

**BIOLOGICAL TREATMENT OF KRAFT CONDENSATES
IN FEEDBACK-CONTROLLED PACKED BED
AND SEQUENCING BATCH REACTORS**

by

Gonzalo Marcelo Daud Milet

B.Sc.Agr.Eng., McGill University, 1993

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE STUDIES

DEPARTMENT OF CHEMICAL AND BIORESOURCE ENGINEERING

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

December 1997

© Gonzalo Marcelo Daud Milet, 1997

In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the head of my department or by his or her representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Chemical and Bioresource Engineering

The University of British Columbia
Vancouver, Canada

Date December 8, 1997

ABSTRACT

In the pulp and paper industry there is an increasing amount of interest in the attainment of a closed cycle mill and in maintaining adequate air quality in and around the mill. As a result of these trends, kraft condensates will have to be treated and reused to a greater extent than is currently practiced. The treatment of a large volume of kraft condensates may be accomplished more effectively by biological oxidation than by the currently available technology of steam stripping.

The self-cycling fermentation (SCF) technique was applied to the control of a laboratory-scale recirculating packed bed reactor (PBR) and a sequencing batch reactor (SBR) treating accumulator condensate and evaporator condensate from a kraft pulp mill. The SCF control strategy uses the level of dissolved oxygen (DO) to dictate the rate at which untreated wastewater is fed to, and treated wastewater is harvested from, a semi-continuous bioreactor.

One PBR run and two SBR runs were performed, each SCF-controlled run lasting approximately one month. During these runs, methanol, which is responsible for the majority of the biological oxygen demand (BOD) of condensates, COD, and the effluent volatile suspended solids (VSS) concentration were routinely measured. Also measured in the SBR were the volatile suspended solids concentration in the reactor (MLVSS) and the influent and effluent concentrations of the odorous total reduced sulfur species (TRS), H_2S , CH_3SH , DMS, and DMDS. Finally, abiotic stripping experiments were performed with the SBR to evaluate the relative amount of TRS removal from the reactor that was due to stripping.

The COD removal efficiency from the accumulator condensate was $88 \pm 5\%$ from an influent COD of 3060 mg/L. The COD removal efficiency from the evaporator condensate was $64 \pm 5\%$ from an influent COD of 1740 mg/L. By triggering a new cycle only when all of the methanol was consumed, the SCF-control strategy ensured these consistent COD removal efficiencies despite significant fluctuations in operating conditions.

Overall, the SBR exhibited a performance that was superior to the PBR. During a representative react phase of the SBR, the COD removal rate was $39 \text{ kg COD/m}^3\text{-day}$. This

removal rate compares very favorably with the removal rate of full-scale activated sludge reactors, and it was seven times greater than the removal rate during a representative cycle of the PBR. The PBR produced an effluent with less than 20 mg VSS/L, but the buildup of biomass in the bed caused some operational problems. Due to some upset conditions that can be avoided in the future, the effluent VSS concentration from the SBR was generally greater than 100 mg/L. However, during the stable operation of the SBR, the biomass exhibited good settleability, with as little as 63 mg VSS/L in the effluent from a cycle that had a MLVSS concentration of 5590 mg/L.

Over 90% of the TRS was removed from the evaporator condensate during treatment in the SBR. The results of the stripping experiments indicate that most, if not all, of the TRS removal during SCF treatment, was due to stripping.

In this study, the SCF-controlled SBR has been shown to be a promising method for efficiently removing methanol, TRS, and COD from kraft condensates that are intended for reuse.

TABLE OF CONTENTS

Abstract	ii
Table of Contents	iv
List of Tables	vii
List of Figures	viii
List of Abbreviations	x
Acknowledgements	xi
 I INTRODUCTION	 1
1.1 KRAFT CONDENSATES	1
1.1.1 Sources of Condensates in the Kraft Process	1
1.1.2 Composition of Kraft Condensates	3
1.2 MOTIVATION FOR SELECTIVE TREATMENT OF KRAFT CONDENSATES	5
1.3 CURRENT SELECTIVE TREATMENT OF KRAFT CONDENSATES	6
1.4 BIOLOGICAL TREATMENT OF KRAFT CONDENSATES	7
1.5 BACKGROUND ON THE BIOREACTORS USED IN THIS STUDY	9
1.5.1 Fixed Film Reactors	9
1.5.2 Sequencing Batch Reactors	10
1.6 AUTOMATIC CONTROL OF BIOLOGICAL WASTEWATER TREATMENT REACTORS	11
1.7 SELF-CYCLING FERMENTATION	12
 II OBJECTIVES	 15
 III MATERIALS AND METHODS	 16
3.1 PACKED BED REACTOR (PBR)	16
3.1.1 Overall Description of the PBR	16
3.1.2 Packed Bed	17

3.2 SEQUENCING BATCH REACTOR (SBR)	18
3.2.1 Stirred Tank	18
3.2.2 Dosing Vessel	19
3.2.3 Sequencing of the SBR	19
3.3 FEEDBACK CONTROL SYSTEM	19
3.4 SEED	20
3.5 FEED	20
3.6 REACTOR OPERATION	21
3.6.1 Run 1	21
3.6.2. Run 2	22
3.6.3 Run 3	22
3.7 STRIPPING EXPERIMENTS	23
3.8 ANALYSES	23
3.8.1 Solids	23
3.8.2 COD	23
3.8.3 Methanol	24
3.8.4 TRS	25
3.8.5 Dissolved Oxygen Measurement	27
IV RESULTS AND DISCUSSION	28
4.1 PERFORMANCE OF THE PACKED BED REACTOR (PBR)	28
4.1.1 Cycling of the PBR	28
4.1.2 Treatment Performance of the PBR	32
4.2 PERFORMANCE OF THE SEQUENCING BATCH REACTOR (SBR)	35
4.2.1 Cycling of the SBR	35
4.2.2 Treatment Performance of the SBR During Run 2	39
4.2.3 Treatment Performance of the SBR During Run 3	42
4.2.4 Operator Intervention of the SBR Operation	48
V CONCLUSIONS	50

VI RECOMMENDATIONS	52
VII REFERENCES	54
VIII APPENDIX	59

LIST OF TABLES

Table 1	List of compounds found in kraft condensates.	3
Table 2.	Properties of TRS compounds.	4
Table 3.	Methanol and COD content of the condensates.	20
Table 4.	Operating conditions employed during the three runs	21

LIST OF FIGURES

Figure 1.	Sources of condensates from a typical kraft mill	2
Figure 2.	Schematic of a multiple effect evaporator	2
Figure 3.	Flowsheet for the SCF control program	13
Figure 4.	Typical DO profile in a SCF	13
Figure 5.	Schematic of the feedback-controlled PBR	16
Figure 6.	Pall rings used in the PBR	18
Figure 7.	Schematic of the feedback-controlled SBR	18
Figure 8.	Sample COD standard curve	24
Figure 9.	Sample methanol standard curve	24
Figure 10.	DMS standard curve	27
Figure 11.	Sample DO profile of the PBR. Dosing rate was 1%	28
Figure 12.	Sample DO profile of the recirculating liquid at the top and bottom of the PBR	29
Figure 13.	Sample DO profile of the PBR. Dosing rate was 10%	29
Figure 14.	Sample DO and methanol profile of the PBR. Dosing rate was 10%	30
Figure 15.	Sample DO profile of PBR cycles. Dosing rate was 10% and DO setpoint was 20%	31
Figure 16.	Sample DO and methanol profile of a PBR cycle. Dosing rate was 10% and DO setpoint was 20%	32
Figure 17.	Cycle time and dosing rate of the PBR	33
Figure 18.	Removal of organics in the PBR	33
Figure 19.	Influent and effluent VSS during Run 1	35
Figure 20.	DO profile throughout the four stages of a typical SBR cycle	36
Figure 21.	Profile of methanol, pH, and DO during the react phase of a typical cycle	36
Figure 22.	DO profile of several SBR cycles	39
Figure 23.	React time of the SBR during Run 2	40
Figure 24.	Influent and effluent COD in the SBR during Run 2	40
Figure 25.	MLVSS and effluent VSS in the SBR during Run 2	41

Figure 26. React time of the SBR during Run 3	43
Figure 27. Removal of organics in the SBR during Run 3	43
Figure 28. MLVSS and effluent VSS in the SBR during Run 3	44
Figure 29. TRS removal in the SBR during Run 3	46
Figure 30. Stripping of TRS and methanol in the SBR with no biomass	47
Figure 31. Extent of operator intervention in the SBR during Run 2	49
Figure 32. Extent of operator intervention in the SBR during Run 3	49

LIST OF ABBREVIATIONS

BOD	biological oxygen demand
CH ₃ SH	methyl mercaptan
COD	chemical oxygen demand
DMDS	dimethyl disulfide
DMS	dimethyl sulfide
DO	dissolved oxygen
H ₂ S	hydrogen sulfide
HAP	hazardous air pollutant
HRT	hydraulic retention time
MBR	membrane biological reactor
MLVSS	mixed liquor volatile suspended solids
PBR	packed bed reactor
SBR	sequencing batch reactor
SCF	self-cycling fermentation
TRS	total reduced sulfur
VOC	volatile organic compound
VSS	volatile suspended solids

ACKNOWLEDGEMENTS

I am very grateful to Dr. Sheldon Duff for providing indispensable input and supervision for this project, while at the same time fostering an atmosphere where I could learn by carrying out much of the work in a self-directed manner. I would also like to thank Dr. John Sheppard for providing the expertise and equipment for the start-up of the SCF control strategy, to Stephan Müller for helping out during the initial stages, and to Dr. David Cooper and his students for providing the Turbo Pascal version of the control program that was used as a template. I am very grateful for the co-operation offered by Jeanne Taylor and other staff at Western Pulp Ltd., who generously delivered a weekly supply of foul condensate. Special thanks to Pierre Bérubé, for assisting me in carrying out the TRS analysis procedure that he developed. I am also indebted to Paula Parkinson in the Civil Engineering lab, for her extensive technical support with the gas chromatograph. Thanks also to the staff at the UBC Pulp and Paper Center and at the Chemical and Bioresource Engineering shop for their help with equipment and library resources. Finally, I gratefully acknowledge the financial support that was provided by means of an FCAR Scholarship and an NSERC Collaborative Project Research Grant.

I INTRODUCTION

1.1 KRAFT CONDENSATES

Kraft condensates are condensed process vapours originating from the digester, the blow tank, and the multiple effect evaporator of a kraft pulp mill. "Clean" condensates are reused within the mill to minimize fresh water use and effluent discharge. "Foul" condensates are considered to contain a high concentration of dissolved organics, hereby prohibiting their reuse as process water. An NCASI survey (1995) of 18 U.S. kraft mills revealed that the total volume of condensates ranged from 5.3 to 11.9 m³ per air dry ton of pulp produced (m³/adtp), with an average of 8.6 m³/adtp.

1.1.1 Sources of Condensates in the Kraft Process

The sources of condensates from a typical batch, softwood, kraft process are illustrated in Figure 1. In the digester, the wood chips are mixed with white liquor, consisting of Na₂S and NaOH, and are cooked at an elevated temperature and pressure. This operation softens the chips and dissolves approximately 80% of the lignin (Smook, 1992). Among the organic compounds that are dissolved by the oxidation reactions, are volatile organic compounds (VOC's), which have a sufficiently low molecular weight to be released into the vapour phase. The vaporous digester emission, containing a high concentration of VOC's, is subsequently condensed, and the condensate is then sent to a turpentine decanter for turpentine recovery. The underflow from the decanter comprises one of the foul condensate streams.

In a batch pulping process, the softened chips from the digester are then sent to the blow tank, where the chips are disintegrated into fibers. The resulting vaporous emission is condensed in the accumulator, where the hot condensate is used to indirectly heat process water. The colder condensate from the bottom of the accumulator becomes a source of foul condensate. The vapours given off from the accumulator are condensed, the resulting liquid being typically sent to the turpentine decanter.

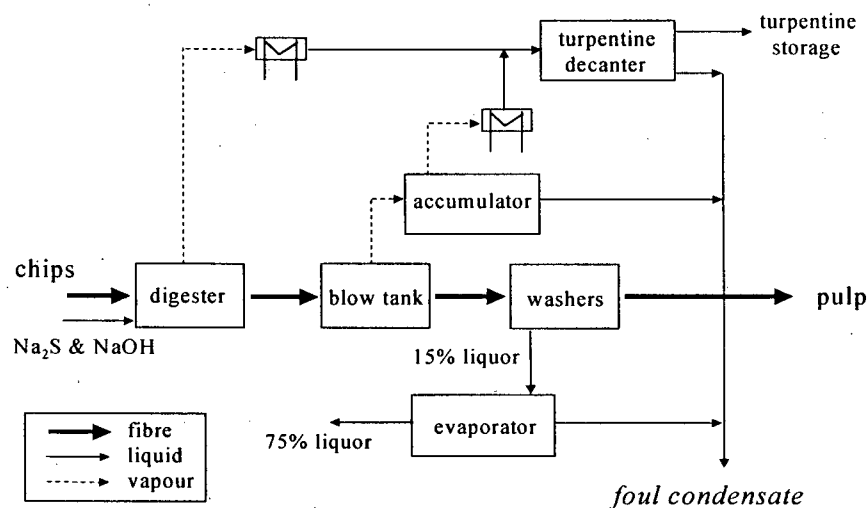


Figure 1. Sources of condensates from a typical kraft mill pulping softwood in batch digesters.

From the blow tank, the pulp is sent to the brown stock washers, where the weak black liquor, containing dissolved organics and the spent cooking chemicals, is washed from the pulp, which is subsequently sent to the bleach plant. In the multiple effect evaporators, the black liquor is concentrated from a consistency of 15% to 75%, so that the resulting strong black liquor can then be burned in the recovery boiler for eventual recovery of the cooking chemicals.

In the multiple effect evaporators, the vapour that is released from each effect is used to heat liquor in the next effect (Figure 2). As the vapour gives its latent heat to the liquor, the vapour condenses, and thereby forms another source of foul condensate. The vapours given off

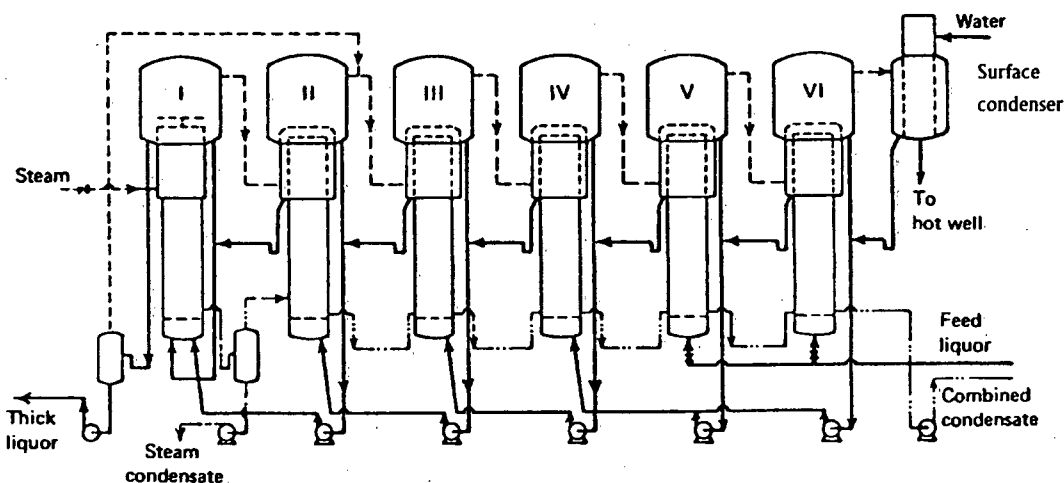


Figure 2. Schematic of an end-fed multiple effect evaporator (adapted from Smook, 1992).

by the weaker black liquor are the most contaminated. The vapours given off by the first-stage evaporation of weak black liquor are indirectly condensed by cooling water in the surface condenser. The resulting surface condenser condensate is typically the most contaminated of all the evaporator condensates (Blackwell et al., 1979).

1.1.2 Composition of Kraft Condensates

The various compounds that have been found in kraft condensates, and their maximum reported concentrations, are listed in Table 1.

Table 1. List of compounds found in kraft condensates, and their maximum reported concentrations (adapted from Blackwell et al., 1979).

Compounds	Concentration (mg/L)
TRS: H ₂ S	660
CH ₃ SH	5,300
DMS	7,400
DMDS	4,100
BOD: methanol	12,000
ethanol	3,200
acetone	500
methyl ethyl ketone	27
terpenes	25,000
phenolics	82
resin acids	230
total BOD ₅	13,000
sodium	370
suspended solids	70
pH	6 - 11.1

The main contaminants of concern in kraft condensates are methanol and reduced sulfur compounds. The four major volatile sulfur compounds in condensates are hydrogen sulfide (H₂S), methyl mercaptan (CH₃SH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS), and these are referred to as total reduced sulfur (TRS). Methanol and TRS are discussed in further detail below. Since sodium ions and resin acids are non-volatile, these compounds are only present in condensates when black liquor is entrained (Blackwell, 1978). Terpenes are unsaturated, cyclic, aliphatic hydrocarbons of the form (C₅H₈)_n, which are present

in softwood. They can account for a substantial portion of the condensate BOD if they are not removed. However, the standard practice is to use a turpentine decanter to remove most of the terpenes from the digester relief condensate and from the accumulator vent condensate (NCASI, 1995).

Methanol

Methanol, CH_3OH , is the predominant BOD component in condensates. One gram of methanol exerts 1.5 g of COD and approximately 1.1 g of BOD (Gay, 1974). It is also toxic to humans, and the U.S. EPA classifies methanol, as well as acetaldehyde and methyl ethyl ketone, as a hazardous air pollutant (NCASI, 1995). With a boiling point of 65 °C, methanol is only moderately volatile. In the NCASI survey (1995), the total condensate methanol content ranged from 7.3 to 11.4 kg/adtp, and averaged 9.5 kg/adtp.

