Comparison of Powdered Activated Carbon and Activated Sludge Treatment of a Kraft Pulp Mill Wastewater

by
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Dedication

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ABSTRACT

The Powdered Activated Carbon Treatment™ (PACT™) process consists of powdered activated carbon addition to the activated sludge treatment process.

Objectives were 1) to compare treatment of kraft pulp mill wastewater using activated sludge versus PACT™, by measuring toxicity, organic load, adsorbable organic halides (AOX) and metals and 2) to assess how three operating conditions: (1) carbon dose; (2) hydraulic retention time; (3) solids retention time, affected performance.

Findings were:

Lengthy hydraulic retention times are unnecessary. Short hydraulic retention times (4 h) provide adequate treatment.

Activated sludge treatment alone removes most biochemical oxygen demand, PACT™ offers no improvement. PACT™ improves removal of soluble chemical oxygen demand. PACT™ improves removal of AOX. Powdered activated carbon dose is the sole determinant of this increased removal.

Activated sludge treatment alone removes Microtox™ toxicity. PACT™ slightly improves treatment of highly toxic wastewaters. Significant chronic toxicity towards *Ceriodaphnia* remains in effluents from both activated sludge and PACT™. Both

treatments remove toxicity to *Ceriodaphnia*, but PACT™ effluents are more toxic. Powdered activated carbon alone exhibits toxicity to *Ceriodaphnia*.

The effect of PACT™ on removal of metals is inconclusive.

PACT™ treatment of kraft mill wastewater would be very expensive.

PACT™ has limited benefits over activated sludge for the treatment of kraft mill wastewater, therefore PACT™ is not recommended for treatment of kraft mill wastewater.

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GLOSSARY

Parameters (typical units in parentheses):

a	empirical constant used in Freundlich analysis (mg/L)
b	empirical constant used in Freundlich analysis (mg/L)
C	equilibrium concentration of adsorbate in solution (mg/L)
C_0	initial or feed concentration of adsorbate (mg/)
C_x	concentration of substance x, depending on context (mg or g/L)
d	day
G	gravity
h	hour
K	empirical Freundlich constant
k	maximum specific growth rate (d^{-1})
k_d	endogenous decay coefficient (d^{-1})
K_s	half-velocity constant (mg/L)
M	mass concentration of carbon (mg/L)
min	minute
n	empirical Freundlich constant
N	number of *C. dubia* offspring produced in test group
N_0	number of *C. dubia* offspring produced in control group
S	effluent substrate concentration (BOD or COD, mg/L)
S_0	influent or feed substrate concentration (BOD or COD, mg/L)
V	volume (L)
X	volatile biological solids concentration (mg/L)
x	mass concentration of adsorbate adsorbed onto carbon (mg/L)
yr	year
Y	yield coefficient (mg/mg)
Z	standardized normal variate
θ	hydraulic retention time or HRT (h or d)
θ_c	solids retention time or SRT (d)

Parameter Subscripts/Prefixes:

Eff	effluent
F	feed
ML	mixed liquor
S	soluble
T	total

Terms:

daphnid	A generic term for *Ceriodaphnia* and *Daphnia* spp. In the present context it refers to *C. dubia.*
kraft	A process for producing pulp from wood. It involves cooking wood chips at high temperature and pressure in an alkaline solution of Na_2S. Synonymous with sulphate.
effluent	Effluent from laboratory reactors (i.e., treated wastewater).
feed	Wastewater as fed to reactors (i.e., partially clarified, nutrified and sometimes adjusted for pH).
sulphate	Sulphate process pulp production - see kraft.
wastewater	Wastewater sampled from pulp mill, used in preparing feed for reactors.

Abbreviations / Acronyms (typical units in parentheses)

ADI	Acceptable daily intake (mass of substance/d).
ADT	Air-dried tonne.
AOX	Adsorbable organic halide. It should be noted that as far as the kraft industry is concerned, organic halogen is synonymous with organic chlorine, since other halogens are insignificant. See also TOX.
AS	Activated sludge.
ASB	Aerated stabilization basin.
BKME	Bleached kraft mill effluent.
BOD	Biochemical oxygen demand (mg/L).
CBOD	Carbonaceous biochemical oxygen demand (mg/L).
CM	Completely mixed.
COD	Chemical oxygen demand (mg/L).
CTMP	Chemi-thermomechanical pulp.
DO	Dissolved oxygen (mg/L).
EAAS	Extended aeration activated sludge.
ECxx	Effective concentration, *xx* percent. A measure of toxicity. Refers to the concentration of test sample at which a specified effect occurs. For example, a Microtox™ EC50 of 7.5% refers to a sample which, at a concentration of 7.5%, causes a 50% reduction in light output of the test bacteria.
EffTSS	Effluent total suspended solids (mg/L).
EPA	Environmental Protection Agency (USA)
FTSS	Feed total suspended solids (mg/L).
GAC	Granular activated carbon.
HRT	Hydraulic retention time (h).
ICxx	Inhibiting concentration, *xx* percent. A measure of toxicity. Refers to the concentration of test sample at which a specified inhibition occurs. For

	example, a *C. dubia* chronic toxicity IC50 of 35% refers to a sample which, at a concentration of 35%, causes a 50% decrease in daphnid reproduction.
MISA	Municipal/Industrial Strategy for Abatement (Ontario).
MLTSS	Mixed liquor total suspended solids (mg/L).
MLVSS	Mixed liquor volatile suspended solids (mg/L).
$MLVSS_{biol}$	Biological mixed liquor volatile suspended solids (mg/L).
NDPES	National Pollution Discharge Elimination System (USA)
NOEC	No observed effect concentration. A threshold measurement of toxic effect. Refers to the maximum concentration of test sample below which a specified effect is not observed. For example, in *C. dubia* chronic toxicity testing, an NOEC of 23% refers to a test sample which does not affect daphnid reproduction below 23% concentration.
OME	Ministry of the Environment (Ontario).
PAC	Powdered activated carbon.
PACT™	Powdered activated carbon treatment. A patented process in which PAC is mixed into the mixed liquor of activated sludge.
RCF	Relative centrifugal force (gravity).
RMOC	Regional Municipality of Ottawa-Carleton.
rpm	Revolutions per minute.
Rx	Unique reactor identification number (R1 through R18).
SCOD	Soluble COD (mg/L).
SRT	Solids retention time (d).
TCDD	Tetrachloro-dibenzo-p-dioxin. The 2,3,7,8-tetrachloro congener is the most toxic form and is used as the benchmark for expressing TEQs.
TCDF	Tetrachloro-dibenzofuran.
TCOD	Total COD (mg/L).
TEQ	Toxic equivalents based on 2,3,7,8-tetrachlordibenzo-p-dioxin.
TMP	Thermomechanical pulp.
TOX	Total organic halide (should not be confused with toxicity), see also AOX.
TSS	Total suspended solids (mg/L).
USEPA	See EPA.
WAR	Wet air regeneration. A method of regenerating powdered carbon for reuse.
YAT	Yeast, alfalfa, Tetramin™ - food for *Ceriodaphnia.*
YCT	Yeast, Cerophyll™, trout chow - food for *Ceriodaphnia.*

CHAPTER 1

INTRODUCTION

Pulp and paper is an important industry in Canada, both for good and bad reasons. Direct and indirect economic benefits are among the good reasons. But there are significant downsides to the industry as well: environmental degradation and pollution. Forests and associated ecosystems are often destroyed to supply wood fibre for raw material. Air, land and, in particular, water pollution are substantial. Although the industry has made significant improvements over the past 20 years or so and continues to improve, there is still much concern that current discharges to the environment are far from inocuous.

The first wave of environmental controls in the 1970s resulted in the reduction of solid discharges and some concommitant reduction in organics through the use of primary treatment facilities. In the 1980s concerns were focused on organic loads, nutrients and toxic pollutants, and the need for secondary biological treatment became apparent. Environmental legislation promulgated during this period provided timetables for industry to clean up. The beginning of the current decade saw goals of this legislation come to fruition, and currently secondary treatment of effluents is the rule rather than the exception. Although secondary treatment is a substantial improvement, the quality of effluent can still not be described as benign. Conceptions about what constitutes pollution continue to evolve along with the ability to detect and measure it. This is especially true

with respect to toxic pollutants, where early concepts were simplistic and shortsighted. Now emphasis has shifted to questioning the subtle, long-term effects posed by persistent, accumulative, xenobiotic compounds, in particular the organochlorine byproducts of pulp bleaching.

This study examined the use of powdered activated carbon (PAC) as an additive to aerobic activated sludge (AS) treatment of wastewater from a bleached kraft pulp mill, a patented process known as Powdered Activated Carbon Treatment™ (PACT™). While aerobic treatments like AS and aerated lagoons have proven to be effective treatment methods and are currently the secondary treatments of choice in the pulp and paper industry, the study sought to determine if further improvements in effluent quality could be obtained with the use of PACT™.

Objectives of the study were, first to compare conventional AS treatment of pulp mill wastewater with PACT™ treatment, with respect to removal of toxicity, organic load, adsorbable organic halide (AOX), and metals. Second, to assess and describe the effects on the above mentioned parameters of three operation/design variables: 1) carbon dose; 2) feed rate (hydraulic retention time or HRT); 3) solids retention time (SRT).

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Pulp and Paper Industry - Brief Overview

Although its share of the economy has been in steady decline, pulp and paper remains an important industry in Canada, typically contributing 3% of Canada's GNP during the past 25 years (Sinclair 1990). The industry is an important employer throughout the country. According to the Canadian Pulp and Paper Association's statistics for 1994, 242 000 people representing 1.83% of the Canadian workforce were employed directly in the forest industry sector (pulp and paper, logging, lumber and panels, and others) with an additional 5.48% indirect or induced jobs contributing to employment. Pulp and paper mills alone accounted for 63 000 jobs, or 0.48% of the Canadian workforce (see Table 2-1).

Table 2-1 Selected Canadian Pulp and Paper Industry Statistics for 1994 (CPPA 1995b)

Production (pulp, paper and paperboard)	27 929 000 tonnes
Value of sales	$19 307 000 000
- as percentage of Canadian manufacturing	12.7%
Value of exports	$17 057 000 000
Net earnings (losses)	($372 000 000)
Employment	63 000
- as percentage of Canadian workforce	0.48%

In many regions, particularly in remote, rural communities, it is the singular base of the economy. For example one out of every three jobs in Northern Ontario is directly or

indirectly provided by the pulp and paper sector (OME 1993). Many communities in northern Ontario and Quebec are mill towns which rely solely on the basis of the local mill's employment. Pulp and paper companies, workers and supporters will often use this argument that the economic value, employment, economic spin offs, tax base provision, way of life, and so on, outweigh the need to protect the environment. Though this attitude is persistent, fortunately provincial governments have had the will to impose upon the industry to clean up its effluent. Witness Ontario's Municipal/Industrial Strategy for Abatement (MISA) program (OME 1992b) and the Quebec government's regulations requiring secondary treatment. A case in point is the mill from which samples were taken for the present study. During the course of the study, it was pleasing to follow progress in construction of the mill's secondary treatment facility which came into operation in the spring of 1995. Prior to that, about 70 000 cubic meters of effluent were discharged to the local river each day, the only treatment being primary settling of gross solid material in a lagoon with a retention time of 14 h.

2.2 The Kraft Pulping Process

Of all pulp mills operating in Canada, kraft mills account for approximately 50.1% percent of production. Of that total, 44.2% is bleached/semi-bleached, the remaining 55.8% is unbleached (CPPA 1995a). Kraft pulp is used in-house for the production of paper or sold as market pulp. The qualities desired in the final product have an effect on the manufacturing process. As far as bleached kraft pulping is concerned this means strong, clean, bright pulp. To this end the process must minimize fiber (i.e., cellulose) losses and damage, remove as much lignin and undesirable material as possible, and bleach

the remaining fibers to the desired standard. Kraft pulping (also known as sulphate pulping) is a chemical process that involves cooking wood chips in an alkaline solution of 10% Na_2S and NaOH, known as white liquor. Wood chips are typically cooked at about 165°C for 1 h to solubilize lignin. The spent cooking liquors, known as black liquor, contain solubilized lignin, various organic compounds from the wood and excess cooking chemicals. Black liquor is washed out of the pulp, concentrated and treated to recover the Na_2S and NaOH, which are reused in the cooking process. Organic residue from the black liquor, mostly lignin, organic acids and other organic compounds, is burned in a recovery boiler to generate steam for the cooking process. Cooked pulp, or brownstock, is washed to remove the lignin and cooking chemicals. Wastewater from brownstock cleaning, called white water, is discharged as part of the mill effluent. The pulp then moves onto the bleaching process. Until recently, the most common bleach system used an initial treatment with chlorine gas to convert lignin to an alkali-soluble form which is then extracted with NaOH. The solubilization/extraction process is repeated twice more, using chlorine dioxide or sodium hypochlorite instead of chlorine. But now the initial chlorination step is routinely replaced by chlorine dioxide, since it produces not only fewer organochlorine byproducts, but these also have a lower degree of chlorine substitution. The bleaching stage is of course the source of all organochlorines in the process and currently there is a push to eliminate chlorine in favour of hydrogen peroxide or oxygen, the latter also known as oxygen delignification.

Bleaching is the final process stage in kraft pulping per se. Bleached pulp continues on to a dryer where it is pressed and dried, then sold as market pulp. Alternatively, in an integrated pulp and paper mill it is processed into paper or paper products on site.

2.3 Environmental Legislation

Although the Canadian federal government suggests effluent limits for the pulp and paper industry, in practice it is left to the provincial environmental ministries to set and enforce their own regulations and timetables. Indeed the federal government admits that "as is the case with both regulations and guidelines, the success of these mechanisms (i.e., waste reduction programs) in reducing the amount of waste discharged from the pulp and paper industry, to a very large extent, depends on the goodwill of the provinces and industry" (Sinclair 1990).

As an example of environmental regulation, the author will review regulations of the most relevant jurisdiction of which he has the most knowledge, viz., the province of Ontario. As of 1989, Ontario had 27 pulp and paper mills which discharged effluent directly to the environment. Nine of these were bleached kraft mills. All 27 mills had at least primary treatment, 6 mills had secondary treatment. The Ontario Ministry of the Environment (OME) began to seriously control pulp and paper mill effluents in the mid 1980s as part of MISA. Created in 1986, the MISA program aims to "identify and reduce the pollutants discharged from municipal and industrial sources, towards the goal of virtual elimination of toxic contamination of Ontario's lakes and rivers (OME 1992b)." The program's three main principles are:

1. Pollution prevention.

2. Bans or phase-outs of persistent toxic chemicals.

3. No cross-media transfer of pollutants.

Industrial pollution from nine sectors were targeted, including pulp and paper. Key elements for all sectors included:

1. Effluent limits for sector-specific parameters.

2. No acute aquatic toxicity.

3. Banning or phasing out of specific persistent toxic substances.

4. Reduction of persistent toxic substances which are not slated for zero-discharge or otherwise limited.

After an initial monitoring program to assess the nature and scope of the problem, MISA set sector-specific regulations for effluent quality. Pulp and paper sector limits came into effect on January 1, 1996, encompassing ten different parameters. These are shown in Table 2-2, along with some of the guidelines for Quebec and the federal governments suggested guidelines. In Ontario, specific limits are set for each individual mill, within the ranges outlined in Table 2-2.

Table 2-2 Some Canadian effluent standards for pulp and paper mills (OME 1993).

Parameter[a]	Ontario	Quebec	Federal (suggested)
BOD_5[b]	2.91-5.00	5.0-9.0	7.5
TSS[c]	4.57-7.87	8.0	11.25
Total phosphorous	0.05-0.08		
Chloroform	0.001-0.002		
Toluene	0.0001-0.0002		
Phenol	0.0002-0.0004		
2,3,7,8-TCDD[d]	n.d.[e]	low[f]	n.d.
2,3,7,8-TCDF[d]	n.d.	low[f]	n.d.
Toxicity	non-acutely lethal	non-acutely lethal	non-acutely lethal
AOX[g]	1.5 (as of 31/12/1995) 0.8 (31/12/1999) 0.0 (31/12/2002)	1.5-2.5 (31/12/1993) 1.0-2.0 (31/12/1995) 0.8 (31/12/2000)	

[a] Values are monthly limits in kg/tonne of air-dried pulp
[b] BOD_5 - 5-d biochemical oxygen demand
[c] TSS = total suspended solids
[d] TCDD = tetrachloro-dibenzo-p-dioxin, TCDF = tetrachloro-dibenzofuran
[g] AOX = adsorbable organic halides
[e] n.d. = not detectable
[f] Total of dioxins and furans not to exceed 15 ppq as 2,3,7,8-TCDD

All mills must adhere to these regulations, which came into force January 1, 1996 (Ontario regulation 760/93). Limits are set for 5-d biochemical oxygen demand (BOD_5), total phosphorous, total suspended solids (TSS), chloroform, toluene, phenol and AOX. Quarterly monitoring for 2,3,7,8-tetrachloro-dibenzo-p-dioxin (TCDD), 2,3,7,8-tetrachloro-dibenzofuran (TCDF) and toxic equivalence of their congeners is also required. Concern over organochlorines has led to a push for elimination of these compounds by the year 2002. The Canadian industry has greatly reduced its AOX discharges in recent years (Figure) primarily due to a reduction in the use of elemental chlorine in the bleaching process. Ontario was the first province to address AOX discharges (Dubelsten and Gray 1990). The ultimate goal is elimination of AOX discharges by the year 2002.

The study of Bonsor et al. (1988), commissioned by OME, examined Ontario kraft mill effluents. Most of their recommendations were incorporated into the OME's regulations for kraft mill effluents. One notable exception however, was the difference of opinion with regard to toxicity standards. Bonsor et al. argued that concentration based toxicity standards are not appropriate since the objective of effluent discharge regulation is to "protect organisms in the receiving water after dilution, not in the end of the effluent pipe". Furthermore concentration based testing " discourages technical development of certain environmentally desirable technologies, such as oxygen delignification, dry debarking and water conservation in general." Therefore the Expert Committee on Kraft Mill Effluents recommended a mass flow limit of toxins, with toxicity testing normalized to 175 m^3 water/tonne pulp. However, OME (1989) dismissed the recommendation, preferring to maintain the criterion of non-lethal effluent, with no allowance for water credit. The ministry's rationale was that it is important to determine the toxicity of the wastes as they are being discharged from each outfall. Ironically, the ministry says it considers water conservation and toxicity as important albeit separate issues, but this statement is contradictory. If one uses a concentration based toxicity criterion, then water use and "toxicity" are directly related. Thus it seems that the OME position on toxicity is a statement of principle rather than logic. Furthermore, since water use is not regulated, a mill can conceivably increase water consumption to meet the toxicity requirements. By allowing this loophole, OME contradicted its stated concern about water conservation as well as its stated opposition to the notion that "dilution is the solution."

2.4 Water Pollution in the Pulp and Paper Industry

The pulp and paper industry is an enormous polluter in Canada, polluting the air, land, water (both chemically and physically when floating logs to markets) and causing environmental degradation from logging. The following discussion of pollution is restricted to water only. To give some idea of the relative contribution of pulp and paper industry to water pollution, consider that the Regional Municipality of Ottawa-Carleton (RMOC), with a population 700 000, discharges treated municipal wastewater averaging 2.15 tonnes carbonaceous (C)BOD/d (i.e., 430 000 m^3/d @ 5 mg/L total CBOD, (RMOC 1996)). Whereas the daily discharge from the mill sampled in this study, prior to installation of secondary treatment facilities, was 35 tonnes CBOD/d (i.e., 70 000 m^3/d of effluent with a soluble CBOD of 500 mg/L). This is more than 16 times that of RMOC from a single mill.

Although the industry remains a serious source of pollution, it has nevertheless made and continues to make improvements to effluent discharges. Even though production continues to increase (Figure), the absolute tonnage of AOX, BOD_5 and suspended solids discharged to the environment has steadily decreased over the past decade (Figures 2-2 to 2-4).

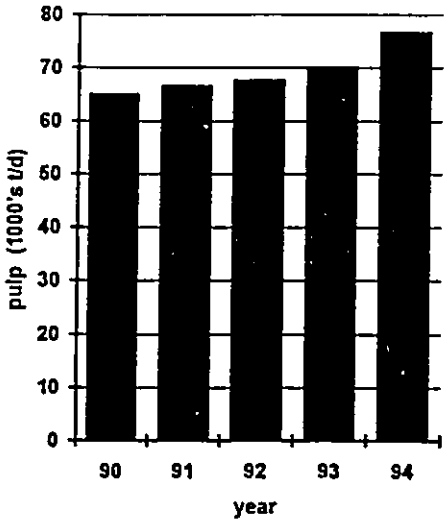


Figure 2-1 Pulp production in Canadian pulp and paper mills, calculated from data in CPPA 1995 Reference Tables, (CPPA 1995b).

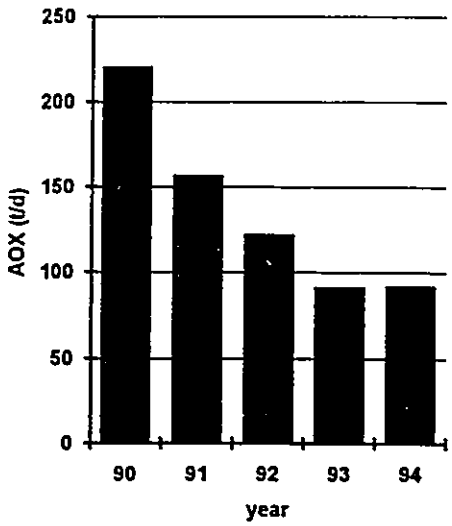


Figure 2-2 AOX in mill effluent discharged to the environment from Canadian pulp and paper mills, calculated from data in CPPA 1995 Reference Tables, (CPPA 1995b).

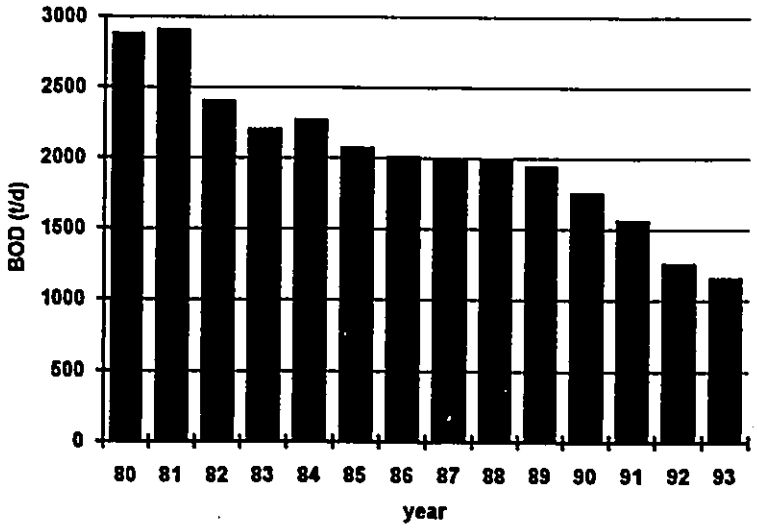


Figure 2-3 BOD discharged to the environment from Canadian pulp and paper mills (CPPA 1995b).

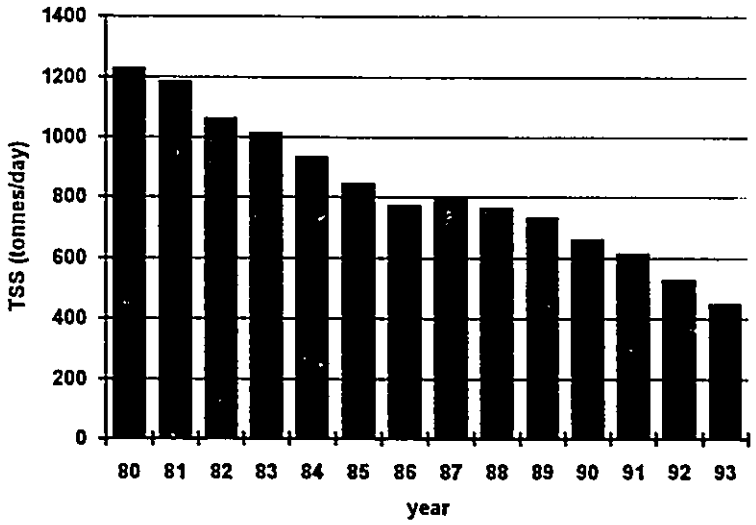


Figure 2-4 Total suspended solids discharged to the environment from Canadian pulp and paper mills (CPPA 1995b).

It is interesting to note that only about 40% of wood is cellulose, which is the main constituent of paper; therefore the remaining 60% of wood mass is a potential waste.

As outlined above, secondary treatment is becoming the industry norm, and it significantly improves the quality of effluent. Data in Table 2-3 give an indication of typical performance of secondary treatment of bleached kraft mill effluent (BKME). BOD removals are excellent, often >90. Few mills test chemical oxygen demand (COD) since BOD_5 is the more common regulatory parameter, so it is difficult to generalize about COD removal. AOX removal is variable, probably reflecting differences in wood furnish, delignification and bleaching processes, all of which affect the amount and type of organochlorine byproducts. McCubbin et al. (1989) reports "typical" AOX removal of 30 to 60 percent for Ontario mills.

Table 2-3 Performance of secondary treatment systems for BKME.

No. of Mills /Treatment/HRT(d)	% Removal[a]			Source
	BOD	COD	AOX	
4 /AS[b]/?			48 to 65	Dubelsten & Gray 1990
1/AS/?	91 to 96	33 to 49	15 to 36	Saunamäki 1994
1/AS/0.3			20 to 30	Saunamäki et al. 1991
1/EAAS[c]/4	98		40	Barkley & Bryant 1990
1/EAAS/1			40 to 50	Saunamäki et al. 1991
4/ASB[d]/7 to 13	91		47	Barkley & Bryant 1990
4/ASB/5	75 to 89		25 to 30	Dubelsten & Gray 1990
1/ASB/6	88	62	56	Fein et al. 1992
1/ASB/7	>90		15 to 47	Tomar & Allen 1991
"typical"/ASB/?			30 to 60	McCubbin et al. 1989

[a] Removal refers to change in parameter concentrations in secondary effluent when compared to primary effluents.
[b] AS = activated sludge
[c] EAAS = extended aeration activated sludge
[d] ASB = aerated stabilization basin (lagoons)

2.5 Toxicity of Wastewater

2.5.1 Perceptions of Toxicity

In recent years the issue of toxicity (as opposed to solids and organic loading) has probably been the strongest motivation in the effort to reduce pulp and paper mill pollution.

A shift in thinking with respect to toxicity is evident when the literature over the past two decades is examined. Early toxicity testing was limited to acute effects on fish. Indeed, even as late as the mid 1980s, toxicity testing using species other than fish still had the aura of a new and not quite routine nor standardized procedure. The value of alternate test protocols (e g., daphnids, Microtox™) was evaluated mainly in terms of their utility as a quicker, cheaper proxy for fish rather than as bona fide tests for their representative groups of organisms. But as evidenced in the McLeay (1987) review of Canadian pulp and

paper mill effluents, emphasis did begin to shift from the narrow, anthropocentric and utilitarian view *of does it kill (economically important) fish?* to *what are the long term consequences for the environment as a whole?* The latter view prevails today.

One of the difficulties in assessing toxicity is the complex nature of the wastewater, making it difficult to pinpoint cause and effect. Like the changing attitudes towards toxicity testing, the relative interest in different toxins has evolved too. Initially, discussions of toxicity were limited to compounds which were responsible for obvious effects of acute toxicity. McLeay (1987) gave most attention to acutely toxic compounds: chlorophenols, resin acids and fatty acids. Dioxins and furans were not mentioned. The current concern is over long term effects; organochlorines in particular, because of their persistence and bioaccumulation. But both the public and scientific interest shown in particular toxins can still be a function of whichever happens to be in vogue. An example is the emergence in the late 1980s of chlorinated dioxins and furans as a *cause célèbre*, even though these compounds make up an exceedingly small proportion of the total organochlorines present. Bonsor et al. (1988) estimated that the average kraft mill released 11 milligrams of 2,3,7,8-tetrachloro-dibenzo-p-dioxin (TCDD) toxic equivalents (TEQ)/d, and that all Ontario kraft mills combined generate only 1/400th of the total TEQ discharge from all sources (combustion, incineration, byproducts in chemical production, etc.) The acceptable daily intake (ADI) for humans is 0.7 ng 2,3,7,8-TCDD TEQ/d. Nevertheless, since these compounds are water-insoluble and tend to accumulate in living organisms, some frequent fish eaters may exceed the ADI in parts of Ontario. McCubbin et al. (1989) argued that focusing on a few specific organochlorine congeners is ineffective

since there are likely thousands present in pulp wastewater, noting that as much as 90% of organochlorines remain undescribed. Furthermore, the long term fate and effects of organochlorines are unknown. For example, high molecular weight chlorolignins can persist for decades in the environment, and although they have relatively low toxicity, they degrade to smaller, more toxic forms. So, reasoning that organochlorines as a group are known to be toxic, persistent and bioaccumulative, they recommend that the total amount of organochlorines should be reduced using a broadly based definition, such as total organic halides (TOX). The test for AOX has since been accepted as the standard protocol for the determination of organochlorines (see Environment Canada 1992b for description of protocol). AOX roughly equals TOX less the approximately 5% of volatile organohalogens present in untreated whole pulp mill effluents.

If dioxin and furan reduction remains a preoccupation, Bonsor et al. (1989) note that two bleach process modifications can virtually eliminate them 1) avoid using furan-containing defoamers upstream of the bleach plant and 2) use higher substitutions of chlorine dioxide instead of Cl_2.

2.5.2 AOX

Although, as discussed above, AOX is considered to be an unacceptable pollutant, demonstrating that it is toxic in the context of current acute and chronic toxicity assays is difficult. A number of studies have failed to show correlation between organochlorine levels in effluents (AOX, TOX) and toxicity as measured with bioassays using fish, daphnids, algae and others.(O'Connor et al. 1992a; Shimp and Owens 1993; Charlet 1991). But one must realize that even nominally "chronic" toxicity assays are short term

when considered in the context of their environmental persistence. Therefore it is unwise to accept these observations as tacit proof that organochlorines are nontoxic.

The most effective means of reducing organochlorine discharges are in-plant modifications, particularly, but not limited to, bleaching operations. Murray and Richardson (1993) pointed out that up to 80% of lignin is removed in the first bleach stage, thus this effluent stream has high organochlorine content. Substitution of chlorine gas by chlorine dioxide in the first stage significantly lowers organochlorine byproduction. But the cost of chlorine dioxide is about twice that of chlorine gas, based on oxidizing power. Oxygen bleaching increases delignification by 25% thus less Cl or ClO_2 is required. Hydrogen peroxide (H_2O_2) is entirely chlorine free. Peroxide has the advantages of not affecting pulp strength, decreasing brightness reversion, and low handling cost. Disadvantages are that it corrodes titanium, and costs 3 times more than chlorine. Hypochlorite bleaching, a major chloroform producer, is being removed in modern bleach plants.

Shimp and Owens (1993) noted that substitution of elemental chlorine with chlorine dioxide not only reduces the total quantity of AOX but the chemical character of the remaining AOX changes from highly substituted species (i.e., 3 to 4 chlorines) to species with only 1 or 2 chlorines. Hence discharges of the more ecotoxic, bioaccumulative and persistent highly-substituted species are reduced. Tomar and Allen (1991) noted that hardwood pulp bleaching produces 1.34 kg AOX/air-dried tonne (ADT) versus 3.60 kg AOX/ADT for softwoods since hardwoods have much less lignin and

require less chlorine during bleaching. Sjoblom and Mjoberg (1990) discussed various in-plant methods for reducing chlorine consumption and hence AOX discharges.

2.5.3 Components and Sources of Toxicity

Pulp and paper mill wastewater toxicity arises from a number of processes in the mill. In terms of acute and chronic toxicity as defined by current assays (i.e., fish, daphnids, etc.), the major sources of toxicity in kraft mill wastewater are leaks/spills, brownstock washings, bleach plant streams, blow heat condensates and woodroom wastewater. One of the most important factors in controlling toxicity is in-plant measures: controlling spills (especially black liquor soaps which contains high concentrations of resin and fatty acid salts) and use of countercurrent brownstock washing. An illustration of the extreme toxicity of black liquor soaps occurred in 1983 when a 20-minute spill from a soap tank caused a massive fish kill along 45 km of the Spanish River (Bonsor et al. 1989). Table 2-4 shows some of the major contributors to toxicity.

Table 2-4 Main toxic components of kraft mill effluents (Bonsor et al. 1988.)

Effluent stream	Major toxic contributors[a]	Lesser toxic contributors[a]
Debarking	Resin acids - isopimaric - dehydroabietic - abietic - pimaric	Diterpene alcohols - pimarol - isopimarol - dehydroabietal
Pulping (unbleached whitewater)	Resin acid sodium salts - Na isopimarate - Na abietate - Na dehydroabietate - Na pimarate	Fatty acid sodium salts - Na palmitoleate - Na oleate - Na linoleate
Acid chlorination	Chlorolignins - 4,5-dichlorocatechol - 3,4,5-trichlorocatechol - tetrachlorocatechol	?
Caustic extraction	Chlorinated stearic acids - epoxystearic - dichlorostearic Chlorinated resin acids - monochlorodehydroabietic - dichlorodehydroabietic Chlorinated phenolics - tetrachloroguaiacol - trichloroguaiachol	Liquid pitch dispersants
[a] Subitems listed in order of prominence.		

Although resin and fatty acids are highly toxic, they are natural compounds present in wood and can be decomposed by secondary treatment (the principle of "microbial infallibility"). They do not pose a persistent toxic hazard in the environment. For this reason, they are not as worrisome as the persistent xenobiotic compounds produced as byproducts during bleaching. For example, Gibbons et al. (1992) showed that AS and aerated lagoon treatments of chemi-thermomechanical (CTMP) and thermomechanical (TMP) effluents removed wood extractives >99% efficiency (but moderate acutely lethal toxicity still remained towards *Ceriodaphnia*). McLeay (1987) also noted that better than 90% of (unchlorinated) resin acids are removed during biological treatment.

Given that resin acids are highly toxic, it is not surprising (though often overlooked) that the type of wood used for pulping is an important determinant of effluent toxicity. Kovacs and Voss (1992) characterized toxicity and chemical composition of mill primary effluents (exclusive of kraft mills). The main findings were that mill furnish rather than process type seemed most important in determining toxicity.(e.g., most toxicity with pine>spruce/balsam>hardwoods). General sensitivity of test organisms was: most sensitive *Ceriodaphnia*>minnows/trout>bacteria>algae. O'Connor et al. (1992b) showed also that wood species affects toxicity, based on tests using simulated pulping effluents. In order of decreasing chronic toxicity towards *Ceriodaphnia*: balsam fir>hemlock>white pine> black spruce=aspen. They noted that dehydrojuvabione, a component of balsam fir, was particularly toxic (0.5 ug/L chronic threshold) for *Ceriodaphnia*.

In the context of all biota in the environment, organochlorine discharges and toxicity testing are rather gross assessments of pollution and its consequences. So the search for deleterious effects of mill pollutants has in recent years become more sophisticated. Many studies investigate the more subtle effects upon biota. For example, Rao et al. (1994) examined BKME and found that although whole effluent was non-acutely toxic and effluent fractions were only mildly toxic to Microtox™ and *Daphnia magna*, both whole and fractionated effluents were mutagenic. Some of the more insidious effects on fish in receiving waters that have been reported include alterations in enzyme and steroid levels, gonad and liver size, despite few apparent effects on *Ceriodaphnia* (Munkittrick and Van Der Kraak 1993). Also, liver enzyme function and reproductive

performance effects have been described among fish in receiving waters exposed to BKME (Robinson et al. 1994).

2.5.4 Toxicity Assays - Microtox™ and *Ceriodaphnia dubia*

The Microtox™ and *Ceriodaphnia dubia* toxicity assays provide a means of comparing the performance of treatment systems such as PACT™ and AS.

Microtox™ is a patented toxicity assay produced by Microbics Corporation of Carlsbad, CA, USA. This assay uses a light-emitting marine bacterium, *Photobacterium phosphoreum* and measures the decrease in light output in response to a 5 or 15 min exposure to toxicant. Toxicity of a sample is generally reported as an *effective concentration 50%* (EC50), meaning the concentration of test sample at which there is a 50% reduction in bacterial light production. Values may also be reported as EC10 or EC20, the concentrations at which respectively 10% and 20% reductions in light output are observed. Reported EC values are inversely proportional to toxicity, i.e., the lower the EC value, the more toxic the sample. It is a relatively new method, first used in the 1980s. The main advantage of the Microtox™ assay is its speed and convenience. If the equipment and reagents (incubator/analyzer unit and freeze-dried bacteria) are in place, a test can be conducted in less than 1 h. Its disadvantage is relative insensitivity compared to other bioassays. Its relevance has also been questioned, the argument being that a marine bacterium is not a good surrogate for freshwater organisms.

