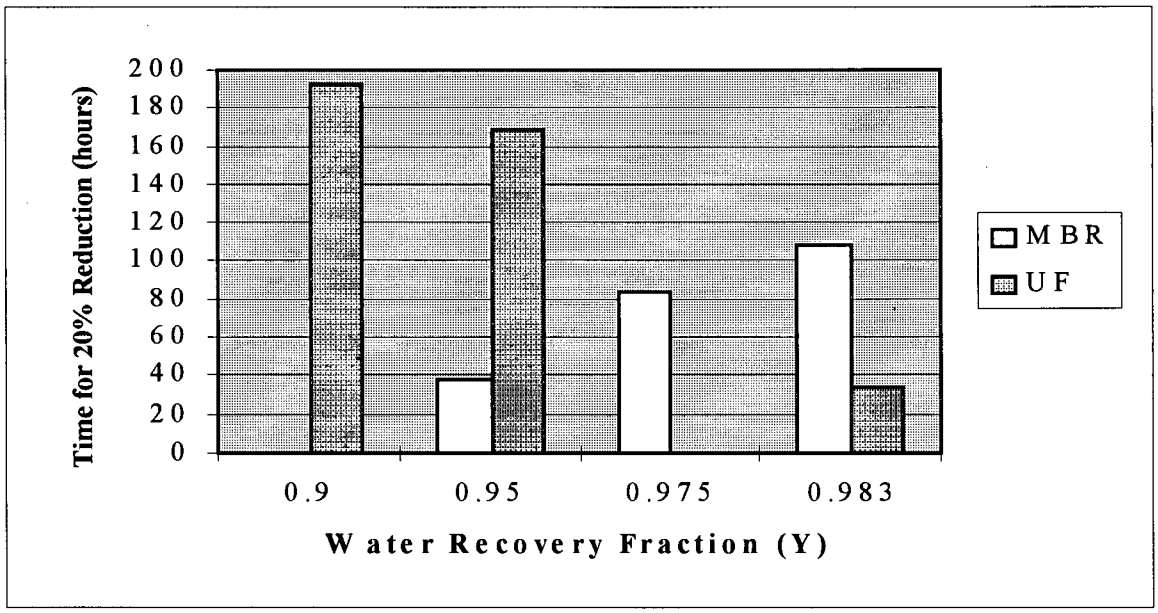

Figure 5-33: Time for a 20% Reduction in Permeate Flux in the Membrane Bioreactor and Ultrafiltration Systems as a Function of Water Recovery Fraction

In the case of the membrane bioreactor, fouling of the membrane surface was likely caused by a number of factors, including: inorganic precipitation of phosphorus compounds (e.g. struvite $MgNH_4PO_4 \bullet 6H_2O$); extracellular matrix excreted by certain bacteria in the mixed liquor (Fane *et al.*, 1994; Hodgson and Fane, 1992) and granular cell material (e.g. glycogen and cell

wall fragments) released during cell lysis resulting from shear stresses induced by pumping (Shimizu *et al.*, 1994).

The rate of fouling significantly decreased with increasing water recovery fraction, suggesting that these factors played a less significant role as the hydraulic residence time was decreased (and the concentration of mixed liquor volatile suspended solids increased), possibly due to changing composition of the mixed microbial culture.

5.3.4 Characteristics of Retentate

Suspended solids (SS) and mixed liquor suspended solids concentrations were estimated in two different ways. In the first case, the dissolved solids were subtracted from the total solids and in the second case (demarked with an asterisk) the average total solids in the effluent (which was equivalent to the dissolved solids in the effluent) were subtracted from the total solids in the retentate. It was noted that biomass was able to pass through the filter used for the determination of suspended solids in this experiment, such that the traditional procedure used for the determination of MLVSS concentration, as a measure of biomass, was inaccurate.

Table 5-2 and Table 5-3 present the characteristics of the concentrate in the MBR treatment system for each of the experimental conditions. All values were rounded to the nearest 5 mg/L.

Table 5-2: Characteristics of the MBR Retentate (pt. I)

Y	TS mg/L	VS mg/L	TDS mg/L	VDS mg/L	SS mg/L	SS* mg/L	MLVSS mg/L	MLVSS* mg/L
0.95	17675	12280	13460	8485	4220	14460	3795	13010
0.975	27585	20910	15625	10015	11960	23870	10890	21735
0.983	31470	25425	23545	18045	7930	27820	7380	25885

(asterisk (*) refers to calculation of suspended solids by means of subtracting permeate solids from total solids - see explanation previous)

SS* = Suspended Solids (TS - MBR Solids)

MLVSS* = SS* * (VS/TS)

MLVSS* concentrations in the MBR system appeared to increase substantially with lower HRT, while MLVSS concentrations did not. MLVSS* appears to be a better indication of active biomass, based on its dependence to hydraulic residence time.