Total Reduced Sulfur (TRS)

Foul condensates contain a major portion of the total mill TRS, ranging from 0.1 to 0.9 kg TRS/adtp (Sarkanen et al., 1970). The reduced sulfur compounds impart an estimated 75 to 95% of the toxicity in condensates (Environment Canada, 1979; Blackwell et al., 1979; Blackwell et al., 1980). Due to their high volatility and low odour threshold (Table 2), they are also responsible for most of the strong odour of condensates. The volatilization of H_2S and CH_3SH occur only via their unionized forms. The pK of H_2S and CH_3SH at 25 °C is approximately 7.1 and 10.2, respectively (Blackwell et al., 1980). Thus at neutral pH, approximately half of the H_2S and virtually all of the CH_3SH are in their volatile forms.

Table 2. Properties of TRS compounds (Sarkanen et al., 1970; Cook et al., 1973).

Compound	Boiling Point, °C	Odour Threshold in Ambient Air, ppb	Toxicity LC_{50} , mg compound / L
H_2S	-62	0.4 - 5	1 ¹
CH_3SH	5.8	2 - 3	0.5 ¹
DMS	38	~ 1.0	23 ²
DMDS	118	-	4 ²

¹ Using fish as test organism

² Using water flea as test organism

1.2 MOTIVATION FOR SELECTIVE TREATMENT OF KRAFT CONDENSATES

On average, 75% of the total condensate volume from surveyed kraft mills in the U.S. was directly reused within the mills (NCASI, 1995). These "clean" condensates were reused in the brown stock washers and in the recausticizing area. Although approximately one in five kraft mills in the U.S. steam strip and subsequently reuse the foul portion of condensates, the majority of the mills discharge the foul condensate to the secondary treatment system with the combined mill effluent (NCASI, 1994a). It is believed that growing concerns regarding air quality will make it necessary for mills to selectively treat a significant portion of the supposedly "clean" condensates. In addition, for mills to attain the goal of closed cycle operation, the selective treatment and reuse of the foul portion of condensates will be a necessity. Thus, to simultaneously achieve adequate air quality and closed cycle operation of kraft mills, a system is required that can effectively treat a large volume of kraft condensates.

Selective treatment for improving air quality

There is an increasing awareness and concern about the ambient air quality in and around pulp and paper mills. The reuse of contaminated condensates within the mill, and the discharge of these condensates to the secondary treatment system results in the emission of odorous TRS and of hazardous air pollutants (HAPs) including methanol, methyl ethyl ketone and acetaldehyde, among others (NCASI, 1995). The original draft of the EPA's Cluster Rules (Roche, 1995), which has subsequently been revised (Swan, 1995), stated that any stream that contains greater than 500 mg/L methanol should be treated such that 90% of the methanol is removed prior to wastewater treatment. The draft goes on to state that all vaporous emissions from such a stream should also be collected and treated so as to destroy the HAPs. As stated previously, the cleaner 75% of the condensate volume, on average, is already reused within the NCASI-surveyed kraft mills (1995). However, these supposedly "clean" condensates had a mean methanol concentration of 680 mg/L, which exceeds the EPA's original 500 mg/L methanol limit. If the condensates were treated prior to their reuse, then this would eliminate any concerns related to the emission of HAPs or TRS.

Selective treatment for achieving closed cycle operation

In an attempt to deal with ever-increasing restrictions on the discharge of liquid effluents to the environment, the pulp and paper industry is striving to achieve closed cycle operation of their mills. In such a mill, the input of fresh water and chemicals and the discharge of liquid effluent are minimized, and theoretically eliminated. In striving to achieve closed cycle operation, individual waste streams are being evaluated for their suitability to in-mill treatment and subsequent reuse. Target streams would be those that constitute a significant hydraulic or organic load to the effluent treatment system and that could be treated for reuse.

In the kraft pulping process, the discharge of condensates may contribute only 5% of the total effluent volume from a bleached kraft mill (Blackwell et al., 1979, NCASI, 1995¹). However, in the past, these condensates accounted for as much as 25 to 40% of the total BOD in untreated bleached kraft mill effluent (Blackwell et al., 1979). During the past two decades, these condensates have been increasingly targeted for reuse. By discharging as little as 25% of the condensate volume, condensates now account for only 10 to 20% of the untreated bleached kraft mill effluent BOD¹. The direct reuse of all of the condensates, including the 10 to 20% of foul condensates that are currently discharged, is not possible, since this would lead to excessive levels of TRS and HAP emissions, as well as excessive concentrations of organic compounds dissolved in the process water. The use of process water with high BOD and COD concentrations leads to problems such as the growth of biological slime. The reuse of foul condensates in a closed cycle mill will therefore require a treatment system that can remove TRS, HAPs, and COD from the condensates.

1.3 CURRENT SELECTIVE TREATMENT OF KRAFT CONDENSATES

The conventional method of treating kraft condensates is by air stripping for TRS removal or steam stripping for TRS and BOD removal. There are very few full-scale air strippers

¹ The results of four surveyed mills were used, and the following was assumed 1) 100 m³/adtp and 20 kg/adtp of total bleached kraft mill effluent flow and BOD, respectively. 2) Methanol contributes 1.1 g BOD₅ / g methanol (Gay, 1974), and methanol is the sole contributor to condensate BOD.

in operation, and approximately one in five kraft mills in the U.S. uses a steam stripper (NCASI, 1994a). The methanol concentration in and out of the surveyed steam strippers averaged 4830 and 610 mg/L, respectively. Note that the average methanol concentration of these stripped condensates exceeds the original 500 mg/L EPA limit.

For a steam stripper with a given condensate-to-steam ratio and a given condensate hydraulic retention time, the rate of methanol removal is solely determined by the methanol transfer rate from the liquid phase to the vapour phase. The mass transfer rate is proportional to the methanol concentration gradient across the two phases. Therefore, a cleaner condensate will experience less overall methanol removal than a more contaminated condensate. In other words, the stripping of cleaner streams is more expensive, per unit of methanol removed, than the stripping of foul condensate streams.

1.4 BIOLOGICAL TREATMENT OF KRAFT CONDENSATES

Biological treatment is an alternative process for removing the TRS, HAPs, and COD from condensates. In contrast to steam stripping, the operating cost of biological treatment is proportional to the strength of the stream to be treated, due to the costs associated with nutrients, aeration, and sludge handling. The biological oxidation of condensate contaminants may therefore be a more cost-effective technology than steam stripping if a large volume of lower strength condensate streams are to be treated for subsequent reuse, as is expected to occur in the near future.

However, due to the volatility of methanol and especially TRS, the design of any aerobic biological treatment system for treating condensates must consider the potential stripping of these compounds from the aerated reactor. In addition, the mesophilic treatment of condensates would require cooling the condensates, which have a temperature of around 75 °C (Sebbas, 1991).

Literature Review on the Aerobic Treatment of Kraft Condensates

The only full-scale bioreactor for the exclusive treatment of kraft condensates was

reported at a Finnish kraft mill (Vettenranta, 1976; cited in Blackwell, 1986). From 1975 to at least 1985, kraft condensates were treated in a trickling filter system. By a combination of biological oxidation and air stripping, the trickling filter achieved removal efficiencies of 60% for methanol, 100% for H_2S and CH_3SH , 77% for DMS, and 44% for DMDS. The stripped gas was passed through a biofilter, which oxidized the TRS to non-odorous compounds.

A cost comparison was made for a hypothetical pure-oxygen activated sludge system and a membrane biological reactor (MBR), both treating kraft condensates (NCASI, 1994b). For a hypothetical mill producing 1000 adtp/day of pulp, a condensate flowrate of 2,000 gal/adtp and a methanol loading rate of 13 lb/adtp, the capital cost for both reactors was estimated at \$9 million, and the operating costs for the activated sludge system and the MBR were estimated to be \$620,000 and \$1,000,000 per year, respectively. In the Civil Engineering Department of the University of British Columbia, the laboratory-scale thermophilic treatment of condensates in a MBR is currently under investigation (Bérubé, unpublished).

Literature Review on the Anaerobic Treatment of Kraft Condensates

The anaerobic treatment of kraft condensates has been studied on a laboratory-scale by a number of researchers (Carpenter and Berger, 1984; Cocci et al., 1985; Pipyn et al., 1987; Qiu et al., 1988). However, the performance of these reactors was often quite unstable, exhibiting long lag periods after shutdown, and achieving BOD removal efficiencies ranging from 40 to 90%. The best performance in condensate treatment occurred with a combination anaerobic filter and effluent membrane filtration with filtrate recirculation (Yamaguchi et al., 1990). The pilot-scale reactor was operated with a temperature of 53 °C and the influent BOD was approximately 18,000 mg/L. The reactor was subjected to a low loading of 11.0 kg BOD/m³/day and a high loading of 35.5 kg BOD/m³/day. For these conditions, the BOD removal efficiency was 85 and 93%, respectively. Although good performance was obtained in the latter study, the difficulties encountered in most of these studies suggest that the aerobic treatment of condensates may be a preferable treatment option.

Aerobic Growth on Methanol and TRS Compounds

Methanol is aerobically degraded by a number of methylotrophic bacteria, including

Pseudomonas sp., *Hyphomicrobium* sp., *Methylobacillus* sp., and *Bacillus* sp., (Erickson and Tuitemwong, 1991), with growth yields ranging from 0.30 to 0.54 gram of dry cell weight per gram of methanol consumed (Jung et al., 1981; Chudoba et al., 1989; Erickson and Tuitemwong, 1991). Various *Thiobacilli* sp. have been reported to aerobically oxidize H_2S (Buisman et al., 1991; Ongcharit et al., 1991; Janssen et al., 1995), CH_3SH , DMS, and DMDS (Erickson and Tuitemwong, 1991). *Hyphomicrobium* sp. has been found to oxidize DMS (Pol et al., 1994), and *Desulfobulbus propionicus* can oxidize H_2S (Fuseler and Cypionka, 1995).

Toxicity of Hydrogen Sulfide

Hydrogen sulfide, at concentrations in the nanomolar to micromolar range, is extremely toxic to most aerobic organisms. The toxicity results from the binding of sulfide to the iron in cytochrome c oxidase, a key enzyme in the electron transport chain. Sulfide inhibition of cytochrome c oxidase is reversible, and aerobes exposed to sulfide-rich environments can employ several defense mechanisms for dealing with the toxicity (Vismann, 1991). Since kraft condensates contain H_2S , some degree of inhibition may be encountered when aerobically treating foul condensates.

1.5 BACKGROUND ON THE BIOREACTORS USED IN THIS STUDY

1.5.1 Fixed Film Reactors

Fixed film reactors have been used for wastewater treatment since the 1870's, when the first trickling filter was reported. Fixed film reactors rely on the ability of microbes to form a biofilm on a surface. The biofilm consists of microbial cells and of extracellular polymeric substances, which form a gel-like matrix. The extracellular polymer matrix can account for as much as 50 to 90% of the biofilm organic carbon, and is composed predominantly of polysaccharides. The biomass concentration in a biofilm reactor may be as high as 20 g/L, which allows them to achieve higher treatment rates than is possible with suspended-growth reactors. A high treatment rate is especially desirable for an in-mill treatment process, where space is less likely to be available. In addition to providing a high treatment rate, another advantage of

biofilm reactors compared to suspended-growth reactors for wastewater treatment is that the requirements for sludge settling are reduced and sometimes eliminated (Characklis and Marshall, 1990).

Various fixed film treatment processes have been applied to the treatment of pulp and paper effluents. Some of these applications include packed beds operated in a downflow mode, otherwise known as trickling filters (Séguin et al., 1993; Stuart et al., 1994;), packed beds operated in an upflow mode (Beaudry et al., 1991; Landry et al., 1991; Lavallée et al., 1993; Möbius and Cordes-Tolle, 1994; Kantardjieff and Jones, 1996), rotating biological contactors (Mathys et al., 1993; Moubayed and Gray, 1993; Marshall et al., 1995), and fluidized bed reactors (Fahmy et al., 1994; Rusten et al., 1994; Dalentoft and Thulin, 1996; Malmqvist et al., 1996).

1.5.2 Sequencing Batch Reactors

A sequencing batch reactor (SBR) is operated semi-continuously and cyclically in five stages, namely, the fill, react, settle, draw, and idle stages. Prior to the fill stage, typically 25% of the reactor volume contains settled sludge. During the fill stage, the remaining 75% of the reactor volume is filled with raw wastewater. The reactor is then agitated and aerated during the react phase, and it is during this phase that most of the BOD reduction occurs. The agitation and aeration are turned off for the settle phase, to allow the biomass to settle as a concentrated sludge blanket at the bottom of the reactor. During the draw phase, the supernatant, or treated effluent, is then drawn off, leaving behind the concentrated sludge blanket. The reactor may then remain in an idle mode until it is filled again, marking the beginning of another cycle. To achieve continuous operation, several reactors are used sequentially. Typically, the fraction of time spent in each stage is 25% for the fill stage, 35% for the react, 20% for the settle, 15% for the draw, and 5% for the idle stage (Tchobanoglous and Burton, 1991).

The following advantages have been claimed for SBRs over the standard, activated sludge reactors: better sludge settling due to completely quiescent conditions; no secondary clarifier required, resulting in less equipment and lower capital costs; their modular nature makes them very flexible with regards to reactor layout, sizing, maintenance, and spill management;

reduced labour costs; better control of bulking conditions; less odour production since the sludge is less likely to go anaerobic; and the possibility of automatically controlling the hydraulic retention time (HRT) to deal with fluctuations in the organic load (Villeneuve and Tremblay, 1995).

SBRs have been in existence since 1914, and they predate activated sludge reactors. However, in the 1920's this technology was abandoned due to the lack of control equipment. In the 1980's, SBRs made a comeback, largely due to developments in programmable logic controllers and control valves. Currently, there are hundreds of SBR systems installed throughout the world. However, only a handful of full-scale SBRs have been reported in the pulp and paper industry, including the ones at Stone-Consolidated Corporation's two newsprint and two groundwood specialty mills in Quebec, two other installations in Quebec (Villeneuve and Tremblay, 1995; Courtemanche et al., 1997), one installation at a New Brunswick groundwood mill (Cocci et al., 1997), and another one at an Austrian cardboard recycle mill (Goronszy and Jaeger, 1996). The effluent from the latter SBR was reused in the mill after it was subjected to sand filtration, micro filtration, membrane separation, and evaporative recovery of the water phase from a multiphase crystallizer, hereby enabling 95% of this mill's water flow to be recovered.

1.6 AUTOMATIC CONTROL OF BIOLOGICAL WASTEWATER TREATMENT REACTORS

Wastewater treatment plants are typically subject to persistent fluctuations in the composition of the influent flow. As a result, they must be carefully monitored and controlled in order to maintain adequate levels of treatment. For the aerobic removal of BOD, the most important variables to be controlled are the biomass concentration, the HRT, and the dissolved oxygen (DO) concentration. With the availability of variable-output aeration systems and reliable DO sensors, the automatic control of the DO concentration is straight forward and is common practice. If there is a capacity to store wastewater, then the HRT can be controlled by changing the influent flowrate. The biomass concentration of an activated sludge reactor can be

controlled by adjusting the sludge return rate.

In conventional wastewater treatment, the biomass concentration and HRT are controlled manually. This is largely due to the fact that the standard method of estimating the extent of organic carbon removal is by performing the BOD and/or the COD test. These tests can only be performed manually, and they take days or hours, respectively, to complete. Manual control based on the BOD and COD test is labour intensive and excessively slow; only after a laboratory analysis reveals poor treatment can remedial action be taken. The adoption of automatic control could therefore greatly lower the operating costs and improve the performance of wastewater treatment plants.

Automatic control requires the on-line measurement of a performance-related variable. Recently, there have been developments in the construction and application of various sensors for the automatic control of biological wastewater treatment systems. For nitrogen and phosphorous removal, oxidation-reduction potential probes have been used to control the duration of the aerobic, anoxic and anaerobic phases of full-scale activated sludge reactors, and to adjust the DO setpoint of the aeration phase (Charpentier et al., 1989; Sasaki et al., 1993). NADH probes and various ion probes also show promise for optimizing nitrogen and phosphorous removal (Vassos, 1993). For BOD removal, respirometry-based control, whereby a respirometer measures the activity of the sludge and/or the strength of the wastewater, is gaining increased attention (Klapwijk et al., 1993).

1.7 SELF-CYCLING FERMENTATION

Another method that can be used for automatically controlling the removal of substrate in biological reactors has been developed by Sheppard (1989), and is called self-cycling fermentation (SCF). SCF was originally conceived for and applied to the control of pure culture fermentations for the production of microbial products of commercial interest (Sheppard and Cooper, 1990a; Brown and Cooper, 1991; Zenaitis and Cooper, 1994). The SCF technique controls the hydraulic retention time of a semi-continuous reactor by automatically adjusting the duration of each cycle (cycle time) according to on-line DO measurements. The principle behind

SCF is that when all of the readily biodegradable substrates have been depleted from a reactor that is aerated at a constant rate, this results in an increase in DO that can be detected by the control system.

Figures 3 and 4 show a basic flowsheet of the SCF control program and a typical DO profile during one cycle. At the beginning of each cycle, the reactor receives untreated feed. As the microbes oxidize the substrate from the reactor, they take up oxygen from the solution, which results in a DO concentration that is somewhat below its saturation value. Once the microbes have depleted the readily degradable substrates, the oxygen uptake rate suddenly decreases, causing the DO to increase. This increase in DO signals the control system to start another cycle by harvesting a portion of the treated water and feeding the same volume of untreated wastewater. In previous SCF studies, the increase in DO was detected when the current DO measurement exceeded the lowest DO measurement of that cycle by a specified amount. In this study, the increase in DO was detected when the current DO value exceeded a setpoint. Since the reactor is fed only when the microorganisms have consumed all of the substrate, this control strategy can ensure the complete removal of the biodegradable contaminants from the process stream, while achieving this removal with the minimum required HRT. Whereas respirometry-based control relies on a sophisticated apparatus containing DO sensors, biological sludge, and wastewater, the SCF control strategy relies solely on the measurement of DO in the reactor. Although the two methods rely on the same fundamental principles, SCF control is simpler and therefore has the potential to be more reliable.

The SCF technique has also been used in the treatment of synthetic wastewater using pure cultures with a solids retention time of about an hour (Sarkis and Cooper, 1994). The conditions in that study, however, do not represent a realistic wastewater treatment scenario. At McGill University, current research involves the application of SCF to the treatment of brewery wastewater using suspended and fixed-film mixed cultures (unpublished). Self-cycling fermentation has not been previously applied to the treatment of wastewater from the pulp and paper industry.