A number of studies have investigated the use of Microtox™ for testing pulp and paper industry wastewaters (see Table 2-5). Many of these tried to correlate Microtox™

with standard bioassays (i.e., fish and algae) in the hope that the latter more expensive and cumbersome tests could be replaced. Blaise et al. (1987) compared Microtox™ to algal and fish toxicity tests. Biological treatment of CTMP effluent reduced Microtox™ toxicity from about 5% to >100%. Very low toxicity remained with respect to trout, and moderate toxicity with respect to algae. Fish were generally the least sensitive, Microtox™ was moderate, and algae were most sensitive. They remarked that reliance on a single toxicity test is too narrow and that to accurately assess the total effects of an effluent on the receiving environment, a gamut of tests ought to be considered. They ranked various types of mills based on a combination of toxicity assays (see Table 2-6). Although such a toxicity ranking is instructive in the design of treatment facilities and to assess the immediate impact in the receiving waters, the toxicity rankings also reflect the amount of water used per tonne of production, hence the net discharge of toxins will not necessarily be the same as the toxicity ranking on a concentration basis.

Table 2-5 Reported toxicity for mill primary and secondary effluents.

Type	Treatment	Microtox™: 15 min. EC50 (%)		*Ceriodaphnia* chronic: NOEC[c] (%) except where noted		Source
		1°[a]	2°[b]	1°	2°	
Integ. BKME	Mod. AS				10,30,32,75	Kraus 1990
BKME	none	11.5 to 37				Lavallee et al. 1992
BKME	AS				56	Kraus 1990
BKME	"secondary"	~ 17	100	2	75	Firth & Backman 1990
Various	"secondary"		8,45,60, 75,100		2,12,25,43,75, 100	Firth & Backman 1990
BKME	ASB			IC25[d]: 1.2 to 10.2 (ave 4.3, 4 mills)	IC25: 1.4 to 83 (ave 26.1, 7 mills)	O'Connor et al. 1992
BKME	ASB	7.9	93	0.1	75	Fein et al. 1992
3 CTMP	"secondary"	4.5	>100			

[a] 1° = primary effluent
[b] 2° = secondary effluent
[c] NOEC = No observed effect concentration
[d] IC25 = Inhibiting concentration for 25% inhibition of reproduction

Table 2-6 Toxicity ranking of mills based on pulping process (source Blaise et al. 1987)

Mill type	Combined toxicity units (algal, trout, Microtox™)
Fine paper (no pulping)	9
CTMP	36.7
Kraft	40.4
Recycled, deinked fiber	43.3
MP/TMP	53.7
Bisulfite	169

As an example of the labile nature of Microtox™ toxicity in pulp and paper wastewaters, Fein et al. (1993) investigated fine paper mill effluent treatment with the Acticontact process. They showed that Microtox™ toxicity was unstable if samples were allowed to sit at room temperature, sometimes toxicity decreased from ~15 to 100% within 24 h. Holding samples at 4°C resulted in a decrease from 15 to 35% toxicity after 9 d.

The Microtox™ data in Table 2-5 reflect its insensitivity to toxicity in secondary treated effluents. Indeed, McLeay (1987) noted that with regard to secondary treated effluent, "this test (Microtox™) is relatively insensitive and cannot detect any residual, sublethal activity" and that "... the relative insensitivity of acute lethal (or Microtox™) bioassays renders them of little value in assessing residual toxicity for samples of receiving waters or biotreated ("detoxified") effluents" (McLeay 1987).

Given the insensitivity of the Microtox™ assay to low levels of toxicity, another test is needed to differentiate PACT™ and AS treatment. The *Ceriodaphnia* chronic toxicity test assesses the effect of longer term exposure of toxins on animal reproduction. The great advantage is that this test can assess the sublethal, chronic toxicity for a complete life cycle in less than 7 d. To perform the test, *Ceriodaphnia* are grown in various concentrations of test sample (e.g., mill waste water, reactor effluents). A control group is grown in pure water only. The number of offspring produced by animals exposed to each sample concentration is compared to the control group. A reduction in the number of offspring provides an measure of toxicity. Results are typically reported as IC50 (inhibiting concentration 50%), that is, the concentration of sample that will cause a 50% reduction in the number of offspring.

Ceriodaphnia testing is becoming widely used. For example, it is commonly required for NPDES (National Pollution Discharge Elimination System) permits in the United States (Reed 1992; Firth and Backman 1992).

Like Microtox™, *Ceriodaphnia* is a relatively new test, the protocol having been developed and standardized in the late 1980s (US EPA 1989). Some aspects of the

protocol have been recently debated: for example, the choice of diet used for culturing *Ceriodaphnia* and its effects on test results. Norberg-King and Schmidt (1993) showed that *C. dubia* may be cultured on various diets and that toxicity test results among different diets were comparable when tested with wastewater treatment plant, refinery or industrial effluents. However, diets consisting solely of algae did not support reproduction that met the minimum requirements. Cerda and Olive (1993) reported similar findings, that algal diets did not support or poorly supported reproduction. Furthermore, animals fed only algae were more sensitive to toxicant (copper). But the effect of diet on test results for specific chemicals is inconsistent. For example, in contrast to the results cited above, some studies showed decreased sensitivity to copper by animals fed on algae (Norberg-King and Schmidt 1993; Cowgill et al. 1985 and Belanger et al. 1989) The emerging consensus is that relatively poor diets (e.g., algae alone) are problematic. Whereas rich diets of algae supplemented with yeast-cereal-fishfood are best, meeting the reproduction requirements in control animals and giving consistent test responses. The current diet recommended by both Environment Canada (1992a) and USEPA (1989) is the alga, *Selenastrum capricornutum*, plus yeast-Cerophyll®-trout food. Substitutions for one or more components of the diet may be made at the discretion of the individual laboratory, as long as minimal health standards are met (Environment Canada 1992a). The choice of alga sometimes varies between laboratories, for example, *Ceriodaphnia* can be cultured successfully with *Ankistrodesmus convolutus* (Olde 1995).

The accepted statistical method for calculating IC50s is that of probit analysis (Environment Canada 1992a and 1992b). Finney (1964) defines it as "the probit of the

proportion P is the abscissa that corresponds to a probability P in a normal distribution with mean 5 and variance 1." In this case the standard deviation is also 1. A probit is therefore equivalent to the normal standard variate $Z+5$. The original rationale for using probits rather than Z was to simplify calculations by avoiding negative values of Z. Now, however, computers render the problem irrelevant. The author prefers to work directly with Z, since readers with basic statistical knowledge are more familiar with it and may find the term probit confusing. The relationship between the observed data and Z for the analysis are as follows:

If N is the number of offspring produced per daphnid in a test group and N_0 that of the control group, then the standardized variate, Z, is related to reproduction, N/N_0, according to Eq. 2-1.

$$\frac{N}{N_0} = \Phi(z) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{z} e^{-u^2/2} du \qquad (2\text{-}1)$$

The underlying assumption in probit analysis is that the dose-response relationship between the toxicant and test animal follows a log-normal distribution. Finney (1964) notes that extreme values of Z, outside the range –2.5 to 2.5, carry little weight and can be disregarded. Points within this range are used to calculate a weighted regression line from which the IC50 and corresponding confidence limits are interpolated. Other transformations of the ordinate (concentration) can be considered if a simple logarithmic transformation fits poorly. If the aim of the statistical analysis is to determine an IC50 alone, it will suffice to consider only those points near 50% reproduction. Some readers may consider the choice of which points to include subjective. However, one should not

be tempted to include all points in the data set for the sake of completeness. It must be kept in mind that the log-normal distribution is being fitted to the data and not vice versa. The IC50 value must be representative of the data and not an artifact of imposing a theoretical relationship on the observations. For this reason it is always recommended to plot raw data, that is, reproduction versus concentration, to see the real behaviour.

2.6 PACT™ Process

Since biological wastewater treatment systems such as AS are in wide use, e.g., the treatment of municipal wastewater, it is assumed that readers are familiar with their basic theory and design, and a review is unnecessary here. The author recommends Tchobanoglous and Burton (1991) and Grady and Lim (1980) as references.

Powdered activated carbon treatment™ (PACT™) is a modification of the AS process in which PAC is added to the mixed liquor. Biomass grows directly on the carbon particles, thus the mixed liquor suspended solids (MLTSS) is a combined mass of carbon and biomass. This patented process was developed by DuPont in the 1970s at the Chambers Works chemical plant in Deepwater, New Jersey. The patent license is owned by Zimpro Environmental Inc. of Rothschild, Wisconsin.

A number of advantages of PACT™ over standard AS treatment are cited (Dietrich et al. 1988; Hutton 1990; Lankford and Eckenfelder 1990; Meidl 1990):

1. Improved COD and BOD removal.
2. Stability of operation with variability in influent concentration and composition.

3. Enhanced removal of toxic substances and priority pollutants.

4. Effective colour removal.

5. Improved solids settling.

6. Suppressed stripping of volatile organics.

Data presented in Table 2-7 and Table 2-8 demonstrate improved treatment of various wastewaters with PACT™ compared to AS. Enhancement of COD removal varies depending on the biodegradability of the waste. It is usually assumed that enhanced COD removal occurs when non or slowly biodegradable material is taken up by the carbon. It is still being debated whether additional COD removed is only adsorbed on the PAC or subsequently taken up by bacteria growing on the PAC particles, allowing more material to adsorb (a process known as bioregeneration of carbon). If bioregeneration is indeed occurring, the advantage of PACT™ is that substrates adsorbed onto PAC remain in the system for one SRT, rather than an HRT, and thus bacteria have more time to consume slowly biodegradable compounds. For example, Vuoriranta and Remo (1994) ostensibly showed that bioregeneration of carbon was responsible for increased adsorptive capacity of granular activated carbon (GAC) treating secondary effluent from BKMF. However, they did not actually determine if carbon adsorption/bioregeneration per se was responsible for the observations, only that GAC plus bacteria results in better overall performance.

In contrast to COD, improvement in BOD removal is minor or negligible, suggesting that AS biomass and PACT™ biomass consume essentially the same substrates. To paraphrase, what is readily edible in the wastewater will be consumed

regardless of the type of biomass growth. PACT™ is a better remover of organics and metals. PACT™ has been shown to reduce stripping, that is, off-gas hydrocarbon levels were reduced from 208 to 78 ppm (Zimpro 1986).

Table 2-7 Comparison of AS and PACT system performance. Percent removal of various wastewater components.

Waste	BOD_5		COD		Basic/Neutral Extractables[a]		Acid Extractables[b]		Metals (Cu, Cr, Ni)		Source
	AS	PACT	AS	PACT	AS	PACT	AS	PACT	AS	PACT	
Organic chemical plant	99.6	99.7	97.1	99.0							Meidl 1990
Chemical plant					66.0	96.8	21.3	96.0			Meidl 1990
Chemical plant	99.0	99.0							12 33 33	90 78 56	Meidl 1990
Shale oil retort effluent	85.9	99.6	64.4	89.4							Dietrich et al. 1988
Organic chemical plant	96.6	98.1			94.1	96.4	69.3	94.3			Hutton 1990

[a] Basic/Neutral Extractables (organics): chlorobenzenes, nitrotoluenes, nitrobenzenes
[b] Acid Extractables (organics): chlorophenol, nitrophenols

Table 2-8 Comparison of AS and PACT system performance. Final concentration of components in effluent.

Waste	BOD_5 (mg/L)		COD (mg/L)		Basic/Neutral Extractables[a] (ppb)		Acid Extractables[b] (ppb)		Metals (Cu, Cr, Ni) (mg/L)		Source
	AS	PACT	AS	PACT	AS	PACT	AS	PACT	AS	PACT	
Refinery wastewater			80	33							Meidl 1990
Not specified					1.7 950 18	0.1 53 0.1	22 86 830	1.3 0.1 29			Meidl 1990
Chemical plant	3	2							0.36 0.06 0.35	0.04 0.02 0.23	Meidl 1990

[a] Basic/Neutral Extractables (organics): chlorobenzenes, nitrotoluenes, nitrobenzenes
[b] Acid Extractables (organics): chlorophenol, nitrophenols

Some examples of PACT™ system operating parameters are shown in Table 2-9 , arranged according to loading rate of mg COD/mg PAC. The operating conditions vary widely, quite different from Zimpro's original design guidelines, especially between different applications. For example, the highest and lowest loading rates (mg COD/mg PAC) differ by a factor of 28 (i.e., 0.36 to 10.1). Nevertheless, the treatment efficiency based on COD removal was high for all systems, 8 of the 10 examples removed more than 90% COD. Several of these studies also reported that treatment efficiency improved with increasing PAC dose. Lankford and Eckenfelder (1990) reported similar findings, and also showed that although removal of specific contaminants increases with increasing PAC concentration, a plateau is reached beyond which additional PAC does not improve treatment. Systems compared in Table 2-9 are most similar in their mixed liquor carbon suspended solids (MLCSS), which range from 4 470 to 27 100 mg/L, a factor of 6.1, perhaps reflecting the operational limitation of high solids content in mixed liquor.

Table 2-9 Comparison of various PACT™ system operating conditions.

Waste	HRT (d)	SRT (d)	PAC dose (mg/L)	MLCSS (mg/L)	influent COD (mg/L)	Loading mg COD/ mg PAC	effluent COD (mg/L)	COD, % removal	Source
Chemical plant runoff	1.1	8.3	1790	13500	636	0.36	19	97.0	Meidl 1990
Chemical plant runoff	1.1	8.3	940	7100	643	0.68	14	97.8	Meidl 1990
Pesticide wastewater	4.3	10	8600	20000	9110	1.06	93	99.0	Dietrich et al. 1988
Landfill leachate	1.0	11.2	2420	27100	2950	1.22	191	93.4	Dietrich et al. 1988
Organic chemical plant	0.329	36	121	13240	171(BOD)	1.41(BOD)	6.7(BOD)	96(BOD)	Hutton 1990
Pharmaceutical	5.3	31.7	2440	14590	6020	2.47	380	93.7	Dietrich et al. 1988
"Stringfellow quarry" Superfund site	0.74	15	667	13520	1788	2.68	467	73.9	Meidl 1990
Hazardous waste pondwater	2.3	5.8	2270	5725	11780	5.19	1580	86.6	Dietrich et al. 1988
Spent solvent	3.8	20	850	4470	7140	8.4	390	94.5	Dietrich et al. 1988
Metal coating	4.2	19.3	1140	5240	11510	10.1	186	98.4	Dietrich et al. 1988
Original Zimpro design guidelines	0.17	5 - 20	>100	15 - 20 gTSS/L					Lankford & Eckenfelder 1990

Only one example of applying PACT™ to the treatment of pulp and paper industry wastewater was found in the literature (Verrault and Dupuyt 1992). However, the particular application was papermaking rather than wood pulping. The study reported on the use of PACT™ to treat spent cooking liquors from cotton fiber and cellulose fiber pulping at a fine paper mill. A prefabricated, batch mode treatment unit purchased from Zimpro Passavant treated 56 m^3/d of high strength wastewater (COD ranging from 18 000 to 25 000 mg/L, and BOD from 9 000 to 10 000 mg/L). Reactor feed was nutrified with ammonium phosphate, and pH adjusted to 7 to 8. Operating temperature was 25-35°C. The PAC dosage was 1.21 g/L. The authors reported good treatment, 90-92% removal of COD and >98% removal of BOD. The high efficiency of COD removal reflects a higher degree of biodegradability in the organic components of this wastewater than for a wood pulping operation. Although two bench-scale experiments were performed to test different operating conditions (i.e., seeding conditions, PAC dosage) there was no comparison of PACT™ with AS or sequencing batch reactor (SBR), so one cannot judge if the system performed better than non-PAC treatments.

Cost is an important consideration in PACT™ systems. A single pass system in which virgin PAC is added to the aeration basin, collected with the sludge, and then discarded is extremely expensive. PAC must be regenerated in order to save on purchase costs and render the system economically viable. However, experience in municipal wastewater treatment plants suggests that in practice PAC regeneration is problematic. Deeny et al. (1989) reviewed the performance of PACT™ systems using wet air regeneration (WAR) in 11 American municipalities. They cited various problems:

1. Substantial buildup of BOD, ammonia and insoluble phosphates.
2. Buildup of insolubie metallic salts in MLTSS.
3. Effluent quality violations of BOD, ammonia, selected heavy metals.
4. Substantial increases in ash content of MLSS.
5. Inaccuracies in the PAC concentration analytical procedure.
6. Incomplete biomass oxidation by the WAR process.
7. Increased loadings on tertiary filters.
8. Additional operational and maintenance requirements with respect to standard AS.

Care must be exercised when evaluating reports regarding the performance of a treatment system. That is, the studies ought to be as objective as possible. With this in mind, readers should note that Hutton (1990); Meidl (1990); and Dietrich et al. (1988) are affiliated with Zimpro.

CHAPTER 3

EXPERIMENTAL APPROACH

3.1 General

Whole mill waste water from a bleached Kraft pulp mill (James MacLaren Inc., Thurso, Que.) was collected in several batches. This effluent represents the total mill wastewater from all processes (e.g., wet drum debarking, excess decker washing white water, condensates, bleaching effluents and overflows/spills). Of the total wood furnish processed in the mill, the proportion of softwood used was typically 11%. Typical pulp production at the mill was 735 ADT/d with water usage of 71 000 m^3/d. The mill used chlorine dioxide bleaching followed by caustic extraction. The bleach sequence was DEDED (D=chlorine dioxide, E=caustic extraction). Oxygen delignification was not used. Within the mill the wastewater was screened to remove gross debris but was otherwise untreated. Wastewater was collected at the pipeline discharge into the mill's settling lagoons and stored in 200 L plastic barrels. After transportation to the laboratory, samples were frozen at −10°C to −20°C. Samples were cooled to 0°C within 24 h of sampling but did not freeze for several days. For feeding to reactors, individual barrels were thawed as needed and wastewater stored in a 110 L reservoir at 2°C. To mimic primary treatment in a settling basin and to minimize solids content, thawed samples were allowed to settle for 24 h before the wastewater was pumped into the reservoir. Phosphorous and nitrogen were added as nutrients to maintain an approximate degradeable-COD:N:P ratio of 100:5:1. Phosphorous was added as K_3PO_4 or K_2HPO_4, nitrogen as NH_4Cl or $(NH_4)_2SO_4$.

One sample batch of waste water was acidic, pH less than 4, and was therefore neutralized to approximately pH 6 with KOH. Wastewater samples received no other pretreatment.

Six lab-scale, completely mixed (CM) 5 L reactors were operated in continuous mode (at least one of which was a non-PAC control). Inoculum for seeding the first batch of reactors was obtained from a municipal wastewater facility (Outaouais Urban Community Wastewater Treatment Plant, Gatineau, Que.). Thereafter reactors were seeded with mixed liquor from previous batches, or converted to new operating comditions of HRT, SRT and PAC dose. Wastewater feed was continuously delivered to the reactors through peristaltic pumps fitted with either Tygon™ or Masterflex Norprene™ tubing. Reactors were a combined CM chamber/clarifier design, built of clear, 6 mm Plexiglas™, with a moveable (up/down) baffle separating the two chambers. Reactor dimensions (inside) were: height 30 cm, depth 15.5 cm, width 22.5 cm (clarifier 8.5 cm, CM chamber 14 cm). Water depth and thus operating volume in the reactor were controlled by adjusting the height of the overflow tube in the clarifier. The nominal 5 L operating volume of the reactors is defined as the volume in the CM zone when the baffle is completely closed (lowered). Clarifier volume is approximately 2.2 L. Mixing and aeration in the CM zone were provided by a double airstone connected to the laboratory compressed air supply. Dissolved oxygen levels in the reactors were maintained above 2 mg/L, with one exception noted in the Results and Discussion chapter. Tops of reactors were covered with Plexiglas™ to minimize losses from splatter and evaporation. Reactor design, operation and laboratory setup are shown in Figures 3-1 to 3-4.

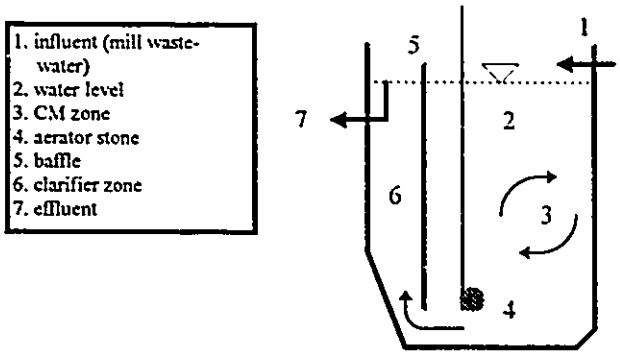


Figure 3-1 Reactor schematic, side view. Flow proceeds from right to left.

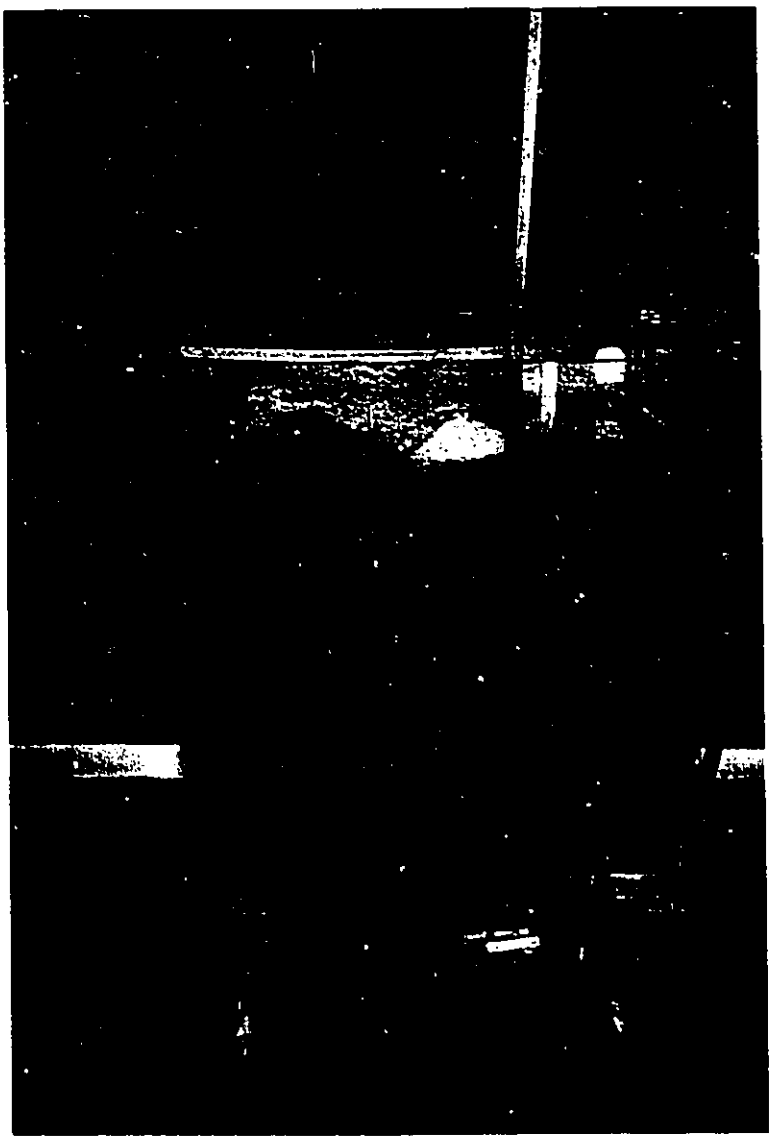


Figure 3-2 Side view of reactor in operation (no PAC).

Feed and air tubes enter from the left side. Airstone and bubbles can be seen in the CM chamber (left side). Note the thick sludge blanket in the clarifier (right side) and dark, clear effluent in the upper 2 to 3 cm. This particular reactor had a slightly modified baffle, the lower half of which was angled toward the outer wall of the clarifier. This prevented sludge accumulation in the clarifier bottom.

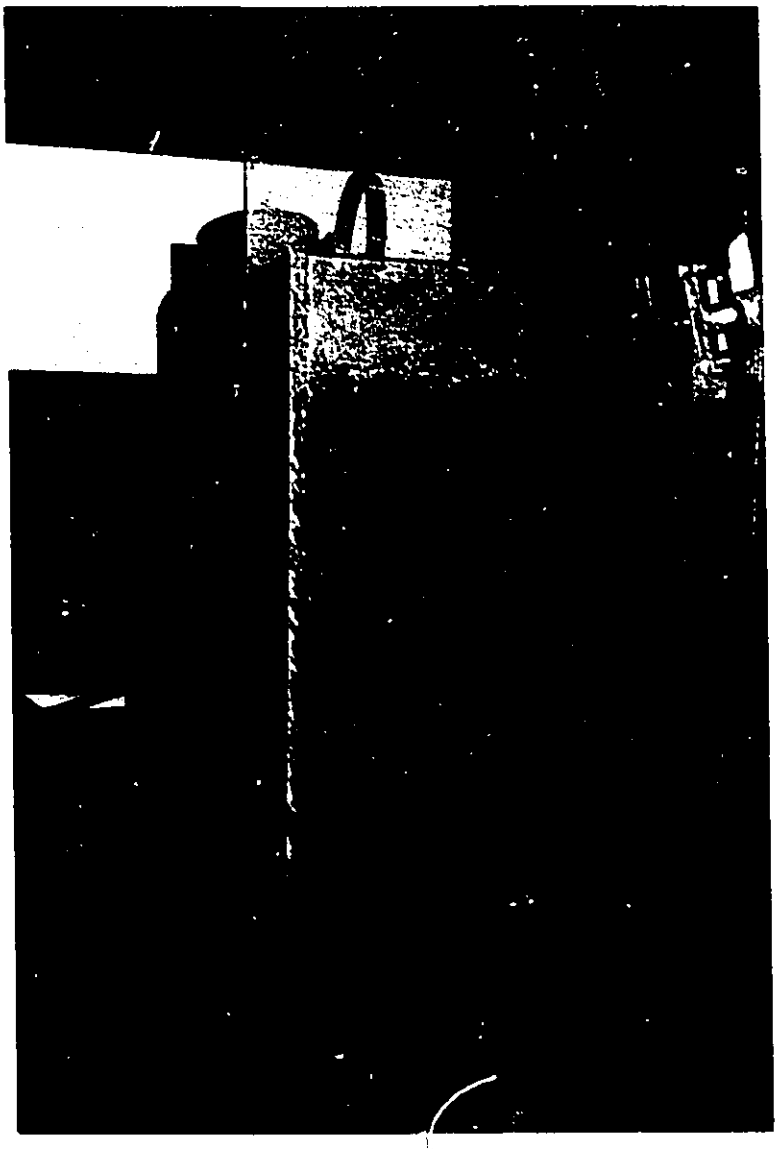


Figure 3-3 End view of reactor (no PAC), clarifier zone.

The sludge blanket can be clearly seen in the lower portion of the clarifier, with dark, clear effluent above.

Figure 3-4 Laboratory setup. Feed is stored in a refrigerated reservoir (on right), fed through pumps to each reactor (on bench at left).

The various operating conditions are shown in Table 3-1. A total of 17 conditions were examined over 18 separate runs.

Table 3-1 Reactor operating conditions[a].

HRT (h)	4	8			24			72
SRT (d)	5	5	10	15	5	10	15	5
PAC (g/L)								
0	R17,D	R13,C & R4,A	R5,A	R6,A		R2,A	R3,A	R1,A
0.1		R7,A	R9,A					
0.2		R8,A						
0.5	R18,D	R14,C	R16,C					
1.0		R15,C			R10,B	R11,B	R12,B	

[a] Shading indicates condition tested). Numbers in each box are unique identifying numbers for each reactor operated at a given condition, letters refer to feed batch A, B, C or D.

This reactor design sometimes suffered the problem of sludge accumulation in the bottom of the clarifier and bottom corners of the CM zone, especially if the flow from or position of the airstones was improperly adjusted. Daily manual stirring of the reactor bottom helped to prevent large accumulation of solids. To alleviate this problem, the author recommends that reactors be built tall rather than wide, thereby minimizing floor space and dead corners where sludge can accumulate. One may also consider placing baffles in the CM zone to direct flow more evenly and increase scour -see Saunamäki (1994) for a novel reactor design.

SRT was controlled daily by manual removal of the required volume of mixed liquor (ML). ML was taken from the CM chamber and discarded, and replaced with an equal volume of reactor effluent. The value of SRT reported was calculated according to Eq. 3-1.

$$SRT = \frac{\text{total mass of solids}}{\text{mass of solids removed per day}} = \frac{X_{T,ML}V_{CM}}{X_{T,ML}V_{MLdiscarded} + X_{T,EFF}V_{EFFdiscarded}} \quad (3\text{-}1)$$

Now since the volume of mixed liquor discarded/sampled is replaced with effluent, the volume of effluent actually discarded is not equal to the throughput, but rather:

$$V_{EFFdiscarded} = V_{EFFthroughput} - V_{MLdiscarded} \quad (3\text{-}2)$$

The value for SRT reported on a given day was a moving average calculated according to:

$$SRT = \overline{X}_{T,ML}V_{CM} \Big/ \left(\overline{X_{T,ML}V_{MLdiscarded} + X_{T,EFF}V_{EFFdiscarded}}\right) \quad (3\text{-}3)$$

The averages in Eq. 3-3 (i.e., average total mass of solids in the numerator, and average mass of solids removed daily in the denominator) were taken over the number of days equal to the nominal SRT. For example, the reported value in a reactor with a nominal 5 d SRT is given as the average taken over the preceding 5 d (inclusive). Note that $V_{MLdiscarded}$ refers to the total volume of mixed liiquor removed for both sampling and SRT maintenance. $V_{EFFdiscarded}$ refers to the volume effluent discarded and sampled minus the volume used to replace mixed liquor.

The PAC used was WPX-Z grade (Calgon Carbon Corporation[1]), produced from reactivated (recycled) granular coal-based carbon. Specifications for WPX-Z are shown in Table 3-2. PAC was dried at 105°C before weighing. Make up PAC was added once per day, after the daily solids wasting, as a PAC-effluent slurry.

[1] Addresses and telephone numbers for suppliers of special materials and analyses are given in Appendix A.

Table 3-2 Calgon™ WPX-Z grade PAC specifications.

Molasses Relative Efficiency	70 minimum
Iodine No., mg/g	800 minimum
Ash, by weight	15% maximum
Moisture, by weight, as packed	2.0% maximum
Screen Size, U.S. Sieve Series through 200 mesh through 325 mesh	 80% minimum 60-70%

3.2 Analyses

Flowrates in the reactors were checked daily. Feed, mixed liquor and effluent were sampled daily for solids and COD. Unless otherwise noted, procedures used were those in *Standard Methods* (APHA et al. 1989). Typically two and three day composite samples were measured for solids and COD. Samples were stored at 2°C during the composite period. Solids were filtered and ashed on Whatman™ GF/C glass filter paper. Samples were ashed at 550°C for 2 h to ensure complete volatilization of PAC. COD measurements employed the ferrous ammonium sulfate titrimetric method. *Soluble* COD was measured on supernatants of samples centrifuged for 20 min at 10 000 rpm in Sorvall SS-34 rotor (i.e., RCF of 12 100 G). Elsewhere the term *soluble* refers to filtrate from samples filtered through Whatman™ GF/C filters.

Samples for other analyses were typically composites taken during the final 2 or 3 d of a particular reactor run, as indicated in the results section. Dissolved oxygen (DO) was measured directly in the CM zone using an Orion™ oxygen meter. Final samples for AOX, CBOD, metals and toxicity were blended, filtered and stored at −10°C to −20°C. AOX analyses were performed on soluble samples only busing a Dohrman AOX analyzer (Seprotech Laboratories). Metals were analyzed using inductively coupled plasma (ICP) at

the Ottawa-Carleton Geoscience Centre Geochemistry Laboratory, University of Ottawa. Soluble samples were submitted directly to ICP. Total samples were first digested in hot acids (nitric followed by perchloric) according to protocol 3030E in *Standard Methods* (APHA et al. 1989). Carbonaceous BOD (CBOD) was the standard 5 d, 20°C BOD test, using 2-chloro-6-trichloromethyl pyridine as nitrification inhibitor.

PAC dosage as reported is based on the known make up rate of PAC (i.e., the nominal dosage) and the average actual HRT during a particular reactor run. Additionally, a nitric acid digestion was performed on grab samples of ML at the end of runs to confirm that ML carbon suspended solids concentrations (MLCSS) were in the range expected, based on PAC dosage, HRT and SRT. Mixed liquor samples (typically 20 or 25 mL) were digested in an equal volume of concentrated nitric acid for 2 h at ca. 90°C to destroy volatile organics. Residue, consisting of PAC and a small amount of indigestible material, was filtered through Whatman™ GF/C filters, and solids determined according to standard methods (APHA et al. 1989). Control samples of pure PAC and non-PAC mixed liquor were also digested to determine respectively PAC recovery and the fraction of non-digestible material in biomass.

Toxicity testing using the Microtox™ system followed protocols in the Microtox™ manuals, either the *Basic Test Protocol, 100% Protocol* or the *Extended Dilution Range Protocol.* A Microbics M500 analyzer unit was used for the incubations and testing. Reagents were obtained from Microbics Corporation. Data reduction and statistical analysis were performed by Microbics statistical software which is part of the test system. Results are determined as follows: For each test concentration in a series of

dilutions, the analyzer unit measures the light emitted by the test bacterium before and after exposure to each test dilution. It then calculates the ratio of light decrease to light remaining after exposure. This ratio is called *gamma*. Thus by definition the EC50 is the concentration where *gamma* is 1, that is, the light loss equals the light remaining. The dose response of the bacterium to toxicant is assumed to be logarithmic, therefore a log-log plot of *gamma* against concentration should be linear. The data are linearly regressed and the EC50 (i.e., concentration where *gamma* is 1) interpolated from the regression line.

3.3 Toxicity Testing with *Ceriodaphnia dubia*

The protocol used was essentially that of Environment Canada (1992a). Because procedures for toxicity testing with *Ceriodaphnia* are somewhat involved and a single standard procedure has not been strictly defined, the description below is given in greater detail than other experimental procedures. Any deviations from Environment Canada's (1992a) protocol are noted, as are the author's recommendations based on his experience.

3.3.1 Culturing Conditions

Ceriodaphnia dubia starter cultures were graciously donated by Linda Olde of PAPRICAN. Culture water was municipal water (RMOC, Source - Ottawa River). Water was dechlorinated by autoclaving in 20 L glass carboys for 90 min at 121°C, cooled and aerated for at least 24 h. To avoid oil contamination during aeration, a diaphragmatic aquarium pump was used rather than the building's compressed air supply. Dissolved oxygen was 90 to 100% saturation and pH 7.5±0.3, adjusted with KOH or HCl as required. Typically 6 mass cultures were maintained in covered 1 or 2 L glass beakers (Figure). Water was replaced 3 times weekly. Cultures were thinned once per week to

approximately 10 daphnids per litre. Temperature was 25±1°C. Lighting cycle was 16 h light, 8 h dark, provided by a bank of 6 × 40.4 cm, 15 watt Cool White™ fluorescent lamps, mounted end to end, 90 cm above cultures.

All daphnids used for testing met (and typically exceeded) the required health criteria : ≤ 20% mortality and ≥ 15 young per daphnid produced weekly in broods and controls, ≥ 6 young produced per brood, no ephippia (egg cases) present.

Brood and test animals were grown in 15 mL of water or test solution in flat-bottomed, 1 oz (31 mL) clear plastic (LDPE) condiment cups (Plastics Inc., purchased from Saalfeld Paper Co., catalog No. PLAPI-1). For each brood or test group, sixty cups (6 rows of 10) were supported in holes drilled through sheets of rigid, 3.75 cm thick Styrofoam™ insulation. Cups were covered with sheets of clear Plexiglas™ to prevent evaporation or contamination. This setup allowed easy handling and direct counting of broods and test groups in situ (Figure). Entire brood or test boards of 60 cups were placed over a light table for observation and counting of neonates (Figure 3-7). The light table was constructed of 5 × 60.8 cm Cool White™ fluorescent lamps mounted side by side, below a sheet of translucent white Plexiglas™ (i.e., similar to those used for viewing X-ray films and photographic slides). It should be noted that counting daphnids is a tedious and time-consuming chore. A single test board of 60 cups required about 45 minutes of work each day for counting, mixing daily test solutions, and transferring animals. The setup described above is preferred by workers at PAPRICAN (Olde 1995) and recommended by Environment Canada (1992a). The author advises against using a different setup that may render counting the animals more difficult, for example, using

round-bottomed cups or test tubes, or a different lighting system. A poor setup can easily increase the counting time by two to three fold. The proper equipment should be obtained rather than using unsatisfactory materials at hand. This investment will save a great deal of labour.

Figure 3-5 *Ceriodaphnia dubia* mass cultures.

A simple setup using covered beakers was employed. Dark material in the bottom of beakers is settled algal food.