Table 5-3 presents the chemical oxygen demand and the resin and fatty acid concentrations in the MBR retentate. Chemical oxygen demand appeared to accumulate to a greater extent than resin and fatty acids in the MBR with increasing water recovery fraction. This indicates a greater degree of degradation of resin and fatty acids than COD at short hydraulic residence times.

Table 5-3: Characteristics of the MBR Retentate (pt. II)

Y	COD mg/L	Resin Acids mg/L	Fatty Acids mg/L	RFA mg/L
0.95	25425	225	270	595
0.975	44770	410	365	775
0.983	52655	590	490	1080

Table 5-4 and Table 5-5 present the equivalent information for the ultrafiltration system.

Table 5-4: Characteristics of the UF Retentate (pt. I)

Y	TS	VS	TDS	VDS	SS	SS*	MLVSS	MLVSS*
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
0.9	12690	9306	10490	7380	2204	8710	1930	7620
0.95	16795	12635	13580	9555	3215	13090	3080	12430
0.983	29030	24580	21800	17730	7230	24990	6855	23680

Solids concentrations in the UF system were generally lower than in the MBR system, where a greater proportion of the solids entering the reactor were retained in the system, and biomass growth would account for the retention of contaminants as biological solids.

Table 5-5: Characteristics of the UF Retentate (pt. II)

Y	COD	Resin Acids	Fatty Acids	RFA
	mg/L	mg/L	mg/L	mg/L
0.9	19420	431	384	515
0.95	20523	538	650	1288
0.983	48325	1274	1421	2695

Similarly, the Chemical Oxygen Demand of the concentrate in the MBR system was found to be higher than that of the UF system, as a result of the higher retention of particulate COD by the MBR and the higher solids (biomass and influent) concentration in the MBR.

Resin and fatty acid concentrations were markedly higher in the UF system, most likely a result of two factors. A greater fraction of RFA were retained by the UF system (and would be present in the concentrate), and the biological oxidation of resin and fatty acids within the membrane biological reactor would result in lower concentrations in the MBR retentate.

Some deposition of contaminants was evident on the walls of each of the treatment systems - resulting in some operational difficulties (sticking of floats and fouling of membranes). In the MBR system, these deposits were dark brown in color, and would often float on the surface of the reactor contents, while in the UF system, the deposits were primarily on the walls of the reactor and were light brown in color.

5.3.5 Solids Mass Balance

Figure 5-34 and Figure 5-35 present cumulative solids mass balance data for each of the treatment systems. Cumulative mass balances were determined by calculation of mass flow rates of solids entering the systems (via the influent) and leaving the system (via the effluent and the concentrate wasting) plus the mass of solids retained in the system. Sampling for chemical analysis was always performed from material already being wasted, such that it did not contribute to solids loss. In both systems, some fraction of solids was unaccounted for in the balance.

Total solids out of the system was calculated using the following equation:

Total Solids out (g) = Permeate Solids (g) + MBR Solids (g) (5.1)

Figure 5-34 indicates that not all solids were accounted for in the balance - i.e. The Total Solids out (g) was always less than the Total Solids in(g), indicating that some solids were destroyed in the MBR system.

In the case of the MBR system, solids could have left the system by two mechanisms: deposition as particulate matter on the walls and bottom of the reactor; and destruction by aerobic metabolism., although these were not accounted for in the balance, nor were they measured