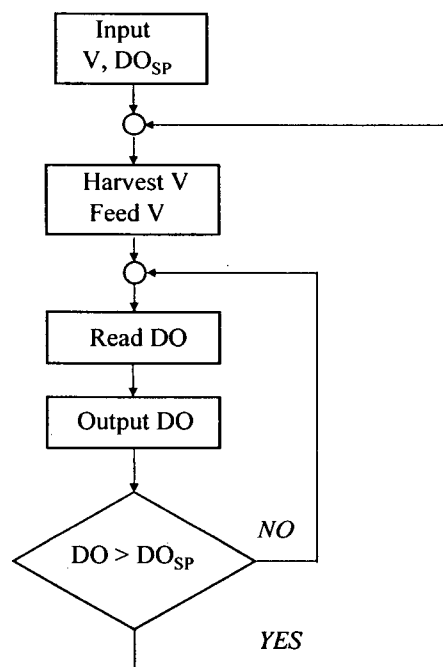


Figure 3. Flowsheet for the SCF control program. V is volume, DO_{SP} is DO setpoint.

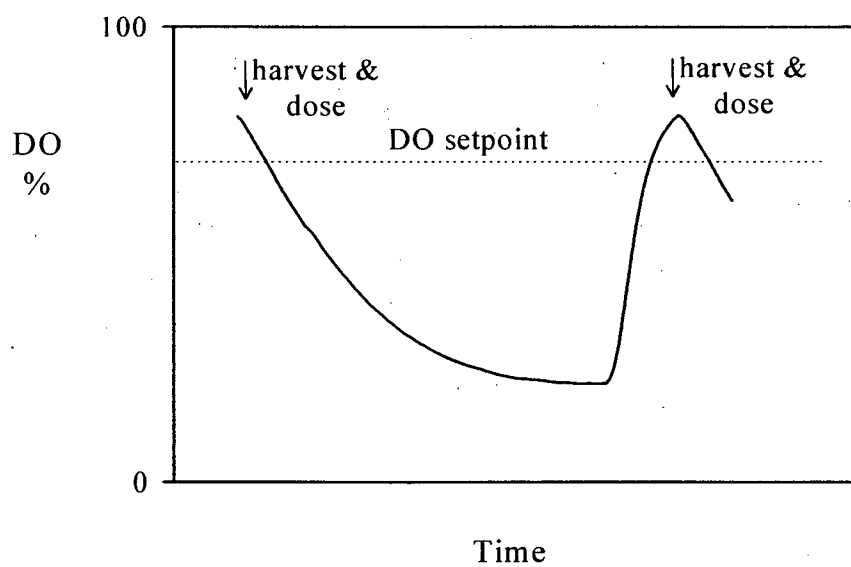


Figure 4. Typical DO profile in a SCF.

II OBJECTIVES

The objectives of this study were as follows, in descending order of priority:

- To evaluate the suitability of using the SCF technique to control the cycle time of reactors treating kraft condensates.
- To assess the biotreatability of kraft condensate methanol, COD and TRS, with the intention of reusing the treated condensate as kraft process water.
- To determine the extent of stripping of methanol and TRS during biological treatment.
- To modify a cyclone column bioreactor to function as a recirculating packed bed bioreactor.
- To design and assemble a laboratory-scale stirred tank to be operated as a SBR.
- To modify the pre-existing SCF control program to function properly with both reactors.

III MATERIALS AND METHODS

3.1 PACKED BED REACTOR (PBR)

3.1.1 Overall Description of the PBR

In this study, a cyclone column bioreactor was adapted for use as a recirculating packed bed reactor (PBR). The cyclone column bioreactor has been used previously in all of the above-mentioned suspended-growth SCF studies, and was originally developed by Dawson et al. (1971). In contrast to a stirred tank, the cyclone reactor achieves mixing and oxygen transfer by the recirculation of the liquid from the bottom to the top of the cyclone column, where the liquid descends in a swirling motion along the walls of the column, hereby providing much of the interfacial area required for oxygen transfer.

A schematic of the PBR used in this study (1.5 L working volume) is shown in Figure 5. A glass cyclone column (7 cm ID X 58 cm) contained a packed bed of Pall Rings, which served as biofilm support elements providing a large surface area for microbial growth and attachment. As the condensate passed through this bed, the biodegradable organics were

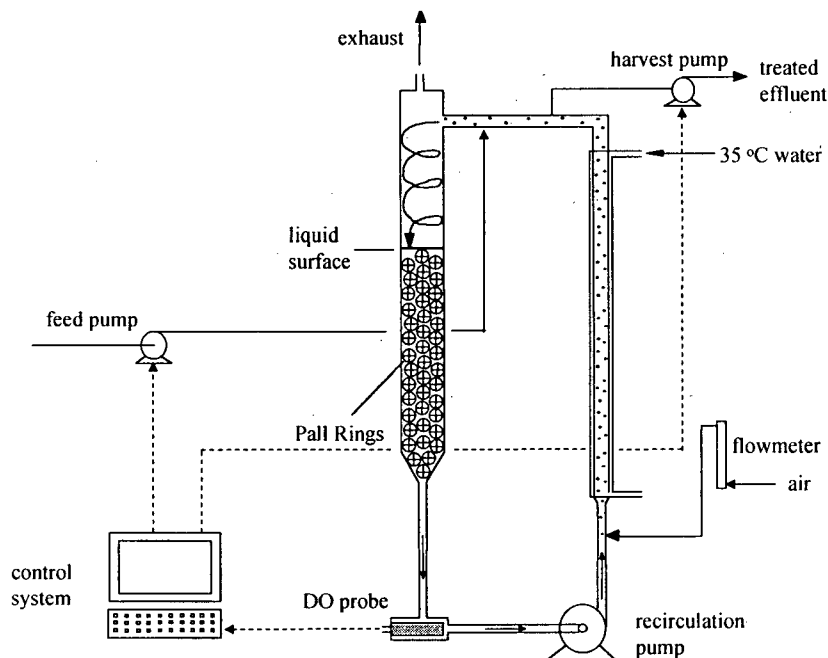


Figure 5. Schematic of the feedback-controlled recirculating packed bed reactor (PBR).

oxidized by the biofilm. The condensate was recirculated from the bottom of the bed back to the top of the column with a gear pump. As a result of biological growth, there was a gradual increase in the pressure drop across the bed throughout the duration of the PBR, which resulted in a decrease in the rate at which the liquid passed through the bed. To ensure that the liquid surface remained level with the top of the bed, the pump recirculation rate was gradually decreased throughout the PBR run. At the start of the run, when there was a negligible amount of biomass, the recirculation rate was at its maximum of 4 L/min.

The DO concentration in the condensate as it exited the bed was measured with a polarographic DO probe and amplifier (Cole Parmer Models 05726-00 and 01971-00, Labcor Technical Sales Inc., Anjou, Quebec). Compressed air was injected into the recirculation loop, the flowrate being measured by a flowmeter (Cole Parmer Model 03295-22, Labcor Technical Sales Inc., Anjou, Quebec). A constant temperature of 35 °C was maintained by recirculating water from a temperature-controlled water bath through a glass tube-in-tube heat exchanger (1.5 cm ID X 48 cm) in the recirculation loop. The condensate finally reentered the top of the column tangentially, where further oxygen transfer occurred from the headspace to the liquid as it swirled down the inside walls of the column. When the DO level reached the setpoint, the feed and treated effluent were simultaneously dispensed with peristaltic pumps (Cole Parmer Masterflex). The feed was stored at 4 °C in a refrigerated vessel. The volumes that were delivered for a given cycle ranged from 5 to 150 mL, corresponding to a dosing rate of 1 to 10% (fraction of working volume that was dosed and harvested each cycle).

3.1.2 Packed Bed

The bed consisted of a packing of polyethylene Pall Rings, which are shown in Figure 6. Each Pall Ring was 2.5 cm in diameter, and had a volume of 3.0 mL not including the void space. When they were packed into the column, they displaced 11% of the liquid volume. The bed of 50 Pall Rings was 33 cm high and had a total volume of 1.25 L. Therefore, 74% of the liquid volume was in contact with the bed at a given time, and the remainder was passing through the recirculation loop.

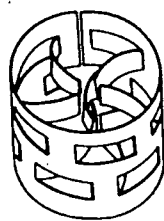


Figure 6. Pall Rings used in the packed bed.

3.2 SEQUENCING BATCH REACTOR (SBR)

3.2.1 Stirred Tank

The SBR consisted of a 19 cm \times 11.5 cm ID plexiglass stirred tank, equipped with four 1 cm-wide baffles and a water jacket to maintain the temperature at 35 °C (Figure 7). A harvesting port was located at a height of 8 cm. Agitation of the 1.5 L working volume was provided by a teflon-coated impeller with six 2 cm-radius blades and a variable-speed drive (Cole Parmer 4558, Labcor Technical Sales Inc., Anjou, Quebec). The flowmeter controlled the flowrate of air or oxygen that was sparged into the bottom of the reactor through an air stone. The DO probe was inserted through a port at the bottom of the reactor, such that the membrane of the probe was flush with the inner wall of the tank.

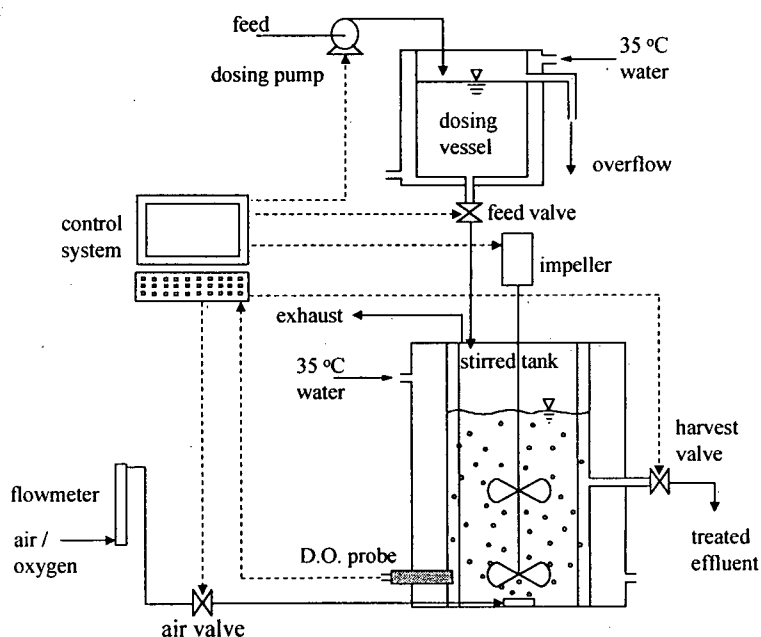


Figure 7. Schematic of the feedback-controlled sequencing batch reactor (SBR).

3.2.2 Dosing Vessel

Untreated condensate was dispensed from a refrigerated vessel (4 °C), using the peristaltic dosing pump (Cole Parmer Masterflex), into a glass, jacketed dosing vessel. The volume of condensate that was pumped into this vessel was slightly in excess of the required volume of 0.725 L; the excess flowed into the overflow outlet, hereby assuring that exactly 0.725 L was delivered to the dosing vessel. Water at 35 °C flowed through the jacket surrounding the dosing vessel to preheat the condensate prior to its addition to the reactor.

3.2.3 Sequencing of the SBR

One cycle of the SBR consisted of a settle, harvest (otherwise known as "draw"), dose (otherwise known as "fill"), and react phase. The duration of each of these phases was fixed, except for the react phase, which was terminated when the DO reached the setpoint of 70% air saturation. For the settle phase, the impeller and air were turned off for 30 minutes. This was followed by a 1.5-minute harvest phase during which the top 0.725 L, or 48%, of the reactor liquid was discharged from the reactor by the opening of the solenoid harvest valve (Skinner Valve 71215, New Britain, Connecticut). The subsequent opening of the feed valve for the duration of 0.5 minutes discharged the dosing vessel contents onto the 0.775 L of settled liquor in the reactor. The impeller and the air valve were then turned on throughout the whole duration of the react phase, and during the first 4 minutes of this phase, the dosing pump was turned on in order to refill the dosing vessel.

3.3 FEEDBACK CONTROL SYSTEM

The amplified DO signal was sent to a 286 PC via a data acquisition and control board (Strawberry Tree Inc., Model Acjr, Sunnyvale, California). The DO value was saved in a file and displayed on a monitor once every two seconds and was continuously displayed on a chart recorder. The duration of each cycle was also stored in a file. Since the duration of the settle, harvest and dose phases were constant and totaled 34 minutes, the duration of the react

phase (react time) was equal to the total cycle time minus 34 minutes.

Two programs were used, one for controlling the PBR and the other for controlling the SBR (see Appendix I for copies). Both programs are in Turbo Pascal and are modifications of a program written by researchers at McGill University, the latter program being based on one that was written by Sheppard (1989).

3.4 SEED

For all runs, the reactors were seeded with 500 mg/L VSS of biomass from a 35 °C laboratory-scale activated sludge reactor treating combined mill effluent from Western Pulp Ltd.'s kraft pulp mill in Squamish, B.C.

3.5 FEED

Accumulator condensate and surface condenser condensate (evaporator condensate) were used as feed to the bioreactors. These condensates were obtained weekly from the same mill as indicated above and were stored at 4 °C in sealed 20 L plastic containers until used. The composition of the condensates used throughout the three runs of this study is shown in Table 3.

Table 3. Methanol and COD content of the condensates.

		<i>Condensate</i>	
		<i>Accumulator</i>	<i>Evaporator</i>
Methanol (mg/L)	Minimum	620	340
	Average	850	630
	Maximum	1020	840
COD (mg/L)	Minimum	1100	1160
	Average	3060	1740
	Maximum	4340	2120

3.6 REACTOR OPERATION

A summary of the major operating conditions employed in the three runs is shown in Table 4.

Table 4. Operating conditions employed during the three runs.

<i>Run</i>	<i>Reactor</i>	<i>Days^a</i>	<i>Dosing Rate, %^b</i>	<i>Carbon Source^d</i>	<i>Nutrients</i>	<i>Oxygen Source</i>
1	PBR	0-20	1	accumulator	40 mL/L NH ₄ OH & 2 mL/L H ₃ PO ₄	air
		21-27	2	accumulator	40 mL/L NH ₄ OH & 2 mL/L H ₃ PO ₄	air
		28-29	4	accumulator	40 mL/L NH ₄ OH & 2 mL/L H ₃ PO ₄	air
		29	10 ^c	accumulator	40 mL/L NH ₄ OH & 2 mL/L H ₃ PO ₄	air
2	SBR	0 - 19	48	accumulator	40 mL/L NH ₄ OH & 2 mL/L H ₃ PO ₄	air
		20 - 29	48	accumulator	40 mL/L NH ₄ OH, metals ^e	air
3	SBR	0 - 6	48	1 g/L methanol	20 mL/L NH ₄ OH, metals	air
		7 - 21	48	evaporator	20 mL/L NH ₄ OH, metals	air
		22 - 33	48	evaporator	20 mL/L NH ₄ OH, metals	oxygen

^a excludes start-up period.

^b % of working volume replaced each cycle

^c cycles with a 10% dosing rate were fed and harvested manually rather with the pump.

^d accumulator is accumulator condensate, evaporator is evaporator condensate

^e 1mL/L of each of the following solutions: phosphate buffer, magnesium sulfate, calcium chloride and ferric chloride. Concentrations as in Standard Methods, 5-day BOD test (1992).

3.6.1 Run 1

During Run 1, accumulator condensate was treated for 29 days in the PBR operating in an automatic mode. Prior to automatic operation, a 1-day start-up period was utilized, during which cycling was controlled manually based on operator observation of DO. For nutrient supplementation, 40 mL/L of 28% ammonium hydroxide and 2 mL/L of 85% phosphoric acid were added to the condensate to obtain a BOD:N:P ratio of approximately 100:5:1. The pH of the feed was lowered from its initial value of 10 to 11 to approximately 8.7 with sulfuric acid. The air flowrate was varied upto a maximum of 3 L/min. The DO setpoint was 80%, except for

two of the cycles on day 29, which were operated with a setpoint of 20%, when the dosing rate was 10%.

3.6.2 Run 2

During Run 2, the SBR was used to treat accumulator condensate. Following a 10-day start-up period, the reactor was operated in an automatic mode for 29 days. Upon observing sub-optimal performance during the first 9 days, the feed was supplemented with a metals solution beginning with the 10th day, in order to make up for a suspected deficiency. The reactor pH was maintained between 7 and 9 by adding sulfuric acid to the feed. The impeller speed ranged from 350 to 500 rpm, and the air flowrate was varied upto a maximum of 3 L/min. The DO setpoint was 70% air saturation throughout this run.

3.6.3 Run 3

Evaporator condensate was used as the feed source to the SBR for most of Run 3. The manually controlled start-up period was reduced to two days for Run 3. For this start-up period, and for the first 6 days of Run 3, the reactor was fed a synthetic wastewater containing approximately 1 g/L methanol in distilled water as the sole carbon source. When the feed was switched from the synthetic wastewater to the evaporator condensate on day 7, an additional 200 mg/L of seed was added to the reactor in order to increase the diversity of the microbial population. On day 7, an antifoam system was installed which fed 1.4 g of Foam-trol 387 (BetzDearborn, Surrey, BC), diluted 10-fold in distilled water, during the dosing phase of each cycle. The air flowrate ranged from 0.2 to 3 L/min during the first 8 days. From day 9, which is the day that TRS monitoring began, until day 21, the air flowrate was 3 L/min. On day 22, the input of air into the reactor was replaced with 0.03 L/min of pure oxygen. Pure oxygen was used in order to determine whether a lower gas flowrate would reduce the extent of stripping and therefore increase the amount of biological oxidation of TRS. During the first 10 days of operation, the impeller speed was varied from 300 rpm to 1000 rpm, whereas for the remainder of the run, the speed was kept at 1000 rpm. The reactor pH was maintained between 7 and 9 by

adding sulfuric acid to the feed. As in Run 2, the DO setpoint of Run 3 was 70% air saturation.