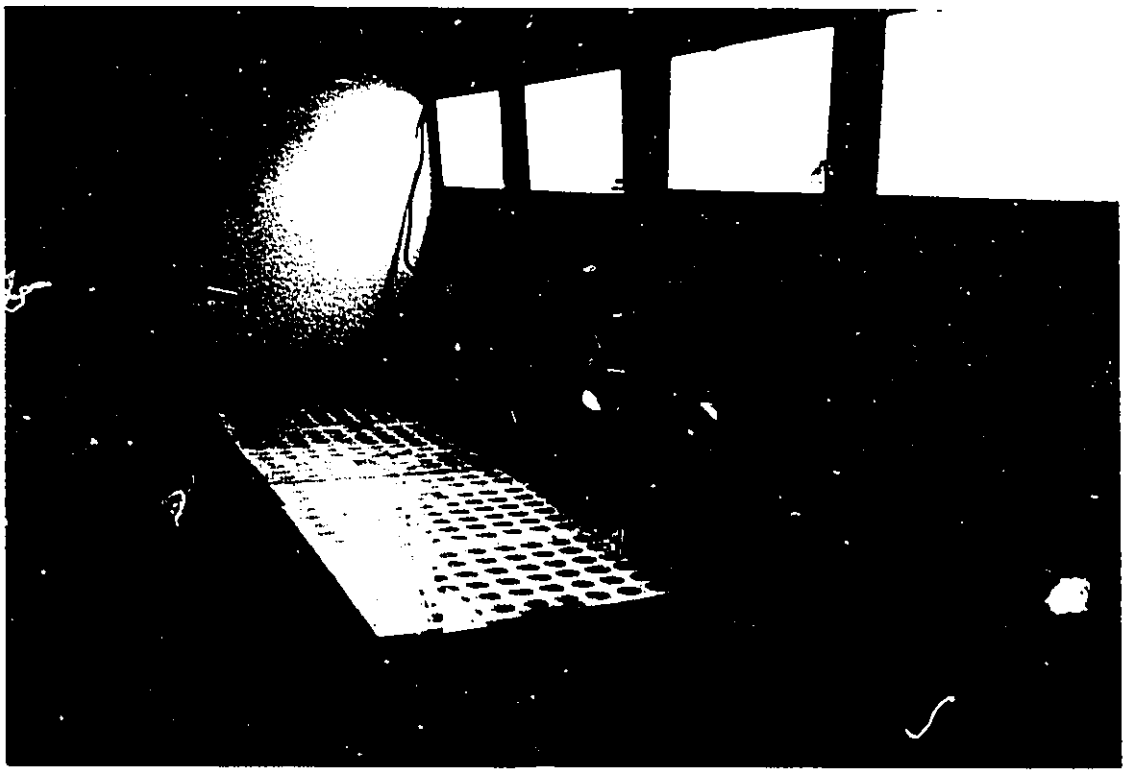


Figure 3-6 Setup for *Ceriodaphnia dubia* brood and test boards.

Covered sheets of Styrofoam™ each held 60 cups, a single neonate daphnid was grown in each cup. The bank of fluorescent lamps in the upper right portion of the photo was timed to provide 16 h light, 8 h darkness per 24 h.

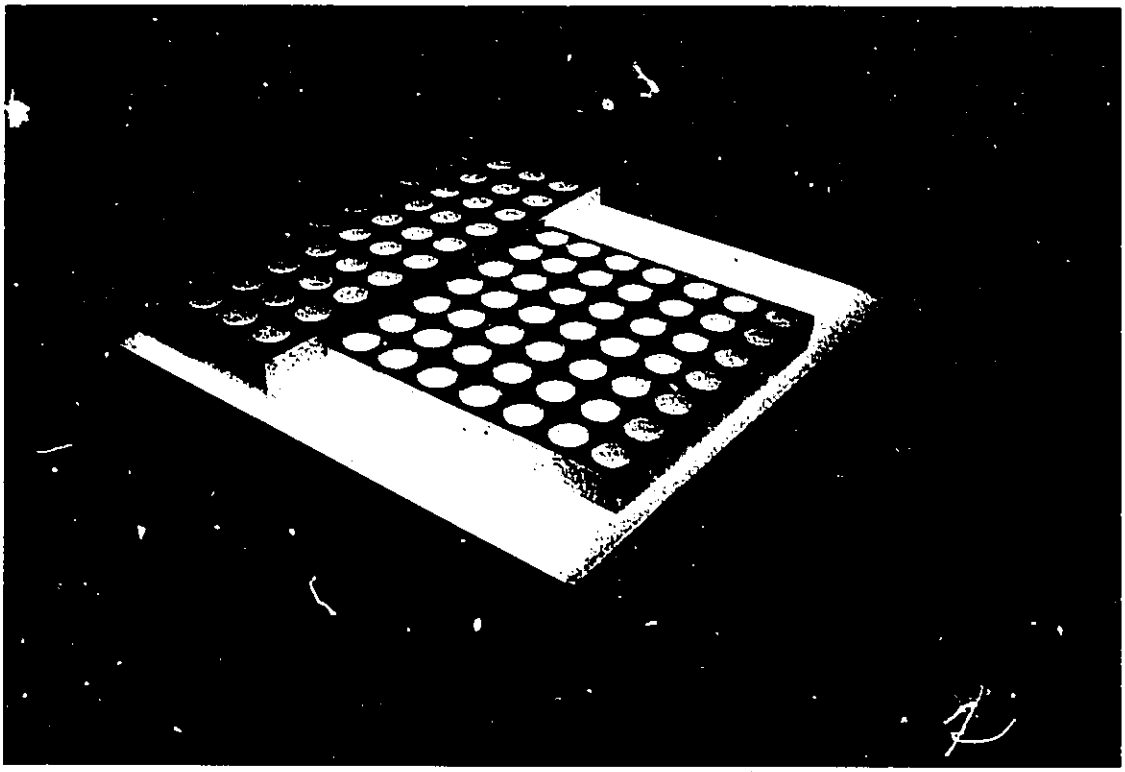


Figure 3-7 Setup for observing daphnids. Brood and test boards are placed on light table. Counting is done in situ.

3.3.2 Food Preparation

Daphnids were fed a modified version of the standard, two-part diet of yeast-Cerophyll™-trout chow (YCT) mixture and algae. Following Environment Canada (1992a) recommendations with respect to substitutions for YCT, Cerophyll™ was replaced with ground alfalfa leaf, Phytovie™ Alfalfa, available at health food stores and pharmacies. Trout chow was replaced with Tetramin™ Staple Food, a commercially available tropical fish food. The yeast used was commercial baker's yeast. The yeast-alfalfa-Tetramin™ (YAT) was prepared as described in Environment Canada (1992a). YAT was stored frozen in 200 mL batches until needed. Thawed portions of YAT for daily feeding were stored at 4°C.

For the algal portion of the diet, two types of algal culture were used. Because of delays in starting a pure algal culture, daphnids in the first set of mass cultures and toxicity tests were fed a mixed algal culture. A mixed inoculum consisting of *Ankistrodesmus* sp. was obtained from the Dept. of Biology, University of Ottawa. A single batch of this culture was grown in a 20 L glass cylinder using 1 g of Difco™ Bacto Tryptic Soy Broth as nutritive supplement in 20 L of distilled deionized water. The culture was grown with aeration and mixing for 10 d at approximately 20°C in ambient light (north-facing window). Algae were harvested and concentrated as described below.

In the second and third sets of tests, the alga fed to daphnids was a pure culture of *Selenastrum capricornutum* obtained from the University of Toronto Culture Collection. Growth media and conditions were as described in Environment Canada (1992a). Glass

Erlenmeyer flasks were used as culture vessels. Flasks were only half-filled with growth medium to maintain enough head space and surface area for adequate gas exchange. That is, a maximum of 2 L of medium in a 4 L flask. Cultures were grown in batches of 6 x 2 L for 10 d at ambient temperature (ca. 20°C) with gentle mixing on rotary shaker tables, illuminated from above and one side by a total of six 121.6 cm Cool-White™ fluorescent lamps, at a distance of ca. 20 cm. Care should be taken to avoid heating of the cultures by the shaker units or lamps, since algae appear to grow better at cooler temperatures. Algal cultures were concentrated prior to feeding to daphnids. Cerda and Olive (1993) reported that the desired algal concentration of 3.0 to 3.5 x 10^7 cells/mL had a spectrophotometric absorbance of 1.5 at 665 nm. However the author notes that accuracy of spectrophotometers is poor beyond an absorbance of 1.0. Thus the following harvest method was employed for algae: cultures were concentrated by centrifugation, typically 20 min at a relative centrifugal force of approximately 4 000 G, with a Sorvall Fixed Angle GSA rotor at 5 000 rpm. The algal pellets held together better and were easier to manipulate if the centrifugation was performed at 4°C. Algal concentration was adjusted as needed (i.e., further concentration or dilution with supernatant) to obtain an absorbance of 0.75 at 665 nm. This solution was again centrifuged and the algal pellet resuspended in 50% of the volume to obtain the final desired concentration noted above. Algal concentrate was stored at 4°C.

In order to conserve the laboratory supply of algae, mass culture animals were fed only with YAT (7.0 mL YAT/L of culture/d, 5 times weekly). Individual neonates in brood boards, as well as all test animals, were fed the standard YAT-algal diet.

Daphnids in brood boards and test cups were fed algal concentrate and YAT each at a rate of 0.1 mL/15 mL. Food, dilution water and test sample were mixed in 250 mL graduated cylinders for each test group of 10 daphnids. Food was added prior to dilution water to avoid altering the final concentration of test sample. Resulting mixtures were tested for dissolved oxygen (minimum of 90% saturation) and pH (adjusted to range 7.5±0.3 with HCl or KOH as required.)

3.3.3 Test Conditions

Test solutions were renewed daily. Test duration for the required three broods in 60% of control animals was typically 7 d, in one set of tests it was 8 d. Test samples of pulp mill wastewater and reactor effluents were frozen at −15°C until needed, thawed and adjusted for concentration, pH, dissolved oxygen and temperature as described above. Dilution water prepared as described above was used for dilution of test samples. Each test concentration employed 10 neonate *Ceriodaphnia*.

3.3.4 Key Points and Recommendations

Ceriodaphnia are sensitive animals. The following key points regarding their care should be noted to ensure success.

Mass cultures are sensitive to overcrowding and fouling of the culture water, therefore maintenance requirements given in Environment Canada's guidelines (1992a) should be followed to avoid mass die-offs. Food should be used only as long as recommended and discarded earlier if fouled. (NB. fresh algal concentrate is bright green without dead, brown solids; fresh YAT should have a pleasant, yeast-pineapple smell).

Glassware and equipment used for *Ceriodaphnia* handling should be kept separately from other laboratory equipment to avoid the risk of chemical contamination.

It may happen that reproduction in the brood cultures drops below minimum standards without apparent reason. In this case the author recommends performing a reproduction test for various combinations of food and water (e.g., autoclaved tapwater or springwater with YAT alone or algae alone, etc.) to determine where the problem lies.

Multiple culture vessels should be maintained so that the entire stock of animals will not be lost due to a population crash. As an additional safeguard, a large volume (5 L) cylinder was kept in a separate location as a reserve mass culture. It was initially inoculated with 10 animals and 75 mL of algal concentrate. The culture was self-supporting, natural light encouraged mild algal growth. No maintenance was needed except occasional addition of distilled water to replace evaporation losses. The reserve culture was worthwhile insurance against a catastrophic loss of laboratory stock. During the study, one set of *Ceriodaphnia* tests was abandoned because of insufficient reproduction in the control animals. Shortly thereafter the entire laboratory population died off. New cultures were started using animals from the reserve culture. After testing the water and foods, it was discovered that a batch of algal concentrate had fouled. A new batch restored reproduction to normal.

3.3.5 Statistical Procedures

To determine IC50s, the standardized variate, Z, is calculated from the observed reproduction at each test concentration. Recall (Equation 2-1) that Z is derived from the

normal cumulative frequency distribution for each observed proportion of reproduction. (i.e., the proportion of the number of offspring in test group versus the number in control group).

IC50s were interpolated from plots of Z versus the logarithmic sample concentration. The IC50 corresponds to the concentration at which Z is zero.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Opening Comments

Before the results are discussed in detail, it is helpful to recall the central goal of this study, in order to provide a context within which the value of observations can be evaluated. Namely, the aim was not to determine absolute and quantitative values, nor deterministically describe the behavior of the treatment systems. Rather it was to compare two types of treatment, PACT™ and standard AS, which can be done with confidence. But as for conclusions regarding the absolute efficacy of treatment, these would rest on the assumption that wastewater samples used in the study were typical of all kraft mills.

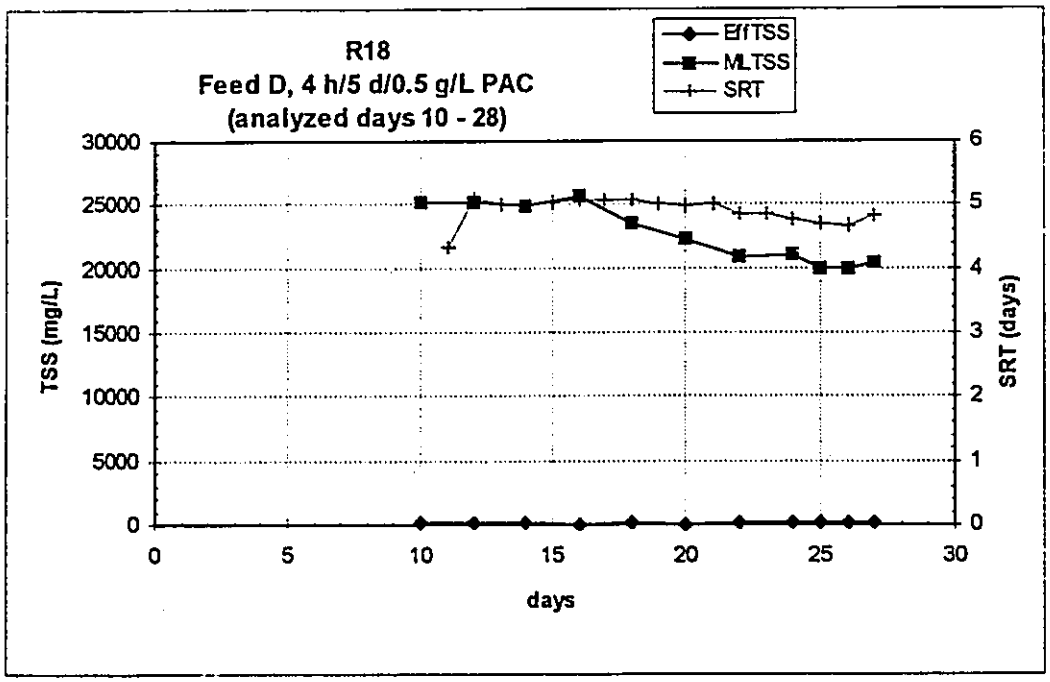
The foregoing is not meant to denigrate the data, only that their context should be kept in mind by the reader. The data represent results from a particular case of 4 samples of kraft mill wastewater, but the limited sample size is a real-world constraint that the experimenter must tolerate.

A complete set of graphs showing solids and COD performance for all reactor runs is shown in Appendix C. An example of typical solids and COD performance of a reactor is shown in Figure 4-1. In this figure, (and those shown in Appendix C also), each of the four different batches of feed is identified by A, B, C and D. Each reactor run is given a unique number from R1 to R18. Day zero is the point where the reactor operation began. Graph titles indicate operating conditions according to feed batch (A, B, C or D), HRT

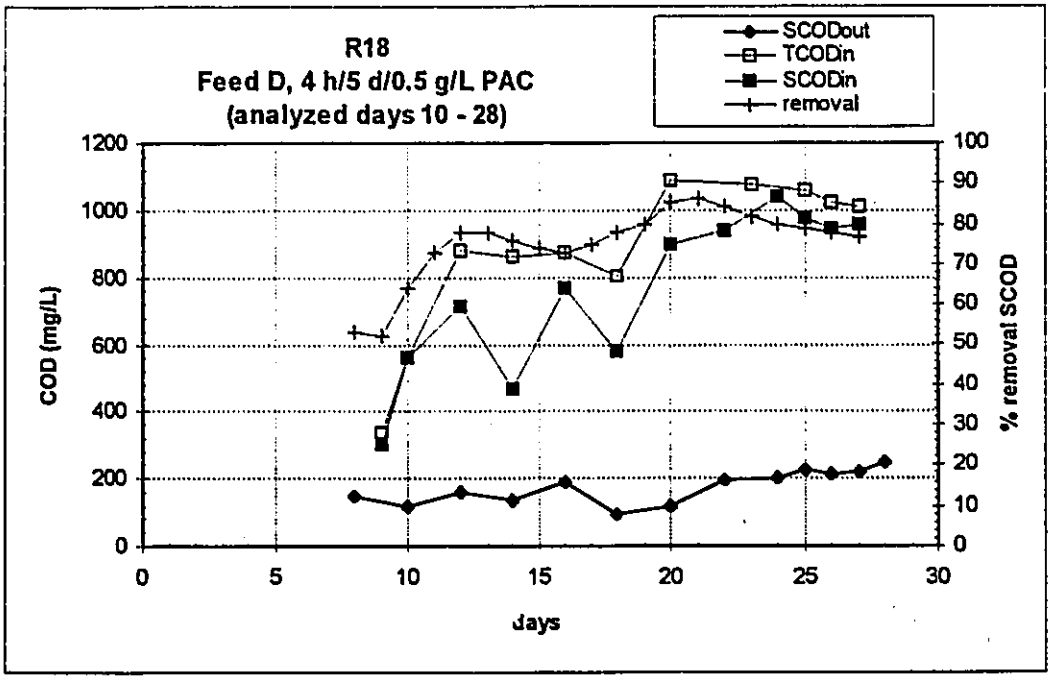
(h), SRT (d) and PAC dose (g/L), respectively. For reactors where two feed types are shown, the letter in parenthesis indicates which batch was used to start the run. However, all reactors in a given feed group received the same feed during that portion of the run which was analyzed for determining average COD and solids values. The portion of the run used for these analyses is also indicated (e.g., days 20 to 43 for R1). Each data point represents the value of a two or three day composite sample. Readers are referred to Appendix B for daily data which details reactor maintenance, sampling and test results.

The choice of which portion of the run to include in the analyses was based mainly on stability of MLTSS and whether the SRT calculated from the observed solids levels was close to the target nominal value, that is, the portion of the run which was as close to a steady state as possible. The analyzed portion of the run also had to include sufficient COD measurements.

Tables 4-1 to 4-3 summarize operating conditions and analyses.



(A)



(B)

Figure 4-1 Example of typical reactor performance, (A) solids, (B) COD removal.

Table 4-1 Summary of average operating conditions, solids and COD values for reactor runs[a].

R	Nominal[b] Conditions	HRT (h)	SRT (d)	std. dev. (%)	PAC (mg/L)	FTSS[c] (mg/L)	MLTSS (mg/L)	std. dev. (%)	MLVSS[d] (mg/L)	EffTSS (mg/L)	std. dev. (%)	SCODin (mg/L)	std. dev. (%)	SCODout (mg/L)	std. dev. (%)	SCOD removal (mg/L)	SCOD % removal	std. dev. (%)
R1	A/72/5/0	69.2	5.0	17	0	NM[e]	368	32	306	99	44	541	8	303	14	237	44.0	5
R2	A/24/10/0	24.8	7.5	18	0	NM	687	28	615	33	57	583	29	181	21	402	69.0	7
R3	A/24/15/0	24.1	12.0	7	0	NM	1208	15	1163	59	52	601	34	124	37	477	79.4	8
R4	A/8/5/0	7.7	5.0	6	0	35	1846	8	1655	30	36	344	26	114	13	230	66.9	8
R5	A/8/10/0	7.8	8.9	16	0	35	3076	10	2750	64	62	344	26	106	19	238	69.3	3
R6	A/8/15/0	7.9	15.0	8	0	34	3519	9	3085	35	68	343	25	117	23	226	66.0	9
R7	A/8/5/0.1	7	5.0	3	96	35	3789	10	3452	21	60	344	26	104	21	240	69.8	9
R8	A/8/5/0.2	7.8	5.1	5	194	33	5413	5	4978	41	17	342	24	100	29	242	70.8	10
R9	A/8/10/0.1	7.9	9.5	6	99	35	5613	12	5187	93	19	344	26	119	16	225	65.5	10
R10	B/24/5/1	24.8	4.8	6	1032	81	5959	8	5580	172	48	566	4	113	17	452	79.9	5
R11	B/24/10/1	24.9	10.0	10	1038	81	11901	27	11118	175	67	569	20	141	27	428	75.2	3
R12	B/24/15/1	23.4	16.3	7	975	NM	15914	2	15009	214	57	554	4	82	14	471	85.1	6
R13	C/8/5/0	7.8	5.5	10	0	28	2589	24	NM	58	57	569	35	213	26	356	62.5	5
R14	C/8/5/0.5	8.3	5.1	3	517	28	11282	10	10664	60	69	569	35	132	22	437	76.8	17
R15	C/8/5/1	8.3	5.1	3	1038	30	17948	14	NM	99	52	606	33	72	30	534	88.1	8
R16	C/8/10/0.5	8.2	10.8	8	513	28	21003	11	NM	99	42	569	35	114	22	455	80.0	6
R17	D/4/5/0	4.1	5.0	9	0	36	4976	7	4579	67	77	791	24	350	26	442	55.8	13
R18	D/4/5/0.5	3.8	4.9	4	480	37	22930	10	21247	99	33	766	25	165	28	601	78.5	5

[a] Averages are taken over the period "analyzed days" described in Appendix C.
[b] Nominal conditions refer to feed batch, and target values for HRT (hr), SRT (d) and PAC dose (g/L) respectively.
[c] FTSS = feed total suspended solids
[d] MLVSS = mixed liquor volatile suspended solids
[e] NM = not measured

Table 4-2 Summary of BOD, AOX and metal analyses[a].

R	Nominal[b] Conditions	soluble CBODin (mg/L)	soluble CBODout (mg/L)	soluble CBOD % removal	AOXin (mg/L)	AOXout (mg/L)	AOX % removal	Heavy Metals (Cd, Cr, Cu, Ni, Pb, Zn)[c]					
								total in (mg/L)	soluble in (mg/L)	mixed liquor (mg/L)	total out (mg/L)	soluble out (mg/L)	mass balance in:out
R1	A/72/5/0	NM[d]	NM		10.3[e]	NM		NM	NM	NM	NM	NM	
R2	A/24/10/0	355	8.4	97.6	NM	5.3		NM	NM	NM	0.14	0.033	
R3	A/24/15/0	355	6.7	98.1	NM	5.0		0.044	NM	NM	NM	0.1	
R4	A/8/5/0	NM	NM		4.1	3.3	20	0.336	0.039	0.81	0.52	0.13	0.62
R5	A/8/10/0	NM	NM		4.1	3.5	15	0.336	0.039	0.6	0.128	0.096	2.31
R6	A/8/15/0	NM	NM		4.1	3.3	20	0.336	0.039	1.88	0.26	0.11	1.14
R7	A/8/5/0.1	NM	NM		4.1	3.2	22	0.336	0.039	3.24	0.356	0.1	0.72
R8	A/8/5/0.2	NM	NM		4.1	2.4	41	0.336	0.039	3.61	0	0.071	
R9	A/8/10/0.1	NM	NM		4.1	2.7	34	0.336	NM	9.56	0.84	0.05	0.34
R10	B/24/5/1	289	5.6	98.1	9.8	NM		NM	NM	NM	NM	NM	
R11	B/24/10/1	289	11.6	96.0	9.8	1.4	86	NM	0.171	NM	NM	0.035	
R12	B/24/15/1	289	3.7	98.7	10.3[e]	2.1[e]	80	NM	0.048	NM	NM	0.26	
R13	C/8/5/0	333	4.5	98.6	12.0	5.9	51	0.564	0.384	2.02	0.204	0.256	1.81
R14	C/8/5/0.5	333	3.1	99.1	12.0	3.2	73	0.564	0.384	11.45	1.608	0.274	0.37
R15	C/8/5/1	333	2.1	99.4	12.0	1.9	84	0.564	0.384	30.95	0.592	0.114	0.41
R16[f]	C/8/10/0.5	333	79.3	76.2	12.0	5.5	54	0.564	0.384	17.35	0.924	0.18	0.58
R17	D/4/5/0	506	11.9	97.6	10.5	8.0	24	0.232	0.384	0.67	NM	0.1	
R18	D/4/5/0.5	506	16.7	96.7	10.5	6.4	39	0.232	0.384	10.45	NM	0.122	

[a] Samples for these analyses were typically composites from the final 3 d of a reactor run.
[b] Nominal conditions refer to feed batch, and target values for HRT (hr), SRT (d) and PAC dose (g/L) respectively.
[c] Heavy metal mass balance ratio based on: *in*; feed and PAC, *out*; mixed liquor wasting and effluent.
[d] NM = not measured
[e] AOX analysis on sample taken from middle of run.
[f] R16 suffered from biomass washout during the final 3 d of the run. Thus performance appears uncharacteristically poor.

Table 4-3 Selection of pH, dissolved oxygen and temperature conditions for reactor runs.

R	Nominal Conditions	pH feed	pH effluent	mixed liquor DO (mg/L)	mixed liquor temp. (°C)
R1	A/72/5/0	6.6	6.0		
R2	A/24/10/0		6.1		
R3	A/24/15/0		5.6		
R4	A/8/5/0	6.8	6.2	8.8	17.3
R5	A/8/10/0	6.8	5.7	9.3	15.4
R6	A/8/15/0	6.8	6.1	9.3	15.5
R7	A/8/5/0.1	6.8	6.1	9.0	16.3
R8	A/8/5/0.2	6.8	5.9	9.3	17.1
R9	A/8/10/0.1	6.8	5.6	8.1	17.0
R10	B/24/5/1	6.6	6.6	8.9	18.4
R11	B/24/10/1	6.6	6.4	8.0	17.3
R12	B/24/15/1	6.6	6.0		
R13	C/8/5/0	ca. 7			
R14	C/8/5/0.5	ca. 7			
R15	C/8/5/1	ca. 7			
R16	C/8/10/0.5	ca. 7			
R17	D/4/5/0	6.8	7.0	0.7[a]	19.0
R18	D/4/5/0.5	6.7	6.7	5.5	19.4

[a] Despite vigourous aeration and mixing, the mixed liquor DO level in R17 was very low. The author is unable to explain this observation.

4.2 Solids

General operation of the reactors is considered first. Readers should refer to the graphs in Appendix C to examine reactor performance over time. These graphs show solids content as MLTSS and effluent TSS (EffTSS), and organic load as SCOD in the feed and effluents, as well as SCOD removal and SRT. These data are summarized in Table 4-1, which shows the averages and standard deviations for various parameters over the period analyzed for each reactor. Examining the solids, the MLTSS in many of the runs varied considerably. The average standard deviation was 13% for all runs during the *analyzed days* period, and even greater over the total time course of runs. Before discussing reactor stability, the exact meaning of the term stability in the present context is

explained. Consider the apparent stability, manifested by stable MLTSS, as the net result of two groups of processes. There is no direct control over the first of these, namely the biochemical processes of biomass growth and decay. It is possible however to control the physical operation of the reactors, the operating parameters of HRT, SRT and PAC dose. Implicit in the aim of the study is the assessment of the biochemical functioning of the system, which ought to be stable in order to make comparisons between different operating conditions. Hence in order to judge biochemical stability *per se*, the physical stability of the system, as evidenced by SRT, must be assured. Stated in other words, before claiming that the process is unstable as a whole, one needs to look at the variability of SRT to judge whether instability is merely an artifact of poor physical operation of reactors.

An examination of the reactor time courses reveals that much of the MLTSS variability was due to poor control of solids handling. For example, R1, R2, R4, R5 and R6 (all non-PAC) showed wide fluctuations in MLTSS in the earlier portion of their runs which corresponded with unstable SRT. SRT instability was due to two factors. First, particularly in the early runs (batch A), some time was needed for the experimenters to familiarize themselves with the operation of lab scale reactors. Second, because the amount of ML wasted each day in order to achieve a desired SRT is a function of both MLTSS and EffTSS, both of which were measured as 2 or 3 d composites, it required some time before the operator knew how much ML wasting was required to acheive a target SRT. Thus for most reactors, the SRT is unstable during the initial period, before stabilizing at the end of the run. Another problem arose during operation of the first group

of reactors with high (1 g/L) PAC dose, R10, R11 and R12. Due to very high MLTSS at this PAC dose, sludge had a tendency to settle on the bottom of the CM chamber. Consequently some of the observed MLTSS values were deceptively low, and actual MLTSS in reactors was probably more stable than it appeared. This is confirmed by the fact that EffTSS remained stable (and low) for these reactors, hence most of the short term MLTSS crashes observed in high PAC reactors were due to sludge settlement rather than washout (see R11). This problem was corrected by additional mixing, adjustment of baffles and aerator stones. MLTSS stability improved during the latter portion of the runs.

Besides high MLTSS causing operational problems, low MLTSS was also problematic, as demonstrated by R1 and R2. Low MLTSS was susceptible to washout. R1, operated at HRT of 72 h was close to failure and stability was poor. It had the poorest quality effluent of all reactors in terms of SCOD, only 44% removal, and effluent solids concentration was highest among non-PAC reactors, 99 mg/L.

The amount of PAC added to reactors was known exactly. Nevertheless, carbon concentration in the ML (MLCSS) was directly measured using nitric acid digestion and these values compared to the expected MLCSS (see Table 4-4). One should bear in mind that this is only a rough comparison since the expected MLCSS is calculated based on the known PAC dose, SRT and HRT over the entire analyzed days period, whereas the measured MLCSS was for the final 3 days of the run. Out of 9 tests, 6 showed observed MLCSS in good agreement with expected values, within ±10%. Three reactors, R11, R15 and R18 were respectively 14, 18 and 25% lower than expected. Among the reactors which showed the greatest discrepancy, R11 and R18, it was observed that their SRTs

dropped towards the end of the run, contributing to a lower than expected MLCSS during sampling.

Table 4-4 Comparison of measured and expected mixed liquor carbon suspended solids (MLCSS) in PAC reactors.

R	Nominal[a] Conditions	measured MLCSS[b] (mg/L)	expected MLCSS[c] (mg/L)	discrepancy %
R7	A/8/5/0.1	1664	1505	+10.6
R8	A/8/5/0.2	3091	3049	+1.4
R9	A/8/10/0.1	2902	2855	+1.6
R10	B/24/5/1	4885	4777	+2.3
R11	B/24/10/1	8155	9965	-18.2
R12	B/24/15/1	NM[d]		
R14	C/8/5/0.5	6869	7675	-10.5
R15	C/8/5/1	12984	15202	-14.6
R16	C/8/10/0.5	16212	16178	+0.5
R18	D/4/5/0.5	11033	14710	-25

[a] Nominal conditions refers to feed batch, HRT (h), SRT (d), and PAC dose (g/L), respectively.
[b] Measured MLCSS based on nitric acid digestion, typically sampled as composites over final 3 days of a run.
[c] Expected MLCSS = PAC dose × SRT / HRT
[d] NM = not measured

SRT stability was the key parameter used in choosing the *analyzed days* period for determining averages of reactor performance. With some exceptions, averaging period was chosen such that SRT did not vary more than ±20% of the target nominal value, and that the final average SRT was as close to the target as possible. For example 12 of 18 reactors were within 5% of target, 3 were between 5% and 10%, and 3 were between 10% and 20%. The exceptions were R2, R3 and R5, which had SRTs more than 20% below target.

A second criterion for determining the *analyzed days* period was COD data. There had to be sufficient COD measurements taken, and only a single feed batch used. In some cases this constrained the analysis to a shorter period (see R4, R5 and R6).

The strength of wastewater fed to the reactors was variable, SCOD ranged from 341 to 791 mg/L. While it would have been desirable to have a single uniform feed for all reactor conditions, it was not practical to collect and blend a single large sample. The total volume of effluent collected during the study was roughly 1 000 L. Because of limitations in transportation and storage, a maximum of only 6 000 L could be obtained in a single batch, hence 4 separate batches were collected. Even within a given batch there was considerable variability in strength (see R16 and R17). Since all barrels within a batch were treated equally, it seems unlikely that this amount of variability was caused by differences in handling and degradation of wastewater in individual barrels from the same batch. Although wastewater was warm upon collection (ca. 40°C), barrels were placed in storage freezers within 3 h of collection. It was noted that all barrels cooled to 0°C within 16 h after placement in storage freezers. If degradation had occurred during handling, one would expect percent SCOD removal during treatment to vary with SCOD of the feed. That is, loss of biodegradable SCOD during handling or storage would result in an apparent decrease in removal efficiency of total SCOD, as the fraction of biodegradable SCOD became smaller. But Figure 4-2 shows no correlation existed between percent SCOD removal and $SCOD_{in}$. It seems that the SCOD of the mill wastewater was not uniform as it left the discharge pipe. Although the mill operated 24 h/d on a nominally continuous production line, various processes do come on and off line intermittantly, thereby changing the quality of the wastewater. For example, the mill employed batch rather than continuous chip cooking, hence effluent quality varies as cooking batches are finished and enter the production circuit. Recall also that one-time events such as spills

affect wastewater quality. Although the strength of wastewater fed to the reactors was quite variable in some runs, the above argument allows that it is probably representative of the variations which a full scale system would encounter in the field.

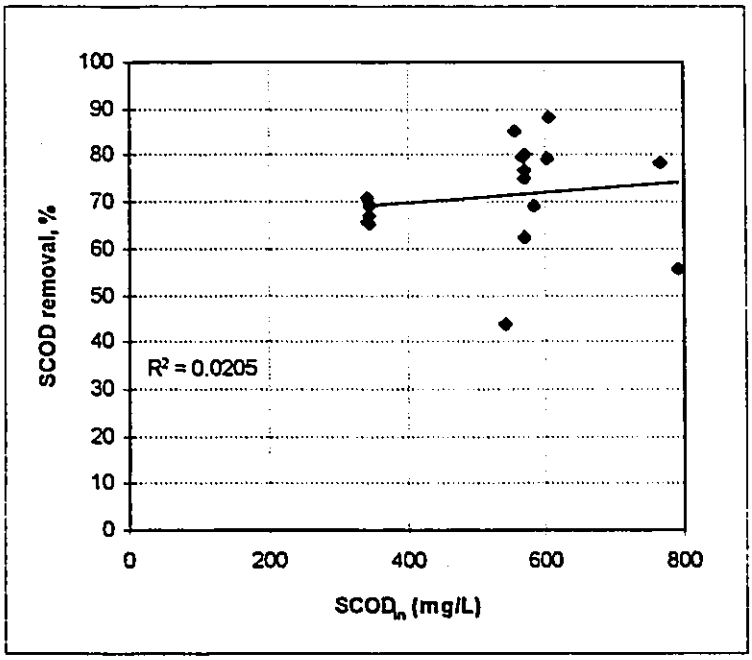


Figure 4-2 Percent SCOD removal versus SCOD of feed for all reactors.

Note that the correlation coefficient, R2 , is low at only 0.02, suggesting no correlation exists between these parameters.

Owing to these differences in feed strength (and perhaps composition) among the various batches, where possible only reactors which received a common feed are compared directly. In comparing runs from different batches, results have been normalized with respect to the control reactor for that batch.

4.3 Organics Removal

The most important determinant of reactor performance is removal of organics, as determined by COD and BOD. The latter is summarized in Table 4-2. Soluble CBOD

removal was consistently high in the 10 reactors tested, irrespective of operating parameters. With the exception of R16 (76% removal), soluble CBOD removal averaged 98%, with a standard deviation of 1.1%. Recall that R16 suffered from some washout of sludge during the final days of the run, thus performance was uncharacteristically poor. Reactors operated under a wide range of conditions, HRT ranged from 4 to 24 h, SRT from 5 to 15 d and PAC dose from 0 to 1.0 g/L. The importance of these results is that conditions in the control reactors were adequate to remove CBOD to low levels, and PAC did not improve treatment. This suggests that practically all of the readily biodegradable organic load is consumed by the biomass and that uptake by PAC is insignificant.

Despite the negligible effects of PAC on BOD, it was shown that PAC does indeed improve removal of COD. But before discussing COD removal, a brief review of the Monod kinetics model is instructive, so that the effects of SRT or HRT on substrate removal can be discussed. Using such a model in the context of kraft mill effluent is admittedly simplistic. The Monod-based model assumes that only a single substrate is present, and ignores the byproducts of metabolism and decay. A complex wastewater such as kraft mill effluent has many substrates, as well as toxins which can inhibit microbial growth. More complex models have been developed for wastewater treatment, but the Monod-type model is a *de facto* standard. The study's goal was not to describe the process deterministically, nor to elucidate constants for model fitting. Rather it was to compare AS and PACT™ systems. Keeping this in mind, the reader should not interpret the foregoing discussion as an endorsement of one model over another. Rather, it is an

attempt to provide a qualitative argument for describing AS system behaviour with respect to operating parameters of HRT and SRT.

Using the Monod type kinetics AS model, performance of a complete mix reactor with recycle is described according to:

$$S = \frac{K_s(1+\theta_c k_d)}{\theta_c(Yk - k_d) - 1} \tag{4-1}$$

where S = effluent substrate concentration (mg/L)
K_s = half-velocity constant (mg/L)
θ_c = SRT (d)
k_d = endogenous decay coefficient (d^{-1})
Y = yield coefficient (mg/mg)
k = maximum specific substrate removal rate (d^{-1})

Note that reactor performance as measured by effluent substrate concentration, S, is a function of only one control parameter, SRT, since all other terms in Equation 4-1 are constants. Conversely, performance is independent of HRT. In practice however, extremes of HRT will lead to solids handling problems, that is, biomass washout can occur if MLTSS is very low for long HRTs and settling problems may occur at high MLTSS for short HRTs.