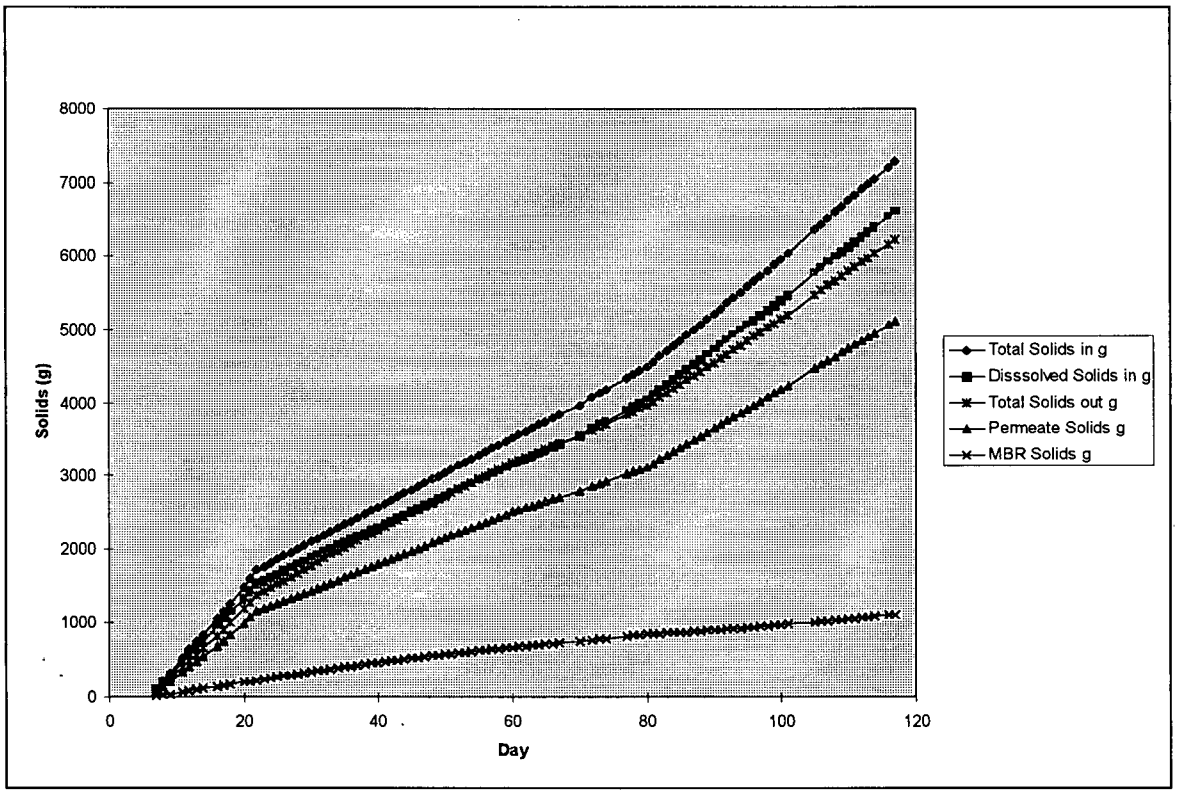

Figure 5-34: Cumulative Solids Mass Flows: MBR, as a Function of Time

The complete biological oxidation of organic solids would result in the mineralization of solid material to final products of carbon dioxide and water. Measurements of the specific oxygen uptake rate (SOUR), which ranged from 1.38 - 2.00 mg O_2/ (g MLVSS*•min) over the course of the experimental period indicated that aerobic respiration was occurring. Tardif (1996) reported SOUR values of 0.35 - 2.42 mg O_2/ (g MLVSS*•min) for a similar system.