3.7 STRIPPING EXPERIMENTS

To assess the relative contribution of stripping to the removal of TRS and methanol in the SBR, experiments were performed whereby evaporator condensate, at 35 °C, was neutralized to a pH of 8.0, and for 40 minutes, was aerated and agitated at 1000 rpm in the SBR with no seed added. Two experiments were performed, with air flowrates of 3 L/minute and 0.03 L/minute, corresponding to the flowrates of air and oxygen, respectively, during the TRS monitoring period of Run 3.

3.8 ANALYSES

3.8.1 Solids

Volatile suspended solids (VSS) were measured using Standard Methods (A.P.H.A., 1992). The VSS concentration of the feed was measured routinely during Run 1. Since the concentrations hereby obtained were very low, the feed VSS concentrations were not measured during Runs 2 and 3. During these SBR runs, the effluent VSS and the mixed liquor volatile suspended solids (MLVSS), the latter taken at the beginning of the react phase, were each measured in triplicate.

3.8.2 COD

The chemical oxygen demand (COD) of the feed and of the treated effluent of all three runs were routinely measured in triplicate using Standard Methods (A.P.H.A., 1992). All samples for COD analysis were filtered through a 1.5 µm glass microfibre filter (Whatman Inc., Clifton, NJ) and were then frozen until subsequent analysis. For each lot of samples, a calibration curve was prepared from at least four standard samples of potassium hydrogen phthalate. Of the 9 standard curves that were prepared in this study, the minimum and average of the R^2 values were 0.95 and 0.99, respectively. A sample curve is shown in Figure 8.

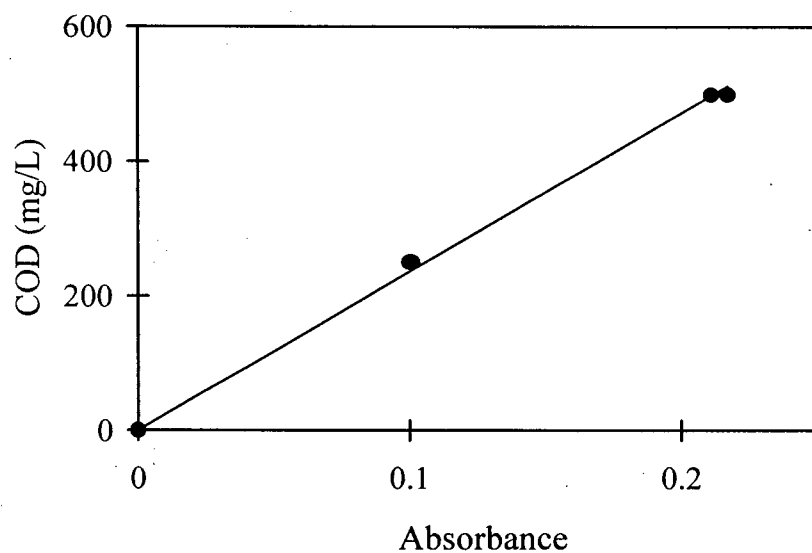


Figure 8. Sample COD standard curve.

3.8.3 Methanol

Methanol, being a HAP and being the major BOD constituent of condensates, was routinely measured during Runs 1 and 3. Samples for methanol determination were filtered and analyzed by gas chromatography using a HP 5890 (Mississauga, ON) equipped with a fused silica capillary column (Supelco 2-4049, Oakville, ON) and a flame ionization detector, set at 45

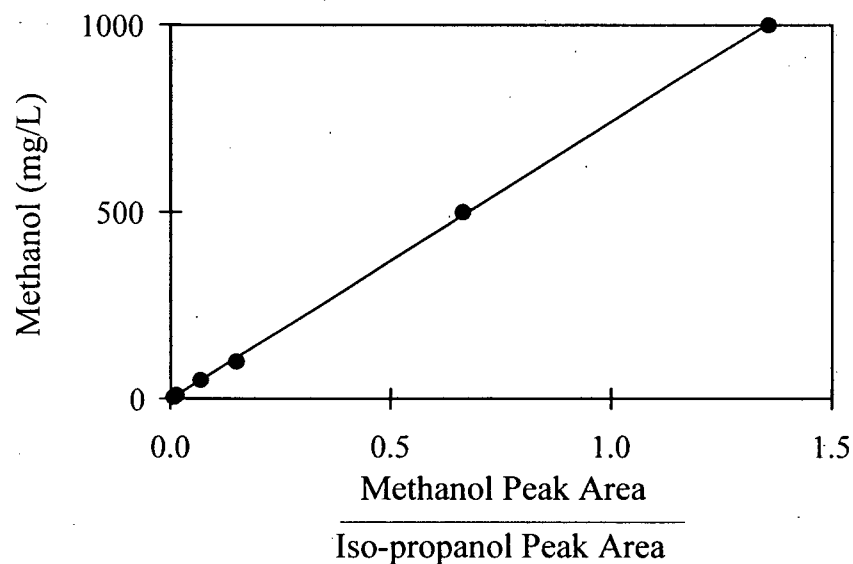


Figure 9. Sample methanol standard curve.

and 200 °C, respectively. To each vial containing 1 mL of sample, 100 µL of 5.5 g/L isopropanol was added as an internal standard. A sample standard curve is shown in Figure 9. Of the 7 standard curves that were prepared in this study, the minimum and average of the R^2 values were 0.988 and 0.998, respectively.

3.8.4 TRS

TRS Measurement

The TRS measurement procedure and the TRS standards preparation procedure used in this study were developed by Pierre Bérubé (unpublished). During Run 3, samples of the untreated and of the treated evaporator condensate were taken for TRS analysis. The pH of these unfiltered samples was immediately lowered to below pH 4.0 with 20% H₂SO₄, to prevent the dissociation of H₂S and CH₃SH, and frozen until analysis. For analysis, 20 mL of the thawed TRS sample were placed in 60 mL serum vials, which were subsequently capped with teflon-coated silicone septa (Chromatographic Specialties Inc., Brockville, ON). If necessary, the sample was diluted before being transferred to the serum vial, to reduce the TRS concentrations to a value that was less than 3 times the concentration of the standards. The vials were kept in an incubated shaker at 55 °C for at least 1 hour, after which 50 µL of the head space was immediately manually injected into a gas chromatograph (Hewlett Packard 5890), which was equipped with an Rtx-Volatiles column (Chromatographic Specialties Inc.) and a flame photometric detector. The temperature of the column was maintained at 40 °C for 2 minutes, followed by a 30 °C/minute ramp to 230 °C, which was maintained for an additional 2 minutes. The detector was maintained at 250 °C.

TRS Standards Preparation

For each lot of TRS samples that were analyzed, at least two standard vials were prepared, each of which contained all four TRS compounds. The standard vials were prepared to have TRS concentrations of 2.20 mg S/L of H₂S (Fisher Scientific Ltd., Vancouver, BC), 2.21 mg S/L of CH₃SH, 2.90 mg S/L of DMS, and 4.75 mg S/L of DMDS (Aldrich Chemical

Company Inc, Milwaukee, WI). For the preparation of the standard vials, a 60 mL serum vial was filled with 59 mL of distilled water and 1 mL of a buffer solution containing 0.2 M HCl and 0.2 M KCl, which lowered the pH of the entire solution to below 3. To this diluted buffer solution was injected 100 μ L of H₂S gas and 100 μ L of CH₃SH gas, both sampled at atmospheric pressure. To this serum vial was also injected 20 μ L of a solution containing DMS and DMDS. The latter solution was made by injecting 20 μ L each of liquid DMS and DMDS into a 2 mL vial containing 1 mL of methanol. The DMS and DMDS were first dissolved in methanol because better dissolution of these compounds is achieved in organic solvents than in water (Hynninen, 1971a). The 60 mL serum vial, containing the four TRS compounds, was then placed in a shaker for 30 minutes to achieve homogeneity. Twenty mL of this solution was transferred into each of two empty 60 mL serum vials, which were subsequently capped and kept in the 55 °C incubated shaker for at least two hours prior to analysis with the gas chromatograph.

TRS Calibration

Since the response of the flame photometric detector is a quadratic function of the sulfur concentration, the following formula was used to calculate the concentration of a particular TRS compound, DMS in this example, in the samples:

$$[\text{DMS}] \text{ (mg S/L)} = \sqrt{\frac{\text{DMS peak area of sample}}{\text{average of standard DMS peak areas}}} \cdot 2.90 \text{ mg S/L}$$

Ten standard vials were used to determine the average standard peak area for each compound, to be used in the above calibration equation. The coefficient of variation of these ten peak areas was 21% for H₂S, 23% for CH₃SH, 15% for DMS and 23% for DMDS, most of this variation arising from the standard preparation procedure. Figure 10 shows the standard curve passing through the average DMS peak area of the ten standard vials, which had a DMS concentration of 2.90 mg S/L.

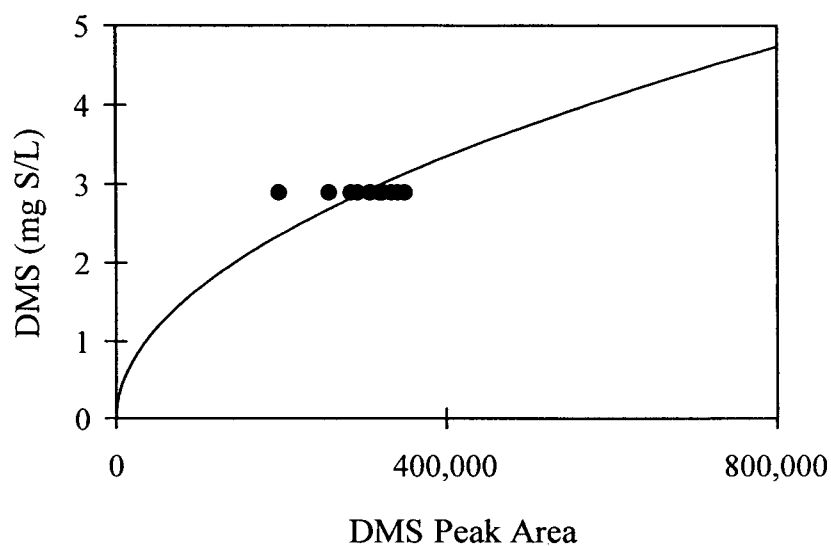


Figure 10. DMS standard curve.

3.8.5 Dissolved Oxygen Measurement

Throughout this study, the DO concentration is reported as percent air saturation. The DO concentration at 100% air saturation for the evaporator and the accumulator condensates was tested and was found to be 7.0 mg/L at the reactor temperature of 35 °C, identical to the saturation concentration of distilled water.

IV RESULTS AND DISCUSSION

4.1 PERFORMANCE OF THE PACKED BED REACTOR (PBR)

4.1.1 Cycling of the PBR

Temporal and Spatial Variation of DO in the PBR

Figure 11 shows the DO profile for four cycles of the PBR. During another cycle, manual DO measurements were also taken of the condensate as it re-entered the top of the packed bed (Figure 12). The near-saturation level of DO at the top, or upstream section, of the packed bed, indicates that the DO that was consumed in the bed was replenished in the recirculation loop.

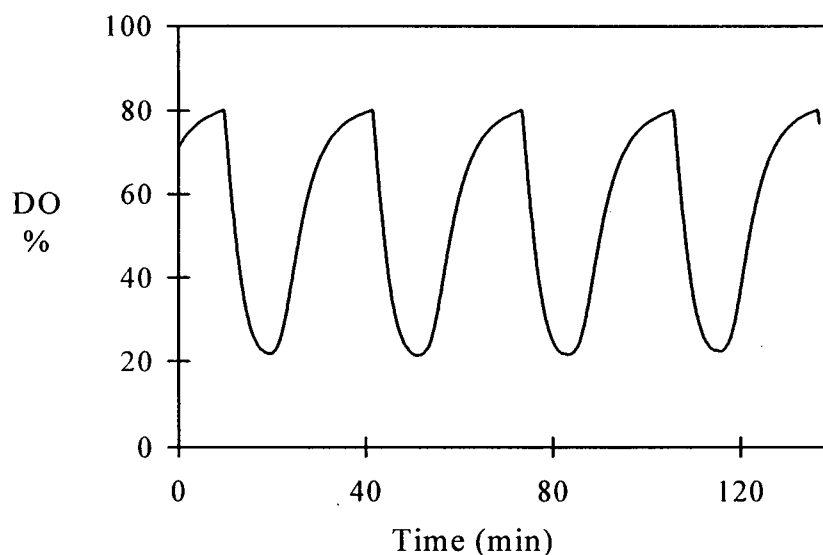


Figure 11. Sample DO profile in the PBR. From Run 1 when the dosing rate was 1%.

Roles of Oxygen and Methanol in Controlling the Cycling Rate of the PBR

Figures 13 and 14 show the profile of DO and methanol for cycles with a 10% dosing rate. During the first half of the cycle in Figure 14, the methanol consumption rate was constant, and the DO was also constant throughout most of this period. The COD removal rate of the cycle in Figure 14 was $6.0 \text{ kg COD/m}^3\text{-day}$ as calculated by the slope of the methanol oxidation curve, or $3.2 \text{ kg COD/m}^3\text{-day}$ if the entire cycle time is taken into account. The DO increased exactly at

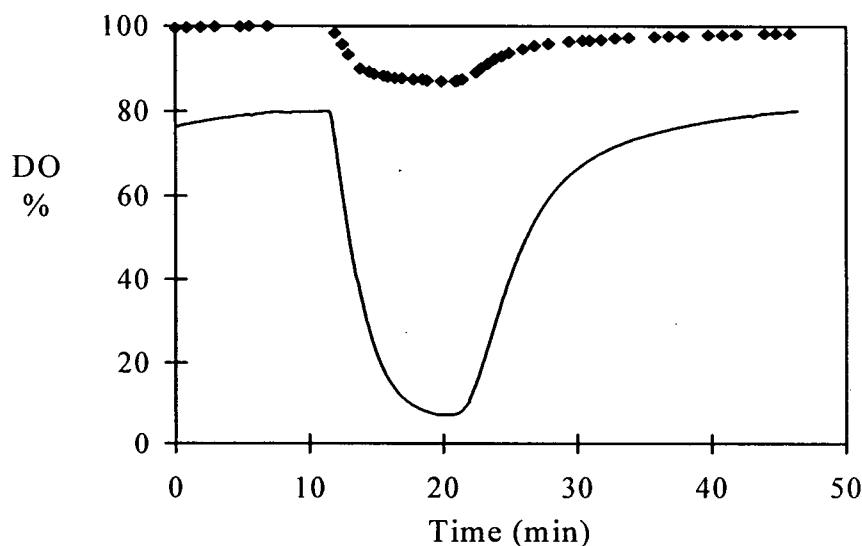


Figure 12. Sample DO profile of the recirculating liquid at the top (♦) and bottom (—) of the PBR. From Run 1 when the dosing rate was 1%.

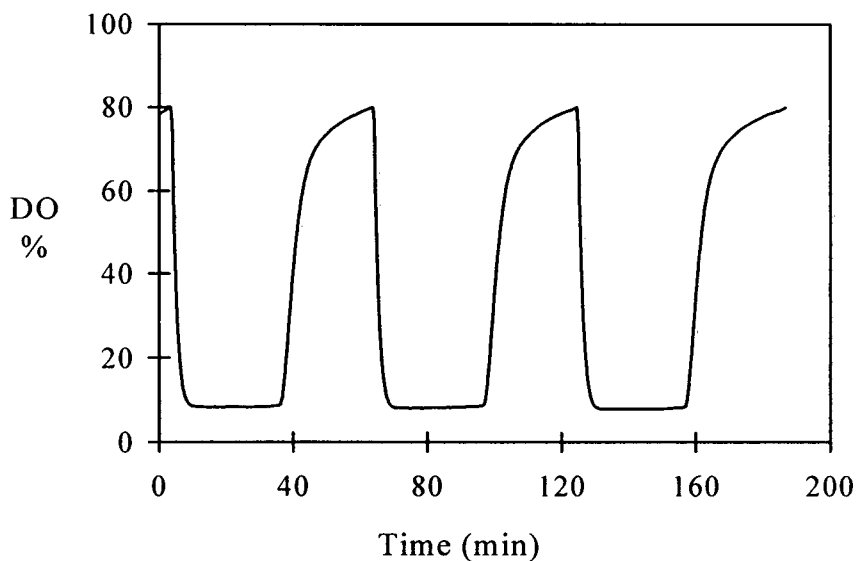


Figure 13. Sample DO profile of the PBR. From Run 1 when the dosing rate was 10%.

the moment that the methanol was completely consumed, suggesting that methanol was the BOD component which controlled the cycling rate.

That the methanol uptake rate was constant for all non-zero methanol concentrations suggests a zero-order relationship between the methanol uptake rate and the methanol concentration. This suggests that it was oxygen, rather than methanol, which was limiting the

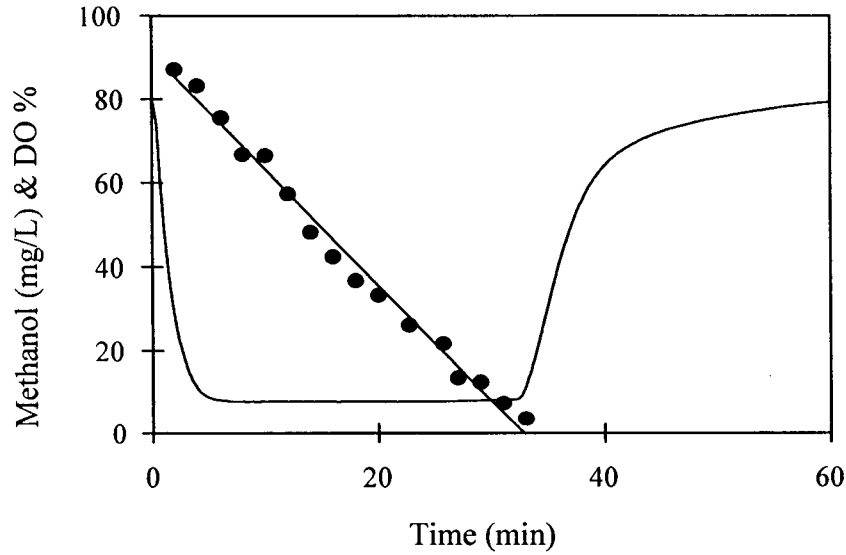


Figure 14. Sample DO (–) and methanol (●) profile of the PBR. From Run 1 when the dosing rate was 10%.

rate of the following biologically-catalyzed overall reaction: $\text{CH}_3\text{OH} + 1.5 \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$.