To determine kinetic coefficients for the above model, the procedure is to operate reactors over a range of SRTs and obtain coefficients from plots of transformed data. Yield, Y, and endogenous decay, k_d, are related according to:

$$\frac{1}{\theta_c} = Y\frac{S_0 - S}{X\theta} - k_d \tag{4-2}$$

where X = biomass concentration or $MLVSS_{biol}$ (mg/L)
θ = HRT (d)
S_0 = influent feed or substrate concentration (mg/l)

A plot of $1/\theta_c$ versus $(S_0 - S)/\theta$ yields a line with slope Y and intercept k_d. However care must be taken selecting data to plot in the context of the present experiment. To determine true yield, one must measure substrate uptake, $(S_0 - S)$, by biomass alone. Hence only control reactors (non-PAC) can be considered because the extent of substrate uptake by PAC is unknown. Also, the value used for X must reflect mixed liquor volatile suspended solids (MLVSS) due to biomass alone, identified here as $MLVSS_{biol}$. To determine $MLVSS_{biol}$, other contributions to MLTSS in the system must be accounted for, that is, feed TSS and PAC. Although wastewater was allowed to settle, significant TSS remained in the feed. Even if this amount is small relative to MLTSS, maintenance of SRT causes it to accumulate in the CM zone as part of the sludge. For example, reactor 4 operated with HRT of 7.7 h, SRT of 5 d and feed TSS of 35 mg/L. Thus feed TSS alone contributed 35 × 5/(7.7/24) = 545 mg/L of TSS to MLTSS, or 29.5% of observed MLTSS of 1846 mg/L.

In a reactor without PAC, $MLVSS_{biol}$ is calculated according to:

$$MLVSS_{biol} = \left[MLTSS - (FeedTSS \times SRT / HRT)\right] \times \frac{VSS}{TSS} ratio \qquad (4\text{-}3)$$

The foregoing development implies three assumptions: that the VSS/TSS ratio of feed TSS was equivalent to that of the biomass, that feed TSS was biochemically inert (i.e., non-biodegradable wood fibres), and that once in the system, its physical behaviour vis a vis settling and removal was identical to biomass. The latter is tantamount to assuming that the ML is a uniform mixture in which equal proportions of PAC, feed TSS

and biomass are removed when sludge is lost, either as TSS in the effluent or sludge wasting.

A yield plot for the 5 non-PAC reactors with known feed TSS is shown in Figure 4-3, from which Y is 0.39 mgVSS/mgCOD and k_d is 0.057 d^{-1}. These values are similar to those reported for AS sludge treatment of domestic wastewater, that is a range of 0.4 to 0.8 for Y (BOD basis) and 0.025 to 0.075 d^{-1} for k_d. (Tchobanoglous and Burton 1991).

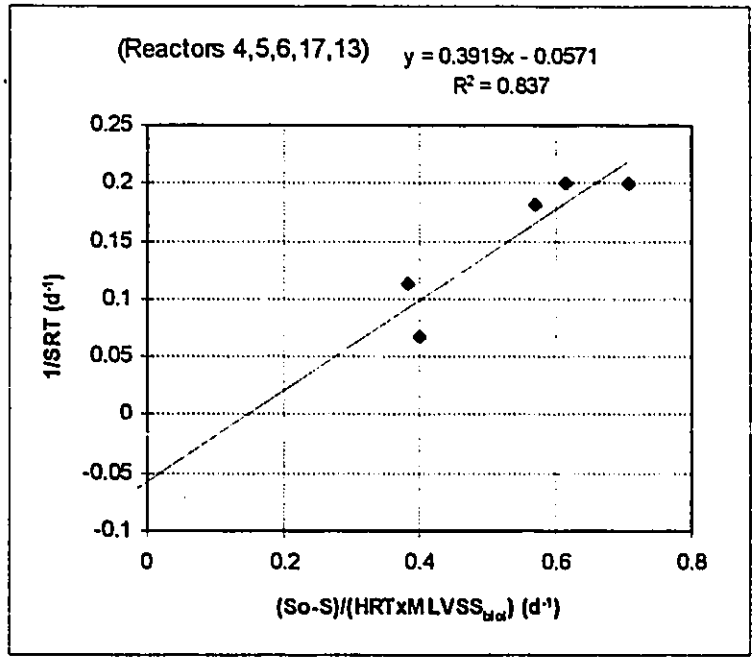


Figure 4-3 Yield plot for reactors with known feed TSS, no PAC.

The remaining coefficients, K_s and k, are related according to:

$$\frac{X\theta}{S_0 - S} = \frac{K_s}{k}\frac{1}{S} + \frac{1}{k} \qquad (4\text{-}4)$$

Normally a plot of terms $X\theta/(S_0\text{-}S)$ versus $1/S$ is used to determine an intercept, $1/k$, and slope, K_s/k. But Equation 4-4 is based on the implicit assumption that the substrate term, S, represents entirely biodegradable material. This assumption is valid if S

is expressed on a BOD basis. But the relationship is not valid if applied on a COD basis that includes inert/non-biodegradable material. The $S_0 - S$ term is valid since it reflects only COD consumed by the biomass, but the S term alone is an artifact of the amount of non-biodegradable material remaining in the effluent. In the present case significant amounts of inert material contributed to COD in the feed and effluents, as demonstrated by high residual COD in the effluents and the increase in COD:BOD ratio from feed to effluents.

Although BOD can be used to determine kinetic coefficients, only a few BOD measurements were made on grab samples at the end of runs, whereas COD measurements were taken throughout. In these circumstances, kinetic coefficients determined from BOD would be of dubious value. Furthermore, BOD data are available for only 2 reactors with known feed TSS, insufficient to apply the analysis. Therefore, kinetic coefficients given later are on a COD basis only.

To discuss the effect of PAC on COD removal, and to compare reactors which were operated under different conditions of SRT and HRT, it is necessary to understand how these latter parameters are likely to affect performance. The relationship in Equation 4-2 predicts that reactor performance is independent of HRT (within a practical range of HRT values). As for SRT, it will affect performance, however only to a small degree. Figure 4-4 shows a plot of effluent substrate concentration, S, as a function of SRT, according to Equation 4.1 , using the observed values for Y and k_d, and literature values for k and K_s. Recall that here S represents only the concentration of biodegradable substrate remaining in the effluent and does not account for inert COD. The significance

of this plot is that beyond a certain value, the observed concentration of substrate in the effluent becomes independent of SRT in practical terms. Note that from 5 to 15 d SRTs, which is the range examined in this study, S is expected to vary by less than 4 mg/L. In terms of the total observed SCOD in the effluents (i.e., residual biodegradable COD plus inert COD), this difference averages only 3% (ranging from 1 to 6%). Indeed Grady and Lim (1980) note that:

"soluble substrate concentration [in the effluent] is relatively independent of SRT within practical limits... in fact... it is unlikely that any effect of SRT upon S could be observed due to the normal variability associated with BOD or COD determinations."

The point of the preceding discussion is that for the range of SRT examined, it is unlikely that any difference can be observed in SCOD removal based on SRT. Therefore, it is valid to compare reactors operated at different SRTs (and HRTs) when comparing the effect of PAC dose.

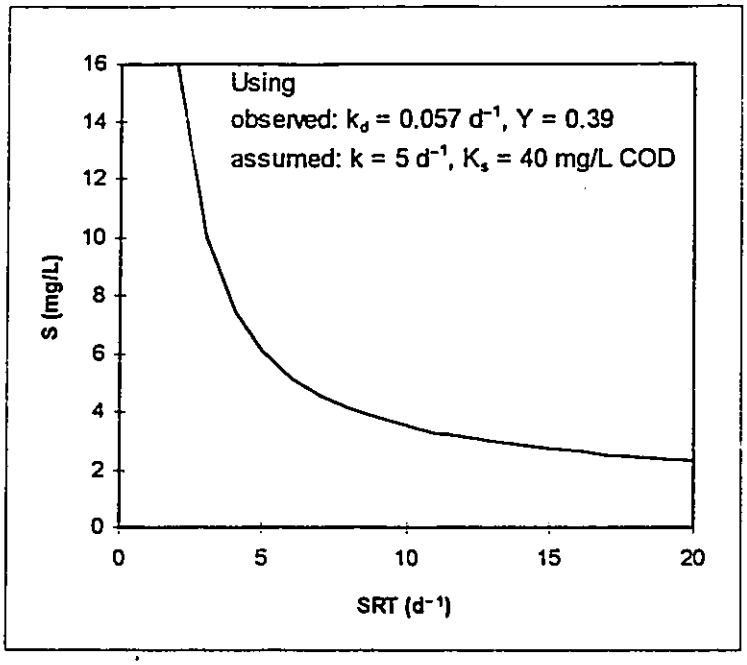


Figure 4-4 Expected reactor performance as a function of SRT.

Plot based on kinetic parameters determined experimentally (k_d and Y) and typical literature values for k and K_s (source: Tchobanoglous and Burton 1991). N.B. This graph is presented for the purpose of discussion and is not meant to wholly represent experimental data.

The foregoing is supported by statistical analysis of the data, presented in the first portion of Table 4-5. Reactors are grouped to compare SRT as the only variable. Percent removal of SCOD is compared using the t-test at a 5% level of significance. Three of the five groups showed no significant difference among reactors. One group showed significant differences (R10, R11, R12) but there was no *progression* of SCOD removal with SRT as one would expect. Only one group of two reactors (R2 and R3) out of a total of 12 groups showed significant differences.

Table 4-5 T-test results to determine if SCOD removal varies significantly with SRT or PACa.

R	Nominal[b] Conditions	SCOD removal, % mean	std. dev.	N	t-stat.	t-crit. at 5%	Significant at 5%	Variable Parameter
R4	A8/5/0	66.9	8.44	18				
R5	A8/10/0	69.2	2.87	18	1.09	2.03	No	SRT
R6	A8/15/0	66	9.36	21	1.39	2.03	No	SRT
R4	A8/5/0	66.9	8.44	18	0.31	2.03	No	SRT
R7	A8/5/0.1	69.8	9.94	18				
R9	A8/10/0.1	65.5	5.45	18	1.61	2.03	No	SRT
R14	C8/5/0.5	76.8	7.77	29				
R16	C8/10/0.5	80	5.78	31	1.82	2.00	No	SRT
R2	A24/10/0	69	6.91	10				
R3	A24/15/0	79.4	8.23	11	3.10	2.06	Yes	SRT
R10	B24/5/1	79.9	2.94	23				
R11	B24/10/1	75.2	6.4	37	3.30	2.00	Yes	SRT
R12	B24/15/1	85.1	5.19	16	5.45	2.01	Yes	SRT
R10	B24/5/1	79.9	2.94	23	3.99	2.03	Yes	SRT
R4	A8/5/0	66.9	8.44	18				
R7	A8/5/0.1	69.8	9.94	18	0.94	2.03	No	PAC
R8	A8/5/0.2	70.8	9.86	21	0.31	2.03	No	PAC
R4	A8/5/0	66.9	8.44	18	1.31	2.03	No	PAC
R13	C8/5/0	62.5	16.53	31				
R14	C8/5/0.5	76.8	7.77	29	4.24	2.00	Yes	PAC
R15	C8/5/1	88.1	7.62	25	5.38	2.01	Yes	PAC
R13	C8/5/0	62.5	16.53	31	7.15	2.00	Yes	PAC
R17	D4/5/0	55.8	13.03	16				
R18	D4/5/0.5	78.5	4.97	18	6.86	2.04	Yes	PAC

[a] The t-statistic shown in each row compares the reactor in that row to the one immediately above.
[b] Nominal conditions refer to feed batch, HRT (h), SRT (d) and PAC dose (g/L), respectively.

Figure 4-5 shows some of the results for removal of SCOD among control reactors (no PAC), operated at various HRTs and SRTs. Only those reactors which received a common feed, A, are compared. With the exception of poor performance in the 72 h HRT reactor which was close to failure (i.e., in effect "starved"), there does not appear to be any trends in SCOD removal with respect to either HRT or SRT.

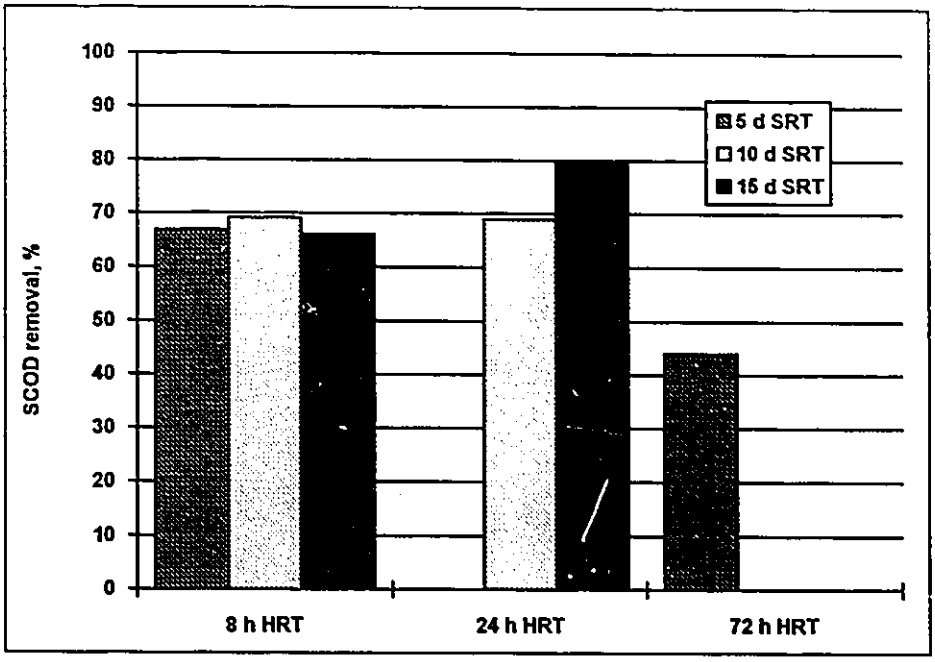


Figure 0-1 SCOD removal for various HRT and SRT for control reactors (0 mg/L PAC), feed batch A.

In contrast to HRT and SRT, PAC dose does have an effect on SCOD removal. The data from Table 4.1 are plotted in Figure 4-6, grouped according to feed batch. Following the argument given above that HRT and SRT do not affect SCOD removal to any observable degree, each bar shown on the graph represents the average SCOD removal for all reactors in that feed batch which were operated at a given PAC dose, irrespective of HRT and SRT.

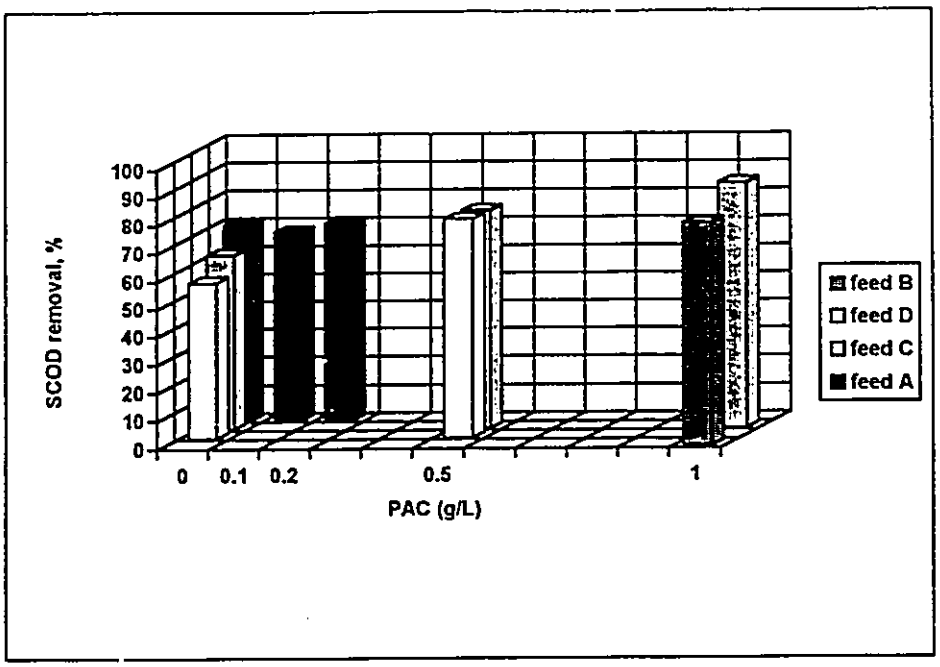


Figure 4-6 Plot of mean percent SCOD removal versus PAC dose for all reactors with HRT of 4, 8 or 24 h.

At low PAC doses of 0.1 to 0.2 g/L (feed A), no improvement in SCOD removal was observed. Test reactors in this group showed no significant differences compared to the control (R4, R7 and R8 in Table 4-5). At higher PAC doses of 0.5 and 1.0 g/L, improvement in SCOD removal is evident. The trend is best exemplified by feed C reactors, in which removal in the control reactor of 62.5% was improved to 78.4 and 88.1% by 0.5 and 1.0 g/L PAC doses, respectively. These observations are statistically significant. Feed D reactors produced similar findings, in which 0.5 g/L PAC improved SCOD removal from 55.8 to 78.5%. This too was statistically significant. Reactors in the feed B group did not include a control, thus direct comparison within that batch is not possible. However in comparison to other batches the performance of these three reactors operated at 1.0 g/L PAC was good, removing 80.1% SCOD.

In Figure 4-7, data are normalized with respect to controls in each batch, to compare batches. The same trends are evident - little or no effect at low PAC dose, noticeable improvement at higher PAC dose.

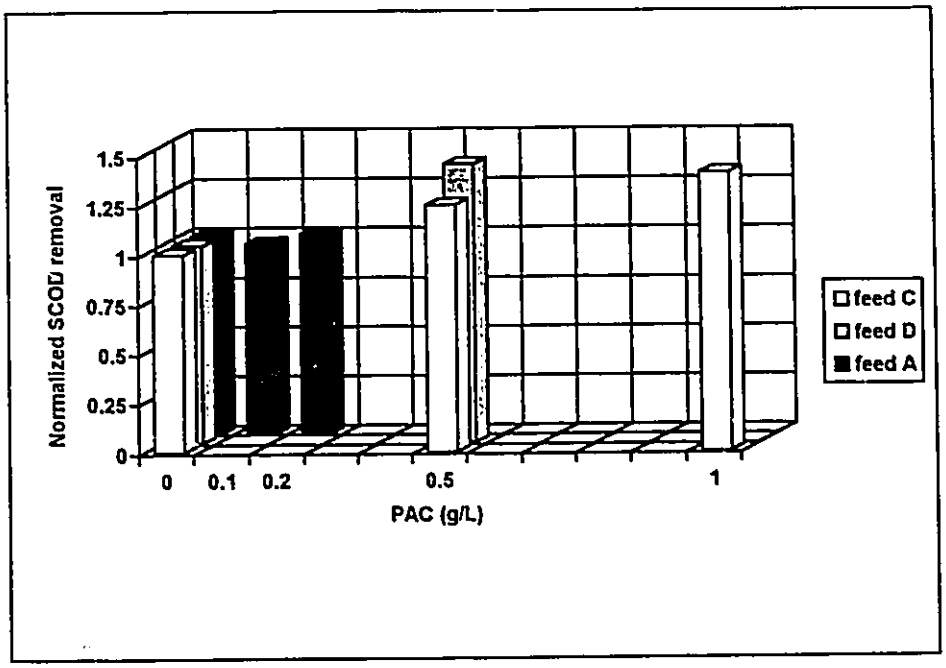


Figure 4-7 Plot of normalized mean SCOD removal versus PAC dose for all reactors with HRT of 4, 8 or 24h.

Batch B is not shown because there was no control reactor.

SCOD and PAC data is also presented. Figure 4-8 shows results for all reactors run at 4, 8 and 24 h HRT. This is a rough comparison because the data are from different feed batches which may not necessarily have the same proportion of biodegradable COD. Nevertheless it is clear that SCOD removal increases with increasing PAC dose. When data are normalized, taking SCOD removal in the control as equal to 1, the trend is more evident. Figure 4-9 and Figure 4-10 compare removal for 4 and 8 h HRT reactors, as plain and logarithmic plots respectively. The correlation coefficient for the logarithmic plot was 0.86, indicating a strong correlation between SCOD removal and PAC.

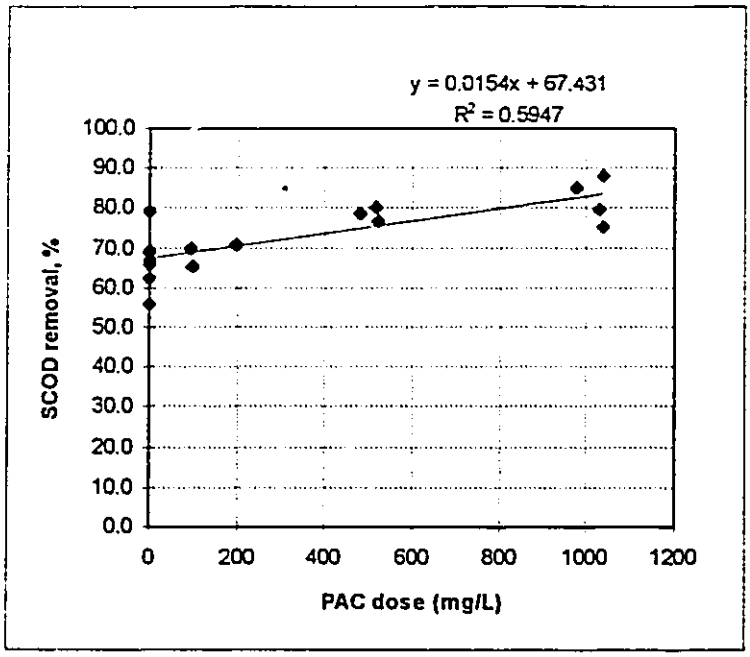


Figure 4-8 SCOD removal versus PAC dose for all 4, 8 and 24 h HRT reactors, various SRTs.

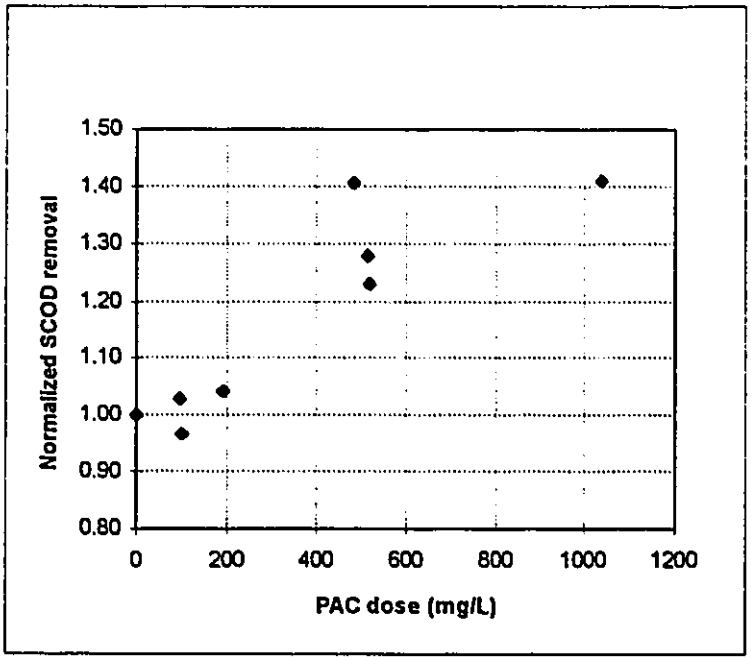


Figure 4-9 Normalized SCOD removal versus PAC, for 4 and 8 h HRTs.

Removal is normalized with respect to control reactors (0 PAC) in each group, such that removal in controls is 1.

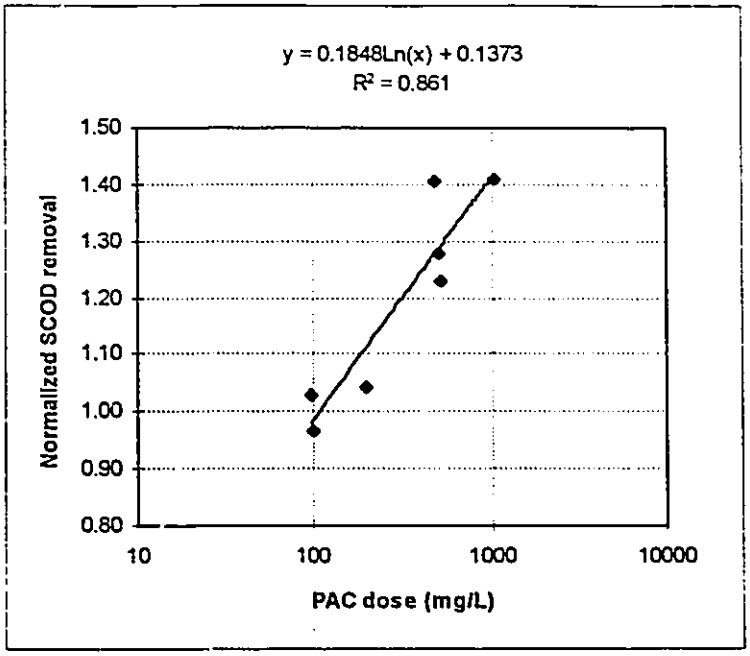


Figure 4-10 Logarithmic plot of normalized SCOD removal versus PAC, for 4 and 8 h HRTs. Removal is normalized with respect to control reactors (0 PAC) in each group, such that removal in controls is 1.

Reactor behaviour with respect to the effect of PAC on biological SCOD removal can be logically hypothesized to occur in three ways, shown in Figure 4-11. Three cases are possible. In case A there is no change. Biological COD removal is constant and any additional removal by PAC occurs strictly through physicochemical processes - adsorption. In process B biological removal is increased. The presence of PAC somehow enhances biological removal. In case C biological removal is compromised by the presence of PAC. Possibly PAC takes up COD, making it unavailable for biodegradation.

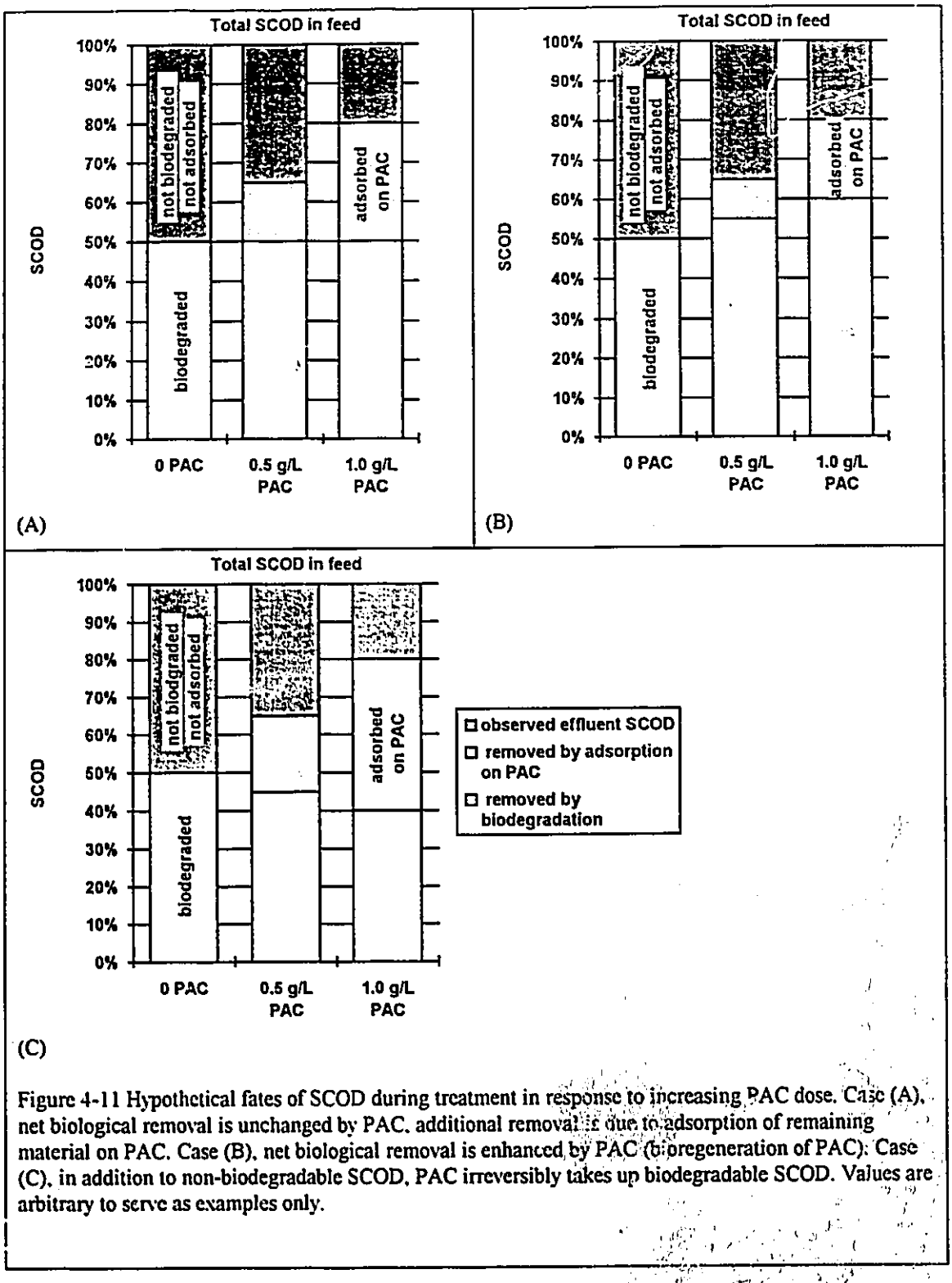


Figure 4-11 Hypothetical fates of SCOD during treatment in response to increasing PAC dose. Case (A), net biological removal is unchanged by PAC, additional removal is due to adsorption of remaining material on PAC. Case (B), net biological removal is enhanced by PAC (bioregeneration of PAC). Case (C), in addition to non-biodegradable SCOD, PAC irreversibly takes up biodegradable SCOD. Values are arbitrary to serve as examples only.

It must be emphasized that the examples in Figure 4-11 represent the ultimate *fate* of SCOD, without regard to the mechanism or intermediate stages of the removal process. If SCOD removal in a PACT™ system is to be fully described, more rigorous data are needed. The following analysis is not definitive. The arguments that follow serve to suggest which one of these three logical alternatives is most plausible.

Given the data in the present experiment, direct measurement of the amount of SCOD removal due to biodegradation alone in PAC reactors is not possible, because only the total amount of SCOD removal (i.e., removal by PAC plus biodegradation) is observed. However, if one assumes that any COD taken up by the biomass is metabolized equally in both control and PAC reactors, that is, yield and endogenous decay are equivalent in each case, then the amount of SCOD biodegradation can be indirectly assessed by examining the amount of $MLVSS_{biol}$ in each reactor. Considering each of the three mechanisms, in case A, increasing PAC dose would have no effect on the amount of SCOD available for biodegradation, hence $MLVSS_{biol}$ would be unaffected by PAC dose. Conversely, in case B, $MLVSS_{biol}$ would increase as more COD is made available to the biomass. In case C, $MLVSS_{biol}$ would decrease as more COD is taken up by PAC.

To examine whether biodegradation was changing, predicted values of $MLVSS_{biol}$ were calculated from the yield, Y, and endogenous decay, k_d, as determined from control reactors. Rearrangement of Equation 4.2 leads to the following expression for $MLVSS_{biol}$ (X):

$$X = \frac{Y(S_0 - S)}{\theta\left(\frac{1}{\theta_c} + k_d\right)} \qquad (4\text{-}5)$$

The ratio of predicted $MLVSS_{biol}$ values to observed $MLVSS_{biol}$ was plotted as a function of PAC dose in Figure 4-12. No correlation was observed between this ratio and PAC dose, suggesting that the net amount of biodegradation was not significantly affected by PAC (Case A).

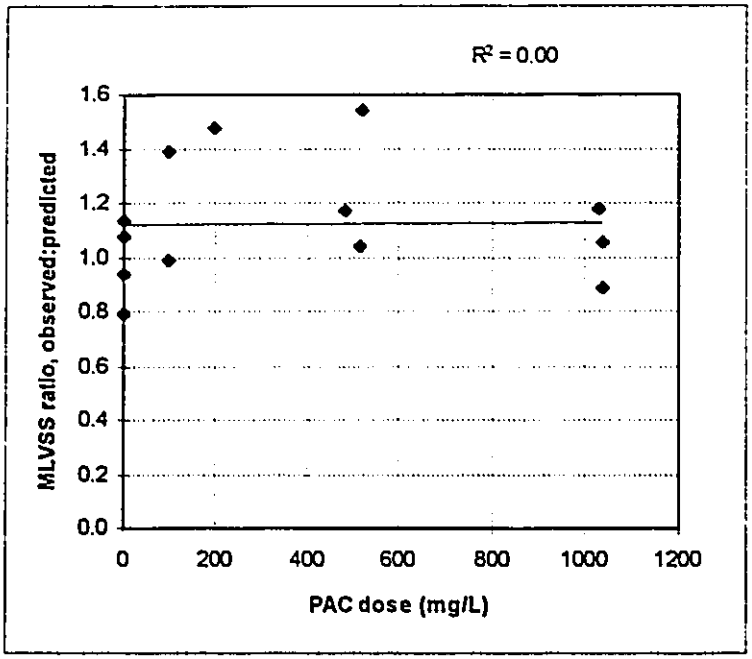


Figure 4-12 Plot of the ratio $MLVSS_{observed}$:$MLVSS_{predicted}$ versus PAC dose.
$MLVSS_{predicted}$ is calculated based on the observed yield, Y, and endogenous decay coefficient, k_d, as determined from control reactor data.

The above analysis is supported when the effect of SRT on SCOD removal is examined. Recall (Figure 4-4 and discussion thereof) that SRT variation is unlikely to affect SCOD removal to any observable degree. However it can be argued that in the presence of PAC, more removal of SCOD could occur at higher SRT (i.e., that SCOD removal varied significantly with SRT due to longer contact time with solids, not only as a functio of PAC dose). This would mitigate an increase in MLVSS. However, this is not

supported by Figure 4-13, which suggests that SCOD removal is not significantly affected by SRT.

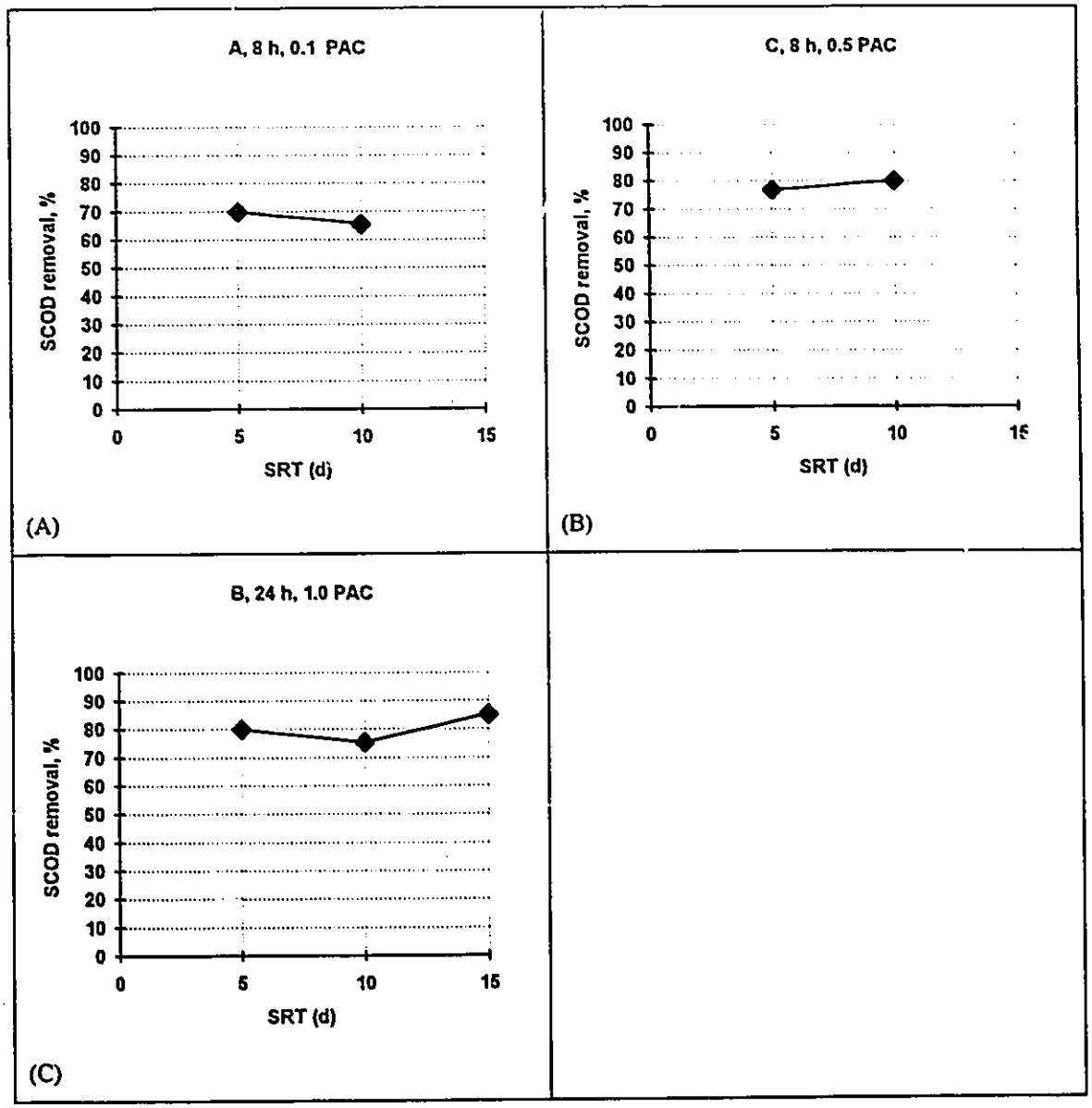


Figure 4-13 SCOD removal as a function of SRT alone.