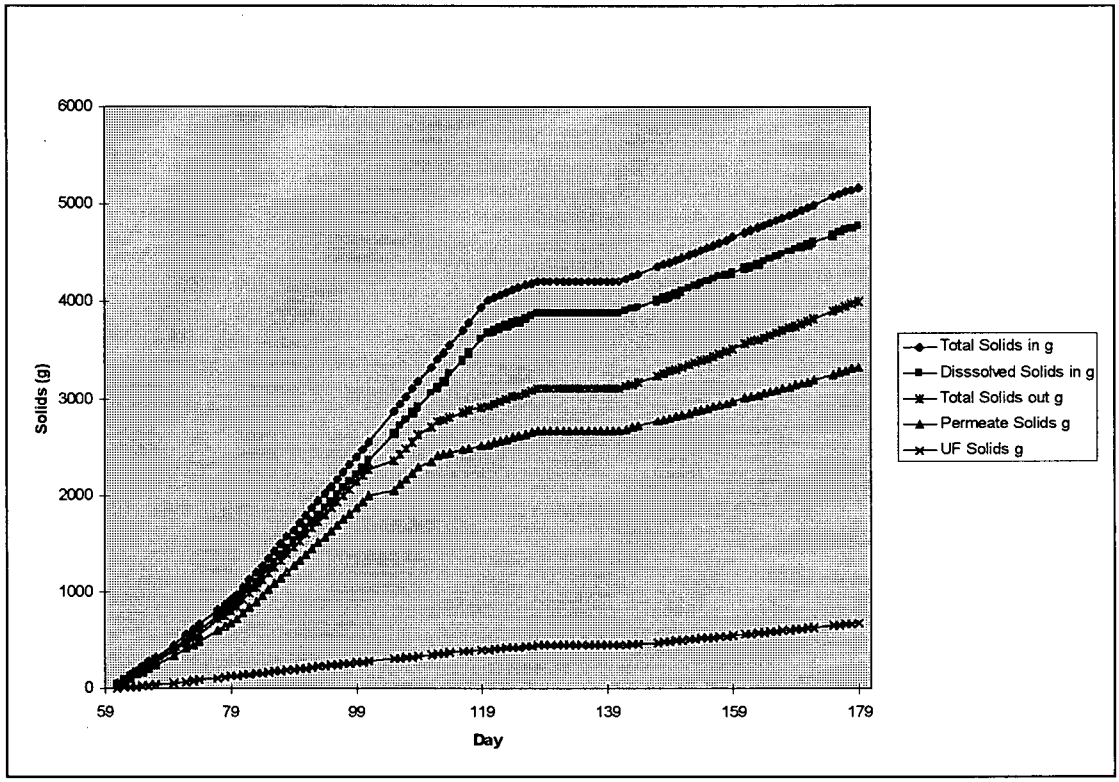

Figure 5-35: Cumulative Solids Mass Flows: UF, as a Function of Time

Figure 5-35 indicates that the mass balance discrepancy for solids was greater in the case of the ultrafiltration system than for the MBR. As was the case with the MBR, abiotic solids loss was likely attributable to precipitation and deposition. As noted earlier, significant deposition was evident in the UF system. These depositions were not measured in the solids mass balance, and deposits were allowed to accumulate over the course of the experiment.

The solids mass balance in the ultrafiltration system shows no change from day 125 to day 140 as the ultrafiltration system was taken off line, and feeding was ceased.

An additional loss of solids in the UF system may have occurred as a result of anaerobic biological activity, since no aeration was provided. The concentration of anaerobes in closed whitewater systems has been reported to be extremely high, and was attributed to high concentrations of organic material and to environmental conditions ideally suited to anaerobic biological growth. The presence of anaerobes in whitewater systems has been linked to operational difficulties, corrosion and problems with paper quality in closed mills (Gudlauski, 1996).

5.4 Biological Activity in the MBR

5.4.1 MLVSS

Mixed liquor volatile suspended solids (MLVSS) concentrations were calculated in two fashions for the purpose of this experiment (MLVSS, and MLVSS*) as discussed in section 5.3.4. As reported in Section 5.3.4, some biomass was unaccounted for in the protocol used for the determination of MLVSS. MLVSS*, however, accounted for all biomass present in the mixed liquor samples.

decreased hydraulic residence time, as predicted by Monod first order kinetics. Figure 5-37 presents the variation of MLVSS* concentration in the MBR observed over the course of the experiment.

Two of the primary operating advantages of the membrane biological reactor over conventional biological treatment are the complete retention of biosolids and the ability to

operate at high concentrations of MLVSS - allowing for higher loading rates, and lower food-to-microorganism ratios.

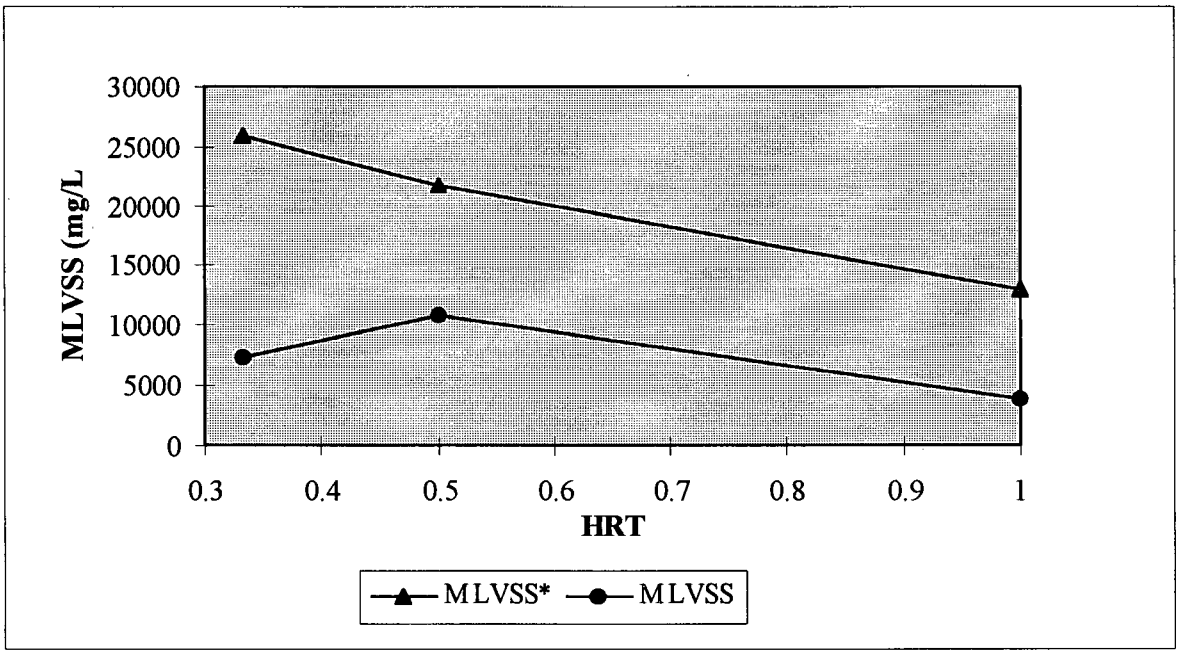

Figure 5-36: MLVSS and MLVSS* Concentrations in the Membrane Bioreactor as a Function of HRT