The rate of methanol oxidation by microbial cells in suspension can be expressed by a multiplicative form of the Monod equation for dual substrate utilization (Shuler and Kargi, 1992):

$$\frac{d[M]}{dt} = \frac{\mu_{\max} X}{Y_{X/M}} \left(\frac{[M]}{K_M + [M]} \right) \left(\frac{[O_2]}{K_{O_2} + [O_2]} \right)$$

, where M is methanol, μ_{\max} is the maximum growth rate, X is the biomass concentration, $Y_{X/M}$ is the yield of biomass on methanol, and K_M and K_{O_2} are the half-saturation constants for methanol and oxygen, respectively.

Whether any substrate limits the reaction rate will depend on the relative magnitude of the half-saturation constant for that substrate and its concentration in the growth medium. If a compound is present at a concentration greater than twice its half-saturation constant value, then it will not limit growth. The half-saturation constant for methanol (K_M) has been reported to be less than 1 mg/L (Chudoba et al., 1989) while DO has been shown to limit growth at 5 – 10% of its saturation concentration in air (Shuler and Kargi, 1992).

In Figure 14, the methanol concentration in the bulk liquid only approached its growth rate-limiting concentration of approximately 1 mg/L in the last 20 seconds of the 33-minute oxidation period. In contrast, the DO concentration in the bulk liquid averaged 8%

during the oxidation period, and therefore was always at, or near, a concentration that would limit growth. In the PBR, the methanol and oxygen must diffuse through the biofilm. Therefore, in addition to the K values, the diffusivity of these compounds must also be taken into account when considering the effect of their relative bulk liquid concentrations on the methanol uptake rate. However, if it is assumed that the diffusivity of methanol and oxygen are of the same order of magnitude, then oxygen will be depleted before methanol when diffusing into the biofilm. The practical significance of this is that influent changes in the methanol concentration will only affect the cycle time, and will not affect the oxygen uptake rate. The other implication is that the treatment rate of the reactor could be increased by operating at a higher DO level.

Effect of the DO Setpoint Value on the Treatment Rate of the PBR

Half of the duration of the cycle shown in Figure 14 was devoted to resaturating the liquid with oxygen. The reason that it took over 20 minutes for the liquid to attain a DO of 80% was likely due to the fact that much of the oxygen that was supplied by aeration diffused into the oxygen-starved biofilm, rather than remaining in the bulk liquid phase. In the cycles of Figures 15 and 16, the overall treatment rate was increased by lowering the DO setpoint, hereby reducing the duration of this oxygen replenishment process. Under these operating conditions, almost the entire duration of the cycle was devoted to the bio-oxidation process. The COD removal rate of

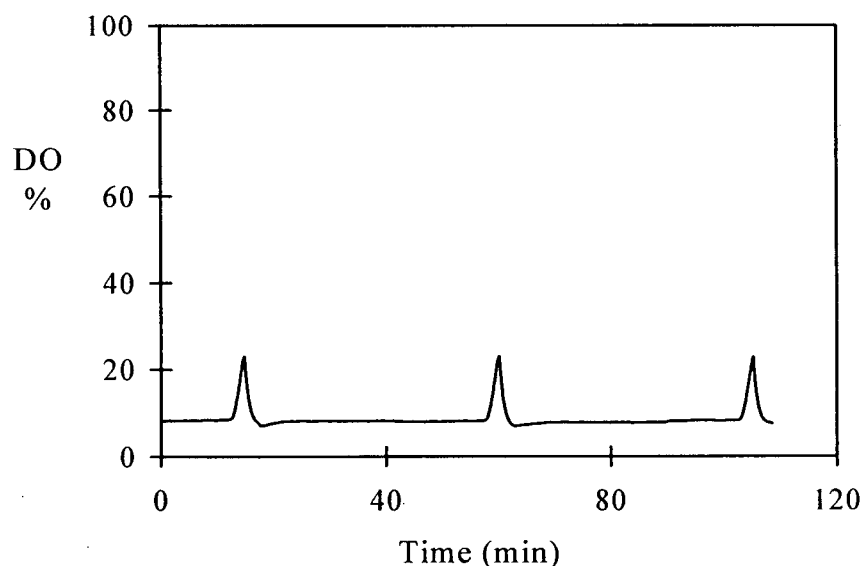


Figure 15. Sample DO profile of PBR cycles from Run 1 with a 10% dosing rate and a 20% DO setpoint.

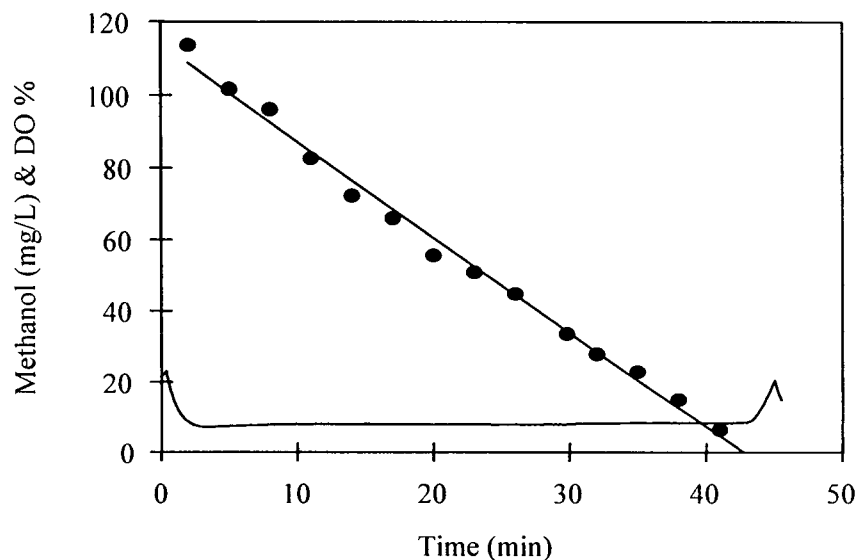


Figure 16. Sample DO (–) and methanol (●) profile of a PBR cycle from Run 1 with a 10% dosing rate and a 20% DO setpoint.

the cycle in Figure 16 was $5.7 \text{ kg COD/m}^3\text{-day}$ as calculated by the slope of the methanol oxidation curve, or $5.4 \text{ kg COD/m}^3\text{-day}$ if the entire cycle time is taken into account.

4.1.2 Treatment Performance of the PBR

Description of Run 1

The performance of the PBR treating accumulator condensate during Run 1 is shown in Figure 17, which plots the cycle time (the duration of each cycle), as well as the applied dosing rate, and in Figure 18, which shows the removal of organics. During this run, the cycle time varied greatly in response to changes in variables other than the influent substrate concentration and the applied dosing rate. On days 2 and 10, the pH in the reactor drifted above a value of 9 ($\downarrow 1$). This resulted in extremely long cycle times, as high as 250 minutes on day 10, which translate to very low treatment rates. When the pH was subsequently lowered to normal levels, the cycle time decreased correspondingly.

On day 21, when the dosing rate was doubled to 2% of the working volume, the reactor responded with a similar increase in the cycle time. However, on day 28, when the dosing rate was again doubled, a corresponding doubling of the cycle time was not evident. On

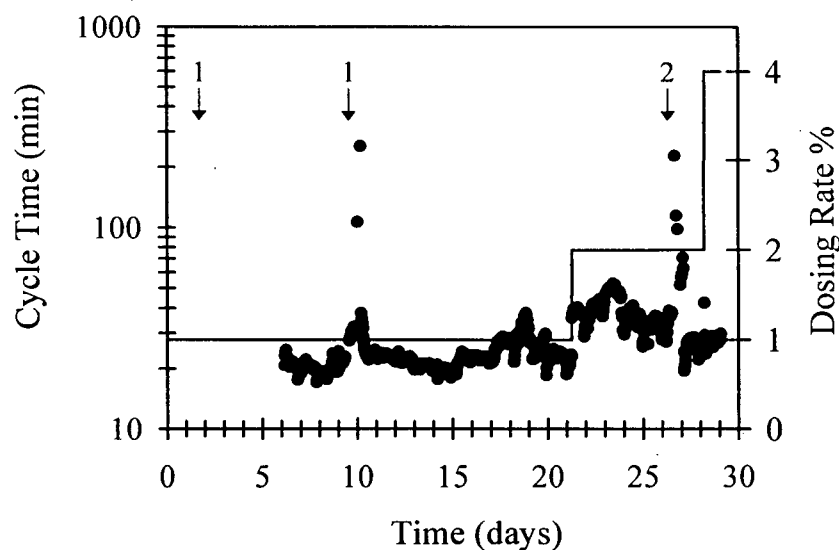


Figure 17. Cycle time of the PBR (●), indicating the dosing rate (–). Data not available for the first 6 days. Not shown are 5 cycles on day 29, which were manually dispensed with a dosing rate of 10%. ↓1 pH upsets; ↓2 recirculation pumping rate decreases overnight.

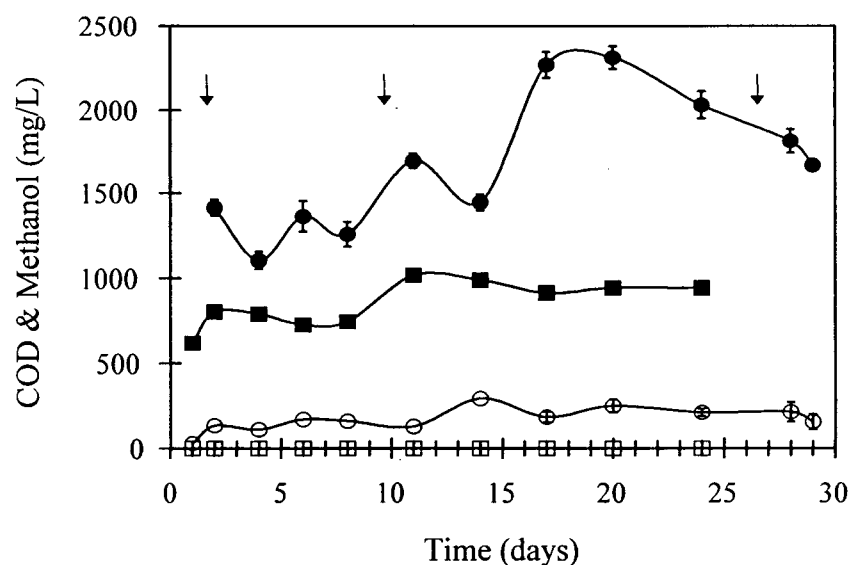


Figure 18. Removal of organics in the PBR. Influent and effluent methanol (■,□); influent and effluent COD (●,○). Error bars represent $\pm 90\%$ C.I. (confidence interval) from COD triplicates. First 7 effluent COD samples were not replicated. ↓ events same as in Figure 17.

day 27, cycles as long as 227 minutes were caused by a significant overnight decrease in the recirculating pump flowrate (↓2), which was believed to be due to fouling of the pump with sloughed biomass. The two most significant variables contributing to the wide variation in the

cycle time throughout this run were the pH and the liquid recirculation rate. The variation in the liquid recirculation rate was due to fouling of the recirculation pump with sloughed biofilm, and also from the deliberate gradual decrease in the pump flowrate in response to the increasing pressure drop across the bed due to the growth of the biofilm.

COD and Methanol Removal in the PBR - Run 1

The methanol concentration in the feed was 850 ± 130 mg/L (average \pm standard deviation). In the SCF-controlled PBR, the methanol was always completely removed (Figure 18). The influent and effluent COD was 1670 ± 400 mg/L¹ and 170 ± 69 mg/L, respectively, representing a COD removal of 1480 ± 380 mg/L and a removal efficiency of $89 \pm 3\%$ ². Assuming an oxygen demand of 1.5 g oxygen / g methanol, methanol accounted for 77% of the influent COD and 85% of the removed COD.

Fate of Solids in the PBR - Run 1

The solids concentration in the effluent from the PBR was always below 20 mg VSS/L (Figure 19). If a sludge yield of 0.3 g VSS/g COD removed is assumed, which is typical for the biological treatment of pulp and paper wastewater (Saunamäki, 1996), then approximately 450 mg of biomass is expected to have been produced per liter of condensate treated. The ability of this PBR to retain the biomass and to produce an effluent low in solids would greatly reduce the need for a solids separation device, if this reactor were to be used in a mill for the regeneration of pulp mill process water. However, this filtering action was achieved at the expense of a plugging of the bed and a fouling of the pump due to biomass sloughing. In a full-scale application, the plugging would result in channeling of the liquid through the bed and in an excessive amount of energy consumption by the recirculating pump. The stable operation of such a reactor in a full-scale application would therefore require a periodic backwashing of the bed. It is believed that for the treatment of high BOD-laden wastewater such as kraft condensate,

¹ For improving legibility, numbers with a value of 100 or greater have been rounded to the nearest 10th digit. For example, 851 was rounded to 850, 1667 was rounded to 1670, and 87 remained unrounded as 87.

² The average and the standard deviation of the removal and of the removal efficiency were calculated from the daily influent and effluent values, and not from the average and standard deviation of the influent and effluent values.

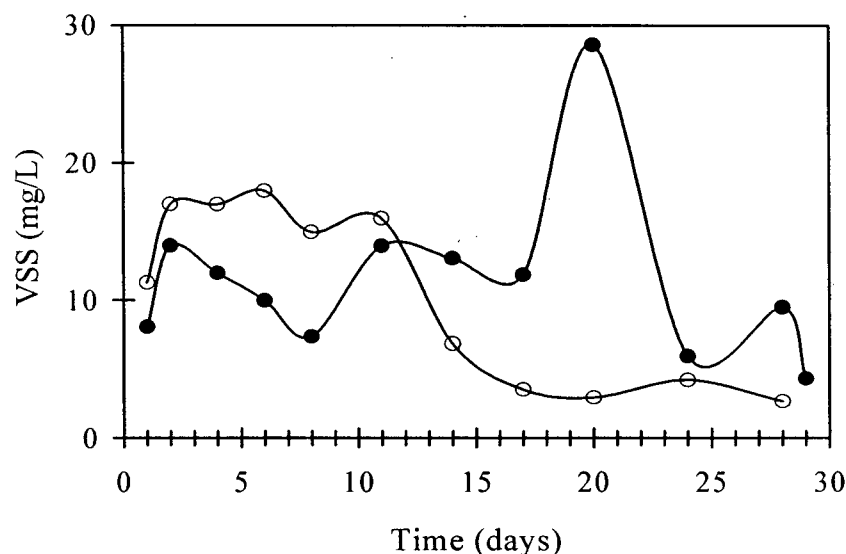


Figure 19. Influent (●) and effluent (○) VSS during Run 1.

a fluidized bed reactor would be more suitable than a packed bed reactor, since with a fluidized bed, the frequent backwashing operation could be avoided completely.

4.2 PERFORMANCE OF THE SEQUENCING BATCH REACTOR (SBR)

4.2.1 Cycling of the SBR

DO Profile During a SBR Cycle

Since the dosing rate was always 48% in the SBR, the concentration of substrates at the beginning of each cycle was always approximately half of what it was in the feed. Figure 20 shows an entire cycle, indicating the duration and location of each phase in relation to the DO profile. The termination of a react phase occurred shortly after time zero, when the DO reached the setpoint of 70%. Subsequently, the impeller and the air supply were turned off for the settle phase. The lack of aeration during this phase resulted in a drop in DO, as the remaining dissolved oxygen was taken up for endogenous respiration and possibly for the slow oxidation of substrates other than methanol. After the 30-minute settle period, the supernatant was harvested from the reactor, new feed was dosed to the reactor, and then the reactor entered another react phase until the DO reached its setpoint again.

Methanol, pH and DO profile during the react phase

The methanol concentration, DO, and pH during the react phase of one cycle is shown in Figure 21. During this cycle, methanol was degraded at a constant rate of 18 mg methanol/L-minute, and the DO remained constant near 4%. The COD removal rate during this cycle, was 39 kg COD/m³-day based on the slope of the methanol consumption curve, or 13 kg COD/m³-day if the duration of the settle, dose, and harvest phases are taken into account. Once

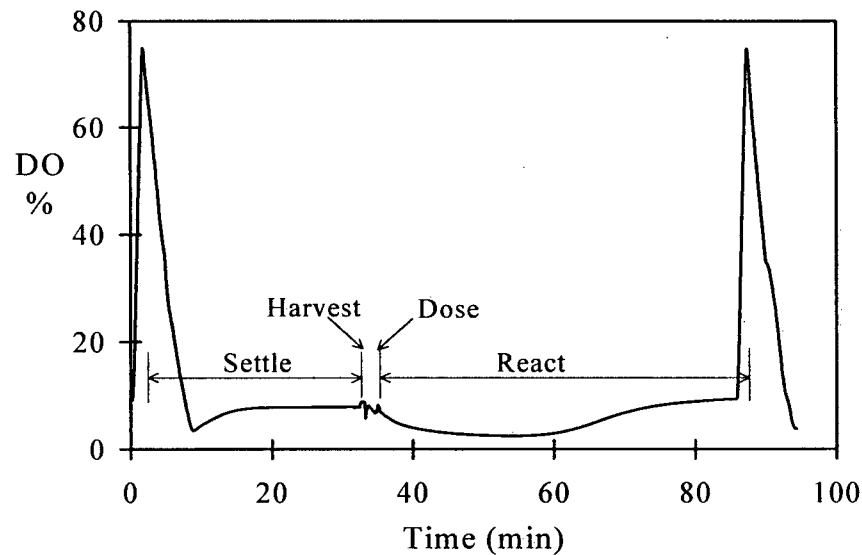


Figure 20. DO profile throughout the four stages of a typical SBR cycle. Cycle obtained from Run 3.