Within each of the three data sets the only variable is SRT. Titles refer to batch, HRT and PAC dose (g/L) respectively..

Adsorption processes in wastewater are most commonly described using the Freundlich isotherm (Langford and Eckenfelder 1990), described by

$$\frac{x}{M} = KC^{1/n} \tag{4-6}$$

$$\log\left(\frac{x}{M}\right) = \log K + \frac{1}{n}\log C \tag{4-7}$$

$$\text{using } x = C_0 - C \tag{4-8}$$

where x = mass of adsorbate adsorbed onto carbon (mg or mg/L)
M = mass of carbon (mg or mg/L)
C = equilibrium concentration of adsorbate in solution (mg/L)
C_0 = initial or feed concentration (mg/L)
K, n = empirical constants

In the present case, the application of Freundlich analysis treats physiochemical removal of SCOD by PAC as being distinct from the biodegradative processes. That is, it is assumed taht the SCOD which was not biodegraded exists in equilibrium in the effluent, partitioned between dissolution in the aqueous phase and adsorption on PAC. Hence the initial concentration, C_0, of Equation 4-8 is taken as the $SCOD_{out}$ concentration from a control reactor. The equilibrium concentration of adsorbate, C, and mass of carbon, M, are taken as $SCOD_{out}$ and carbon dose respectively, for each test reactor. It must be stressed that this conceptualization does not account for intermediate processes or mechanisms. It is an attempt to describe the apparent, end results of the process. This is obviously a rough analysis, and a stricter approach is needed to investigate the process with confidence, for example, traditional isotherm analyses on the feeds and effluents. However, the results given here may serve as a starting point for more detailed investigation.

Data for the Freundlich analysis are tabulated in Table 4-6 and plotted in Figure 4-14. Data are grouped according to feed batch, such that $SCOD_{out}$ from the control reactor

in each batch is taken as the initial concentration, C_0, of adsorbate, and $SCOD_{out}$ concentration in the test reactor is taken as the equilibrium concentration, C, of adsorbate. The plot shows a rough adherence to expected behaviour for a Freundlich isotherm. It should be noted that complex mixtures or solutions which contain non-adsorbable compounds will deviate from the ideal, linear relationship. For example, in the presence of non-adsorbable material, increasing carbon dose does not indefinitely increase adsorbate removal. In such a case the Freundlich plot decreases asymptotically towards some residual value of C, representing the concentration of non-sorbable material.

Table 4-6 Summary of SCOD and PAC data used for Freundlich (Freund.) plot.

R	Parameters[c]	M (=PAC dose) (mg/L)	C (=$SCOD_{out}$) (mg/L)	Freund.$_x$ [b] log C	x (=$C_0 - C$) (mg/L)	x/M	Freund.$_y$ [b] log(x/M)
R4,5,6	A/8/5,10,15/0	0	115	2.06	ctrl		
R7	A/8/5/0.1	96	104	2.02	11	0.117	-0.933
R8	A/8/5/0.2	194	100	2.00	15	0.078	-1.109
R9	A/8/10/0.1	99	119	2.07	-4	0.000	NA
R13	C/8/5/0	0	213	2.33	ctrl		
R14	C/8/5/0.5	517	132	2.12	81	0.157	-0.804
R15	C/8/5/1	1038	72	1.86	141	0.136	-0.867
R16	C/8/10/0.5	513	114	2.06	99	0.193	-0.714
R17	D/4/5/0	0	350	2.54	ctrl		
R18	D/4/5/0.5	480	165	2.22	185	0.385	-0.4151

[a] For each feed batch, SCOD concentration in the control (no PAC) effluent is taken as the *initial concentration* or C_0. Effluent from the test reactors is the *equilibrium concentration* or C. Hence, the amount of adsorbed contaminant, $x = C_0 - C = SCOD_{out,control} - SCOD_{out,test\ reactor}$

[b] Subscripts x and y indicate abscissa and ordinate respectively of Freundlich plot.

[c] Parameters refer to feed batch, HRT (h), SRT (d) and PAC dose (g/L) respectively.

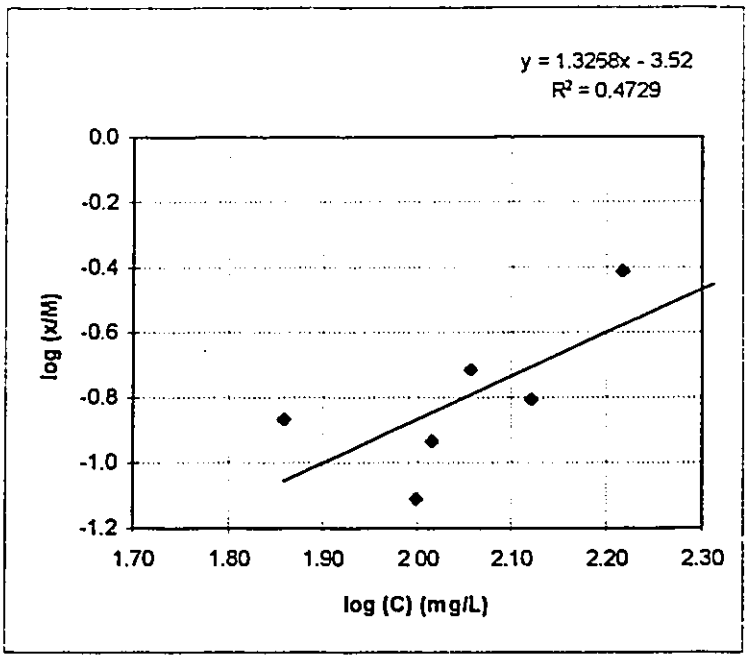


Figure 4-14 Freundlich plot for removal of SCOD by PAC. data from Table 4-6

4.4 AOX

Reactor performance with respect to AOX removal was similar to that for SCOD. Data for AOX removal for three groups of reactors, each of which included a non-PAC control, are shown in Figure 4-15. Although removal of AOX varied depending on the feed batch, overall it is clear that PAC improves AOX removal. In each group AOX removal increased with increasing PAC dose, irrespective of the amount of initial removal in the control. In contrast to SCOD however, even low doses of PAC, 0.2 g/L for example, greatly increased AOX removal efficiency. Figure 4-16 compares AOX data normalized with respect to the control reactors in each batch, while Figure 4-17 shows AOX removal for all reactors as a function of PAC dose, clearly demonstrating improved AOX removal with increasing PAC dose.

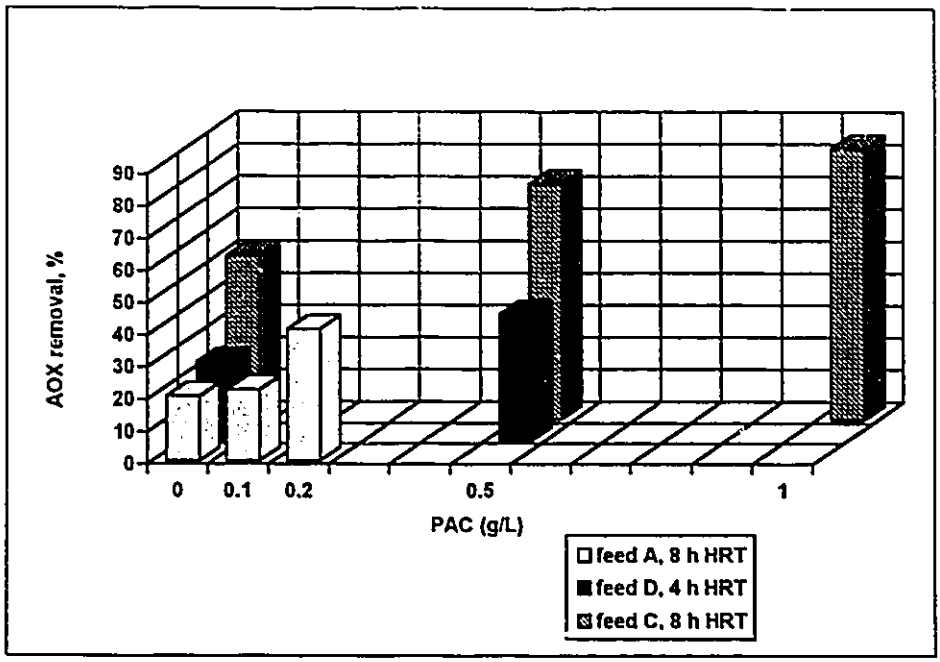


Figure 4-15 AOX removal for 4 and 8 h HRT (all at 5 d SRT) at various PAC doses.

Note that removal efficiency varies with feed batch, even for the same conditions. For example, in the 8 h controls, 20% of AOX was removed in batch A vs. 51% in batch C.

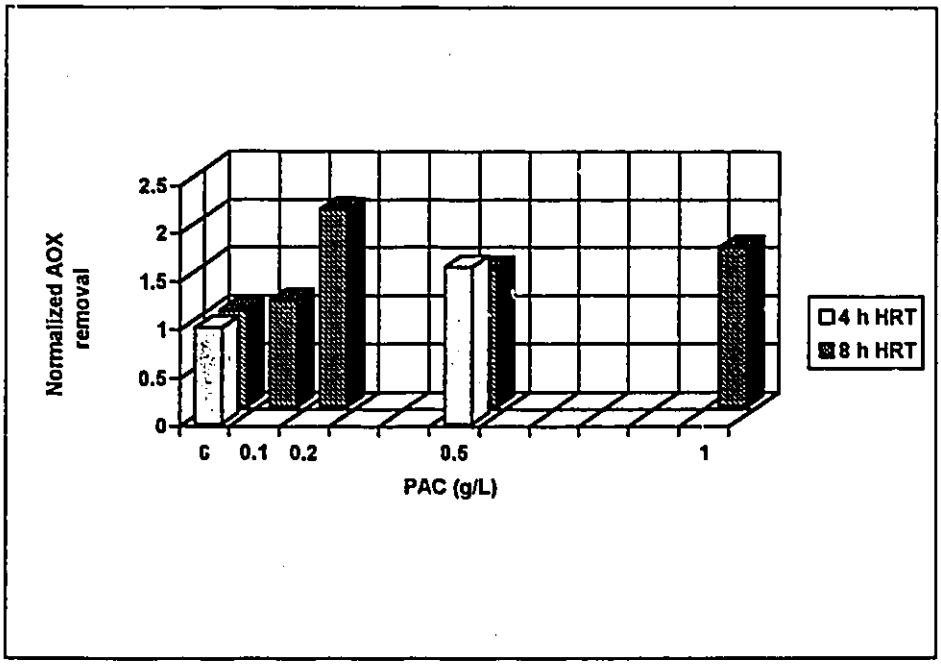


Figure 4-16 Normalized AOX removal for 4 and 8 h HRT (all 5 d SRT) at various PAC doses.

Different feeds were used in the runs represented above, therefore AOX removal in the control reactors (i.e., 0 PAC) has been normalized to 1 to allow for a more valid comparison.

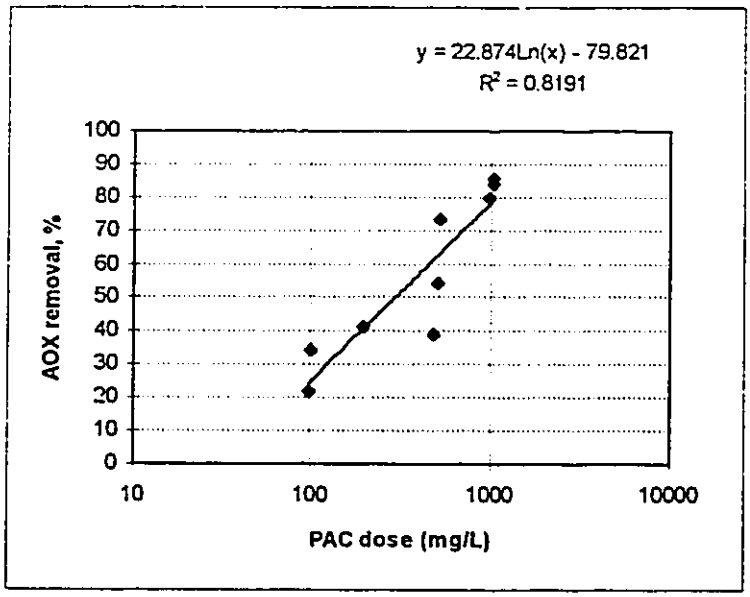


Figure 4-17 AOX removal vs. PAC dose for all reactors.

It has been suggested that solids concentration plays a role in removal of adsorptive compounds such as AOX. Two mechanisms may occur. First, physical removal of AOX by adsorption on solids which are subsequently removed during sludge wasting. Second, biological removal is enhanced because adsorptive compounds remain in the reactor longer. By adsorbing to solids they remain in the system for one SRT rather than one HRT, the implication being that consumption of poorly or slowly biodegradable compounds is enhanced by longer contact with biomass. The latter mechanism has been cited as an ostensible feature of PACT™. If solids played such a role, one would expect changes in AOX removal to occur in response to changing solids concentration.

Before examining the effect of solids concentration on AOX removal, it is necessary to clarify the difference between the terms PAC *dose* and *concentration.* These terms are interrelated but not equivalent. PAC dose (mg/L) refers to the mass of PAC added to the reactor per volume of feed. PAC concentration (mg/L) refers to the

concentration of PAC in the ML. PAC dose partly determines MLTSS, but at a given PAC dose and HRT, PAC concentration in the ML is function only of SRT.

Figure 4-18 demonstrates the effect of MLTSS on AOX removal. Three data sets are presented, each for a particular feed batch at constant HRT and PAC dose. The only variable in each plot is SRT (hence MLTSS). There is little difference in AOX removal at different MLTSS. In case (A), the three reactors showed nearly equal removal. In case (B) an increase was observed, but in case (C) a decrease. Taken together, these observations show no trend in AOX removal with respect to SRT, suggesting that solids concentration has no effect on AOX removal, consequently sorption on solids other than PAC does not occur or is negligible.

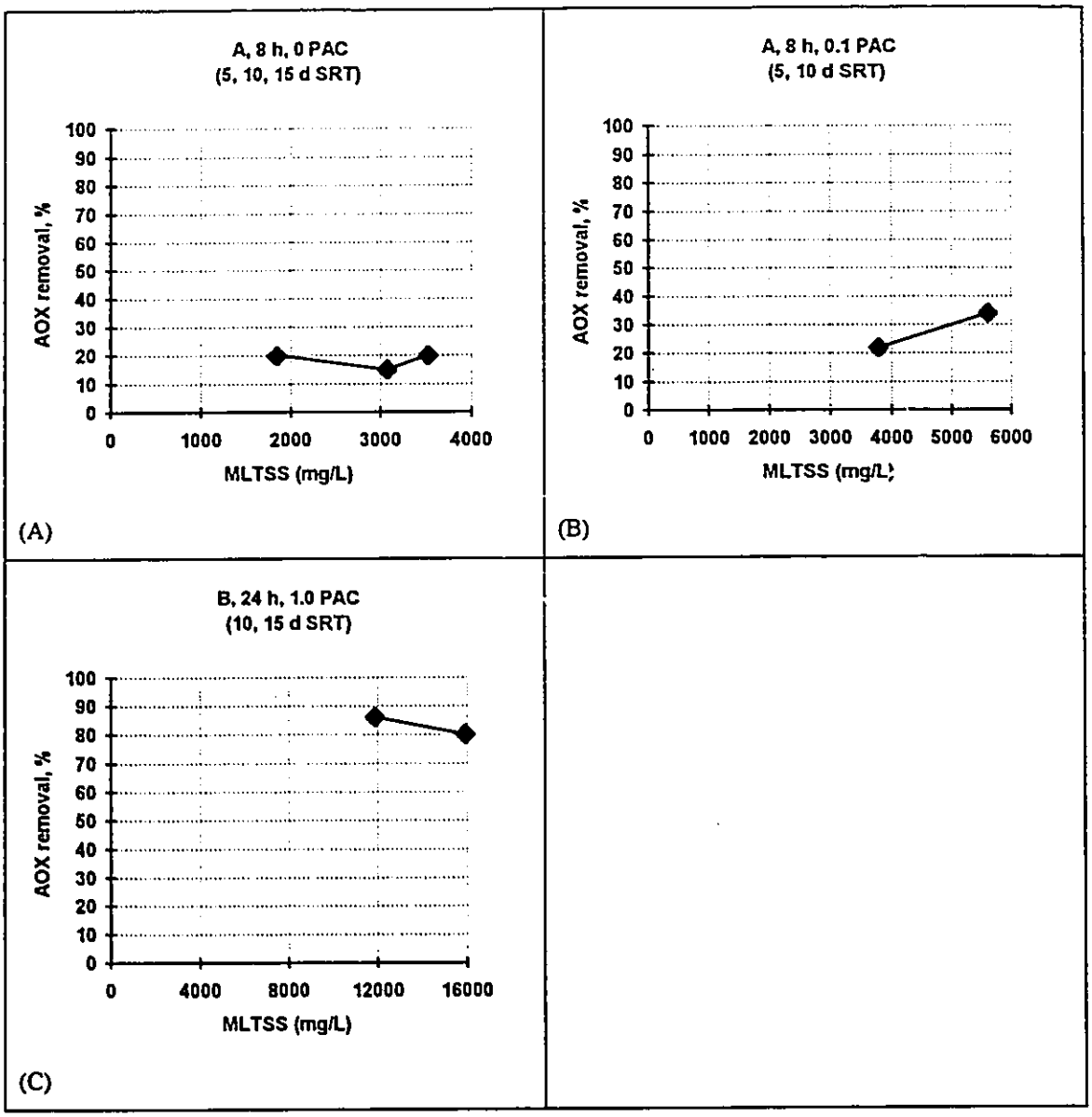


Figure 4-18 AOX removal as a function of MLTSS alone.

Within each of the three data sets the only variable is SRT (hence MLTSS). Titles refer to feed batch, HRT and PAC dose in g/L respectively.

Having established that SRT is not a factor in AOX removal, one can examine the effects of PAC dose. Table 4-7 provides a more detailed summary of AOX data , showing removal (absolute and percentage) at various PAC doses, grouped according to feed batch/HRT. Removal of absolute mg/L AOX behaves as expected, that is more AOX is

removed as AOX concentration increases in the feed (looking down the columns in Table 4-7 for any given PAC dose). But inspection of percent removal reveals that neither absolute AOX or SCOD in the feed nor HRT consistently correlate with AOX removal. For example in the control reactors with no PAC, AOX removal in feed A (344 mg/L SCOD) was 18%. Higher strength feed C (578 mg/L SCOD) showed better AOX removal at 51%, but the hignest strength feed D (779 mg/L SCOD) had poorer AOX removal of only 24%. With respect to HRT, feeds B and C, which were of similar strength (563 and 578 mg/L SCOD), showed nearly identical AOX removal of 84 and 83% at 1 g/L PAC dose, despite having HRTs which differed by a factor of 3 (8 vs. 24 h).This indicates that equilibrium was established in 8 h or less. Lastly, although absolute AOX concentrations in feeds C, B and D were within 20% of each other, percent removal varied substantially among reactors in the 0.5 and 1.0 g/L PAC groups. The key determinant of varying removal efficiency appears to be AOX/SCOD ratio. For example, 1.0 g/L PAC reactors which treated feeds C and B showed similar AOX results (84 and 83%) having similar absolute AOX concentrations and AOX/SCOD ratios (12 and 10 mg/L, 2.08 and 1.78 respectively). In contrast, comparison of 0.5 g/L reactors which treated feeds C and D reveals a reduction in removal from 64% to 39%, corresponding to a reduction in AOX/SCOD ratio from 2.08 to 1.35, despite similar absolute AOX concentration in the feed (12 and 10.5 mg/L). Note that the data in Table 4-7 are arranged in order of decreasing AOX/SCOD ratio. In all cases, whether in control or test reactors, AOX removal efficiency decreases as this ratio decreases. These observations suggest that the

different feeds have variable AOX composition, each feed with a particular distribution of organochlorine species with different biodegradability and/or adsorption.

Freundlich plots of the AOX data shown in Table 4-7 were also prepared, presented in Figure 4-19 (except for batch B which did not include a non-PAC control). The rationale in this analysis is the same as that for SCOD (Figure 4-11A), that the fraction of AOX removed through biodegradation is unchanged as PAC dose increases. Therefore, for the plot in Figure 4-19, the AOX concentration used to calculate the mass of adsorbed adsorbate is that of the control reactor effluent for each batch (i.e., $x = C_0 - C = AOX_{out,control} - AOX_{out,test\ reactor}$). However, the plot shows a negative slope, implying that adsorption decreases with increasing concentration. Evidently the assumption of constant fraction of AOX biodegraded at different PAC doses is incorrect. Before discarding this assumption entirely, recall that the plotted data represent three different feed batches, each with a particular AOX/SCOD ratio. If this ratio also reflected differences in biodegradability and adsorbability of AOX, then one would expect that each batch, with its own population of organochlorines, would show consistent adsorption behavior. That is, each batch would have its own apparent values for the Freundlich constants, K and n. Consequently, a combined Freundlich plot of results for all batches would yield a series of lines, each line representing the data for a particular batch. But when the plot is examined batch by batch, each batch also exhibits a negative slope. This suggests that biodegradation of AOX is indeed changing in response to PAC dose.

Table 4-7 Detailed summary of AOX data.

Feeds				Effluents					
				AOX (mg/L)			AOX removal (%)		
Batch/ HRT (h)	SCOD (mg/L)	AOX (mg/L)	AOX/SCOD (100mg/mg)	0 PAC	0.5 g/L PAC	1.0 g/L PAC	0 PAC	0.5 g/L PAC	1.0 g/L PAC
C/8	578	12.0	2.08	6.1	7.65[a]	10.1	51	64[a]	84
B/24	563	10.0	1.78			8.3[a]			83[a]
D/4	779	10.5	1.35	2.5	4.1		24	39	
A/8	344	4.1	1.19	0.73[a]			18[a]		
[a] Averages for 2 or 3 runs with different SRTs.									

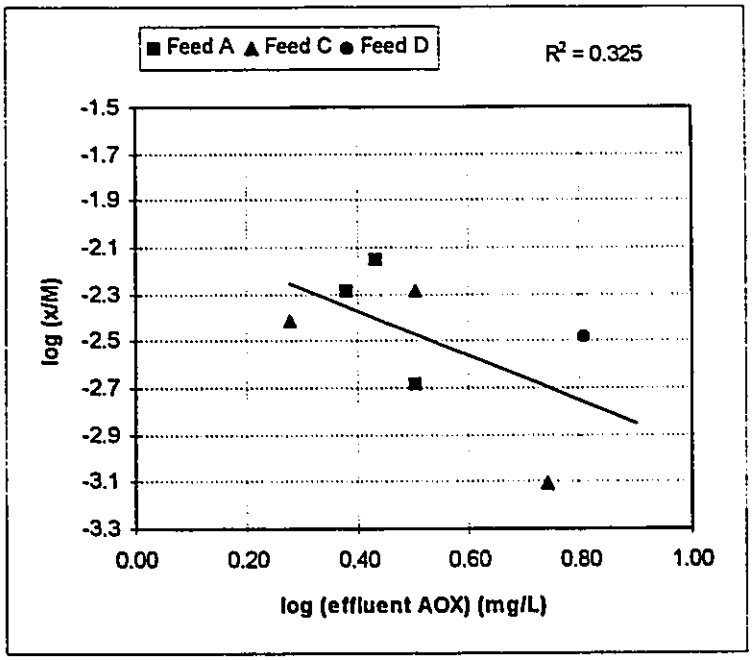


Figure 4-19 Freundlich plot using observed data for removal of AOX by PAC.

Assumes no change in the fraction of biological AOX removal as PAC dose increases, hence $x = C_o - C = AOX_{out,control\ reactor} - AOX_{out,\ test\ reactor}$.

Similar to the case of SCOD, PAC may have one of two possible effects upon biodegradation of AOX, enhancement or inhibition (Figure 4-11 B and C respectively). It is commonly observed that PACT™ systems have greater apparent adsorption than expected from isotherm analysis, due to enhanced biodegradation and bioregeneration of PAC (Langford and Eckenfelder 1990). But one can also hypothesize that a poorly

biodegradable substance with high affinity for adsorption on PAC (such as AOX) might be sequestered on PAC, thereby reducing the net amount that is biodegraded. If the affinity for AOX to adsorb on PAC is much greater than that of microorganisms to take it up, then net degradation of AOX is reduced as AOX is adsorbed on PAC. To examine these possibilities, the author has used two simple models to transform and re-plot the AOX data to see if typical isotherm behaviour, viz. a positive slope, can be observed. Once again, it is emphasized that this approach is rough. Intermediate stages and mechanisms of the process cannot be described with the limited data presented here. It is acknowledged that adsorption processes are complex, especially in solutions containing mixtures of compounds. The presence of microorganisms in PACT™ further complicates description of the process. However, it is hoped that the analysis given here will provide a basis for more rigorous studies in the future.

Consider the case where PAC sequesters AOX (analogous to Figure 4-11C for SCOD). In this case the effective initial concentration of adsorbate, that is, AOX which is not biodegraded, C_0, will increase with increasing PAC dose (i.e., as more AOX is sequestered by PAC, the amount of AOX that is biodegraded decreases, thereby increasing the apparent initial liquid-phase concentration of AOX, C_0, in the Freundlich relationship). One must keep in mind that the value taken as C_0 in this analysis represents the concentration of AOX which is not biodegraded, and is therefore partitioned in the effluent between AOX adsorbed on PAC and AOX in the liquid phase. A simple saturation type mechanism for AOX uptake by PAC was used. The maximal possible increase is the difference between concentration in the feed and effluent in the control, therefore the term

$M/(M+a)$ becomes asymptotic to 1 at high PAC dose. The sequestration case will be referred to as model A:

$$\text{A: } C_0 = C_{control} + \left(C_{feed} - C_{control}\right)\frac{M}{M+a} \tag{4-9}$$

$C_{control}$ = AOX concentration in control reactor effluent (mg/L)
C_{feed} = AOX concentration in feed (mg/L)
M = PAC dose (mg/L)
a = empirical constant (mg/L)

Conversely, consider the case where PAC enhances AOX biodegradation (analogous to Figure 4-11B for SCOD). The effective initial concentration of adsorbate, C_0, will decrease with increasing PAC dose. Consequently the apparent equilibrium concentration of adsorbate will decrease. The same simple saturation type mechanism is used. However in this case, the maximal possible *decrease* in AOX concentration is equivalent to the total amount of AOX in the effluent, therefore the term $M/(M+b)$ becomes asymptotic to 1 at high PAC dose. For this model, B:

$$\text{B: } C_0 = C_{control} - C_{control}\frac{M}{M+b} \tag{4-10}$$

b = empirical constant (mg/L)

The transformed data for each of these two cases are presented in Table 4-8 and plotted in Figure 4-20. The constants, a and b, were numerically determined to provide the best fit for the data, that is, nearest to a positive slope. Model B, that of bioregeneration of PAC, did not improve the fit of the data, slope remained negative (−1.17) and data points were poorly collinear. Model A fitted better, slope increased to −0.05 and data points were more linear. Low values for slope, less than 0.2, and hence large value of n, have been reported for some pure compounds (Langford and Eckenfelder 1990) and it is known

that a large apparent value of n is observed for mixtures of compounds. The latter should apply to AOX which is a generalized measurement for many organochlorines. These results suggest that model A most adequately reflects the mechanisms of AOX removal in the system. that is, PAC sequesters AOX and inhibits its biodegradation.

While the above analysis suggests that sequestration of AOX by PAC is responsible for the observed behaviour, the data are too limited to argue strongly in favor of model A. It is clear however that the fate of AOX is more complex than that of SCOD. More complete data are needed to describe the process.

Table 4-8 Calculations for Freundlich modeling of AOX removal by PAC.

Feed	C_{feed} (mg/L)	C_{eff} (mg/L)	$\log(C_{eff})$	C_{ctrl} (mg/L)	M PAC (mg/L)	Model A[a]		Model B[b]	
						C_o (mg/L)	$\log(x/M)$	C_o (mg/L)	$\log(x/M)$
C	12	1.9	0.28	5.9	1000	10.98	−2.04	4.43	−2.6
A	4.1	2.4	0.38	3.37	200	3.74	−2.18	3.16	−2.42
A	4.1	2.7	0.43	3.37	100	3.61	−2.04	3.26	−2.25
A	4.1	3.2	0.51	3.37	100	3.61	−2.38	3.26	−3.21
C	12	3.2	0.51	5.9	500	10.26	−1.85	5.06	−2.43
C	12	5.5	0.74	5.9	500	10.26	−2.02	5.06	NA
C	10.5	6.4	0.81	8	500	9.79	−2.17	6.86	−3.04

[a] Model A: $C_o = C_{ctrl} + (C_{feed} - C_{ctrl})M/(M+a)$, a = 200 mg/L
[b] Model B: $C_o = C_{ctrl} - C_{ctrl}M/(M+a)$, b = 3000 mg/L

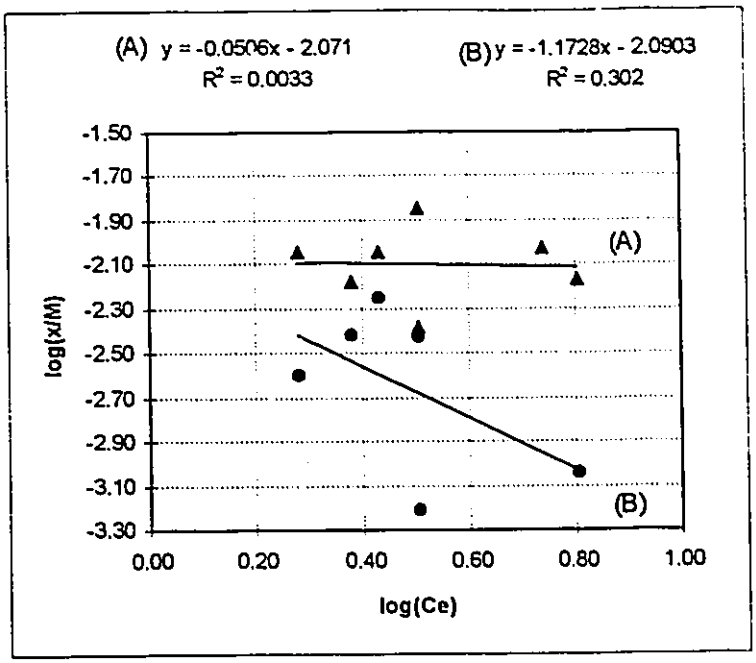


Figure 4-20 Freundlich plots using transformed AOX data, based on two models.

Model A (triangles): PAC decreases AOX available for biodegradation. Model B (circles): PAC increases biodegradation of AOX. Linear regression lines and equations are shown.

4.5 Metals

Results of ICP metals analyses were summarized in Table 4-2. Total masses for six heavy metals, Cd, Cr, Cu, Ni, Pb and Zn are shown. Other metals were not present above the detection limits for the protocol used. A mass balance ratio was calculated based on the average daily input and output volumes and concentrations in the reactors. Input is calculated according to:

$$Input = V_{feed}C_{metals,FT} + V_{feed}C_{PAC}C_{metals,PAC} \quad (4\text{-}11)$$

where

V_{feed} = volume of feed (L)

$C_{metals,FT}$ = concentration of metals in total feed (mg/L)

C_{PAC} = virgin PAC dose (g/L)

$C_{metals,PAC}$ = concentration of metals in virgin PAC (mg/g)

Output is calculated according to:

$$Output = (V_{feed} - V_{ML\_wasted})C_{metals,FT} + V_{ML\_wasted}C_{metals,ML} \quad (4\text{-}12)$$

where

$V_{ML,wasted}$ = volume of ML wasted (L)

$C_{metals,ML}$ = concentration of metals in ML (mg/L)

The mass balance ratio of input to output varied widely (Table 4-2), from a low of 0.37 to a high of 2.31. For this reason, the metals data cannot be commented on with any confidence.

The poor precision of the data may be related to low concentrations in prepared samples which may have been susceptible to very slight contamination. For example, Zn and Cr represented the largest fraction of the five metals, having detection limits of 0.01 and 0.008 mg/L respectively. However even the most concentrated samples, metals were present in small amounts, for example, 0.37 mg/L for Zn and 0.061 for Cr. Typically values were less than half of these. At these low levels, samples are sensitive to even slight contamination. A stricter protocol for sample preparation may be needed.

4.6 Toxicity

The toxicity of feeds and reactor effluents as measured with the Microtox™ assay is summarized in Table 4-9. Recall that the *effective concentration*, ECxx, is inversely proportional to toxicity of a sample, that is a low EC50 indicates high toxicity, a high EC50 indicates low toxicity. Only EC50s have been reported. For some samples , EC20 and EC10 were calculated by the Microtox™ software but were of dubious value because of large confidence intervals. This is to be expected in samples with low toxicity for two reasons. First, the protocol is able to measure toxic response only in samples of 100% concentration. Since EC20 or EC10 values in samples of low toxicity lie near the upper

end of the test range, they are subject to wider confidence intervals. Second, it is difficult to assess whether an observed 10 or 20% reduction in light output in a given sample, that is, a small relative effect, is due to toxicity or natural variation. In other words, the measurement of an effect, whose magnitude is the same as the "noise" expected in the analysis, will exhibit poor reproducibility.

Table 4-9 Microtox™ toxicity of feed and reactor effluents.

Reactor		EC50 (15 min test)		EC50 (5 min test)	
R	Parameters[a]	Feed	Effluent	Feed	Effluent
R1	A/72/5/0	14% (12-16)[b]	ND[c]	16% (16-20)	ND
R2	A/24/10/0		>100%		>100%
R3	A/24/15/0		>100%		>100%
R4	A/8/5/0		>100%		>100%
R5	A/8/10/0		>100%		>100%
R6	A/8/15/0		>100%		>100%
R7	A/8/5/0.1		>100%		92% (59-141)
R8	A/8/5/0.2		>100%		>100%
R9	A/8/10/0.1		>100%		>100%
R10	B/24/5/1	25% (16-62)	>100%	25% (19-34)	>100%
R11	B/24/10/1		>100%		>100%
R12	B/24/15/1		>100%		>100%
R13	C/8/5/0	14% (7-25)	75% (26-217)	17% (11-27)	[d]76% (22-271)
R14	C/8/5/0.5		91% (60-137)		67% (49-93)
R15	C/8/5/1		>100%		[d]99% (30-327)
R16	C/8/10/0.5		>100%		>100%
R17	D/4/5/0	3.1% (3-3.3)	44% (37-53)	5% (4.6-5.5)	46% (39-53)
R18	D/4/5/0.5		66% (51-85)		50% (44-57)

[a] Parameters refer to feed batch, HRT (h), SRT (d) and PAC dose (g/L) respectively.
[b] Values in parentheses are 95% confidence limits calculated by Microtox™ software.
[c] ND = Not Determined
[d] Estimates. Microtox™ software calculated EC50s by extrapolation.

A striking feature of the data is the range of toxicity in the feed. In the 15 min test data, feed B was least toxic with an EC50 of 25%, feeds A and C were equal at 14% and D was most toxic at 3.1%. Although it is well known that toxicity roughly correlates with wastewater strength, COD or BOD, organic strength is not strictly predictive of the

absolute toxicity of a given sample. The progression of toxicity in batches A, B and D parallels increasing feed strength, 340, 570 and 770 mg/L SCOD respectively. However feeds B and C, which were of equal strength at 570 mg/L SCOD, had different EC50s, 25 and 14% respectively. Furthermore, although the trend of higher strength/higher toxicity holds true, it is not a direct relationship. For example, the strength of batches A and D differs by a factor of 2.3 but their EC50s differ by a factor of 4.5. Nor does the ratio of CBOD to SCOD strongly correlate with toxicity. For batches A, B, C and D, this ratio was 0.60, 0.52, 0.56 and 0.65 respectively. Once again considering batches A and D, these showed similar CBOD:SCOD ratios despite having a wide disparity in toxicities. This suggests that variability in feed toxicity reflects not just changes in wastewater strength but in composition as well. Recall from the Literature Review and Theory chapter that some of the most important contributors to toxicity are one-time events (e.g., spills) rather than on-line processes operating at steady-state. The high toxicity in feed D may be such a case.

In contrast to organic strength, AOX content of the feed does not correlate with toxicity. This too has been observed in other studies (discussed in Literature Review and Theory). In the present case, feeds A and C had identical toxicity despite AOX differing by a factor of 3.

The 15 min Microtox™ test is slightly more sensitive than the 5 minute test. (cf. EC50 values for feeds) and is more suited to analysis of low-toxicity samples. For batches A through C (R1 through R16), Microtox™ could not differentiate between the effluents. Out of a total 30 measurements, 24 produced the same result - an EC50 greater than

100%. The 6 samples which did show EC50s of less than 100% had very wide confidence intervals, hence they may well have EC50s greater than 100%. In the majority of cases AS alone was sufficient to remove observable Microtox™ toxicity. In batches A and B, effluent EC50s were greater than 100% (with only one exception). It is important to understand that an EC50 of greater than 100% does not imply that a sample is non-toxic, but rather that the stated response to toxicity could not be detected. Thus these results show only that both AS and PAC treatment removed Microtox™ toxicity to non-detectable levels. Any additional improvement by PAC cannot be detected. There may still exist differences in effluent quality between control and PAC reactors, but in these cases Microtox™ sensitivity was insufficient to detect them.