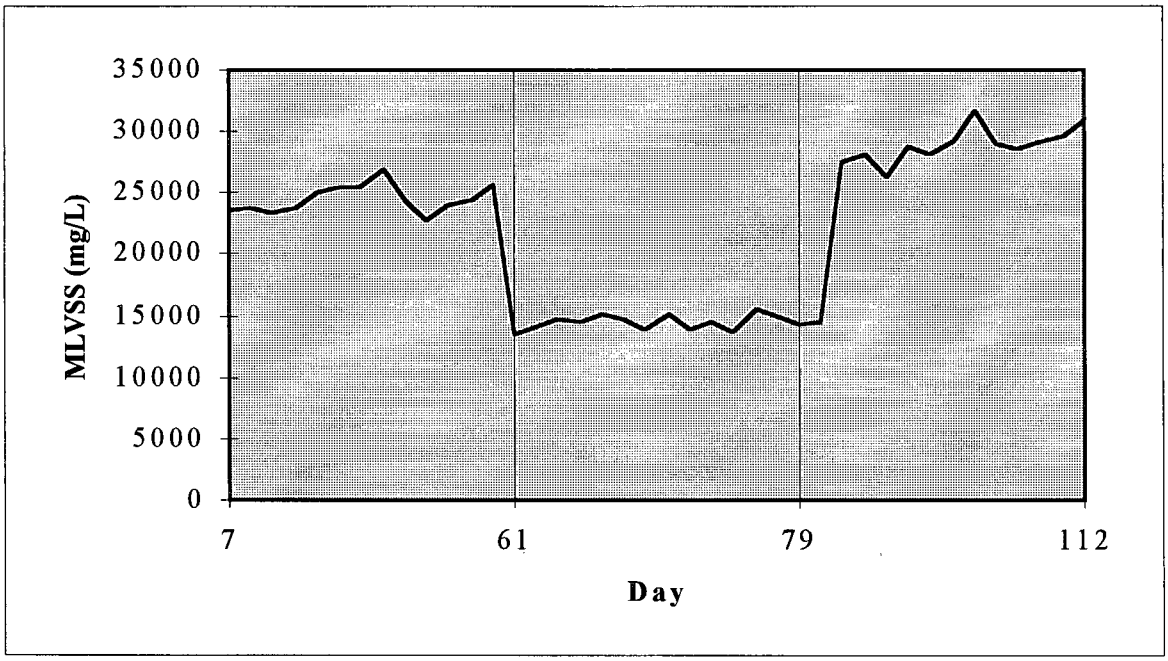

Figure 5-37: MLVSS * Concentrations in the MBR as a Function of Time

5.4.2 Food to Microorganism Ratio

The food-to-microorganism (F/M) ratio is a parameter used in the design and operation of activated sludge systems. Strict control of the food-to-microorganism ratio is important in determination of the type of microorganisms which thrive within a mixed microbial culture and for the prevention of such problematic occurrences as sludge bulking (Metcalf & Eddy Inc., 1991).

The F to M ratio is calculated by the following equation:

$$\frac{F}{M} = \frac{S_o}{\Theta X} \qquad (5.2)$$

where:

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

θ = HRT (d)

X = MLVSS* concentration (mg/L)

For the MBR, the substrate was considered to be the biodegradable chemical oxygen demand (BCOD).

In order to determine what fraction of the whitewater COD was biodegradable at 55 °C, a modified BOD_5 test was performed.

The average concentration of COD from a triplicate series of batch biodegradation tests containing whitewater, nutrients and biomass (at a concentration of 2000 mg/L) was determined and plotted as a function of incubation time. The 5 day consumption of biodegradable COD (BCOD) was plotted and determined to represent approximately 58% of the COD (Figure 5-38).