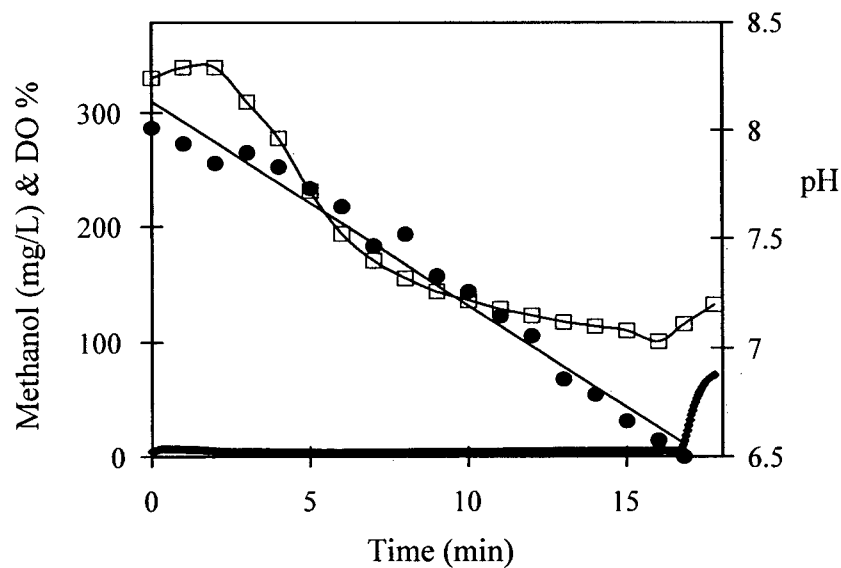


Figure 21. Profile of methanol (●), pH (□), and DO (▪) during the react phase of a typical cycle. Obtained from Run 3.

all of the methanol was oxidized, the DO increased until it reached the setpoint value of 70%, when the start of the next cycle was triggered. A consistent decrease in pH was observed to occur throughout this and other cycles. Much of this pH decrease was presumably due to the formation of carbonic acid from the carbon dioxide that was released by the respiring cells.

That the methanol consumption rate was constant suggests that there was a negligible amount of biomass growth. In general, as in the cycle of Figure 21, the amount of biomass growth that occurred during each cycle was indeed small relative to the biomass concentration in the reactor. In this cycle, for example, the MLVSS concentration was 3500 mg/L at the start of the cycle. If a solids production rate of 0.3 g VSS/g COD removed is assumed, then throughout this cycle, there was 135 mg/L of biomass that was produced, or 4% of the MLVSS.

That the methanol consumption rate was constant was also partly due to the fact that the condensate was preheated in the jacketed dosing vessel, from its storage temperature of 4 °C to the reactor temperature of 35 °C.

Comparison of SBR and PBR Treatment Rates

The COD removal rate, based on the sampled methanol consumption curves, was at least 6 times greater in the SBR compared to the PBR. The SBR cycle of Figure 21 had a removal rate of 39 kg COD/m³-day, whereas the two cycles sampled in the PBR had removal rates of 6 and 5.7 kg COD/m³-day. These results do not support the statement made in the introductory section, that fixed film reactors can achieve higher treatment rates due to their ability to attain higher biomass concentrations. The overall treatment rate of any reactor will depend on the amount of biomass that has access to substrates. In a fixed film reactor, diffusional limitations will prevent the transport of substrates and oxygen into the inner depths of the biofilm. Thus, even though the total amount of biomass may be greater in a fixed film reactor than in a suspended growth reactor, this will not necessarily result in a higher treatment rate if a large portion of the biomass in the fixed film is subject to diffusional limitations. In this study, the biomass concentration in the PBR was not measured, since this would have required weighing the entire bed.

To increase the amount of biomass that is active in a fixed film reactor and thereby

increase the treatment rate, at least four variables can be manipulated: 1) The amount of biofilm that is exposed to the wastewater can be increased. In the PBR of this study, some channeling was observed, which resulted in some of the biomass not being submerged. An upflow PBR or a fluidized bed reactor would help solve this problem. 2) The biofilm surface area to volume ratio could be increased, by employing smaller support particles. 3) For oxygen-limited biofilms such as this one, the bulk liquid DO concentration can be increased. 4) If the transport of the limiting substrate is limited by its rate of diffusion through the liquid film, rather than through the biofilm, then turbulent flow around the biofilm will result in a higher flux of this substrate into the biofilm. Increased turbulence can be achieved by increasing the liquid flowrate in a PBR or by using a fluidized bed reactor.

Comparison of Treatment Rate of SBR with Other Reactors

The COD removal rate of 39 kg COD/m³-day encountered in this cycle was slightly higher than the 33 kg COD/m³-day removal rate obtained in the previously-mentioned anaerobic MBR treating kraft condensates (Yamaguchi et al., 1990).

The COD removal rate in this SBR cycle was more than 10 times the treatment rate of the aeration section of a typical activated sludge plant treating pulp and paper mill effluent (Saunamäki, 1996). However, it must be acknowledged that the hydraulic retention time of combined mill effluent treatment systems is usually designed for toxicity removal, which is a slower process than BOD removal. Additionally, in a full-scale SBR involving multiple reactors, the duration of the various phases might be restricted somewhat in order to achieve an overall continuous process, thereby potentially compromising the treatment rate.

SBR Cycling Reproducibility

As indicated in Figure 22, it was possible to achieve very reproducible cycles, and stable operation, when operating the SBR in the feedback-controlled mode. The dosing vessel was found to be very accurate and reproducible in dispensing exactly 0.725 L of feed each cycle.

This method is believed to be superior to the dosing method employed during Run 1, which relied on peristaltic pumps for delivering the correct volume, since changes in the pump tubing

demand frequent recalibration of the pumping flowrate. The use of this dosing vessel may also offer more reproducibility compared to previous dosing methods in self-cycling fermentations, which employed a load cell to weigh the correct amount of liquid to feed and harvest. In the

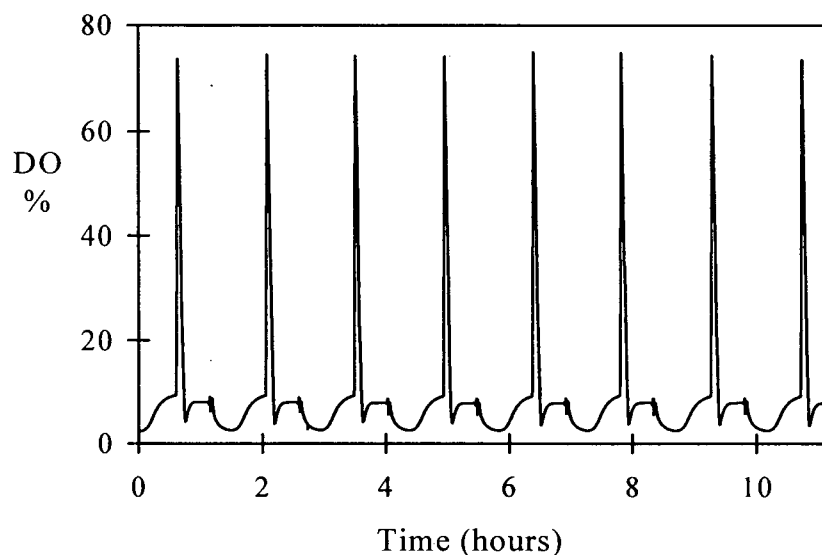


Figure 22. DO profile of several SBR cycles. Sampled from Run 3.

most recent and improved method of volume control for self-cycling fermentations, an average variation in cycle time of 7% was achieved for 77 consecutive cycles (Sheppard, 1993). The 7 cycles in Figure 22 have an average cycle time variation of 0.9%.

4.2.2 Treatment Performance of the SBR During Run 2

Description of Run 2

The performance of the SBR treating accumulator condensate during Run 2 is shown in Figures 23, 24, and 25, which show the react time, the influent and effluent COD, and the reactor and effluent VSS concentrations, respectively. As indicated by Figure 23, the first 6 days of operation were quite unstable. On day 6 especially, an unusually long (18-hour) react time was observed. Immediately following this long cycle, the reactor was reinoculated with 40 ml of activated sludge from a reactor treating whole mill effluent (↓1). This improved the SBR performance, as is evident by the decrease in the react time to a low of 6 hours on day 7.

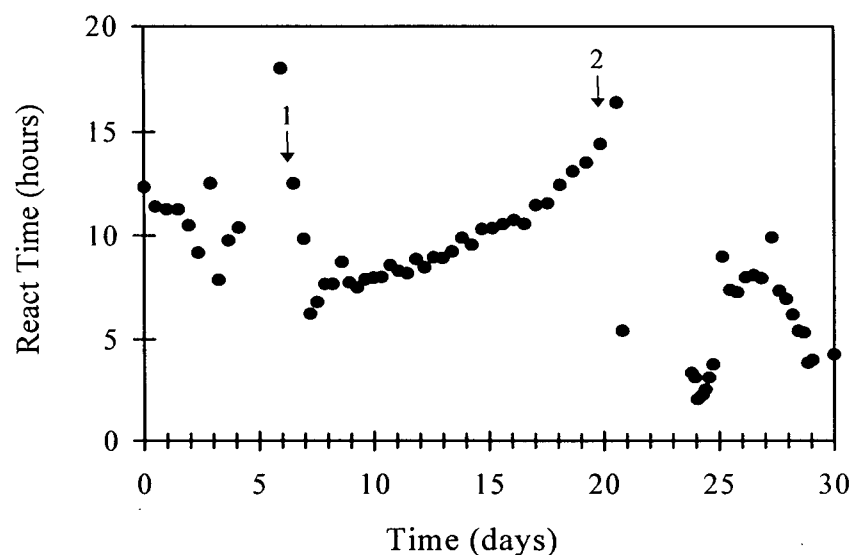


Figure 23. React time of the SBR during Run 2. ↓1 reinoculated with 40 ml activated sludge; ↓2 now supplementing feed with metals.

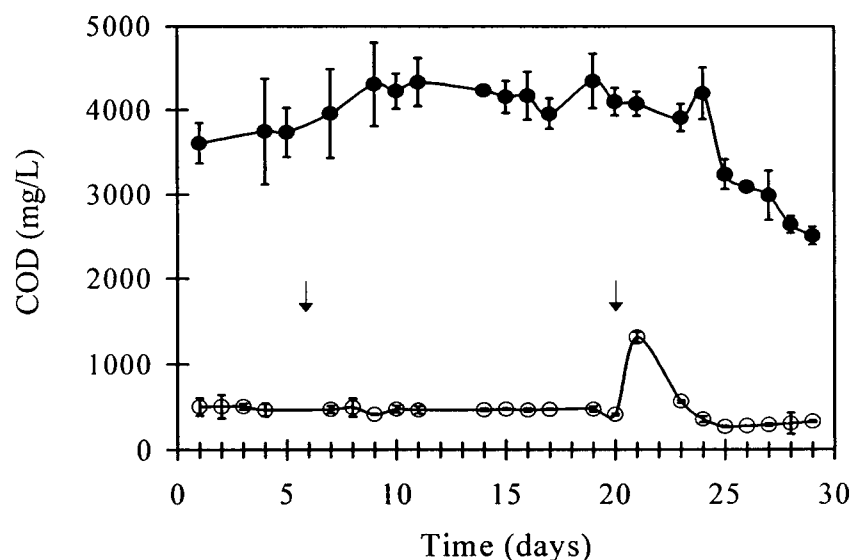


Figure 24. Influent and effluent COD (●,○) in the SBR during Run 2, \pm 90% C.I. from triplicates. ↓ events same as in Figure 24.

Between days 7 and 20, a steady increase in the react time was observed. Since the biomass concentration and the COD removal were relatively constant throughout this period, the specific COD removal rate therefore decreased.

It was suspected that the decrease in the specific COD removal rate between days 6

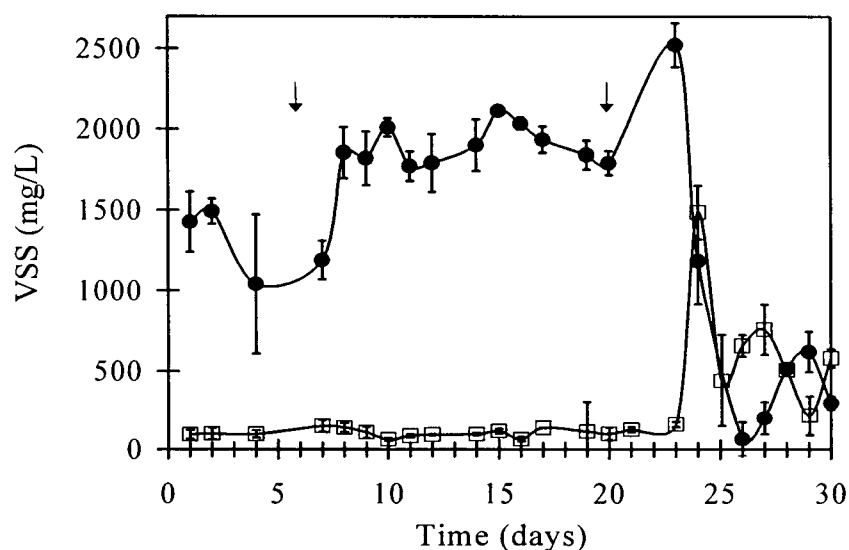


Figure 25. MLVSS (●) and effluent VSS (□) in the SBR during Run 2, \pm 90% C.I. from triplicates. ↓ events same as in Figure 24.

and 20 was due to a metal deficiency. This was confirmed on day 20, when the addition of metals to the reactor (↓2) resulted in an almost immediate 3-fold decrease in the react time. Similarly, the average specific COD removal rate ($\text{Avg} [(\text{COD}_{\text{in}} - \text{COD}_{\text{out}})/(\text{React Time} \times \text{MLVSS})]$) increased three-fold, from 0.20 mg COD/(mg MLVSS · h) for the period prior to metals addition, to 0.62 mg COD/(mg MLVSS · h) for the period following metals addition. However, after the metals addition, some operational problems were encountered in dealing with the higher growth rate, namely, poor settling of the biomass, and low reactor pH values arising from a greater pH drop during each cycle. Consequently, on day 21, the SBR cycled prematurely, resulting in an abnormally high COD in the effluent, and on days 24 to 26, almost all of the biomass exited with the effluent.

Since kraft condensates are generally only comprised of volatile compounds, it is not surprising that the accumulator condensate was deficient in the metals necessary for biological growth. Although the PBR was also treating accumulator condensate that was not supplemented with metals, the operation of Run 1 was more stable than the first 20 days of Run 2. It is speculated that the superior performance during Run 1 was due to the entrainment of black liquor into the accumulator condensate that was used as a feed for Run 1.

COD Removal in the SBR – Run 2

Despite large fluctuations in the COD removal rate due to variations in the biomass concentration and in the activity of the biomass, the feedback-control strategy consistently assured very high levels of treatment, with the exception of day 21, by maintaining the reactor in the react phase until all of the readily biodegradable substrates were consumed (Figure 24). The influent COD was 3780 ± 560 mg/L and the effluent COD was 460 ± 200 mg/L, representing a COD removal of 3330 ± 540 mg/L, and a removal efficiency of $88 \pm 5\%$.

Solids Production in the SBR – Run 2

Despite the slow treatment rate that occurred with the metal deficiency, the biomass exhibited good settleability prior to the solids upset on day 24 (Figure 25). During these first 23 days, the MLVSS concentration was 1780 ± 360 mg/L, and the effluent VSS concentration was 110 ± 27 mg/L.

4.2.3 Treatment Performance of the SBR During Run 3

Description of Run 3

The react time, the removal of organics, and the solids concentration during Run 3 are shown in Figures 26, 27 and 28, respectively. Due to the various upset conditions, the react time and the biomass concentration varied greatly during Run 3. Of these figures, the plot of the biomass concentration (Figure 28) most clearly shows the effects of the various upset conditions. When the reactor feed was switched from the synthetic feed to the evaporator condensate on day 7 (↓1), a loss of solids due to foaming occurred, which was corrected by the installation of the antifoam system (↓2). However, on day 14, the antifoam addition system failed (↓3), which resulted in a loss of most of the biomass. Once the antifoam addition system was repaired, biomass levels recovered. On day 22, the air supply was replaced with pure oxygen (↓4). From this day until shutdown, the reactor pH often went below 7.0 (↓5), which significantly affected the MLVSS and the react time. This was especially the case on day 22, when the react time more than doubled and the biomass concentration halved, and on days 29 and 33, when the biomass concentration halved again.

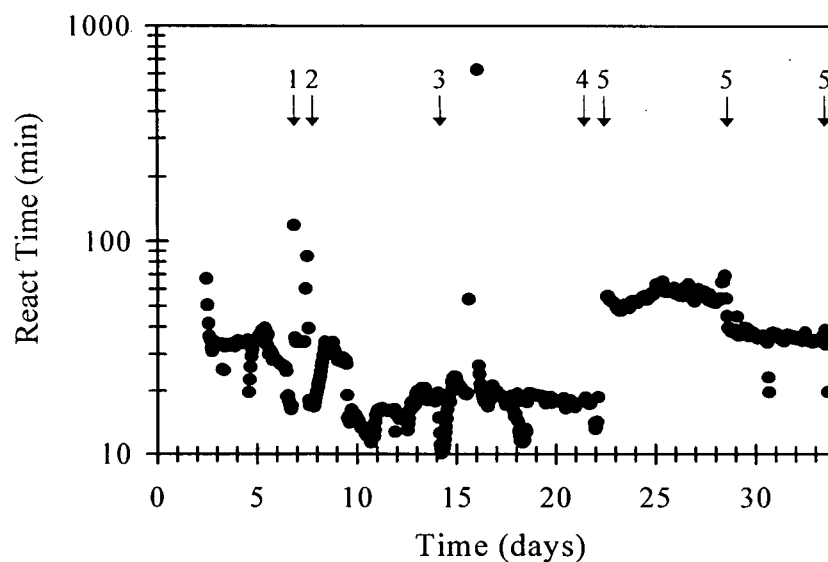


Figure 26. React time of the SBR during Run 3. ↓1 switched from synthetic feed to evaporator condensate; ↓2 foaming incident, installed antifoam system; ↓3 foaming incident; ↓4 switched from air to oxygen; ↓5 pH upset.