However, batches C and D suggest that PACT™ may differ from AS with respect to toxicity removal. In each of these batches, toxicity was lower in PACT™ effluents compared to AS. Figure 4-21 shows improvement in effluent quality with increasing PAC dose. But this batch alone is not strong evidence because the 95% confidence intervals overlap (Table 4-9). The most toxic batch, D, provides more convincing evidence. Figure 4-22 shows the same trend of greater toxicity removal with increasing PAC dose, but confidence intervals are tighter. This suggests that PACT™ does indeed improve toxicity removal compared to AS.

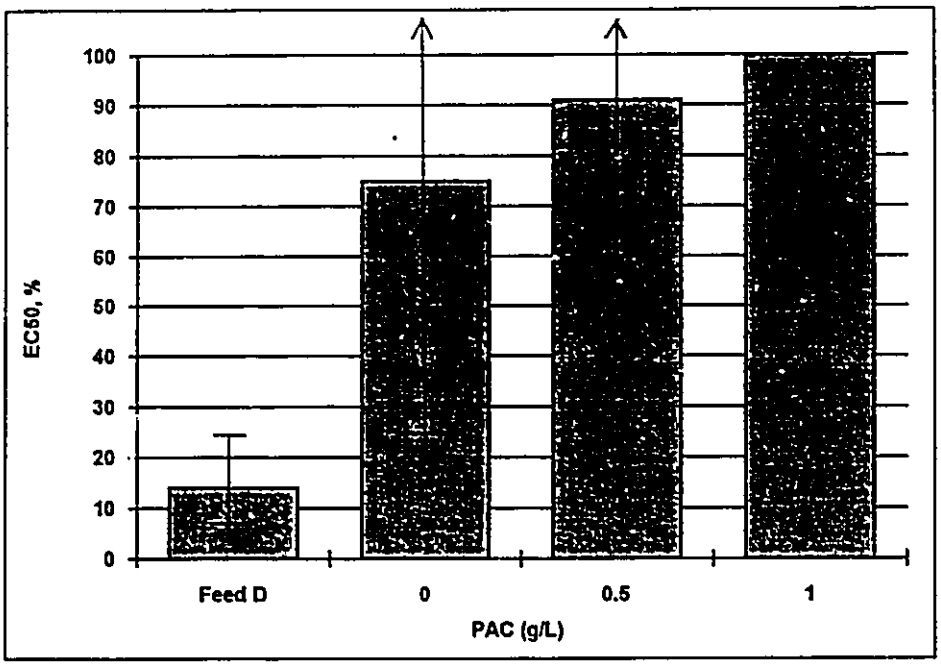


Figure 4-21 Microtox™ toxicity for feed and effluents of batch C reactors, 15 min test. The 95% confidence intervals among the effluents overlapped (see Table 4-9).

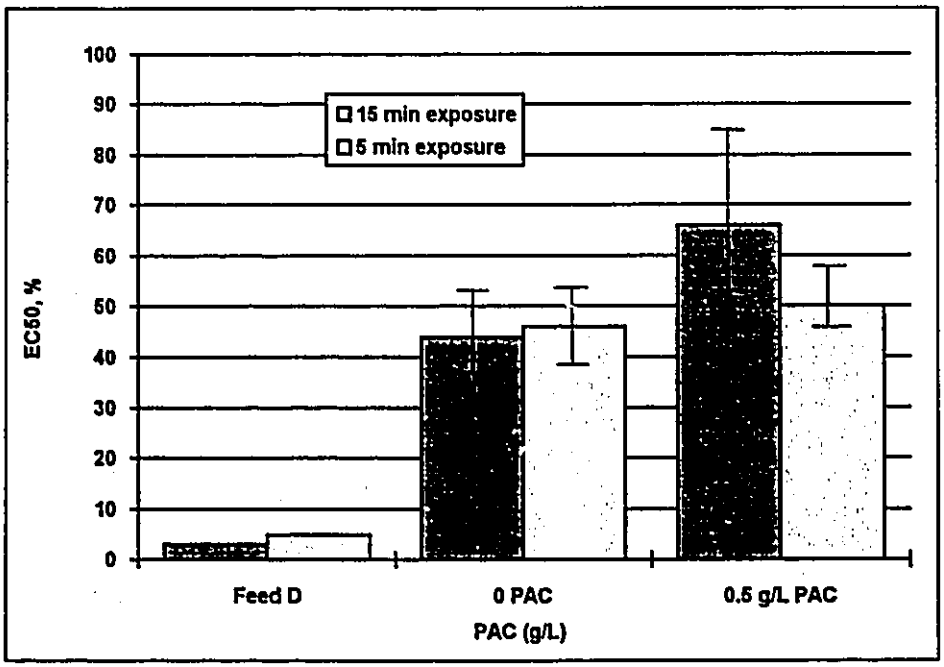


Figure 4-22 Microtox™ toxicity for feed and effluents of 4 h HRT reactors (R17 and 18). This was the only run in which toxicity reduction in control and PAC reactors differed significantly (see Table 4-9).

Although the Microtox™ assay clearly demonstrates that secondary treatment removes toxicity from pulp mill wastewater, low sensitivity of the test limits its utility as a means of comparing effluent quality among different treatment systems.

In contrast to Microtox™ data, the chronic toxicity assay using *Ceriodaphnia dubia* detected significant residual toxicity in effluents and was able to clearly differentiate between control and PACT™ effluent, but results were surprising. Three groups were tested: batch A is shown in Figure 4-23, batch C in Figure 4-24 and batch D in Figure 4-25. These plots show daphnid reproduction as a function of sample concentration. Each line represents the reproduction vs. concentration for a particular feed or effluent. High toxicity is indicated by lines where reproduction decreases sharply from the control value of 1.0 in response to slight increases in concentration.

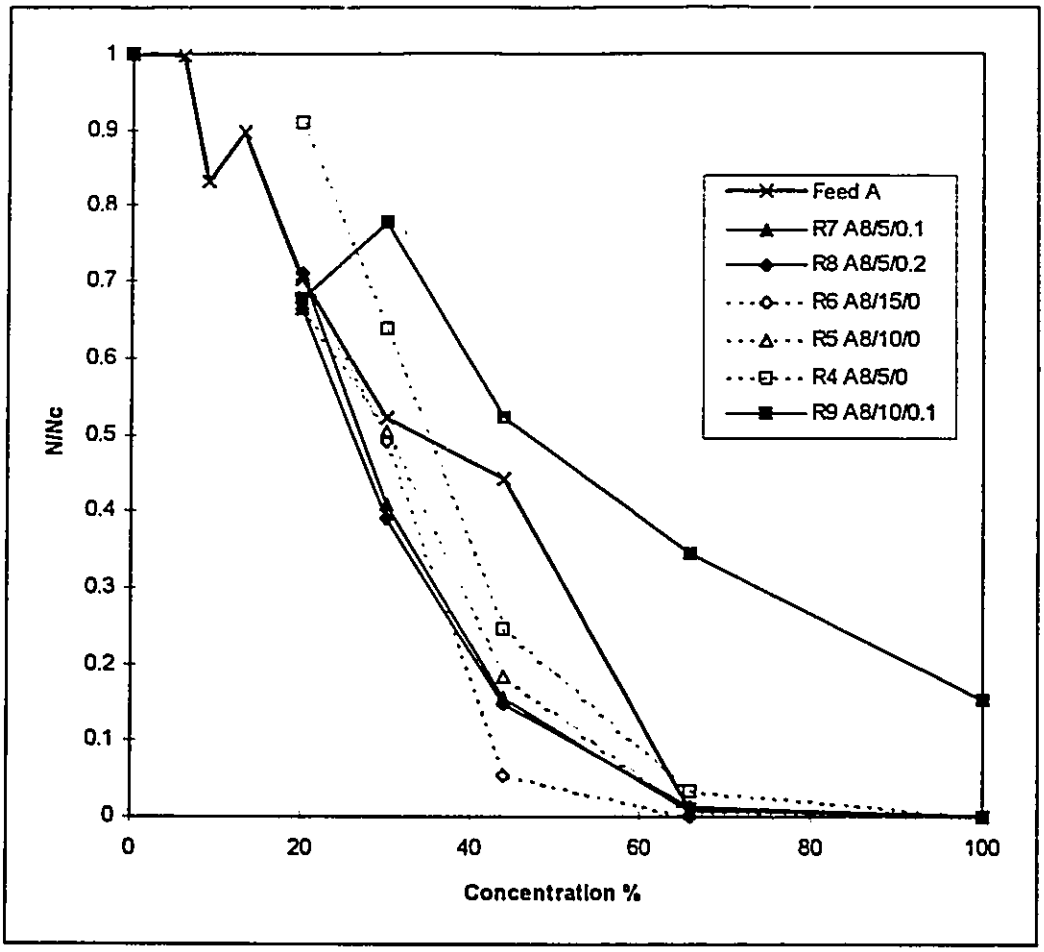


Figure 4-23 *Ceriodaphnia dubia* chronic toxicity assay, batch A, feed and reactor effluents.

Plot of reproduction versus test sample concentration. The ordinate has been normalized with respect to controls. That is, N/Nc is the ratio of offspring produced at a given test concentration versus the number of offspring produced in the control (0% sample concentration) for each group. Lines are drawn beginning at first non-zero concentration, rather than zero, for the sake of clarity. Thick lines are feed, thin lines are PACT effluents, dashed lines are control AS effluents. Reactor parameters refer to feed batch, HRT (h), SRT (d) and PAC dose (g/L) respectively.

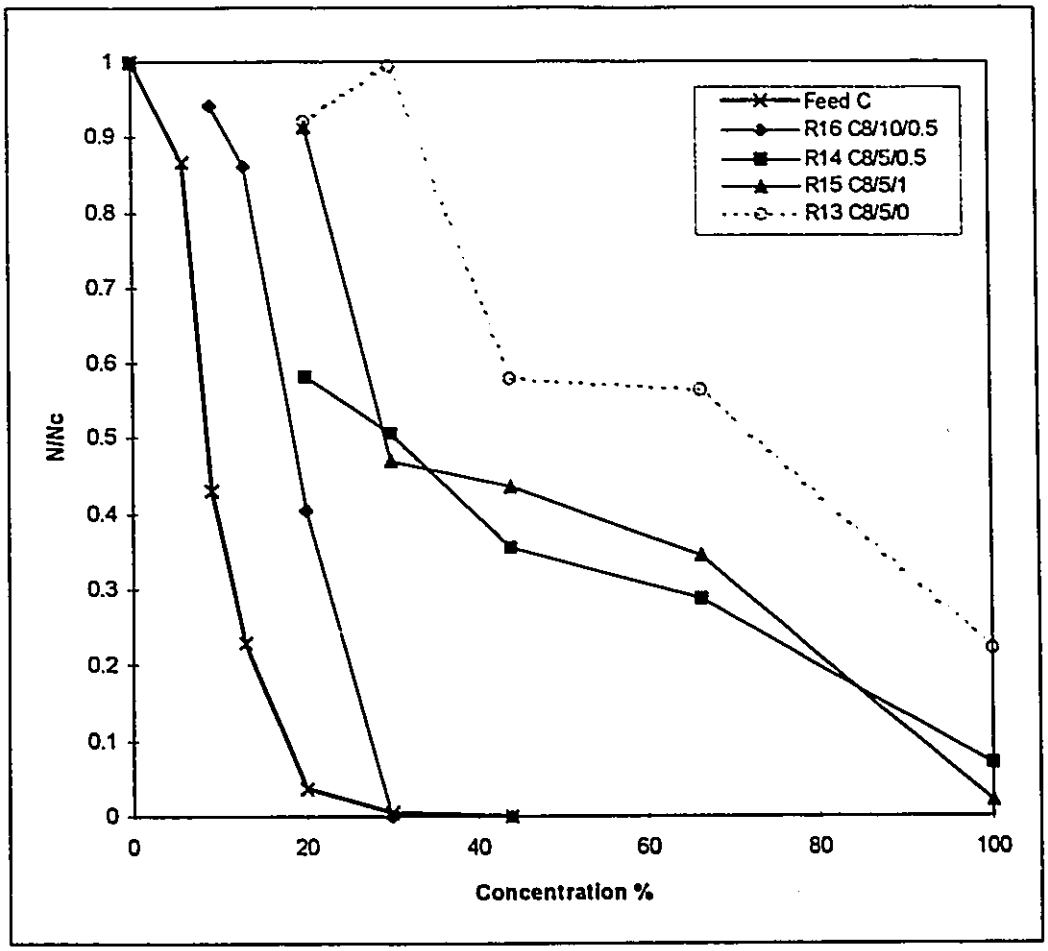


Figure 4-24 *Ceriodaphnia dubia* chronic toxicity assay, batch C, feed and reactor effluents.

Note that effluent from R16, which had washout problems, was significantly more toxic than any of the other three reactor effluents. Thick lines are feed, thin lines are PACT effluents, dashed lines are control AS effluents. Reactor parameters refer to feed batch, HRT (h), SRT (d) and PAC dose (g/L) respectively.

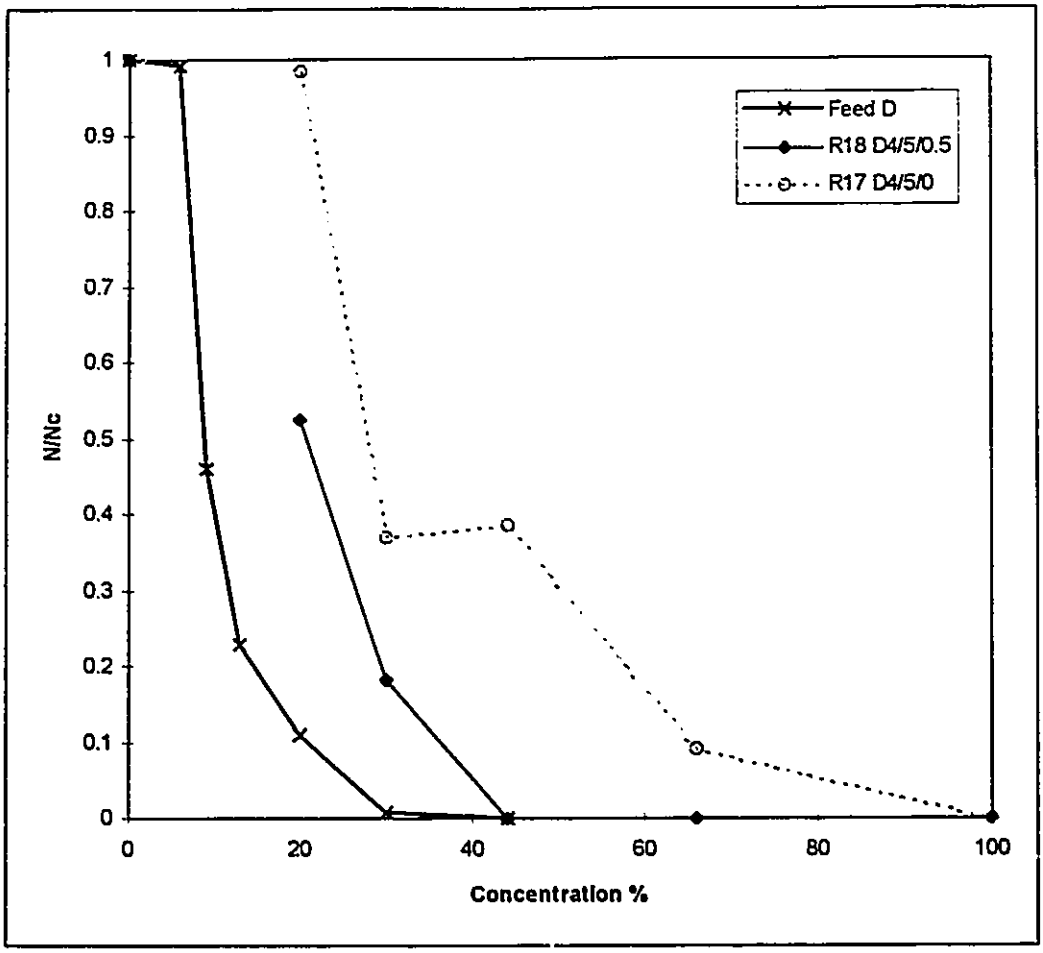
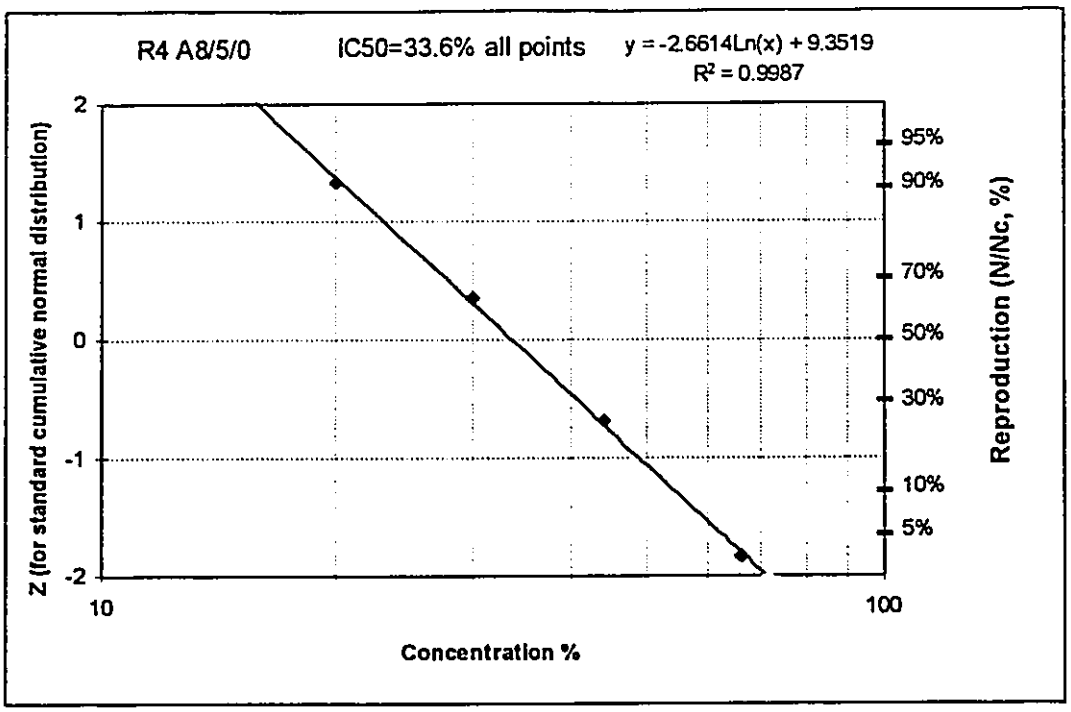


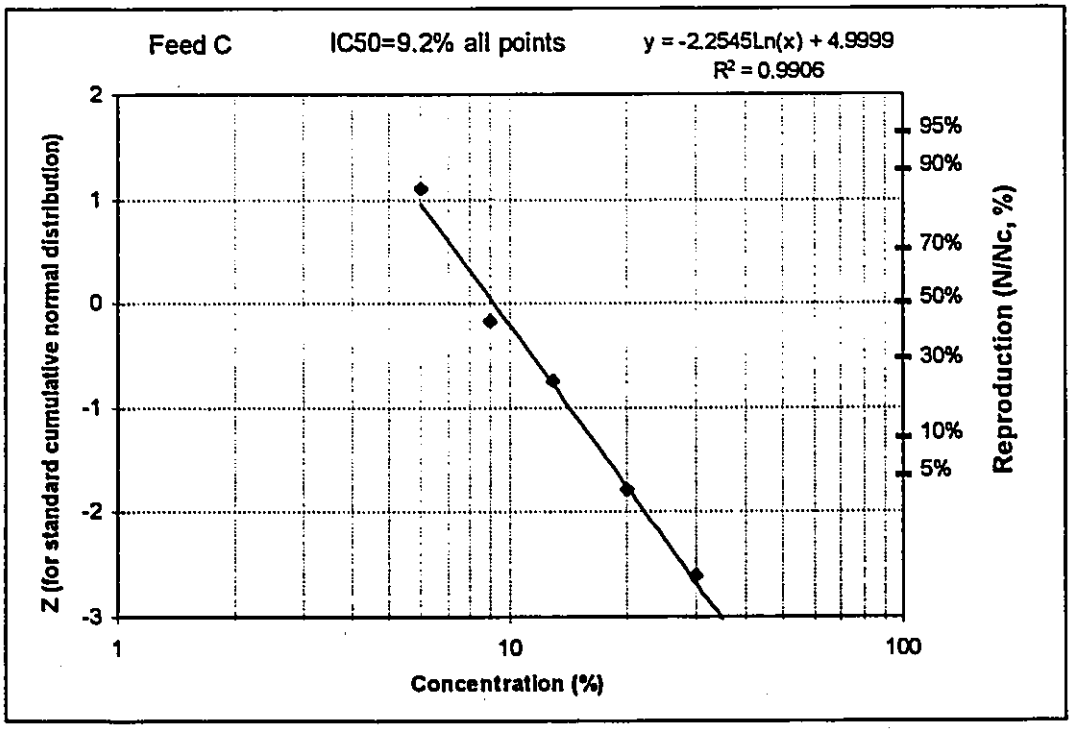
Figure 4-25 *Ceriodaphnia dubia* chronic toxicity assay, batch D, feed and reactor effluents. Thick lines are feed, thin lines are PACT effluents, dashed lines are control AS effluents. Reactor parameters refer to feed batch, HRT (h), SRT (d) and PAC dose (g/L) respectively.

IC50s have been determined in order to compare between samples. Examples of the probit method used to determine IC50s are shown. Figure 4-26 shows probit plots with good linearity, while Figure 4-27 show plots with poorer fit.. Recall that the probit method assumes that the toxicity response follows a log-normal distribution, that is, untransformed data should present an approximately sigmoidal response curve (sigmoidal if log concentration is plotted on the abscissa). Examination of the untransformed data in the plots of raw data reveals that the relationship does not fit well at low concentrations. The curves is not always symmetrically sigmoidal, but rather drop sharply at

concentrations where toxic response begins. Also, some of the reactor effluent toxicities trail off almost linearly at high concentration. It is difficult to say if such a departure from the classic sigmoid response is really anomalous behavior or whether this is typical for *Ceriodaphnia* assays. Other studies do not report raw data, only final *no observed effect concentration* (NOEC) or IC50 values. Much of the data which supports the sigmoidal response model is based on single toxin experiments under strictly controlled conditions. For example, testing of pesticides on insects, or rats. However in the present case, the substances investigated are complex mixtures of compounds, therefore the toxic response may not be as clear cut. Nevertheless, because the probit method remains the standard for interpolation of ICxx, it is used here.



(A)

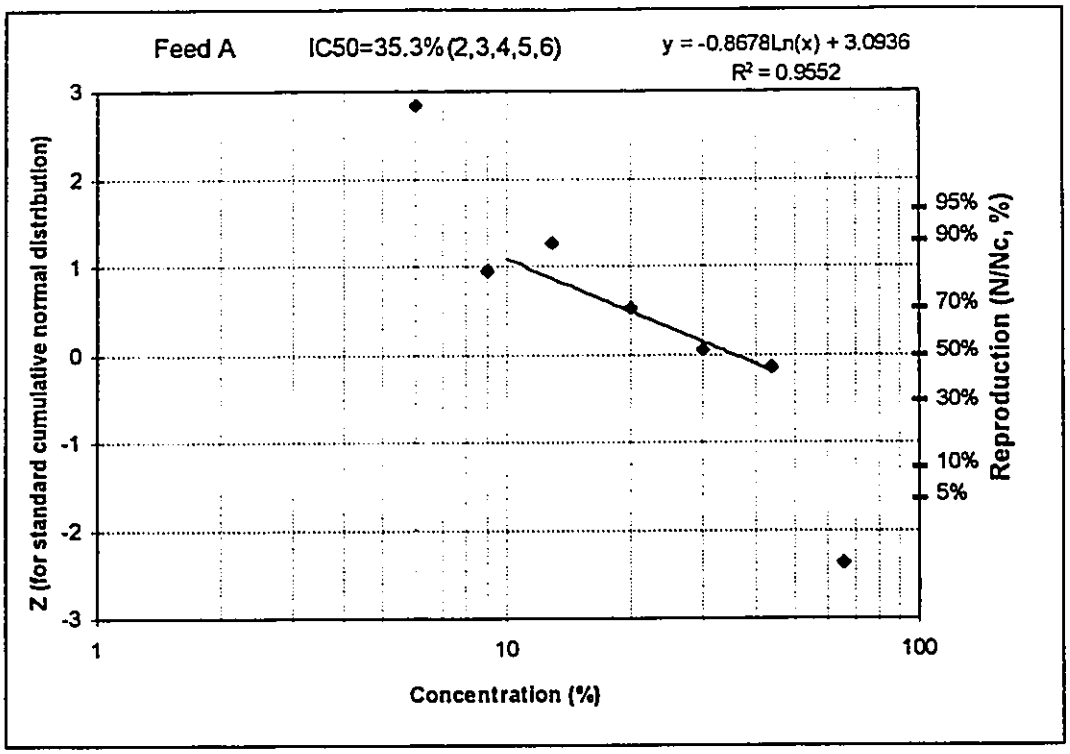


(B)

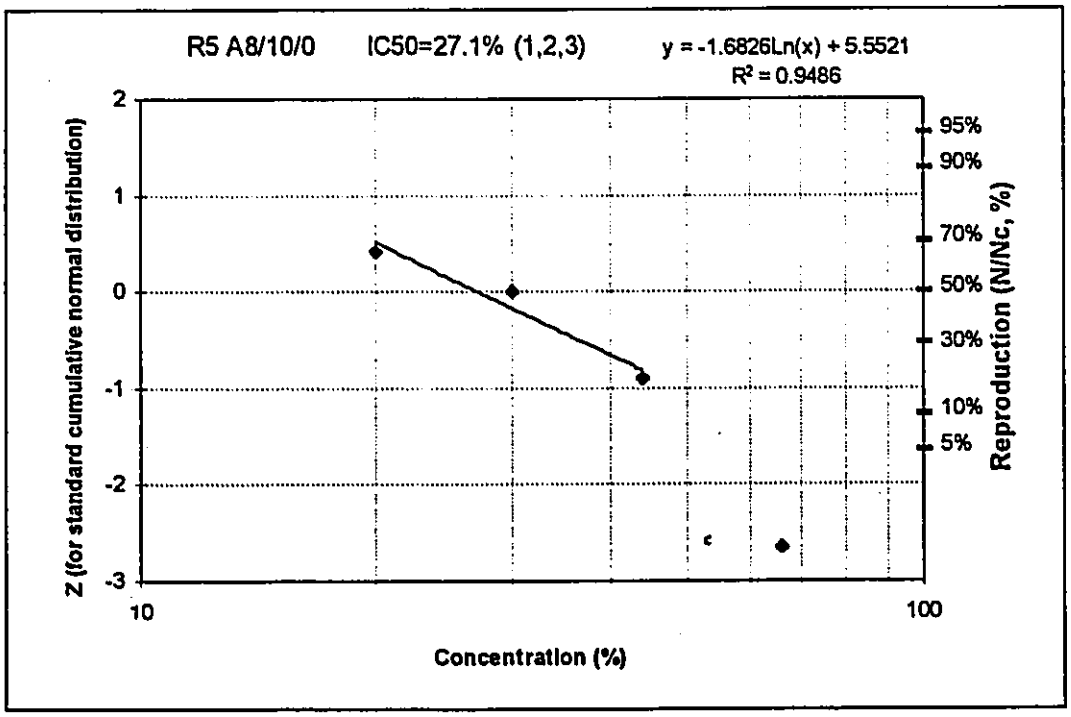
Description overleaf.../

Figure 4-26 (A, B) Probability-log (probit) plots for determining IC50 of *Ceriodaphnia* tests. (previous pg.)

Examples of two data sets which show good linearity throughout. IC50 was interpolated from the regression line shown.



(A)



(B)

Description overleaf .../

Figure 4-27 (A, B) Probability-log (probit) plots for determining IC50 of *Ceriodaphnia* chronic toxicity tests. (previous page)

Examples of two data sets that show poor linearity at the end-points. Numbers in parentheses indicate which data points were included in the regression analysis.

Despite the deviation at the extrema, the transformed plots show good linearity in the middle range, which is most important for determination of IC50s. In plots where endpoints departed from linearity, only those values close to 50% were used for interpolation. It is worth noting that both Finney (1964) and Environment Canada (1990) stress that extrema have less statistical weight and can be ignored in the analysis. The temptation to fit data to the equation must be avoided.

In order to compare whether differences in *Ceriodaphnia* toxicity were statistically significant, T-tests were performed on reproduction data at each test concentration within each batch (Table 4-10). In the analysis of batch A, which was the least toxic feed with IC50 of 35.3%, the majority of effluent toxicity levels were not significantly different. Five of the six effluent samples tested show little difference in toxicity. With the exception of R8 and R4 at 30%, toxicities in effluents from R2, R4, R5, R6 and R8 were not significantly different at any concentration tested. Feed toxicity was not significantly different from these effluents at any concentration except at 44%. One reactor effluent, R9, was noticeably less toxic than the others, particularly at higher concentrations of 66 and 100%. However this same effluent was not significantly different from the feed at lower concentrations. IC50s for this and other batches are summarized in Table 4-11 and plotted in Figure 4-28. No clear trend was observed in this batch, values were within 10% of one another. These results show that there was no appreciable difference in toxicity between control and test reactors, nor indeed between feed and reactor effluents. Batch A was the lowest strength of the four feeds, averaging about 340 mg/L SCOD. Although treatment removed roughly 70% of SCOD, effluent toxicity was equal to that of the feed,

suggesting that the wastewater components responsible for toxicity are poorly or slowly biodegradable. That is, despite approximately 240 mg/L of COD removal from the feed in each reactor, toxicity was not reduced in the effluents.

Table 4-10 Summary of *Ceriodaphnia dubia* chronic toxicity assay results[a].

Reactor		Sample Conc.	N/Nc				t-crit	Significant
R	Parameters	(%)	mean	std. dev.	n	t-stat	at 5%	at 5%
R13	C8/5/0	100	0.351	0.152	10			
R14	C8/5/0.5	100	0.070	0.044	10	5.62	2.10	Yes
R15	C8/5/1	100	0.020	0.050	9	2.35	2.11	Yes
R13	C8/5/0	66	0.895	0.280	10			
R14	C8/5/0.5	66	0.288	0.168	9	5.65	2.11	Yes
R15	C8/5/1	66	0.345	0.109	10	0.89	2.11	No
R13	C8/5/0	66	0.895	0.280	10	5.79	2.10	Yes
R13	C8/5/0	44	0.772	0.317	10			
R14	C8/5/0.5	44	0.355	0.171	9	3.51	2.11	Yes
R15	C8/5/1	44	0.455	0.077	10	1.68	2.11	No
R13	C8/5/0	44	0.772	0.317	10	3.08	2.10	Yes
R13	C8/5/0	30	1.044	0.322	10			
R14	C8/5/0.5	30	0.505	0.181	10	4.61	2.10	Yes
R15	C8/5/1	30	0.471	0.154	10	0.46	2.10	No
R13	C8/5/0	30	1.044	0.322	10	5.08	2.10	Yes
R17	D4/5/0	30	0.368	0.159	10			
R18	D4/5/0.5	30	0.181	0.249	10	2.00	2.10	No
R17	D4/5/0	20	0.098	0.190	10			
R18	D4/5/0.5	20	0.526	0.297	10	3.84	2.10	Yes
R4	A8/5/0	20	0.909	0.222	10			
R5	A8/10/0	20	0.665	0.175	9	2.65	2.11	Yes
R6	A8/15/0	20	0.712	0.314	10	0.40	2.11	No
R7	A8/5/0.1	20	0.709	0.169	10	0.03	2.10	No
R8	A8/5/0.2	20	0.665	0.168	10	0.57	2.10	No
R9	A8/10/0.1	20	0.678	0.294	9	0.11	2.11	No
	Feed A	20	0.691	0.381	9	0.08	2.12	No
R4	A8/5/0	20	0.909	0.222	10	1.54	2.11	No
R4	A8/5/0	30	0.639	0.195	10			
R5	A8/10/0	30	0.503	0.178	10	1.63	2.10	No
R6	A8/15/0	30	0.490	0.260	10	0.13	2.10	No
R7	A8/5/0.1	30	0.409	0.209	10	0.77	2.10	No
R8	A8/5/0.2	30	0.389	0.173	10	0.23	2.10	No
R9	A8/10/0.1	30	0.777	0.191	9	4.64	2.11	Yes
	Feed A	30	0.556	0.351	10	1.67	2.11	No
R4	A8/5/0	30	0.639	0.195	10	0.65	2.10	No
R8	A8/5/0.2	30	0.389	0.173	10	3.03	2.10	Yes
	Feed A	30	0.556	0.351	10	1.35	2.10	No
R9	A8/10/0.1	30	0.777	0.191	9	1.67	2.11	No
R4	A8/5/0	30	0.639	0.195	10	1.55	2.11	No

Table 4-10 continued.

Reactor		Sample Conc.	N/Nc				t-crit	Significant
R	Parameters	(%)	mean	std. dev.	n	t-stat	at 5%	at 5%
R4	A8/5/0	44	0.245	0.084	10			
R5	A8/10/0	44	0.182	0.070	10	1.81	2.10	No
R6	A8/15/0	44	0.054	0.059	10	4.38	2.10	Yes
R7	A8/5/0.1	44	0.154	0.087	10	2.97	2.10	Yes
R8	A8/5/0.2	44	0.148	0.084	10	0.15	2.10	No
R9	A8/10/0.1	44	0.523	0.133	9	7.43	2.11	Yes
Feed A		44	0.442	0.277	10	0.80	2.11	No
R4	A8/5/0	44	0.245	0.084	10	2.16	2.10	Yes
R8	A8/5/0.2	44	0.148	0.084	10	2.59	2.10	Yes
Feed A		44	0.442	0.277	10	3.22	2.10	Yes
R9	A8/10/0.1	44	0.523	0.133	9	0.80	2.11	No
R4	A8/5/0	44	0.245	0.084	10	5.50	2.11	Yes
R6	A8/15/0	44	0.054	0.059	10	5.86	2.10	Yes
Feed A		44	0.442	0.277	10	4.33	2.10	Yes
R5	A8/10/0	44	0.182	0.070	10	2.88	2.10	Yes

[a] The t-statistic shown in each row compares the reactor in that row to the one immediately above. Reactor parameters refer to feed batch, HRT (h), SRT (d) and PAC dose (g/L) respectively

Table 4-11 Summary of *Ceriodaphnia dubia* chronic toxicity assay results[a].

Reactor		*C. dubia* chronic IC50, %	
R	Parameters	Feed	Effluent
R4	A/8/5/0	35.3	33.6
R5	A/8/10/0		27.1
R6	A/8/15/0		26.1
R7	A/8/5/0.1		26.5
R8	A/8/5/0.2		25.4
R9	A/8/10/0.1		43.2
R13	C/8/5/0	9.2	59.1
R14	C/8/5/0.5		27.8
R15	C/8/5/1		38.4
R16	C/8/10/0.5		18.9[b]
R17	D/4/5/0	8.1	26.2
R18	D/4/5/0.5		20.5

[a] The IC50s were determined by interpolation of probability-log plots.
[b] R16 suffered washout. Toxicity probably not representative for operating conditions.

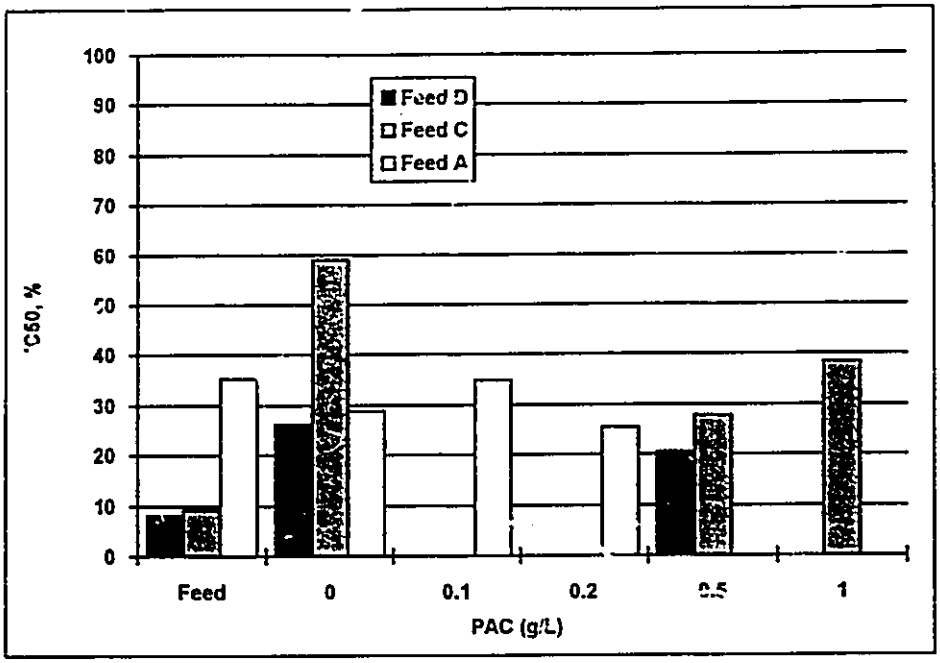


Figure 4-28 Summary of IC50s for *Ceriodaphnia* chronic toxicity assays.