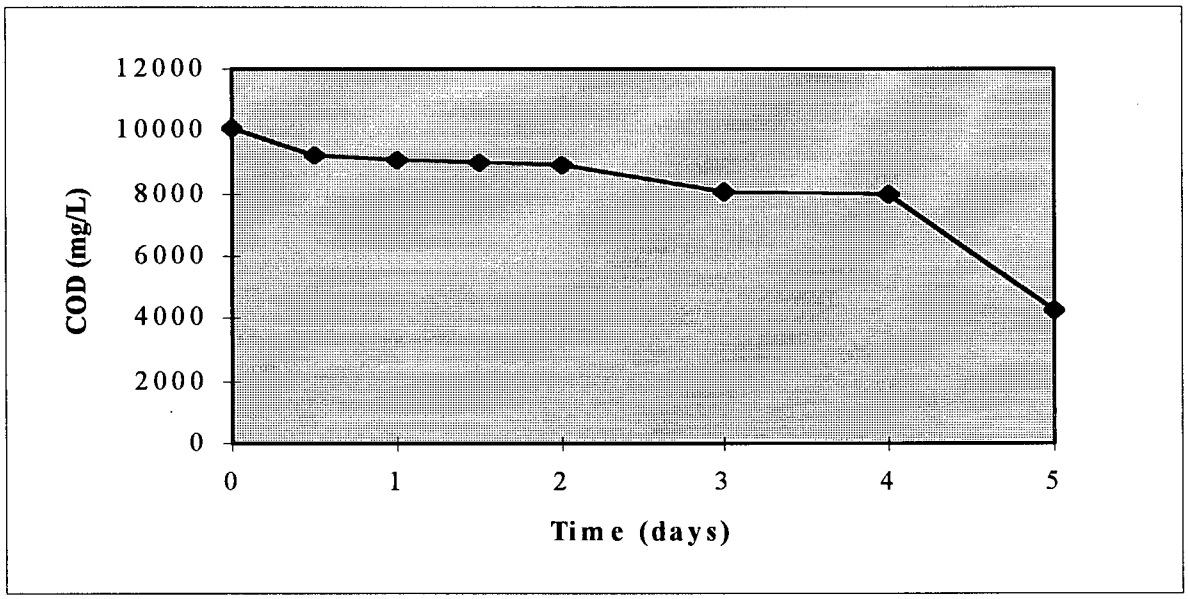

Figure 5-38: Determination of BCOD (mg/L) in the Membrane Bioreactor

Determination of the F/M ratio for 5 day biodegradable COD was as follows:

$$\frac{F}{M}_{(BCOD)} = 0.58 * \frac{F}{M}_{(COD)} \qquad (5.3)$$

Table 5-6 presents the F/M (COD) and F/M (BCOD) for each of the three experimental runs in the MBR.

Table 5-6: F/M Ratios

Y	HRT (d)	F/M COD (d^{-1})	F/M BCOD (d^{-1})
0.95	1	0.388	0.225
0.975	0.50	0.539	0.313
0.983	0.33	0.665	0.386

Typical values for a complete mix activated sludge system are 0.2 - 0.6 mg BOD_5/(mg MLVSS*•d) (Metcalf & Eddy Inc., 1991). One of the primary advantages of an MBR system over activated sludge is the ability to maintain a low F/M ratio under high loading rates, thus minimizing sludge yield (Chiemchaisri and Yamamoto, 1994). The MBR studied in this experiment exhibited F/M ratios ranging from 0.2-0.39, lower than those recommended for activated sludge systems.

5.5 Effect of VRF on Operation of the UF System

One of the objectives of this study was to examine the behavior of an ultrafiltration system operating in a continuous mode over a range of volume reduction factors (VRF). Ultrafiltration systems normally operate at volume reduction factors in the range of 15-20 (Pejot and Pelayo, 1993), and filtration is often performed as a batch operation. At low volume reduction factors the flux through the filters is high, and fouling is kept to a minimum.

In the present study, the operation of the ultrafiltration system in continuous mode at VRF 10, 20 and 60 yielded the following observations.

- Contaminant removal efficiency was only minimally affected by the VRF. Removal of total solids, total COD and dissolved COD was improved with increasing VRF, resin acid, and fatty acid removal decreased slightly with increasing VRF.

- Removal of cationic demand markedly decreased with increasing VRF. As discussed in Section 5.3.2.4, this may have been a result of anaerobic microbial activity resulting in the production of anionic trash at the higher volume reduction factors.
- Maximum flux decreased almost linearly with increasing volume reduction factor. At volume reduction factors of 10 and 20, the UF flux was high enough to be considered an economically viable treatment option (Pejot and Pelayo, 1993).
- The time for a 20% loss of flux decreased almost exponentially with increasing volume reduction factor. At a VRF of 60, the effects of fouling were evident very quickly, and a 20% loss was apparent in less than 48 hours. Other authors have reported similar findings (Pejot and Pelayo, 1993; Ekengren *et al.*, 1993).
- Operation of the UF system at a volume reduction factor of 60 was not possible and was abandoned prior to completion of the run due to the inability to maintain an adequate flux through the filter without daily cleanings.