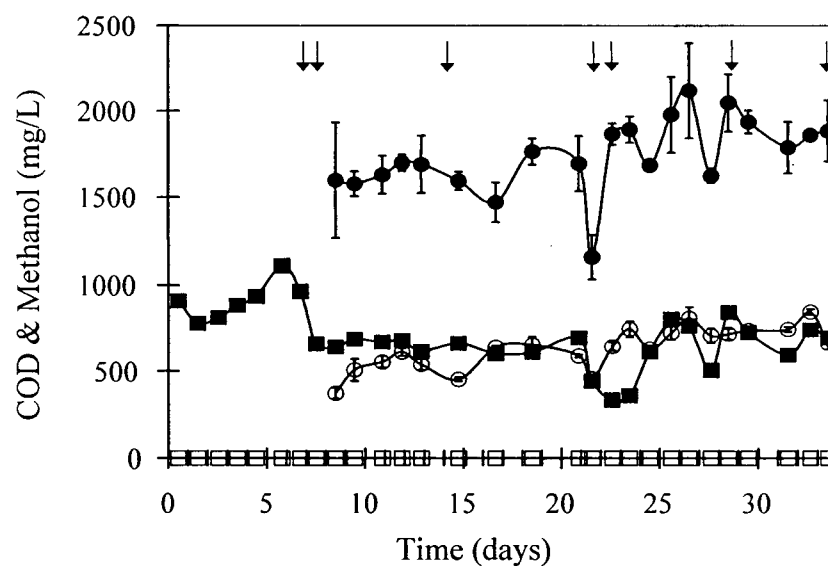


Figure 27. Removal of organics in the SBR during Run 3. Influent and effluent COD (●,○); influent and effluent methanol (■,□), $\pm 90\%$ C.I. from COD triplicates. ↓ events same as in Figure 28.

Aside from the foaming that occurred on day 7, there was no discernible difference in the reactor performance while treating the synthetic methanol feed versus the evaporator condensate. Although a controlled experiment would be required to determine with certainty

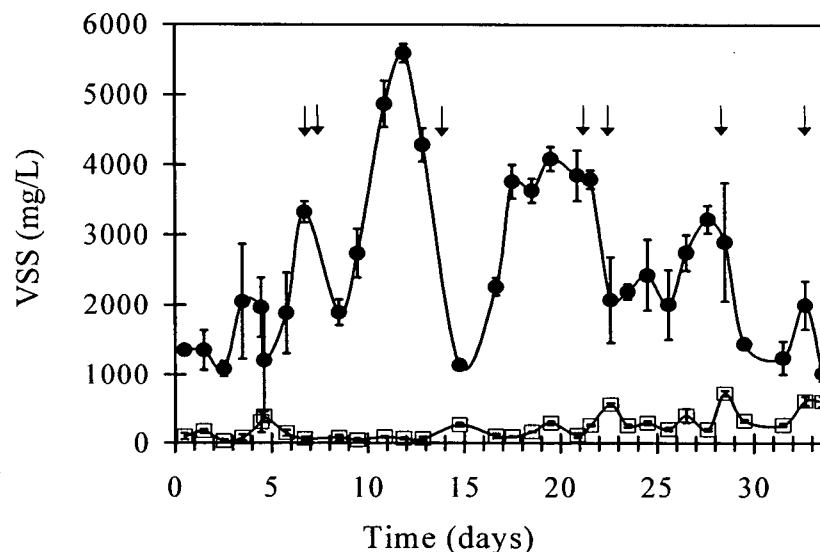


Figure 28. MLVSS (●) and effluent (□) VSS in the SBR during Run 3, \pm 90% C.I. from triplicates. ↓ events same as in Figure 28.

whether the methanol removal rate was affected by other compounds in the condensate, this data suggests an absence of inhibition from the presence of sulfide or any other compounds.

COD and Methanol Removal in the SBR – Run 3

Despite the various upsets that occurred during Run 3, the methanol removal was always complete, and the COD removal was very consistent (Figure 27). During the period that evaporator condensate was fed to the SBR in Run 3, starting on day 7, the influent and effluent COD were 1740 ± 220 mg/L and 630 ± 120 mg/L, respectively, corresponding to a COD removal of 1110 ± 150 mg/L, or 64 ± 5 %. The methanol concentration in the evaporator condensate was 630 ± 130 mg/L, accounting for 54% of the influent COD and 86% of the removed COD.

Solids Production in the SBR – Run 3

The reactor and effluent biomass concentrations during Run 3 were 2520 ± 1210 mg/L and 230 ± 180 mg/L, respectively (Figure 28). Whenever the sludge blanket level reached the effluent port, a higher concentration of solids exited with the effluent since no other means of solids wastage was employed. Other incidences of high effluent VSS were due to the operational problems mentioned above. However, when there were no operational problems, the settleability

of the solids was generally good, as was the case on day 11, when the reactor and the effluent solids concentrations were 5590 mg/L and 63 mg/L, respectively. Depending on the intended location of reuse within the mill, the effluent from the SBR would likely require further processing for solids removal.

TRS Removal in the SBR - Run 3

The removal of each of the four TRS compounds from the SBR-treated evaporator condensate is shown in Figure 29. Throughout the whole run, the removal of H_2S and CH_3SH was $99 \pm 2.1\%$ and $98 \pm 9.0\%$, respectively. Changing the oxygen source from air to pure oxygen on day 22 did not have a significant effect on the removal efficiency of H_2S and CH_3SH . DMS and DMDS also exhibited a high removal efficiency during the aeration period, of $100 \pm 0\%$ and $92 \pm 5.7\%$, respectively. However, when pure oxygen was supplied, the removal efficiency of these compounds was reduced to $82 \pm 5.7\%$ and $76 \pm 9.2\%$, respectively.

From the theoretical oxygen demands of the TRS compounds, the TRS that was removed during Run 3 was calculated to account for 11% of the removed COD during this run. Since, as stated previously, methanol was responsible for 86% of the COD removed from the evaporator condensate, then 97% of the COD removed from the condensate has been accounted for solely by the removal of methanol and TRS.

Stripping Experiments

Abiotic stripping experiments were performed in order to evaluate the extent of TRS removal that was due to the interfacial transfer of TRS from the liquid to the gas phase (Figure 30). In these experiments, gas flowrate did not strongly influence the stripping rate of methanol and TRS. These results differ from those obtained for DMS and DMDS during Run 3, when the 0.03 L/min of pure oxygen flow resulted in less DMS and DMDS removal compared to the 3 L/min of pure oxygen flow. Forty minutes after the start of the stripping experiment, only $18 \pm 4\%$ of the methanol was stripped, regardless of the flowrate. Within 10 minutes of the start of the stripping experiment, all of the H_2S and CH_3SH was stripped. After 40 minutes, 100% of the DMS and 73 - 78% of the DMDS was stripped.

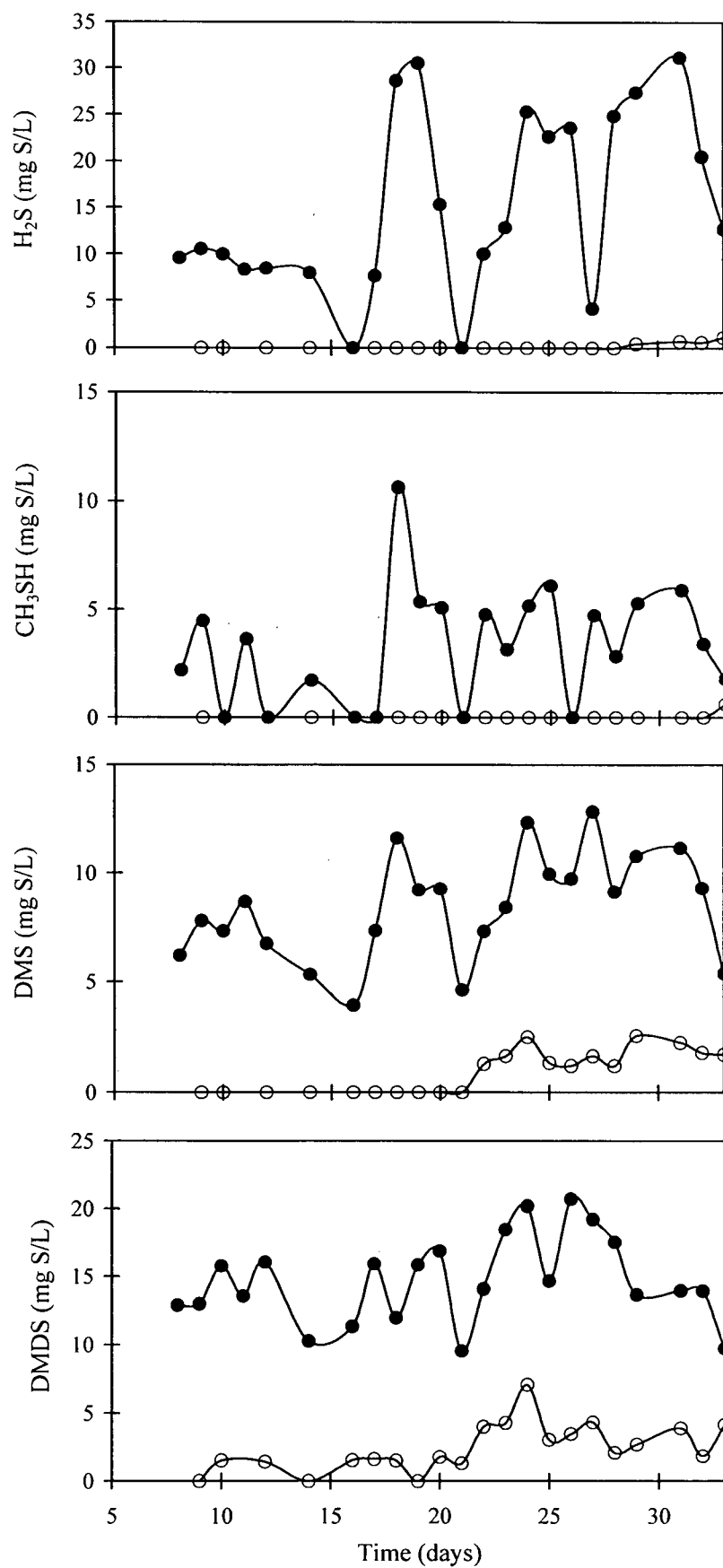


Figure 29. TRS in the influent (●) and effluent (○) of the SBR during Run 3.

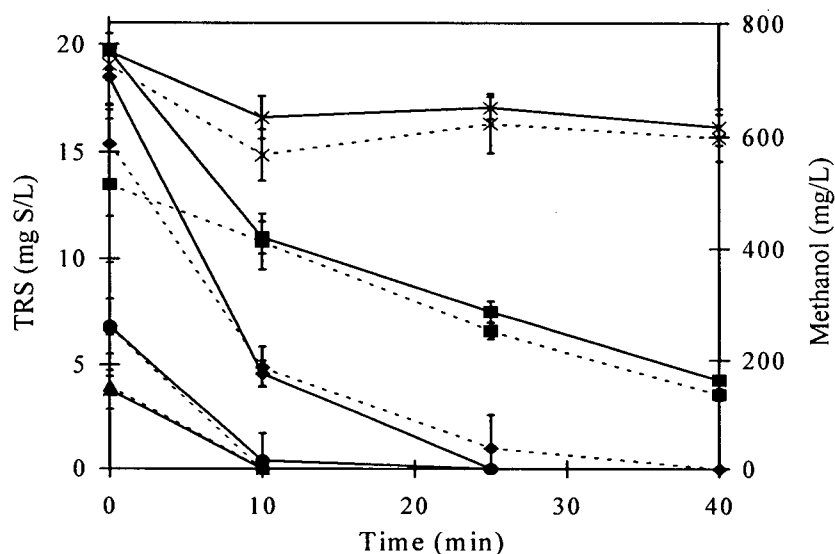


Figure 30. Stripping of H₂S (▲), CH₃SH (●), DMS (◆), DMDS (■) and methanol (×) in the SBR with no biomass, with an airflow rate of 3 L/min (–) and 0.03 L/min (---). Error bars represent $\pm 90\%$ C.I. from four samples.

These results suggest that, during the 30 ± 27 minute react phase of Run 3, there was sufficient time for all of the H₂S, CH₃SH and DMS, and most of the DMDS, to be removed by stripping. It should be noted that in the bioreactor runs, biological or chemical oxidation of TRS might have been a competing removal mechanism. The biological oxidation of TRS was discussed in the introductory section. At neutral pH, CH₃SH is chemically oxidized to DMDS (Hynninen, 1971), and H₂S is oxidized to elemental sulfur. The latter reaction occurs at a maximum rate at a pH of 8, and can lead to further reactions producing polysulfides, sulfite, and sulfate (Chen and Morris, 1972). The measurement of the influent and effluent concentration of either total sulfur or sulfate would have permitted an assessment of the extent of oxidation of TRS. The measurement of sulfate by the colorimetric method was attempted. However, the measurements had excessive scatter, possibly due to interfering compounds in the condensate. In the absence of information about the relative rate of stripping versus oxidation, definitive conclusions about the fate of TRS compounds cannot be made. However, since a significant fraction was likely removed by stripping, reactor off-gas from a full-scale application would have to be collected and treated, either by incineration or by biofiltration.

Finally, the high amount of TRS stripping that occurred in this reactor may provide another reason for treating condensates aerobically rather than anaerobically. In an anaerobic reactor, the extent of TRS removal by stripping is likely to be greatly reduced. In addition, the presence of sulfate in the condensate would give rise to sulfide. Thus, an anaerobically treated condensate would be much more odorous than an aerobically treated one.

4.2.4 Operator Intervention of the SBR Operation

It was previously mentioned that one of the benefits of employing the SCF control strategy was that operator input and laboratory analysis of the wastewater could be reduced or eliminated. While most of the time, the SBR was cycling automatically, there was also a significant amount of intervention required. Since there were large variations in the oxygen uptake rate, it was sometimes necessary to adjust the oxygen transfer rate, by changing either the air flowrate or the impeller rotational speed. If the oxygen transfer rate was too low, then the DO concentration would be reduced to zero during the react phase, thereby compromising the treatment rate. If the oxygen transfer rate was too high, then the DO would increase beyond the setpoint before all of the methanol was consumed, thereby causing premature cycling and a high COD in the effluent. Thus, the oxygen transfer rate had to be manually matched to the current oxygen uptake rate. The number of times that the operator intervened each day, by changing either the air flowrate or the impeller speed, is plotted for Runs 2 and 3 in Figures 31 and 32, respectively. Since the reactor was not stable for much of Run 2, there was, not surprisingly, a considerable amount of operator intervention required during this run. For Run 2, the longest period of uninterrupted automatic operation occurred between days 11 and 16, inclusive. Run 3 was much more stable, and therefore a greater amount of automatic operation was possible, with two periods of fully automatic operation lasting for 11 and 12 days each.

Most, or all, of the fluctuations in the oxygen uptake rate in the SBR were due to the lack of pH and foam control and to the lack of metals supplementation. In a full-scale operation, these problems could be largely avoided. The most significant fluctuations in operating conditions would then be due to changes in the influent BOD and methanol concentration.

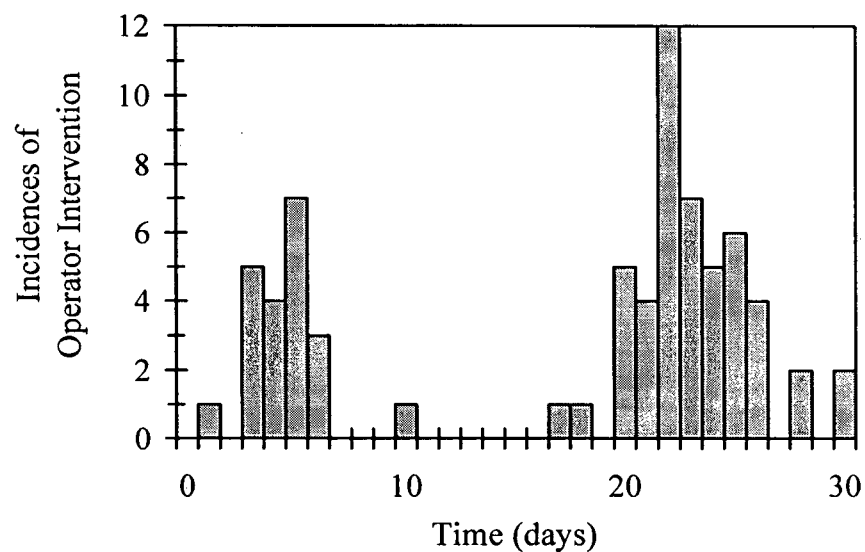


Figure 31. Extent of operator intervention in the SBR during Run 2. A value of zero indicates at least 24 hours of automatic operation.

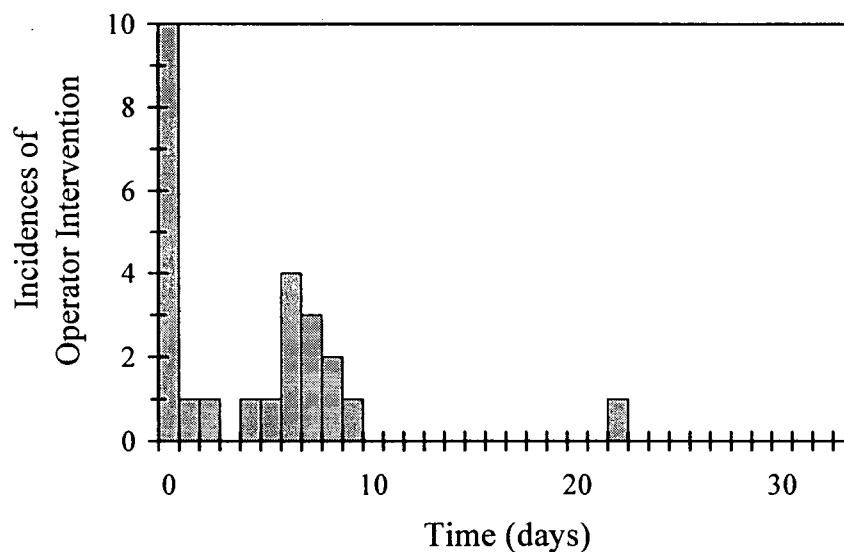


Figure 32. Extent of operator intervention in the SBR during Run 3.

However, as was stated previously, this would not affect the oxygen uptake rate. Thus, in an SBR with adequate pH and foam control and metals supplementation, it would be possible to operate the reactor in a fully automatic mode for much more extended periods of time than occurred in this study.