Toxicity reported for control reactor (0 PAC) in batch A represents average of R4, R5 and R6. R16 is not shown.

In contrast to batch A, batches C and D showed differences in feed and effluent toxicity, but the comparison between control and PAC reactors was surprising. These feeds were considerably more toxic than A, with IC50s of 9.2 and 8.2% respectively. Both control and PAC reactors removed significant toxicity from the feed. In contrast to to feed A, this observation suggests that labile toxins are also present in the wastewater and these can be removed by biodegradation.

Considering batch C first, note that R16 effluent toxicity was high relative to the other effluents. Recall that R16 produced generally poorer quality effluent (e.g., high COD) due to washout, therefore toxicity observations are probably not representative for this reactor. Despite this, the IC50 of R16 effluent was 18.9%, still less toxic than feed. The surprising result for this batch is that the control reactor, not PAC reactors as

expected, produced the best quality effluent. PAC reactors R14 and R15, operating with 0.5 and 1.0 g/L PAC doses, respectively, produced effluents which were not significantly different from one another over the range of 30 to 60% concentration. The IC50s were at the low end of this range, 27.8 and 38.4% respectively, implying a greater difference than what the data suggest as a whole. The control reactor effluent was least toxic with an IC50 of 59.1%. Differences observed between the two test reactors with respect to the control were significant at all concentrations above 20%, and control reactor effluent toxicity was lower at all concentrations.

Results from batch D confirm the observations for C. Both the test reactor, at 0.5 g/L PAC dose, and the control reactor removed toxicity, but the control effluent was least toxic. Control effluent IC50 was 26.2%, less toxic than that for the test reactor effluent at 20.5%. As in batch C, control effluent was less toxic at all concentrations below 100%, and differences between control and test effluent at three of the four sample concentrations were statistically significant (at 20, 40 and 66%). The plot of IC50s in Figure 4-28 summarizes the observations. The data from batches C and D demonstrate that PACT™ effluents are more toxic than control effluents, as measured with *Ceriodaphnia dubia* chronic assay.

The observation that PACT™ effluents have greater toxicity seems paradoxical in light of other data. Recall that the Microtox™ results implied that treatment of highly toxic wastewater with high PAC doses of 0.5 to 1 g/L improves toxicity reduction. The SCOD data also showed that high PAC doses increase COD removal, which is known to correlate with toxicity. Despite this, PAC reactor effluents clearly showed more toxicity

towards *Ceriodaphnia*. This suggests that PAC itself may be responsible for toxicity towards *Ceriodaphnia*.

A test was conducted to assess what effects, if any, PAC alone had on *Ceriodaphnia*. Three groups of daphnids were grown and compared for reproduction, as in the standard chronic toxicity test protocol. A control group, grown in plain dilution water, was compared with groups grown in (i) the same water with 0.1 g/L PAC added and (ii) GF/C filtrate of the 0.1 g/L PAC solution prepared in (i). GF/C filter paper has a nominal pore size of 1.2 μm and is the same filter paper used to prepare effluent samples for toxicity testing. Results are shown in Figure 4-29. Differences in test groups were statistically significant. Reproduction among daphnids grown in 0.1 g/L PAC was markedly depressed, only 42% of that in the control. Additionally, microscopic examination revealed that 60% of these animals had accumulated deposits of a black material in their ventral cavities. Deposits were not observed in the controls, suggesting that the material ingested was PAC. Reproduction among animals grown in the GF/C filtrate was also significantly reduced, only 73% of the control value. Unlike the other test group, no accumulation of particles was observed in these daphnids. Further filtration of GF/C filtrate across 0.45 μm pore filters revealed that some PAC was present. It is clear from these observations that PAC has a toxic effect on *Ceriodaphnia*.

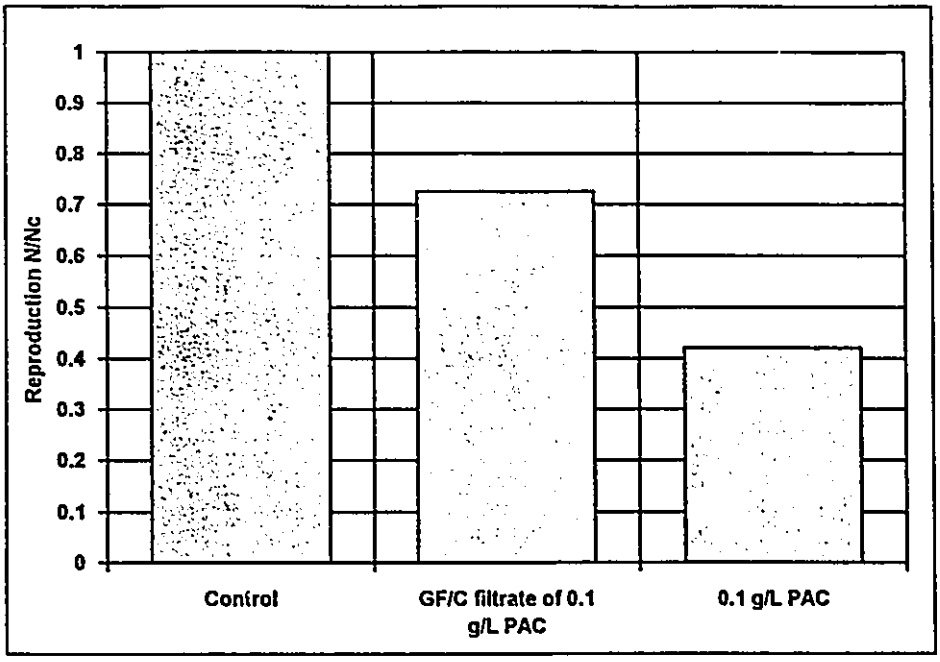


Figure 4-29 Comparison of the effects of PAC alone on *Ceriodaphnia* chronic toxicity assay. The control group was grown in plain water, the test groups in two different PAC concentrations. GF/C filters have a nominal pore size of 1.2 μm.

The data suggest that the toxicity is primarily due to direct ingestion of PAC, rather than uptake of some soluble component of PAC released into the water, because the soluble fraction is the same in each test solution, they differ only in the amount of PAC removed on the filter. Indeed, activated carbon treatment is recommended as a method of removing chlorine from tapwater used for culturing of daphnids, so it seems unlikely that soluble components of PAC are toxic. In light of the other results demonstrating PAC's improvement of effluent quality (i.e., COD, AOX, Microtox™), PACT™ may in fact reduce the soluble portion of toxicity but any beneficial effects are masked by the physical action of PAC on *Ceriodaphnia*. Further tests with smaller pore size filtrates could answer this question. But whether the mechanism which underlies PAC toxicity is physical or chemical is perhaps irrelevant. The practical significance is that GF/C filtrate represents a

better than best case scenario in terms of solids removal from effluent, a level not likely to be achieved in a clarifier, yet toxicity remained in PACT™ effluent. Tertiary filtration may be required.

4.7 Cost Analysis

Implementation of pollution control measures is both economic and legislative decision. Industry will not implement control systems unless required to do so, and then only if economically feasible. A rough but very conservative analysis of PACT™ in the present application reveals high cost. Recall that in order to reduce the operating costs it is necessary to regenerate PAC, rather than rely solely upon virgin carbon. Thermal regeneration of PAC typically results in 5 to 10% loss of carbon, and a slight decrease in adsorptive capacity compared to virgin carbon (Tchobanoglous and Burton 1991; Eckenfelder and Langford 1990). As of early 1996, the bulk price of the PAC grade used in the study (Calgon WPX) was $2.60 Canadian dollars (CAD) per kg, including taxes. The pulp mill sampled in the study had a typical wastewater flow of 70 000 m^3/d, was scheduled to operate about 350 d/yr, and produced approximately 650 ADT pulp/d during a normal day's production. Assume the best possible case of no reduction in adsorbance capacity of PAC, and only 5% losses during regeneration (i.e., 5% of the nominal dose is required as virgin PAC makeup). Treatment of this wastewater at a 1 g/L PAC dose would cost $3.185 million annually, or $14 per ADT kraft pulp. The market price for pulp is volatile and cyclical, in recent years the maximum has been in the area of $1 300 CAD/ADT. At the time of writing, March 1996, prices were in the range of $650 CAD/ADT. Note that the foregoing analysis includes only the cost of PAC, without

capital, operating, maintenance nor sludge disposal expenses. During the years 1991 through 1994, the pulp and paper sector in Canada operated at a loss (CPPA 1995b), additional expenses for pollution control would be difficult to bear. This cost is also difficult to justify in terms of the most significant benefits, namely a moderate improvement in COD and AOX removal. Current legislation does not limit discharge of COD, BOD being the regulated parameter for organic strength. The data showed that BOD removal was practically complete using standard AS, and that PACT™ did not improve BOD removal. Although AOX is regulated, the ultimate goal is complete elimination within five years, however PACT™ reduces but does not eliminate AOX. Zero AOX discharges will probably be achieved only through elimination of chlorine in the bleaching process. The utility of PACT™ treatment of pulp mill wastewater in terms of cost-benefit is poor.

4.8 General Comments

The wider, implicit purpose of this type of study is to reduce pollution from pulp and paper mills. If the wider goal is to be achieved, it may be necessary to change one's focus and attempt to solve the problem using a different approach. It may not be effective to commit resources to a narrow niche when other, fundamental changes can accomplish more. For example, AOX can be completely eliminated by halting the use of chlorine as a bleaching agent and switching to hydrogen peroxide. Bonsor et al. (1989) comment on this attitude towards the cause célèbre of dioxins and furans. They argue that time, effort and funds should not be focused on these compounds, which are present in minute quantities, when the same effort to reduce the totality of toxins in the effluent benefits the

environment more as the whole. Despite this, the MISA program remains committed to eliminating dioxins and furans to non-detectable levels. According to CPPA (1995b) the total yearly discharge of dioxins and furans from all Canadian mills was 2 *grams* in 1994. It is a laudable philosophy that toxins ought not be discharged into the environment, but is this a wise use of resources?

But one problem in choosing where to commit resources and which wastes ought to be controlled is the limited knowledge about their effects. This is especially true with the issue of toxicity. Although toxicity testing has evolved in recent years, for example, ten years ago, *toxicity* meant lethal effects, and the practical definition of *non-toxic* was "does not kill fish within 4 days". Even so-called chronic bioassays such as *Ceriodaphnia* are only seven days in length. These are simplistic and short-sighted in the context of the real environmental effects which are complex and occur over large areas and long time spans. Even ostensibly sophisticated, modern toxicity assays are *grosso modo* in comparison. But in order to render toxicity assessment as practical (economic) as possible, there is pressure to simplify testing. Both industry and government prefer simple yes or no answers. Bonsor et al. (1989) argued that it is simplistic to define effluent quality as good or bad, and that the "we need a freeze-dried, talking, fish-on-a-stick" syndrome should be avoided (ibid., quoting John Cairns, Jr.). There is also a tendency to extrapolate single results to the total environment, for example a large amount of data on correlating of various tests is available, comparing trout, daphnids, bacteria, and so on, the aim being to use a cheaper test as a proxy. But the utility of such data may be limited. That is, such proxy tests may be justified if one is testing only a single chemical, for example, effects of phenol on trout

correlated to Microtox™. But will a given correlation will hold true under different conditions or even different concentrations of the same chemical? We may need to accept the fact that ecosystems are complex, that reactions of different organisms within an ecosystem are varied, and that no single test can ever adequately reflect the totality of a pollutant's effects on an ecosystem. For a testing regime to have real value, it should at the very least try to test organisms from across representative orders, for example, fishes, invertebrates, bacteria, plants, mammals, etc. Admittedly this is expensive on an ongoing basis, and may be more suited to ad hoc assessment of the effects of a particular type of discharge, as opposed to continuous monitoring.

Another problem with toxicity monitoring is that standards are often concentration-based. McCubbin et al. (1989) argue that concentration based toxicity standards are not appropriate since the objective of effluent discharge regulation is to "protect organisms in the receiving water after dilution, not in the end of the effluent pipe". Furthermore concentration based testing " discourages technical development of certain environmentally desirable technologies, such as oxygen delignification, dry debarking and water conservation in general." A mass flow limit of toxins is a more rational approach, for example, toxicity testing normalized to 175 m^3 water/ADT pulp. Yet OME disagreed with this approach and MISA toxicity limits remain concentration-based.

Reduction of pollution is important to the pulp and paper industry, and will become more so as regulations become stricter. Awareness that environment and economy are linked is being realized. A particularly thought-provoking statement from Sinclair

(1990) embodies this philosophy, that environment is a part of the economy, not an extraneous consideration: "if environmental protection requirements are too lenient, then the environment will be unnecessarily degraded. To the degree [that] Canada's environmental laws are less stringent than similar laws in countries importing Canadian pulp and paper products, Canada will be subsidizing other countries by accepting pollution levels not tolerated in customer nations."

Wastewater treatment in the pulp and paper industry will continue to evolve, the longer term outlook sees further changes. For example, increased post consumer recycling of paper products, deinking facilities and chlorine free bleaching will change plant operations and have consequences for effluent treatment systems. The most profound changes will result from in-plant control measures that reduce or close water circuits. Indeed in the future the question of how to best treat effluent may become irrelevant (Edde 1994; Malinen et al. 1994; Myréen 1994).

CHAPTER 5

CONCLUSIONS

Lengthy HRTs are unnecessary since they do not improve treatment. In extreme cases (72 h), reactors may fail. More economical short HRTs (4 h) are adequate for full scale systems.

Activated sludge alone removes a high proportion of of CBOD (ca. 95%) irrespective of conditions, PACT™ does not improve CBOD removal.

Compared to AS, PACT™ improves SCOD removal at high PAC dose (1.0 g/L). HRT and SRT, within the ranges of 4 to 72 h and 5 to 15 d respectively, have no effect on SCOD removal by PACT™.

Increased SCOD removal occurs through increased removal of poorly/slowly biodegradable components of SCOD. Net biodegradation of SCOD is not affected by PAC.

Biodegradability of AOX is variable in kraft mill wastewaters, increasing as AOX:SCOD ratio increases.

PACT™ improves removal of AOX. PAC dose is the sole determinant of increased removal, HRT and SRT (hence MLTSS), within the ranges of 4 to 72 h and 5 to 15 d respectively, do not affect AOX removal. Biodegradation of AOX changes in response to PAC dose. PAC appears to sequester AOX, thereby reducing the amount of

AOX biodegraded with increasing PAC dose. However, more thorough examination of the process is needed to confrim this.

In most cases, Microtox™ is not sensitive enough to assess the efficiency of toxicity removal in secondary treated kraft mill effluents. AS treatment is sufficient to remove nearly all detectable Microtox™ toxicity for wastewaters of low to moderate toxicity. Compared to AS, PACT™ slightly improves treatment of highly toxic wastewaters.

Significant residual chronic toxicity towards *Ceriodaphnia dubia* remains in all effluents, irrespective of treatment type. Both AS and PACT™ remove toxicity, but PACT™ effluents are more toxic, probably due to PAC ingestion.

PAC alone shows chronic toxicity towards *Ceriodaphnia dubia*, probably due to physical ingestion of PAC particles.

The effect of PACT™ on removal of metals is inconclusive.

Considering the cost of virgin PAC makeup alone, and ignoring capital and operating costs, even in the best case, PAC treatment of kraft mill wastewater would be very expensive.

Overall, PACT™ has limited benefits over AS for the treatment of kraft mill wastewater, only slight improvements in SCOD and AOX removal, therefore PACT™ is not recommended for treatment of kraft mill wastewater.

CHAPTER 6

RECOMMENDATIONS FOR FUTURE RESEARCH

Given that PACT™ is not suitable for treatment of kraft pulp mill wastewater, an attempt should be made to assess the use of carbon as tertiary treatment. For example, using GAC columns to polish secondary (AS) effluent.

High MLTSS in PACT™ reactors is problematic at laboratory scale, therefore a better reactor design, which is less susceptible to settling problems, would simplify operation in future studies using PACT™.

Long HRTs do not appear to improve treatment, excessively long HRTs will fail, hence studies can be limited to whichever HRTs are most practical for full scale systems (e.g., 4 h).

Owing to the variability in wastewater strength, toxicity, AOX and other constituents, large, homogeneous samples should be taken to determine kinetic parameters with certainty. Smaller reactor volumes, requiring smaller sample volumes, would help to conserve samples. However, if the high variability in composition is itself typical for kraft mill wastewater, then the relevance of parameters determined from a particular sample may be questionable.

To assess toxicity removal in different treatment systems, sensitive and long term assays are needed. The temptation to assume that limited and short term toxicology assays are good indicators of their long-term environmental fate and effects is naive.

In light of increasingly strict legislation for kraft mill discharges, the best approach to reduce pollution will lie with in-plant controls and process modifications (e.g., AOX can only be eliminated by replacement of chlorine bleaching). Systems such as PACT™ and AS greatly improve the quality of effluent discharges and represent the state of the art. But in the long term they are stop-gap measures. The ultimate goal for all industries should be not only reduction but elimination of pollution.

APPENDIX A: Addresses/contacts for Supplies

Calgon Carbon Corporation: PO Box 717, Pittsburgh, PA 15230-0717, USA, Tel. 1-800-4CARBON.

James MacLaren Inc.: Industries James MacLaren Inc., Division de la pâte kraft, C.P. 400, Thurso, Québec, J0X 3B0, Tel. (819) 985-2233.

Microbics Corporation: 2232 Rutherford Rd., Carlsbad, CA 92008-8883 USA, Tel. 1-800-642-7629.

Outaouais Urban Community: Communauté urbain de l'Outaouais, Usine d'épuration régionale, 858 av. Notre Dame, Gatineau, Québec, Tel. (819) 663-5585

PAPRICAN (Pulp and Paper Research Institute of Canada): 570 Boul. St. Jean, Pointe Claire, Québec, H9R 3J9, Canada, Tel. (514) 630-4100.

Plastics Inc.: St. Paul, MN 55164, USA.

Saalfeld Paper Co.: 4510 Reading Rd., Cincinnati, OH 45229, USA Tel. (513) 641-5000.

Seprotech Laboratories: 2378 Holly Lane, Ottawa, Ontario, K1V 7P1, Canada, Tel. (613) 731-0851.

University of Toronto Culture Collection: Dept. of Botany, Univ. of Toronto, Toronto, Ontario M5S 1A4, Canada, Tel. (416) 978-3641.

APPENDIX B: Reactor Data

Only data for the *analyzed days* portion of reactor runs have been included. *Flow* refers the volume of feed delivered daily to reactors. Note that the time of day (*time*) when flow measurements were taken was not necessarily the same each day, therefore the volumes listed under *flow* should not be understood to represent flowrate per 24 h. Elapsed time must be considered. *Discards* refers to the volume of *ML* removed from the CM zone to maintain the desired SRT. *Discards effluent* represents the throughput (*flow*) less the volume of effluent returned to the CM zone (i.e., to replace *discards ML*.) Both *Solids* and *COD* measurements were typically two or three day composites, without exception indicated by identical values over two or three days respectively. The prefixes *Eff*, *ML*, and *F* refer to effluent, mixed liquor and feed respectively. The calculation of *moving average SRT* is described in the Experimental Approach chapter. Suffixes *T* and *S* in the context of COD measurements refer to total and soluble respectively.

Table B1

R	run days	Flow (mL)	time (24h)	DISCARDS effluent (mL)	DISCARDS ML (mL)	SOLIDS EffTSS (mg/L)	SOLIDS MLTSS (mg/L)	SOLIDS MLVSS (mg/L)	SOLIDS MLVSS/ MLTSS	SOLIDS FTSS (mg/L)	SOLIDS FVSS (mg/L)	TSS Loss (mg)	Moving Average SRT (days)	COD FT (mg/L)	COD FS (mg/L)	COD ES (mg/L)	COD %Removal (ESvsFS)	Notes
1	20	1700	1600	920	780	60	468	368	0.79			420	5.13			350		
1	21	1620	1510	840	780	60	468	368	0.79			415	5.30			350		
1	22	2025	1800	1175	850	118	388	326	0.84			468	4.98	692	572	350	39	
1	23	4775	1550	3925	850	118	388	326	0.84			793	4.16	692	572	350	39	
1	24	2257		1578	679								4.08					
1	25	2018		1446	572								3.71		457	256	44	
1	26	1406		834	572								3.08		457	256	44	
1	27	1910		1338	572	140	296	230	0.78			357	2.97		539	273	49	
1	28	1066		363	703	140	296	230	0.78			259	4.81		539	273	49	
1	29	1344		641	703								4.81					
1	30	1774		1071	703	31	214	152	0.71			184	5.04		539	289	46	
1	31	1566		863	703	31	214	152	0.71			177	5.22		539	289	46	
1	32	1319		821	498								5.84					
1	33	1072		574	498								5.93					
1	34	826		265	561	160	228	230	1.01			170	6.18	856	547.2			
1	35	1064		194	870	160	228	230	1.01			229	5.81	856	547.2			
1	36	1301		486	815								5.70					
1	37	1567		682	885	90	480	416	0.87			486	5.28	640	588.8			
1	38	1832		947	885	90	480	416	0.87			510	5.07		588.8			
1	39	1827		942	885								4.85					
1	40	1822		1178	644	93	502					433	5.12					
1	41	1816		1172	644								5.12					
1	42	1811		1167	644	93	502					432	5.40					
1	43	1885		1241	644								5.81					
2	27	3930	1500	3650	280	17	424	412	0.97			181	3.93		567			
2	28	4950	1600	4650	300	11	470					192	6.34	487	507	153	70	
2	29	4750	1600	4450	300	34							6.34					
2	30	5130	1730	4830	300	10	670					249	7.27	812	732	133	82	
2	31	5480	2030	5180	300	34							7.27					
2	32	3800	1400	3350	450	24	492					302	7.70	492	452	197	56	
2	33	5940	1800	5720	220	34							7.70					
2	34				0								7.81					
2	35	4170	1030	3595	575	27	584	518	0.89			433	7.58					
2	36	5790	1600	5290	500	33	820	690	0.84			585	8.91	522	492	197	60	
2	37	4480	1530	4170	310	18	864	778	0.90			343	9.27	542	432	165	62	
2	38	4240	1500	3900	340	64	938	833	0.89			568	8.81					

Table B1 continued

R	run days	Flow (mL)	time (24h)	DISCARDS effluent (mL)	DISCARDS ML (mL)	SOLIDS EffTSS (mg/L)	SOLIDS MLTSS (mg/L)	SOLIDS MLVSS (mg/L)	SOLIDS MLVSS/ MLTSS	SOLIDS FTSS (mg/L)	SOLIDS FVSS (mg/L)	TSS Loss (mg)	Moving Average SRT (days)	COD FT (mg/L)	COD FS (mg/L)	COD ES (mg/L)	COD %Removal (ESvsFS)	Notes
2	39	5090	1630	4780	310	60	670					495	8.47	982	898	237	74	
2	40	5040	1530	4730	310	64	938	833	0.89			593	8.00					
3	30	6150	1730	6100	50	25	1170					211	10.60	812	732	101	86	
3	31	4635	2030	4155	480	32							11.31					
3	32	3600	1400	3340	260	22	1278					406	12.27	492	452	165	63	
3	33	5650	1800	5370	280	32							13.09					
3	34				0								13.09					
3	35	4090	1030	3630	460	83	962	856	0.89			744	11.63					
3	36	6130	1600	6080	50	113	1146	1178	1.03			744	10.90	522	492	149	70	
3	37	4680	1530	4630	50	54	994	874	0.88			300	11.45	542	432	149	65	
3	38	4670	1500	4670	0	73	1440	1450	1.01			341	12.15					
3	39	5260	1630	5210	50	78	1240					468	12.55	982	898	53	94	
3	40	4900	1530	4900	0	73	1440	1450	1.01			358	13.11					
4	33	14422		13612	810	37	2032	1801	0.89	27	low	2152	5.11	354	289	142	51	
4	34	15362		14552	810	37	2032	1801	0.89	27	low	2186	5.04	354	289	142	51	
4	35	16080		15270	810	37	2032	1801	0.89	27	low	2213	4.90	354	289	142	51	
4	36	12712		11962	750	47	1805			36	low	1912	4.81	236	258	98	62	
4	37	11452		10702	750	47	1805			36	low	1853	4.70	236	258	98	62	
4	38	16460		15710	750	47	1805			36	low	2087	4.62	236	258	98	62	cleaned feed tubes
4	39	23030		22380	650	18	2055	1843	0.90	37	36	1741	4.85	260	271	102	62	
4	40	17530		16880	650	18	2055	1843	0.90	37	36	1641	5.16	260	271	102	62	
4	41	15400		14750	650	18	2055	1843	0.90	37	36	1602	5.48	260	271	102	62	
4	42	16570		15690	880	35	1824	1637	0.90	34	33	2151	5.31	433	498	107	79	
4	43	13540		12660	880	35	1824	1637	0.90	34	33	2045	5.34	433	498	107	79	
4	44	19170		18290	880	35	1824	1637	0.90	34	33	2241	4.95	433	498	107	79	
4	45	15980		15230	750	28	1665	1497	0.90	39	37	1670	4.73	386	328	120	63	
4	46	13710		12960	750	28	1665	1497	0.90	39	37	1607	4.53	386	328	120	63	
4	47	17770		17020	750	28	1665	1497	0.90	39	37	1719	4.66	386	328	120	63	
4	48	16240		15490	750	24	1588	1456	0.92			1567	4.78	605	417			
4	49	14320		13540	780	17	1779	1596	0.90			1613	5.11	605	417	113	73	
4	50	14510		13730	780	17	1779	1596	0.90			1616	5.22	605	417	113	73	
4	51	13740		12960	780	17	1779	1596	0.90			1603	5.29			113		
5	33	14800		14400	400	68	3531	3128	0.89	27	low	2393	8.73	354	289	91	69	
5	34	14840		14440	400	68	3531	3128	0.89	27	low	2396	8.48	354	289	91	69	
5	35	16210		15810	400	68	3531	3128	0.89	27	low	2489	8.01	354	289	91	69	
5	36	16010		15790	220	119	3032			36		2539	7.46	236	258	88	66	

Table B1 continued

R	run days	Flow (mL)	time (24h)	DISCARDS effluent (mL)	DISCARDS ML (mL)	SOLIDS EffTSS (mg/L)	SOLIDS MLTSS (mg/L)	SOLIDS MLVSS (mg/L)	SOLIDS MLVSS/ MLTSS	SOLIDS FTSS (mg/L)	SOLIDS FVSS (mg/L)	TSS Loss (mg)	Moving Average SRT (days)	COD FT (mg/L)	COD FS (mg/L)	COD ES (mg/L)	COD %Removal (ESvsFS)	Notes
5	37	12370		12150	220	119	3032			36		2108	7.68	236	258	88	66	
5	38	16270		16050	220	119	3032			36		2570	7.70	236	258	88	66	
5	39	14900		14875	25	118	2569	2292	0.89	37	36	1814	8.00	260	271	98	64	dirty effluent, diffuser misplaced
5	40	15700		15675	25	118	2569	2292	0.89	37	36	1908	7.59	260	271	98	64	
5	41	15870		15845	25	118	2569	2292	0.89	37	36	1928	7.18	260	271	98	64	
5	42	16090		16065	25	24	3112	2771	0.89	34	33	460	7.40	433	498	141	72	
5	43	14780		14755	25	24	3112	2771	0.89	34	33	429	8.07	433	498	141	72	
5	44	17020		16995	25	24	3112	2771	0.89	34	33	482	8.87	433	498	141	72	
5	45	16340		15940	400	25	3291	2976	0.90	39	37	1711	9.23	386	328	93	72	
5	46	13430		13030	400	25	3291	2976	0.90	39	37	1639	9.86	386	328	93	72	
5	47	18246		17846	400	25	3291	2976	0.90	39	37	1758	10.19	386	328	93	72	
5	48	16550		16150	400	43	3020	2740	0.91			1900	10.67	605	417			
5	49	14410		14010	400	41	2939	2625	0.89			1749	10.85	605	417	124	70	
5	50	14370		13970	400	41	2939	2625	0.89			1748	11.11	605	417	124	70	
5	51	13740		13340	400	41	2939	2625	0.89			1722	11.41			124		Run ends
6	55	14520		14340	180	76	4488	3891	0.87	27	low	1894	14.65	370	333			
6	56	14730		14650	80	77	3441	3019	0.88	27	low	1398	14.46	354	289	154	47	
6	57	14460		14380	80	77	3441	3019	0.88	27	low	1378	14.34	354	289	154	47	
6	58	16350		16270	80	77	3441	3019	0.88	27	low	1523	14.16	354	289	154	47	
6	59	16080		16055	25	48	3075			36	low	841	13.90	236	258	85	67	
6	60	12360		12335	25	48	3075			36	low	664	13.70	236	258	85	67	
6	61	16310		16285	25	48	3075			36	low	852	13.41	236	258	85	67	
6	62	14940		14840	100	24	3552	3131	0.88	37	36	709	13.49	260	271	104	62	
6	63	15290		15190	100	24	3552	3131	0.88	37	36	717	13.93	260	271	104	62	
6	64	15600		15500	100	24	3552	3131	0.88	37	36	724	14.34	260	271	104	62	
6	65	15160		14920	240	17	3541	3079	0.87	34	33	1106	14.60	433	498	145	71	
6	66	14950		14710	240	17	3541	3079	0.87	34	33	1102	14.82	433	498	145	71	
6	67	16710		16470	240	17	3541	3079	0.87	34	33	1132	15.08	433	498	145	71	
6	68	15980		15710	270	22	3397	2975	0.88	39	37	1261	15.37	386	328	120	63	
6	69	13300		13030	270	22	3397	2975	0.88	39	37	1203	15.79	386	328	120	63	
6	70	18373		18103	270	22	3397	2975	0.88	39	37	1314	16.02	386	328	120	63	
6	71	16630		16360	270	11	3572	3176	0.89			1151	16.31	605	417			
6	72	14380		14140	240	17	3765	3308	0.88			1146	16.66	605	417	91	78	
6	73	14320		14080	240	17	3765	3308	0.88			1145	17.19	605	417	91	78	
6	74	13750		13510	240	17	3765	3308	0.88			1135	17.08			91	78	
7	17	15555		14655	900	44	3772	3431	0.91	27	low	4037	4.82	354	289	91	69	

Table B1 continued

R	run days	Flow (mL)	time (24h)	DISCARDS effluent (mL)	DISCARDS ML (mL)	SOLIDS EffTSS (mg/L)	SOLIDS MLTSS (mg/L)	SOLIDS MLVSS (mg/L)	SOLIDS MLVSS/ MLTSS	SOLIDS FTSS (mg/L)	SOLIDS FVSS (mg/L)	TSS Loss (mg)	Moving Average SRT (days)	COD FT (mg/L)	COD FS (mg/L)	COD ES (mg/L)	COD %Removal (ESvsFS)	Notes
7	18	15065		14165	900	44	3772	3431	0.91	27	low	4015	4.85	354	289	91	69	
7	19	15885		14985	900	44	3772	3431	0.91	27	low	4051	4.79	354	289	91	69	
7	20	10645		9795	850	32	3213			36	low	3044	4.84	236	258	132	49	
7	21	9595		8745	850	32	3213			36	low	3010	4.89	236	258	132	49	
7	22	11305		10455	850	32	3213			36	low	3065	5.00	236	258	132	49	cleaned feed tubes
7	23	26245		25375	870	13	4349	3976	0.91	37	36	4122	5.14	260	271	110	59	
7	24	21725		20855	870	13	4349	3976	0.91	37	36	4062	5.30	260	271	110	59	
7	25	19375		18505	870	13	4349	3976	0.91	37	36	4031	5.32	260	271	110	59	
7	26	15735		14775	960	12	4063	3705	0.91	34	33	4083	5.25	433	498	129	74	
7	27	14455		13495	960	12	4063	3705	0.91	34	33	4067	5.20	433	498	129	74	
7	28	16945		15985	960	12	4063	3705	0.91	34	33	4098	5.13	433	498	129	74	
7	29	16215		15255	960	17	3775	3413	0.90	39	37	3878	5.04	386	328	74	77	
7	30	12615		11655	960	17	3775	3413	0.90	39	37	3818	4.95	386	328	74	77	
7	31	17869		16909	960	17	3775	3413	0.90	39	37	3905	4.92	386	328	74	77	
7	32	15965		15005	960	13	3960	3660	0.92			3995	4.91	605	417			
7	33	14785		13845	940	10	3504	3195	0.91			3432	4.94	605	417	87	79	
7	34	12695		11755	940	10	3504	3195	0.91			3411	4.99	605	417	87	79	
7	35	15275		14335	940	10	3504	3195	0.91			3437	5.02			87	79	
8	14	18205		17325	880	26	5955	5437	0.91	27	low	5694	5.52	370	333	128	62	
8	15	15605		14725	880	26	5955	5437	0.91	27	low	5626	5.81	370	333	128	62	
8	16	15255		14375	880	26	5955	5437	0.91	27	low	5617	5.65	370	333	128	62	
8	17	14335		13395	940	48	5484	5059	0.92	27	low	5799	5.32	354	289	142	51	
8	18	15895		14955	940	48	5484	5059	0.92	27	low	5874	5.04	354	289	142	51	
8	19	15915		14975	940	48	5484	5059	0.92	27	low	5875	4.93	354	289	142	51	
8	20	16335		15455	880	47	5376			36	low	5459	4.85	236	258	79	69	
8	21	9715		8835	880	47	5376			36	low	5147	4.83	236	258	79	69	
8	22	20325		19445	880	47	5376			36	low	5648	4.84	236	258	79	69	cleaned feed tubes
8	23	12865		11985	880	42	5449	5029	0.92	37	36	5298	4.93	260	271	62	77	
8	24	17565		16685	880	42	5449	5029	0.92	37	36	5495	5.00	260	271	62	77	
8	25	14305		13425	880	42	5449	5029	0.92	37	36	5358	5.03	260	271	62	77	
8	26	16255		15355	900	41	5376	4945	0.92	34	33	5475	4.97	433	498			
8	27	12975		12075	900	41	5376	4945	0.92	34	33	5339	5.03	433	498			
8	28	18895		17995	900	41	5376	4945	0.92	34	33	5584	4.96	433	498			
8	29	14605		13705	900	37	4976	4575	0.92	39	37	4987	4.96	386	328	88	73	
8	30	14615		13715	900	37	4976	4575	0.92	39	37	4988	4.94	386	328	88	73	
8	31	ND?			900	37	4976	4575	0.92	39	37	4478	5.06	386	328	88	73	

Table B1 continued

R	run days	Flow (mL)	time (24h)	DISCARDS effluent (mL)	DISCARDS ML (mL)	SOLIDS EffTSS (mg/L)	SOLIDS MLTSS (mg/L)	SOLIDS MLVSS (mg/L)	SOLIDS MLVSS/ MLTSS	SOLIDS FTSS (mg/L)	SOLIDS FVSS (mg/L)	TSS Loss (mg)	Moving Average SRT (days)	COD FT (mg/L)	COD FS (mg/L)	COD ES (mg/L)	COD %Removal (ESvsFS)	Notes
8	32	16105		15205	900	47	5176	4792	0.93			5375	5.01	605	417	136	67	
8	33	13775		12875	900	43	5352	4920	0.92			5369	5.05	605	417	88	79	
8	34	14865		13965	900	43	5352	4920	0.92			5415	5.04	605	417	88	79	
8	35	14935		14035	900	43	5352	4920	0.92			5418	5.03			88	79	
9	33	14060		13670	390	102	6881	6308	0.92	27	low	4083	9.46	354	289	129	55	cloudy effluent
9	34	14320		13930	390	102	6881	6308	0.92	27	low	4110	9.26	354	289	129	55	
9	35	16160		15770	390	102	6881	6308	0.92	27	low	4298	9.04	354	289	129	55	
9	36	12850		12560	290	121	5899			36	low	3236	8.91	236	258	82	68	
9	37	11245		10955	290	121	5899			36	low	3041	9.06	236	258	82	68	
9	38	14300		14010	290	121	5899			36	low	3412	9.11	236	258	82	68	feed tubes blocked! all tubes flushed out
9	39	20560		20360	200	100	5661	5236	0.92	37	36	3178	9.28	260	271	110	59	
9	40	16540		16340	200	100	5661	5236	0.92	37	36	2774	9.21	260	271	110	59	clarifier OK but effluent still cloudy MYSTERY!
9	41	15770		15570	200	100	5661	5236	0.92	37	36	2697	9.17	260	271	110	59	
9	42	16040		15800	240	94	4975	4589	0.92	34	33	2684	9.00	433	498	132	73	
9	43	14600		14360	240	94	4975	4589	0.92	34	33	2548	9.13	433	498	132	73	
9	44	16860		16620	240	94	4975	4589	0.92	34	33	2761	9.22	433	498	132	73	
9	45	16350		16130	220	77	4975	4607	0.93	39	37	2331	9.52	386	328	129	61	
9	46	13510		13290	220	77	4975	4607	0.93	39	37	2113	9.74	386	328	129	61	
9	47	18358		18138	220	77	4975	4607	0.93	39	37	2485	9.77	386	328	129	61	
9	48	15900		15680	220	74	5208	4892	0.94			2311	10.05	605	417			
9	49	14300		14080	220	70	5423	5020	0.93			2179	10.41	605	417	129	69	
9	50	14060		13840	220	70	5423	5020	0.93			2162	10.62	605	417	129	69	
9	51	13250		13030	220	70	5423	5020	0.93			2105	10.84			129	69	
10	50	5655		4748	907	136	5926	5632	0.95			6021	5.08		550	104	81	
10	51	5052		4116	936	136	5926	5632	0.95			6107	4.89		550	104	81	
10	52	4789		3853	936								4.89					
10	53	5378		4442	936	191	5722	5474	0.96			6204	4.79		574	108	81	
10	54	4674		3738	936	191	5722	5474	0.96			6070	4.77		574	108	81	
10	55	4880		4217	663								4.73					
10	56	5086		4423	663								4.66					
10	57	5292		4235	1057	118	5528	5306	0.96			6343	4.56	856	547.2	87	84	
10	58	4901		3743	1158	118	5528	5306	0.96			6843	4.36	856	547.2	87	84	
10	59	4510		3719	791								4.19					
10	60	4318		3382	936	169	5534	5100	0.92			5751	4.38	640	588.8	106	82	