Operation of an ultrafiltration system at high volume reduction factors would be preferable since smaller volumes of concentrate would require disposal. At a VRF of 60, however, this advantage is offset by the requirement for frequent cleaning and high costs associated with downtime as a result of the high rate of fouling rate. Based on the results from this study, it would appear that the ideal operating capacity for the UF system is at a VRF of 20.

5.6 Comparison to Other Research

The findings in this study indicate that the design criteria for the MBR and UF systems, when operated under ideal conditions, would be quite different. The MBR system, although not

optimized in this study (it may have been feasible to operate at even lower HRTs) appeared to operate best under a VRF of 60- corresponding to a long SRT and a short HRT while the UF system appeared to operate best at a VRF of approximately 20. This difference in optimal VRF's would result in dramatically different design criteria, with the mixing tank (reactor) of the MBR system being approximately one third the size of that of the UF system, and the UF system producing three times the concentrate requiring disposal. The MBR, however, would require additional equipment (such as nutrient addition and aeration systems) not required by the UF system, increasing the capital and operating costs associated with this treatment system.

Optimal operating conditions for an MBR would differ substantially from the optimal operating conditions for a UF system. Table 5-7 presents a comparison of the two systems. Confidence intervals (90%) are presented in brackets following each percentage removal value.

The results from this suggest that operation of a membrane bioreactor appears to offer no real advantage over an ultrafilter alone for the treatment of low-water use integrated TMP-newsprint whitewater. The MBR did offer marginally improved removals of solids and chemical oxygen demand, and a slight removal of short chained lignins, but the UF system exhibited fewer operational difficulties, lower rate of fouling, and exhibited higher removal efficiencies for both resin acids and cationic demand.

Table 5-7: Comparison of Optimal Operating Conditions

Parameter	MBR System	UF System
VRF	60	20
Water Recovery Fraction (Y)	0.983	0.950
Fraction Concentrate (requiring treatment/disposal)	0.017	0.050
HRT (days)	0.33	1
SRT (days)	20	20
Maximum Flux ($L/(m^2 \cdot hr)$	164	164
Time for 20% loss of flux (hrs)	110	170
Removal of total solids (%)	28.8 (30.4-27.1)	23.3 (24.9-21.6)
Removal of Dissolved Solids (%)	21.5 (23.3-19.7)	17.8 (18.9-16.5)
Removal of COD (%)	48.3 (50.8-45.9)	31.8 (34.2-29.4)
Removal of Dissolved COD (%)	34.2 (37.4-31.0)	3.7 (13.8-(-6.4))
Removal of RA (%)	68.0 (76.2-59.9)	95.3 (100-89.7)
Removal of FA (%)	99.0 (99.1-98.8)	98.7 (99.2-98.2)
Removal of Cationic Demand (%)	47.9 (52.8-43.0)	74.2 (79.4-68.9)
Removal of UV- Lignin (%)	7.21 (10.0-4.4)	-1.2 (2.9-(-5.4))

The conclusion that the MBR system offered no particular advantage over an UF system is specific to this particular study. Different operating conditions, such as lower temperatures and lower hydraulic residence times, or the use of a membrane with a smaller pore size or a hollow-fiber type membrane system would likely improve the performance of the MBR system. Additional research into the treatment of a minimum effluent TMP-newsprint whitewater could include the examination of the use of a hollow fiber MBR.

6. CONCLUSIONS

This chapter summarizes the findings of this thesis and the research to date on treatment options for a minimum effluent integrated TMP-newsprint whitewater.

A summary of the current literature on systems closure and fresh water minimization in a mechanical newsprint mill yielded the following findings regarding the composition of a minimum effluent whitewater.

- The reduction of fresh water levels from current usage of 10-150 m^3/adt, to 2-5 m^3/adt, will require the implementation of such practices as pulp washing and countercurrent flow.
- Closure or partial closure of an integrated mechanical newsprint mill would result in an increase in suspended solids, dissolved and colloidal solids, chemical oxygen demand, resin and fatty acids, lignin and temperature. A decrease in dissolved oxygen in the whitewater would occur.
- To simulate a minimum effluent mechanical newsprint whitewater, TMP-newsprint wastewater streams which would comprise the whitewater in a mechanical newsprint mill following fresh water use reductions should be used to produce a whitewater containing higher levels of the aforementioned contaminants than an open mill whitewater.

6.1 Comparison : MBR and UF Treatment of Minimum Effluent Whitewater

1. The MBR was found to be a relatively stable form of biological treatment at 55 °C but contaminant removals were generally lower than had been found in previous studies. Tardif (1996) using a membrane of nominal pore size of 0.08μm was able to better

remove all contaminants of interest. Although the MBR was able to completely retain suspended solids, removal efficiencies for total and dissolved solids were only 34% and 28% respectively. Maximum removal of other contaminants were as follows: total chemical oxygen demand - 58%; dissolved chemical oxygen demand - 36%; resin acids - 76%; fatty acids - 99%; cationic demand - 48%; and UV-lignin (205 nm) - 12%.