V CONCLUSIONS

The following conclusions can be drawn from this study:

1. The SCF control strategy was successfully modified and applied to the treatment of kraft condensates in a PBR and a SBR.
2. Most of the COD in kraft condensates can be removed by aerobic treatment. The accumulator condensate COD, averaged across Runs 1 and 2, was 3060 mg/L, and 77% of this COD was attributed to methanol. In both runs, approximately 88% of the accumulator condensate COD was removed. The evaporator condensate COD averaged 1740 mg/L, 64% of which was removed by the SBR, and 54% of which was attributed to methanol. Of the COD that was removed from the evaporator condensate, 86% was due to the removal of methanol and 11% to the removal of TRS.
3. Kraft condensates are lacking the metal ions necessary for healthy biological growth, hereby making supplementation necessary for achieving stable bioreactor operation.
4. Due to the feedback nature of the SCF control strategy and to the high correlation between the presence of methanol and the oxygen uptake rate, it was possible to cycle the reactors immediately after the methanol was depleted. Thus, despite the occurrence of a number of upset conditions that prevented steady-state operation, the SCF control strategy was able to ensure the complete removal of methanol from the condensate, and at a minimum HRT.
5. The COD removal rates, based on the slope of the methanol oxidation curve of sampled cycles, were 5.7 kg COD/m³-day in the PBR and 39 kg COD/m³-day in the SBR.

6. Due to the filtering action of the biofilm, the PBR produced an effluent with a VSS concentration of less than 20 mg/L. However, excessive biofilm build-up resulted in a high pressure drop across the bed, and in the fouling of the pump due to sloughed biomass. The stable, long term operation of the PBR would require periodic backwashing.
7. In the SBR, a number of upset conditions occurred which adversely affected the solids concentration in the effluent. These upsets were due to the temporary failures in the antifoam system, the lack of automatic pH control, the temporary deficiency in metals, and the lack of an automatic sludge wasting system. Consequently, the MLVSS concentration averaged 1780 and 2520 mg/L during Runs 2 and 3, respectively, and the effluent VSS concentration averaged 110 and 230 mg/L during Runs 2 and 3, respectively. However, all of the above problems can be easily prevented. During a period of stable SBR operation, the settleability of the solids was good, as exemplified by the MLVSS and effluent VSS concentrations on one day, which were 5590 and 63 mg/L, respectively.
8. All of the TRS compounds were removed by more than 90% in the air-sparged SBR. The stripping experiments indicated that a substantial majority of this removal, if not all of it, was due to stripping.
9. Due to the various upset conditions that occurred, a significant amount of operator intervention of the SBR operation was required. However, when the reactor operation was stable, fully automatic operation was achieved for periods lasting longer than 10 days.
10. The aerobic treatment of kraft condensate shows much promise as a means of regenerating clean water for process reuse. These results suggest that the use of the SCF technique to control the react time of a SBR, can be an effective means of removing the methanol and TRS from kraft condensate, while achieving this with the minimum required HRT.

VI RECOMMENDATIONS

1. Further investigation into SCF-controlled treatment of condensates should be done using the SBR, rather than the PBR, due to the inherent problems associated with the plugging of the packed bed.
2. For the next SCF-controlled SBR, the installation of an automatic pH control system for the bioreactor would greatly improve the stability of operation.
3. The installation of an automatic sludge wasting system for the SBR would allow a pseudo steady-state to be achieved while maintaining high MLVSS and low effluent VSS concentrations.
4. The relative extent of oxidation and stripping of TRS could be determined directly by analyzing the influent and effluent for sulfate or total sulfur, in addition to analyzing for TRS. If sulfate and/or total sulfur analysis is to be performed, then a non-sulfur-containing acid, such as HNO_3 or HCl , should be used for neutralizing the condensate, rather than the H_2SO_4 used in this study. If sulfate is analyzed for, then this should be performed by a method other than the colorimetric one, such as ion chromatography, since the colorimetric determination of sulfate was attempted during this study and was unsuccessful.
5. The extent of bio-oxidation of TRS could also be easily assessed by injecting TRS compounds into a respirometer containing sludge from the bioreactor. In these respirometric tests, the pH could be varied in order to determine the optimal pH for TRS bio-oxidation, especially that of DMS and DMDS, which were not completely stripped from the bioreactor.
6. TRS standard vials with higher concentrations of TRS compounds should be prepared to confirm the quadratic relationship between the flame photometric detector signal and the TRS compound concentration.

7. Biological treatment of condensates should be attempted at a higher temperature. In a full-scale application, this would reduce the cost of cooling the condensates, which occur at a temperature of approximately 65 °C (Blackwell et al., 1984).

8. Eventually, if the SCF-controlled SBR treatment of condensates shows further promise, then a pilot-scale SCF-controlled SBR system should be built and operated. This system would employ more than one reactor, operating with realistic fill, draw and settle phase durations, thereby enabling it to receive feed on a continuous basis.

VII REFERENCES

- American Public Health Association (1992). Standard methods for the examination of water and wastewater. 18th Edition. Washington D.C.
- Beaudry P., DuFour B. and Pezet J. (1991). Application of biological aerated filters for industrial wastewater treatment. *Tappi Proceedings, Environmental Conference*, 85-90.
- Blackwell B.R. (1979). Air stripping of kraft foul condensates to remove volatile impurities including methanol. Ph.D. thesis, Department of Civil Engineering, University of British Columbia, Vancouver.
- Blackwell B.R., Mackay W.B., Murray F.E. and Oldham W.K. (1979). Review of kraft foul condensates. *Tappi* 62(10), 33-37.
- Blackwell B.R., Murray F.E. and Oldham W.K. (1980). Vapour/liquid equilibrium relationships of kraft foul condensates. *Tappi* 63(2), 151-154.
- Blackwell B.R. (1986). Review of methods for treating kraft foul condensates. *Canadian Pulp and Paper Association Annual Meeting*, Montreal.
- Brown W.A. and Cooper D.G. (1991). Self-cycling fermentation applied to *Acinetobacter calcoaceticus* RAG-1. *Applied and environmental microbiology* 57(10), 2901-2906.
- Buisman C.J.N., IJspeert P., Hof A., Janssen A.J.H., ten Hagen R. and Lettinga G. (1991). Kinetic parameters of a mixed culture oxidizing sulfide and sulfur with oxygen. *Biotechnology and Bioengineering* 38, 813-820.
- Carpenter W.L. and Berger H.F. (1984). A laboratory investigation of the applicability of anaerobic treatment to selected pulp mill effluents. *Tappi Proceedings, Environmental Conference*, 173-178.
- Characklis W.G. and Marshall K.C. (1990). *Biofilms*, John Wiley & Sons, Toronto.
- Charpentier J., Godart H., Martin G. and Mogno Y. (1989). Oxidation-reduction potential regulation as a way to optimize aeration and C, N and P removal: experimental basis and various full-scale examples. *Water Science and Technology* 21, 1209-1223.
- Chen K.Y. and Morris J.C. (1972). Kinetics of oxidation of aqueous sulfide by O₂. *Environmental Science and Technology* 6(6), 529-537.
- Chudoba J., Albokova J. and Cech J.S. (1989). Determination of kinetic constants of activated sludge microorganisms responsible for degradation of xenobiotics. *Water Research* 23(11), 1431-1438.
- Cocci A.A., Landine R.C., Brown G.J., Tennier A.M. and Hall E.R. (1985). Anaerobic treatment of kraft foul condensates. *Tappi Proceedings, Environmental Conference*, 67-82.
- Cocci A.A., Almost S., McCarthy P.J. and Brown G.J. (1997). Accelerated design and start-up of an SBR system for groundwood mill wastewater treatment. *Tappi Environmental Conference*, 871-877.
- Cook W.H., Farmer F.A., Kristiansen O.E., Reid K., Reid J. and Rowbottom R. (1973). The effect of pulp and paper mill effluents on the taste and odour of the receiving water and the fish therein. *Pulp and Paper Magazine of Canada*, Convention Issue, 97-106.

Courtemanche M., Tremblay H. and Villeneuve F. (1997). Sequencing batch reactor technology: an old technique successfully applied to the treatment of pulp and paper mill effluents containing high residuals of sulphite. *Tappi Proceedings, Environmental Conference*, 853-863.

Dalientoft E. and Thulin P. (1996). The use of Kaldnes suspended carrier process in treatment of wastewaters from the forest industry. *5th IAWQ Symposium on Forest Industry Wastewaters*, Vancouver, 145-153.

Dawson P.S.S., Anderson M. and York A.E. (1971). The cyclone column culture vessel for batch and continuous, synchronous or asynchronous, culture of microorganisms. *Biotechnology and Bioengineering* **XII**(6), 865-876.

Dubilier N., Giere O. and Grieshaber M.K. (1994). Concomitant effects of sulfide and hypoxia on the aerobic metabolism of the marine oligochaete *Tubificoides benedii*. *The Journal of Experimental Zoology* **269**, 287-297.

Environment Canada (1979). Air pollution emissions and control technology: wood pulping industry. Report EPS 3-AP-77-6, Ottawa, Ontario.

Erickson L.E. and Tuitemwong P. (1991). Growth yields, productivities, and maintenance energies of methylotrophs. in Goldberg I., Rokem J.S. (eds). *Biology of methylotrophs*. Butterworth-Heinemann, Toronto.

Fahmy M., Kut O.M. and Heinzle E. (1994). Anaerobic-aerobic fluidized bed biotreatment of sulphite pulp bleaching effluents--I. Global parameters. *Water Research* **28**(9), 1987-1996.

Fuseler K. and Cypionka H. (1995). Elemental sulfur as an intermediate of sulfide oxidation with oxygen by *Desulfobulbus propionicus*. *Archives of Microbiology* **164**, 104-109.

Gay P.L. (1974). Stripping and disposal of contaminated condensates. *Tappi* **57**(9).

Goronszy M.C. and Jaeger A. (1996). Cardboard recycle mill wastewater reuse using cyclic activated sludge technology. *5th IAWQ Symposium on Forest Industry Wastewaters*, 243-250.

Hynninen P. (1971). On the reactions of methyl mercaptan and its oxidation products in air- or steam stripping of sulfate mill condensates. *Paperi ja Puu/Papper och Trå* **53**(4a), 159-169.

Janssen A.J.H., Sleyster R., van der Kaa C., Jochemsen A. Bontsema J. and Lettinga, G. (1995). Biological sulphide oxidation in a fed-batch reactor. *Biotechnology and Bioengineering* **47**, 327-333.

Jung W.K., Humenick M.J. and Armstrong N.E. (1981). A comprehensive study on the biological treatabilities of phenol and methanol-I. Analysis of bacterial growth and substrate removal kinetics by a statistical method. *Water Research* **15**, 1221-1231.

Kantardjieff A. and Jones J.P. (1996). Practical experiences with aerobic biofilters in TMP, sulfite and fine paper mills in Canada. *5th IAWQ Symposium on Forest Industry Wastewaters*, Vancouver, 227-234.

Klapwijk A., Spanjers H. and Temmink H. (1993). Control of activated sludge plants based on measurement of respiration rates. *Water Science and Technology* **28**(No. 11-12), 369-376.

Landry D., Trudel J.P. and Nicol R. (1991). Biological filtration: a compact process for the treatment of pulp and paper mill wastewaters. *Tappi Proceedings, Environment Conference*, 129-134.

Lavallée P., Trudel J.P., Bergel J.Y., Roberge J. and Zaloum R. (1993). Upflow biological filtration: 80% BOD removal efficiency in less than 20% of the area required for an activated sludge process. *Tappi Proceedings, Environment Conference*, 133-157.

Lizama H.M. and Sankey B.M. (1993). Oxidation of H₂S by *Thiobacillus thiooxidans* is inhibited by substrate and methane. in Torma A.E., Apel M.L. & Brierley C.L. (eds). *Biohydrometallurgical Technologies*. The Minerals, Metals & Materials Society, 339-348.

Malmqvist A., Welander T. and Gunnarsson L. (1996). Suspended-carrier biofilm technology for treatment of pulp and paper industry effluents. *5th IAWQ Symposium on Forest Industry Wastewaters*, Vancouver, 189-194.

Marshall D., Schultz T., Zeni A. and Crabb W.J. (1995). Fixed film biological process solves pulp mills wastewater treatment need. *Tappi, International Environmental Conference Proceedings*, 675-688.

Mathys R., Branion R. and Lo K.V. (1993). CTMP wastewater treatment using a rotating biological contactor. *79th Annual Meeting, Technical Section, Canadian Pulp and Paper Association*, A261-A267.

Möbius C.H. and Cordes-Tolle M. (1994). Advanced treatment of paper mill wastewaters. *Water Science and Technology* **29**(No. 5-6), 273-282.

Moubayed N.N. and Gray N.C.C. (1993). The use of a biofilm reactor to reduce the AOX fraction of kraft mill effluent *79th Annual Meeting, Technical Section, Canadian Pulp and Paper Association*, A103-A108.

NCASI (1994a). Stripping of kraft foul condensates: literature review, operating experience, and field studies. Technical Bulletin No. 661, NCASI, New York.

NCASI (1994b). Kraft mill condensate treatment system conceptual design and order-of-magnitude cost estimate, NCASI, New York.

NCASI (1995). Acetaldehyde, acetone, methanol and methyl ethyl ketone contents of kraft mill condensates. Technical Bulletin No. 702, NCASI, New York.

Ongcharit C., Sublette K.L. and Shah Y.T. (1991). Oxidation of hydrogen sulfide by flocculated *Thiobacillus denitrificans* in a continuous culture. *Biotechnology and Bioengineering* **37**, 497-504.

Pipyn P.M., Eeckhaut M., Ombregt J.P., Teraoka H., Kishimoto Y., Sakamoto H., Kuroda J. and Masue Y. (1987). Anaerobic treatment of kraft pulp mill condensate. *Tappi Proceedings, Environmental Conference*, 173-178.

Pol A., Huub J.M., den Camp O., Mees S.G.M., Kersten M.A.S.H. and van der Drift C. (1994). Isolation of a dimethylsulfide-utilizing *Hyphomicrobium* species and its application in biofiltration in polluted air. *Biodegradation* **5**, 105-112.

Qiu R., Ferguson J.F. and Benjamin M.M. (1988). Sequential anaerobic and aerobic treatment of kraft pulping wastes. *Water Science and Technology* **20**(1), 107-120.

Roche M.P. (1995). Wastewater characterization study to determine mill requirements under the proposed MACT regulation. *Tappi International environmental conference proceedings*, 565-573.

- Rusten B., Mattsson E., Broch-Due A. and Westrum T. (1994). Treatment of pulp and paper industry wastewaters in novel moving bed biofilm reactors. *Water Science and Technology* **30**(3), 161-171.
- Sarkanen K.V., Hrutfiord B.F., Johanson L.N. and Gardner H.S. (1970). Kraft odour. *Tappi* **53**(5), 766-783.
- Sarkis B. and Cooper D.G. (1994). Biodegradation of aromatic compounds in a self-cycling fermenter. *The Canadian Journal of Chemical Engineering* **72**, 874-880.
- Sasaki K., Yamamoto Y., Tsumura K., Hatsumata S. and Tatewaki M. (1993). Simultaneous removal of nitrogen and phosphorus in intermittently aerated 2-tank activated sludge process using DO and ORP-bending-point control. *Water Science and Technology* **28**(No. 11-12), 513-521.
- Saunamaki, R. (1996). Activated sludge plants in Finland. *5th IAWQ symposium on forest industry wastewaters*. Vancouver 251-258.
- Sebbas E. (1991). Reuse of kraft mill secondary condensates. in Coleman M.J. (ed.) *Energy Engineering and Management in the Pulp and Paper Industry*. Tappi, Atlanta, Georgia.
- Séguin F.A., Tremblay B., Zaloum R., Lavallée P. and Lapointe S. (1993). Biofiltration pilot test at the Daishowa pulp and paper mill using the Biocarbene Process. *Water Pollution Research Journal of Canada* **28**(3), 621-634.
- Sheppard J.D. (1993). Improved volume control for self-cycling fermentations. *The Canadian Journal of Chemical Engineering* **71**, 426-430.
- Sheppard J.D. (1989). Feedback control and the continuous phasing of microbial cultures. PhD thesis, Department of Chemical Engineering, McGill University.
- Sheppard J.D. and Cooper D.G. (1990). Development of computerized feedback control for the continuous phasing of bacillus subtilis. *Biotechnology and Bioengineering* **36**, 539-545.
- Shuler M.L. and Kargi F. (1992). Bioprocess engineering. Prentice Hall, Toronto.
- Smook G.A. (1992). Handbook for Pulp and Paper Technologists. 2nd Edition. Angus Wide Publications, Vancouver.
- Stuart P.R., Lagacé P., Arsenault F. and Zaloum R. (1994). Pilot trials using a trickling filter to treat a TMP newsprint mill effluent. *Pulp and Paper Canada* **95**(12), 74-79.
- Swan C.E. (1995). Cluster rules update: new rules will be less stringent. *American Papermaker* **58**(11), 23-25.
- Tchobanoglous G. and Burton F.L. (1991). Wastewater engineering – treatment, disposal, and reuse. 3rd Edition. McGraw-Hill, Toronto.
- Vassos T.D. (1993). Future directions in instrumentation, control and automation in the water and wastewater industry. *Water Science and Technology* **28**(No. 11-12), 9-14.
- Villeneuve F. and Tremblay H. Sequential batch reactor technology: an old technique applied to the treatment of pulp and paper mill effluents. *Tappi International Environmental Conference Proceedings*, 713-718.
- Vismann, B. (1991). Sulfide tolerance: physiological mechanisms and ecological implications. *Ophelia* **34**(1), 1-27.

Yamaguchi M., Tanimoto Y., Ogawa S., Minami K., Okamura K., Naritomi T. and Hake J. (1990). Thermophilic methane fermentation of evaporator condensate from a kraft pulp mill. *Tappi Proceedings, Environmental Conference*, 631-639.

Zenaitis M.G. and Cooper D.G. (1994). Antibiotic production by *Streptomyces aureofaciens* using self-cycling fermentation. *Biotechnology and Bioengineering* **44**, 1331-1336.

VIII APPENDIX

8.1 SCF CONTROL PROGRAMS

Copies of the two programs used to control the PBR and the SBR are available through the Special Collections division of the UBC library. Both programs were written in Turbo Pascal 7.0 for MS-DOS.