2. Solids, COD and UV-lignin removal efficiencies in the UF system were slightly lower than those in the MBR system. Removal efficiency ranges were as follows: total solids: 22 - 20 %, dissolved solids: 18 - 12%; total COD: 37 - 22%; dissolved COD: 14 - (-3)%, UV-lignin: -1 - (-6)%.
3. Removals of resin and fatty acids and cationic demand in the UF treatment system were high: fatty acids: 100 - 93%; resin acids: 100 - 98%; cationic demand: 88 - 68%.
4. Maximum flux through the MBR was high (175-162 L/(m^2•hr)) and was relatively stable at hydraulic residence times of 0.33, 0.5 and 1 day, corresponding to volume reduction factors of 20, 40 and 60.
5. At low volume reduction factors, maximum flux through the UF system was very high - 198 L/(m^2 hr) at a VRF of 10, and 160 L/(m^2•hr) at a VRF of 20. Flux in the UF system decreased linearly with increasing volume reduction factor. Maximum flux at a VRF of 60 was 118 L/(m^2•hr).
6. Fouling of the UF filter in the MBR system was substantial - a 20% loss of flux was observed in 39 hours at an HRT of 1 day; but decreased with increasing volume reduction factors. The time for a 20% loss of flux increased linearly with decreasing hydraulic retention time. The rate of fouling of the UF filter in the ultrafiltration treatment system was highly dependent on volume reduction factor. At a low VRF (i.e. 10) fouling was

slow - 192 hours for a 20% loss of flux, but the time for fouling decreased exponentially with increasing volume reduction factor.

7. Retentate from the MBR system was higher in solids and COD concentrations than the retentate from the UF system, and lower in resin and fatty acids concentrations, when operated at the same VRF, perhaps making it easier to dispose of.
8. Some solids were destroyed in both the MBR and UF systems - most likely as a result of biological degradation and deposition on the walls and bottom of the reactor.

6.2 Conclusions: MBR Biokinetics

1. The MBR system was able to function at high concentrations of mixed liquor volatile suspended solids, up to 25,000 mg/L at an HRT of 8 hours (0.33 days).
2. The imposed HRTs and SRTs used in this experiment produced F/M ratios in the MBR that were lower than typical values for a complete mix activated sludge. This would suggest that the use of an MBR could minimize sludge production.

6.3 Conclusions: Operation of a UF at Varying VRF

1. Most contaminant removal efficiencies were only minimally affected by the VRF - removal of total solids, total COD and dissolved COD was improved with increasing VRF, resin acid, and fatty acid removal decreased slightly with increasing VRF.
2. Removal of cationic demand decreased substantially with increasing VRF. This may have been a result of anaerobic microbial activity resulting in the production of anionic trash at the higher volume reduction factors.

3. Maximum flux decreased almost linearly with increasing volume reduction factor. At volume reduction factors of 10 and 20, the UF flux was high enough to be considered an economically viable treatment option.
4. The time for a 20% loss of flux decreased almost exponentially with increasing volume reduction factor. At a VRF of 60, the effects of fouling were evident very quickly, and a 20% loss was apparent in less than 48 hours.

6.4 Most Viable Treatment Option

Treatment alternatives for the purging of contaminants from a minimum effluent TMP-newsprint whitewater which have been studied to date are: ultrafiltration (10-50 °C); sequencing batch reactor (SBR) at an HRT of 2 days (20-50 °C); ultrafiltration of the SBR effluent (20-40 °C); membrane bio-reactor treatment at HRTs of 0.7-2.8 days (40-55 °C); and a comparative parallel study of ultrafiltration and MBR treatment at HRTs of 0.33 - 1 day(s), VRFs of 10-60 at 55 °C.

A determination of the most appropriate technology requires analysis of the following factors:

A. The removal capabilities of each system with respect to identified contaminants of interest;

B. Time required for treatment (flow through time, or flux), which would determine the space and size requirements of a treatment system; and operational requirements and stability of each system.

The research to date examining potential contaminant purging treatment systems for a minimum effluent TMP-newsprint whitewater, has yielded the conclusion that ultrafiltration of

the whitewater to a volume reduction factor between 10 and 20 would be the most appropriate treatment technology for this application.

This research showed that when an MBR and UF treatment system were operated in parallel there were only marginal differences in contaminant removal, and in some cases the UF outperformed the MBR.

Ultrafiltration offers numerous advantages over biological or combined biological/physical treatment, including reduced power consumption, lower economic costs (no requirement for temperature or pH moderation, aeration or nutrient addition), higher flux and lower rate of fouling.

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