Table B1 continued

R	run days	Flow (mL)	time (24h)	DISCARDS effluent (mL)	DISCARDS ML (mL)	SOLIDS EffTSS (mg/L)	SOLIDS MLTSS (mg/L)	SOLIDS MLVSS (mg/L)	SOLIDS MLVSS/ MLTSS	SOLIDS FTSS (mg/L)	SOLIDS FVSS (mg/L)	TSS Loss (mg)	Moving Average SRT (days)	COD FT (mg/L)	COD FS (mg/L)	COD ES (mg/L)	COD %Removal (ESvsFS)	Notes
10	61	4126		3190	936	169	5534	5100	0.92			5719	4.49		588.8	106	82	
10	62	4737		3801	936								4.53					
10	63	5347		4494	853	238	5398					5672	4.80		566	93	84	
10	64	4953		4100	853								4.80			93		
10	65	4559		3706	853	238	5398					5485	4.84		566			
10	66	4165		3312	853								4.84					
10	67	5286		4135	951								4.84					
10	68	3305		2376	929	344	6466					6823	4.82		531.2	134.4	75	
10	69	5015		4085	930	344	6466			104		7417	4.65		531.2	134.4	75	
10	70	5955		5233	722	92	6402			104		5104	5.00		544	137.6	75	
10	71	5705		4969	736	90	6597	5990	0.91	66	47	5303	5.26			137.6		
10	72	5515		4580	935	90	6597	5990	0.91	66	47	6580	5.21		608	137.6	77	
10	73	4345		3410	935	90	6597	5990	0.91	66	47	6475	5.29		608	137.6	77	Finished run
11	36	5985	1600	5535	450	67	15068	14876	0.99			7151	10.87	522	492	85	83	
11	37	4735	1530	4475	260	118	14820	13986	0.94			4381	12.67	542	432	61	86	
11	38	4865	1500	4384	481	138	12438	11733	0.94			6587	12.05					
11	39	5315	1630	4835	480	96	12744					6581	11.50	982	898	117	87	
11	40	4765	1530	4285	480	138	12438	11733	0.94			6561	11.22					
11	41	ND				138	12438	11733	0.94				11.52					
11	42	5365	1600	4895	470	153	8234	7760	0.94			4619	10.65	1032	852	115	87	
11	43	4945	1600	4475	470	222	8932	8248	0.92			5191	10.43			162		
11	44	4795	1440	4325	470	222	8932	8248	0.92			5158	10.25			162		
11	45	4215	1740	3810	405	457	18230	16716	0.92			9124	10.10	692	572	130	77	
11	46	1620	1530	1215	405	457	18230	16716	0.92			7938	10.21	692	572	130	77	
11	47	5459		5031	428								9.67					
11	48	5192		4832	360								9.70		398	78	80	
11	49	5112		4752	360								9.71		398	78	80	
11	50	5470		5110	360	308	18038	16936	0.94			8068	9.94		550	136	75	
11	51	4995		4525	470.4	308	18038	16936	0.94			9879	9.87		550	136	75	
11	52	4650		4180	470.4								9.97					
11	53	5435		4965	470.4	123	13320	12800	0.96			6876	10.07		574	168	71	
11	54	4696		4226	470.4	123	13320	12800	0.96			6785	10.19		574	168	71	
11	55	4939		4606	333								10.23					
11	56	5183		4850	333								9.92					
11	57	5426		4895	531	268	9646	8914	0.92			6434	9.51	856	547.2	163	70	
11	58	5002		4420	582	268	9646	8914	0.92			6798	9.14	856	547.2	163	70	

Table B1continued

R	run days	Flow (mL)	time (24h)	DISCARDS effluent (mL)	DISCARDS ML (mL)	SOLIDS EffTSS (mg/L)	SOLIDS MLTSS (mg/L)	SOLIDS MLVSS (mg/L)	SOLIDS MLVSS/ MLTSS	SOLIDS FTSS (mg/L)	SOLIDS FVSS (mg/L)	TSS Loss (mg)	Moving Average SRT (days)	COD FT (mg/L)	COD FS (mg/L)	COD ES (mg/L)	COD %Removal (ESvsFS)	Notes
11	59	4577		4157	420								9.14					
11	60	4523		4086	437	261	8942	8302	0.93			4974	8.73	640	588.8	224	62	
11	61	4469		4032	437	261	8942	8302	0.93			4960	8.66		588.8	224	62	
11	62	4998		4561	437								8.66					
11	63	5526		5124	402	163	9012					4455	8.65		566	147	74	
11	64	5026		4624	402								8.36					
11	65	4527		4125	402	163	9012					4293	8.65		566	147	74	
11	66	4027		3625	402								8.65					
11	67	3440		2992	448								8.94					
11	68	3245		2789	456	45	11356					5303	9.85		531.2	150.4	72	
11	69	5065		4615	450	45	11356			104		5316	10.00		531.2	150.4	72	
11	70	5909		5430	479	54	9574			104		4879	10.14		544	128	76	
11	71	5645		5165	480	45	9540	8684	0.91	66	47	4812	10.30			147.2		
11	72	5125		4651	474	45	9540	8684	0.91	66	47	4731	10.27		608	147.2	76	
11	73	4705		4225	480	45	9540	8684	0.91	66	47	4769	10.25		608	147.2	76	Finished run
12	50	6117		5974	143	244	15782	14984	0.95			3714	14.57		539	85	84	
12	51	5038		4788	250.4	244	15782	14984	0.95			5120	15.52		539	85	84	
12	52	4873		4623	250.4								15.66					
12	53	5408		5158	250.4	208	15844	15146	0.96			5040	15.85		539	77	86	
12	54	4692		4442	250.4	208	15844	15146	0.96			4891	16.92		539	77	86	
12	55	4941		4764	177								17.83					
12	56	5189		5012	177								18.87					
12	57	5437		5166	271	348	16372	15246	0.93			6235	17.02	856	547	73.6	87	
12	58	4983		4686	297	348	16372	15246	0.93			6493	15.30	856	547	73.6	87	
12	59	4529		4281	248								14.08					
12	60	4657		4657	0	297	15400	14308	0.93			1382	15.92	640	589	105.6	82	
12	61	4785		4785	0								16.94		589		100	
12	62	5563		5563	0								16.94					
12	63	6341		6057	284	18						296	16.89					
12	64	5546		5262	284								16.89					
12	65	4751		4467	284	18						267	16.30					
12	66	4342		4058	284													
13	24	17443	21:15	17102	341	79	1513					1867	6.02			288		
13	25	12764	17:48	12423	341	79	1513					1497	5.81			288		
13	26	12680	14:15	12339	341	79	1513					1491	5.45	452	314	288	8	
13	27	16290	16:05	16050	240	84	2164			25		1868	5.24	412	432	253	41	

Table B1continued

R	run days	Flow (mL)	time (24h)	DISCARDS effluent (mL)	DISCARDS ML (mL)	SOLIDS EffTSS (mg/L)	SOLIDS MLTSS (mg/L)	SOLIDS MLVSS (mg/L)	SOLIDS MLVSS/ MLTSS	SOLIDS FTSS (mg/L)	SOLIDS FVSS (mg/L)	TSS Loss (mg)	Moving Average SRT (days)	COD FT (mg/L)	COD FS (mg/L)	COD ES (mg/L)	COD %Removal (ESvsFS)	Notes
13	28	13436	13:29	13196	240	84	2164			25		1628	5.31	412	432	253	41	
13	29	15600	15:00	15360	240	84	2164			25		1810	5.74	412	432	253	41	
13	30	15710	15:30	15260	450	55	2023			30		1750	5.87	482	352	157	55	CM solids weak, effluent dark
13	31	17696	19:30	17246	450	55	2023			30		1859	5.91	482	352	157	55	CM solids weak, effluent dark
13	32	16579	21:26	16129	450	55	2023			30		1797	5.88	482	352	157	55	
13	33	12210	16:26	11580	630	63	2272					2161	5.60					
13	34	15290	15:57	14660	630	63	2272					2355	5.35					
13	35	19050	19:41	18420	630	63	2272					2592	5.05		572			
13	36	15440	22:29	14810	630	28	2155					1772	5.15		812	261	68	
13	37	18068	20:15	17438	630	28	2155					1846	5.19		571	261	54	
13	38	18373	19:43	17772	601	28	2155					1793	5.31		532	261	51	Runout
13	39	17772	19:09	17171	601	108	2668					3458	4.98			261		
13	40	11082	12:46	10481	601	108	2668					2735	5.08					
13	41	16691	15:24	16282	409	85	2572					2436	4.98					
13	42	14542	14:41	14133	409	85	2572					2253	4.98					
13	43	15644	16:11	15122	522	114	3164					3376	4.78		715	229	68	
13	44	13375	13:54	12853	522	114	3164					3117	5.08			229		Feed pH 8.4 acidified with H3PO4 to 6.58
13	45	16980	17:27	16503	477	26	3260					1984	5.59					
13	46	15620	18:49	15143	477	26	3260					1949	6.08		789			
13	47	14005	17:36	13528	477	17	3562					1929	6.64		800	157	80	
13	48	14623	17:26	13736	887	17	3562					3393	6.79		981	157	84	
13	49	15522	18:59	14635	887	17	3552					3399	6.79		981	232	76	
13	50	12456	15:27	11523	933	17	3552					3510	6.17		427	232	46	
13	51	16533	17:01	15600	933	22	3084					3221	5.60		427	141	67	
13	52	16491	18:35	15558	933	22	3084					3220	5.03		597	141	76	
13	53	14088	17:22	13155	933	22	3084					3167	4.95		597	141	76	
13	54	16903	19:07	15970	933		2822					2633	4.96		528	160	70	
13	55	14133	16:51	13234	899		2822					2537	5.04		528	160	70	
13	56	16519	20:38	15620	899													
13	57																	
14	26	12895	14:50	12083	812	165	9407	8939	0.95			9632	5.19	452	314	93		
14	27	16715	16:20	15955	760	150	9236	8727	0.94	25		9413	4.96	412	432			
14	28	13685	13:54	12925	760	150	9236	8727	0.94	25		8958	4.87	412	432			
14	29	16275	15:38	15515	760	150	9236	8727	0.94	25		9347	4.96	412	432			
14	30	15745	15:45	14965	780	70	11480	10837	0.94	30		10002	5.13	482	352	157	55	

Table B1continued

- R	run days	Flow (mL)	time (24h)	DISCARDS effluent (mL)	DISCARDS ML (mL)	SOLIDS EffTSS (mg/L)	SOLIDS MLTSS (mg/L)	SOLIDS MLVSS (mg/L)	SOLIDS MLVSS/ MLTSS	SOLIDS FTSS (mg/L)	SOLIDS FVSS (mg/L)	TSS Loss (mg)	Moving Average SRT (days)	COD FT (mg/L)	COD FS (mg/L)	COD ES (mg/L)	COD %Removal (ESvsFS)	Notes
14	31	17440	19:39	16660	780	70	11480	10837	0.94	30		10121	5.30	482	352	157	55	
14	32	16304	21:37	15524	780	70	11480	10837	0.94	30		10041	5.46	482	352	157	55	
14	33	12165	16:37	11245	920	37	13460					12799	5.46					
14	34	14805	16:14	13885	920	37	13460					12897	5.49					
14	35	14341	19:57	13421	920	37	13460					12880	5.39		572			Tubing clogged
14	36	5656	22:46	4736	920	41	11761					11014	5.33		812	125	85	
14	37	15155	20:37	14235	920	41	11761					11404	5.24		571	125	78	
14	38	13047	20:08	12086	961	41	11761					11798	5.18		532	125	77	Runout
14	39	14359	19:26	13398	961	34	11834					11828	5.14			117		
14	40	10605	12:59	9644	961	34	11834					11700	5.10					
14	41	16312	15:50	15352	960	34	10780					10871	5.03					
14	42	13805	14:57	12845	960	34	10780					10786	5.00					
14	43	16266	16:26	15310	956	76	12024					12659	4.95		714	147	79	
14	44	13020	14:10	12064	956	76	12024					12412	4.92			147		
14	45	16069	17:43	15158	911	27	12416					11720	4.96					
14	46	15053	19:13	14142	911	27	12416					11693	5.03		789			
14	47	14041	17:52	13130	911	30	10884					10309	5.08		800	120	85	
14	48	15523	17:46	14554	969	30	10884					10983	5.13		981	120	88	
14	49	15935	19:17	14966	969	40	10306					10585	5.15		981	192	80	
14	50	12909	15:54	11948	961	40	10306					10382	5.08		427	192	55	
14	51	16645	17:19	15684	961	46	11140					11427	4.98		427	107	75	
14	52	15288	18:49	14343	945	46	11140					11187	4.93		597	107	82	
14	53	14084	17:37	13139	945	46	11140					11132	4.94		597	107	82	
14	54	16711	19:15	15766	945		10655					10069	5.02		528	107	80	
14	55	14140	16:53	13198	942		10665					10046	5.08		528	107	80	
14	56	16505	20:41	15563	942													
14	57	11623	19:43	11623														
15	30	15370	15:53	14480	890	91	20741			30		19777	5.03	482	352	77	78	
15	31	17213	19:14	16323	890	91	20741			30		19945	5.10	482	352	77	78	
15	32	16308	21:09	15418	890	91	20741			30		19863	5.15	482	352	77	78	
15	33	12770	16:45	11830	940	62	18677					18290	5.15					
15	34	15870	16:25	14930	940	62	18677					18482	5.17					
15	35	14876	20:07	13936	940	62	18677					18420	5.13		572			Tubing clogged
15	36	9243	23:05	8303	940	53	18279					17622	5.13		812	77	91	
15	37	11611	20:46	10671	940	53	18279					17748	5.11		571	77	87	
15	38	12374	20:20	11421	953	53	18279					18025	5.10		532	77	86	Runout

Table B1continued

R	run days	Flow (mL)	time (24h)	DISCARDS effluent (mL)	DISCARDS ML (mL)	SOLIDS EffTSS (mg/L)	SOLIDS MLTSS (mg/L)	SOLIDS MLVSS (mg/L)	SOLIDS MLVSS/ MLTSS	SOLIDS FTSS (mg/L)	SOLIDS FVSS (mg/L)	TSS Loss (mg)	Moving Average SRT (days)	COD FT (mg/L)	COD FS (mg/L)	COD ES (mg/L)	COD %Removal (ESvsFS)	Notes
15	39	12166	19:33	11213	953	60	18990					18770	5.11			69		
15	40	10900	13:04	9947	953	60	18990					18694	5.11					
15	41	17324	15:59	16368	956	96	18120					18894	5.03					
15	42	14655	15:04	13699	956	96	18120					18638	4.97					
15	43	16344	16:36	15419	925	244	18942					21284	4.84		714	53	93	
15	44	13574	14:20	12649	925	244	18942					20608	4.75			53		
15	45	17025	17:52	16208	817	107	18996					17254	4.82					
15	46	15594	19:24	14777	817	107	18996					17101	4.95		789			
15	47	14251	18:03	13434	817	78	14928					13244	5.07		800	75	91	
15	48	15269	17:56	14349	920	78	14928					14853	5.22		981	75	92	
15	49	15974	19:25	15054	920	92	10440					10990	5.33		981	123	87	
15	50	13382	16:06	12449	933	92	10440					10886	5.20		427	123	71	
15	51	16071	16:46	15138	933	134	18459					19251	5.00		427	53	88	
15	52	14285	18:57	13409	876	134	18459					17967	4.92		597	53	91	
15	53	12402	17:44	11526	876	134	18459					17715	4.96		597	53	91	
15	54	16572	19:25	15696	876		18678					16362	5.14		528	53	90	
15	55	14174	16:54	13276	898		18678					16773	5.26		528	53	90	
15	56	16836	20:42	15938	898													
15	57	13720	19:28	13720														
16	24	17385	21:29	17059	326	177	16713					8468	12.36			100		
16	25	11325	18:11	10999	326	177	16713					7395	12.68			100		
16	26	10740	14:20	10414	326	177	16713					7292	12.54	452	314	100	68	Pump gear slipped
16	27	17170	16:12	16820	350	147	17793			25		8700	12.39	412	432	85	80	
16	28	13997	13:49	13647	350	147	17793			25		8234	12.08	412	432	85	80	
16	29	16610	15:20	16260	350	147	17793			25		8618	11.82	412	432	85	80	
16	30	15140	15:37	14760	380	90	18827			30		8483	11.74	482	352	125	64	
16	31	16968	19:39	16588	380	90	18827			30		8647	11.43	482	352	125	64	
16	32	15921	21:32	15541	380	90	18827			30		8553	11.06	482	352	125	64	
16	33	11720	16:30	11290	430	80	21363					10089	10.73					
16	34	14550	16:03	14120	430	80	21363					10316	10.77					Tubing clogged
16	35	16320	19:48	15890	430	80	21363					10457	10.66		572			
16	36	12751	22:38	12321	430	70	22029					10335	10.60		812	133	84	
16	37	11159	20:25	10729	430	70	22029					10224	10.65		571	133	77	
16	38	12885	19:52	12440	445	70	22029					10674	10.60		532	133	75	Runout
16	39	15437	19:15	14992	445	50	23936					11401	10.62					
16	40	10750	12:53	10305	445	50	23936					11167	10.59					

Table B1continued

R	run days	Flow (mL)	time (24h)	DISCARDS effluent (mL)	DISCARDS ML (mL)	SOLIDS EffTSS (mg/L)	SOLIDS MLTSS (mg/L)	SOLIDS MLVSS (mg/L)	SOLIDS MLVSS/ MLTSS	SOLIDS FTSS (mg/L)	SOLIDS FVSS (mg/L)	TSS Loss (mg)	Moving Average SRT (days)	COD FT (mg/L)	COD FS (mg/L)	COD ES (mg/L)	COD %Removal (ESvsFS)	Notes
16	41	15992	15:30	15522	470	36	23518					11612	10.51					
16	42	12940	14:48	12470	470	36	23518					11502	10.44					
16	43	17198	16:18	16720	478	136	22016					12798	10.22		714	125	82	
16	44	14383	14:03	13905	478	136	22016					12415	10.05			125		
16	45	16860	17:35	16450	410	91	24258					11443	10.09					
16	46	15342	19:03	14932	410	91	24258					11305	10.11		789			
16	47	14050	17:46	13640	410	82	22148					10199	10.11		800	93	88	
16	48	14876	17:38	14431	445	82	22148					11039	10.09		981	93	91	
16	49	15220	19:08	14775	445	63	21242					10384	10.06		981	173	82	
16	50	12058	15:45	11612	446	63	21242					10205	10.02		427	173	59	
16	51	17093	17:09	16647	446	120	21697					11675	9.94		427	99	77	
16	52	16110	18:40	15653	457	120	21697					11794	9.83		597	99	83	
16	53	14260	17:30	13803	457	120	21697					11572	9.93		597	99	83	
16	54	16253	19:09	15796	457		21290					9730	10.14		528	107	80	
16	55	14284	16:52	13865	419		21290					8921	10.24		528	107	80	
16	56	16343	20:40	15724	619		22670					14033	9.91					Forgot that BG already sampled 200mL
16	57	13728	19:18	13728			22670											
17	12	29720	16:20	29100	620	93	4920	4442	0.90	26		5757	4.54	881	713	240	66	
17	13	31820	17:20	31200	620	93	4920	4442	0.90	26		5952	4.36	881	713	240	66	Lengthened intake
17	14	32860	17:50	32410	450	38	5188	4710	0.91	21		3582	4.56	863	469	420	10	Adjusted pump
17	15	27710	16:15	27260	450	38	5188	4710	0.91	21		3384	5.13	863	469	420	10	
17	16	29640	16:05	28850	790	52	5432	4960	0.91	25		5777	5.24	872	769	480	38	
17	17	25950	14:40	25160	790	52	5432	4960	0.91	25		5587	5.39	872	769	480	38	Adjusted pump
17	18	32780	18:35	32050	730	25	5034	4584	0.91	28		4476	5.76	806	581	218	63	Adjusted pump
17	19	26000	17:10	25270	730	25	5034	4584	0.91	28		4307	5.55	806	581	218	63	Adjusted pump
17	20	27780	16:20	26920	860	33	4892	4476	0.91	35		5095	5.12	1088	900	323	64	Adjusted pump
17	21	25200	13:10	24340	860	33	4892	4476	0.91	35		5010	5.17	1088	900	323	64	Adjusted pump
17	22	40200	21:06	39390	810	57	5362	4934	0.92	82		6588	4.95	1078	938	443	53	
17	23	25100	20:25	24290	810	57	5362	4934	0.92	82		5728	4.78	1078	938	443	53	Runout. Adjust pump to make up
17	24	38830	18:17	38170	660	76	4768	4436	0.93	41		6029	4.44	1078	1040	425	59	
17	25	11130	16:40	10910	220	241	4240	3892	0.92	38		3557	4.57	1059	975	360	63	Pump stalled
17	26	29270	16:20	28570	700	45	4676	4328	0.93			4545	4.61	1022	947	300	68	
17	27	29550	16:10	29290	260	115	4620	4664	1.01	28		4570	4.84	1013	956	300	69	
17	28	29400	17:50	29400		60	4640					1764	5.61			311		SVI 510mL from 1L in 30 min in 1L cylinder

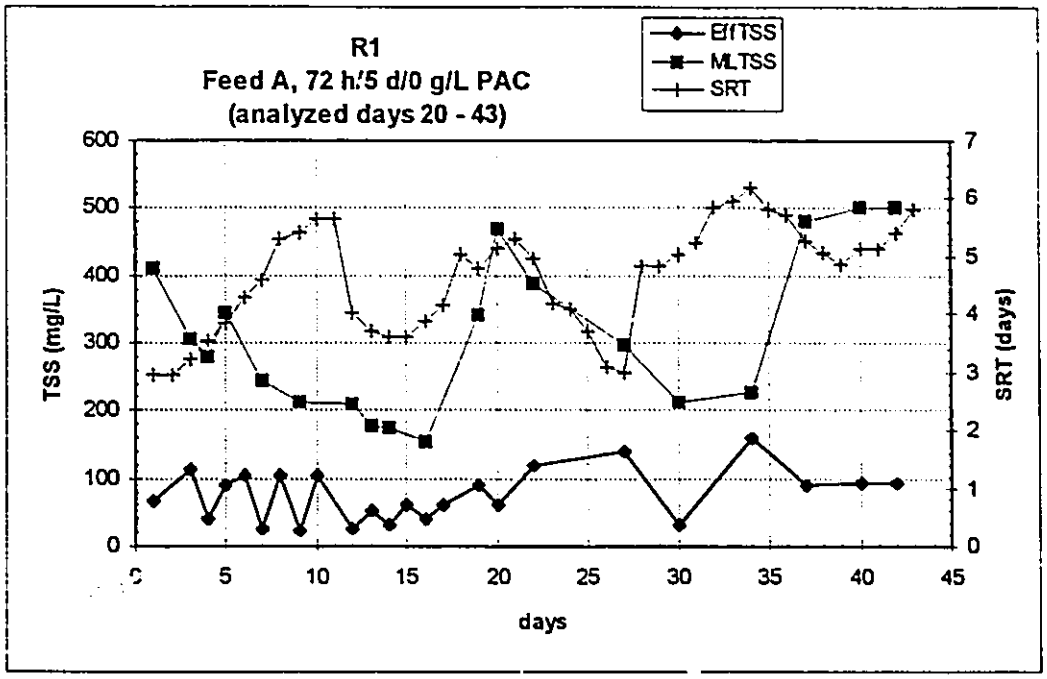
Table B1continued

R	run days	Flow (mL)	time (24h)	DISCARDS effluent (mL)	DISCARDS ML (mL)	SOLIDS EffTSS (mg/L)	SOLIDS MLTSS (mg/L)	SOLIDS MLVSS (mg/L)	SOLIDS MLVSS/ MLTSS	SOLIDS FTSS (mg/L)	SOLIDS FVSS (mg/L)	TSS Loss (mg)	Moving Average SRT (days)	COD FT (mg/L)	COD FS (mg/L)	COD ES (mg/L)	COD %Removal (ESvsFS)	Notes
18	12	29110	15:50	28240	870	120	25230	23372	0.93	26		25325	5.10	881	713	158	78	
18	13	32240	17:10	31370	870	120	25230	23372	0.93	26		25699	5.01	881	713	158	78	
18	14	30990	17:40	30120	870	79	24928	23062	0.93	21		24067	4.98	863	469	135	71	
18	15	27650	16:05	26780	870	79	24928	23062	0.93	21		23803	5.05	863	469	135	71	
18	16	28610	15:55	27700	910	70	25608	23602	0.92	25		25242	5.07	872	769	188	76	
18	17	30640	14:30	29730	910	70	25608	23602	0.92	25		25384	5.08	872	769	188	76	
18	18	37920	18:20	37000	920	79	23516	21754	0.93	28		24558	5.06	806	581	97	83	
18	19	30740	18:05	29820	920	79	23516	21754	0.93	28		23991	5.01	806	581	97	83	
18	20	31270	16:05	30365	905	50	22318	20654	0.93	35		21701	4.99	1088	900	120	87	
18	21	28100	13:05	27195	905	50	22318	20654	0.93	35		21544	5.00	1088	900	120	87	
18	22	43847	21:14	42907	940	96	20844	19422	0.93	82		23712	4.87	1078	938	195	79	
18	23	29000	21:00	28060	940	96	20844	19422	0.93	82		22287	4.85	1078	938	195	79	
18	24	28070	18:00	27200	870	181	21072	19600	0.93	41		23242	4.77	1078	1040	202	81	
18	25	28970	16:25	28100	870	134	20014	18586	0.93	38		21178	4.69	1059	975	225	77	
18	26	27990	16:05	27190	800	129	20012	18568	0.93			19504	4.68	1022	947	210	78	
18	27	26910	15:50	26070	840	108	20420	18932	0.93	28		19968	4.82	1013	956	221	77	
18	28	35480	17:40	35480		105	18734									247		SVI 1000mL to 190mL in 30 min in 1 L cylinder

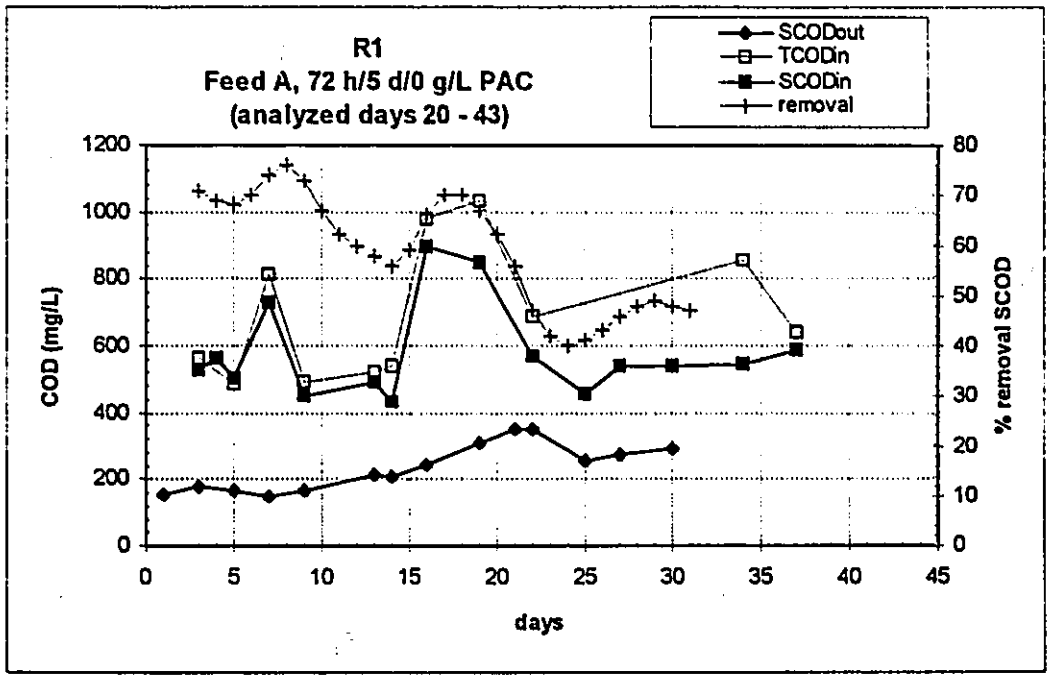
APPENDIX C: Reactor Runs

This Appendix contains graphs of the time courses of solids and COD performance for each of the 18 reactor runs in the study. Each of the four different batches of feed is identified by A, B, C and D. Each reactor run is given a unique number from R1 to R18. Graphs indicate operating conditions according to feed batch (A, B, C or D), HRT (h), SRT (d) and PAC dose (g/L), respectively. For reactors where two feed types are shown, the letter in parenthesis indicates which batch was used to start the run. However, all reactors in a given feed group received the same feed during that portion of the run which was analyzed for determining average COD and solids values. Day zero is the point where the reactor operation began. The portion of the run used for these analyses is also indicated (e.g., days 20 to 43 for R1). Single data points for COD and solids usually represent the values of composite samples taken over 2 or 3 d. Refer to Appendix B for details of the daily measurements.

As noted previously, the choice of which portion of the run to include in the analyses was based mainly on stability of MLTSS and whether the SRT calculated from the observed solids levels was close to the target nominal value, that is, the portion of the run which was as close to a steady sate as possible. The analyzed portion of the run also had to include sufficient COD measurements.

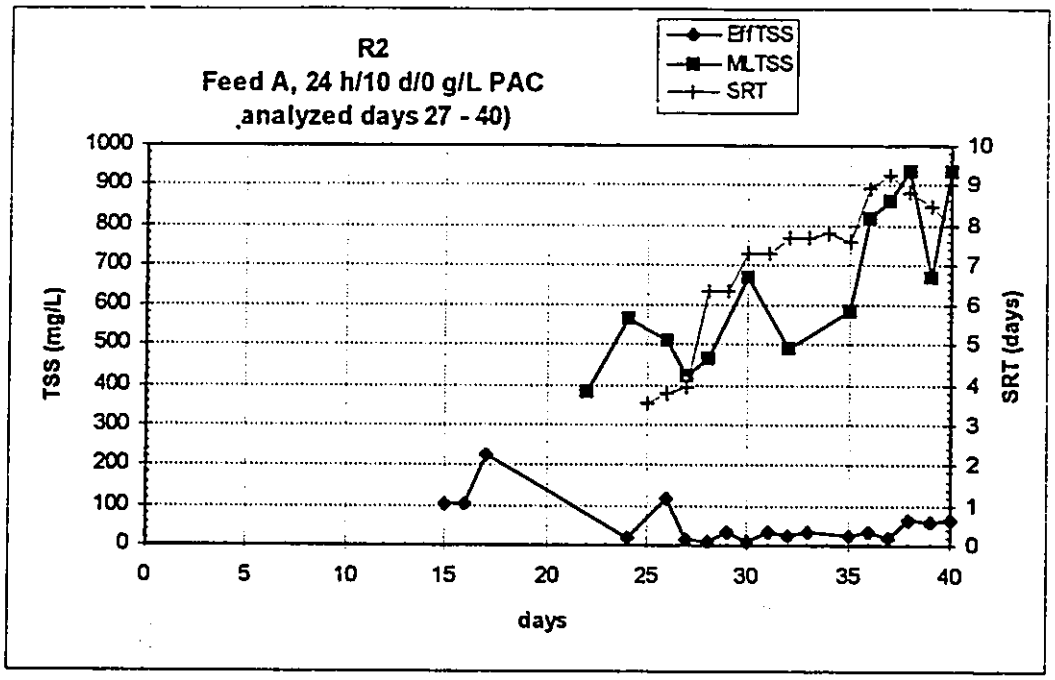


(A)

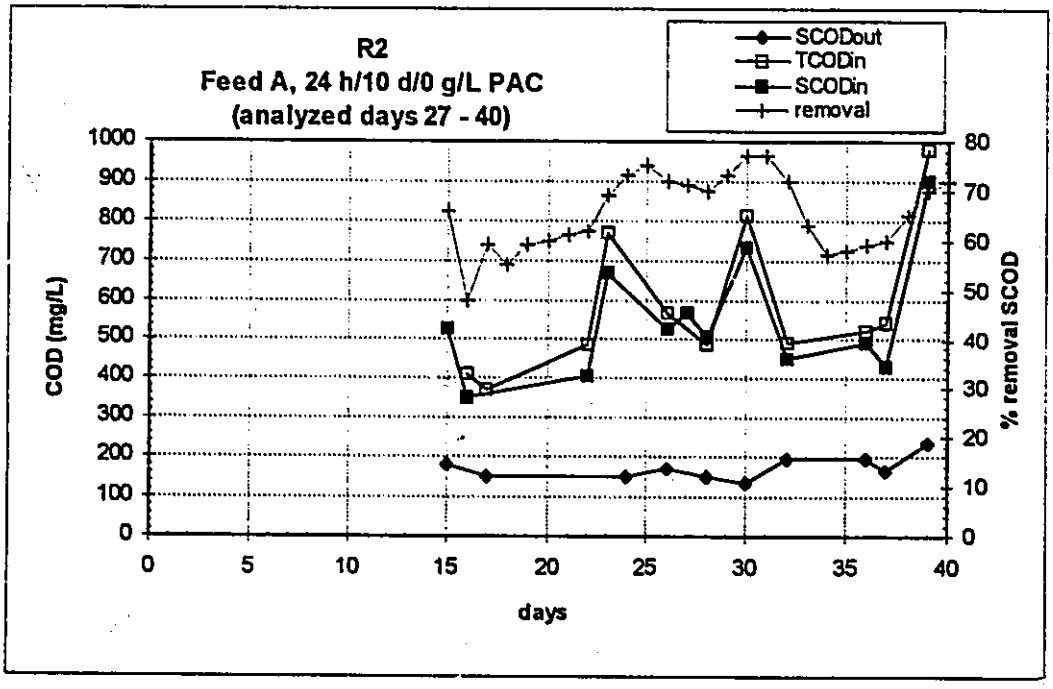


(B)

Figure C-1 Reactor performance (A) solids, (B) COD removal.

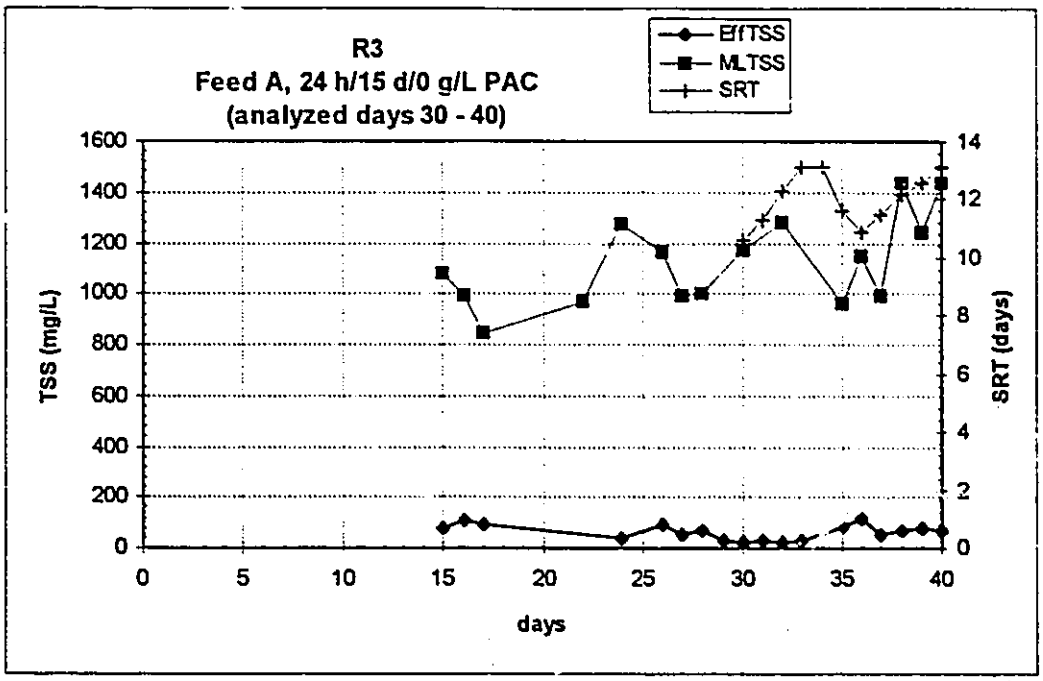


(A)

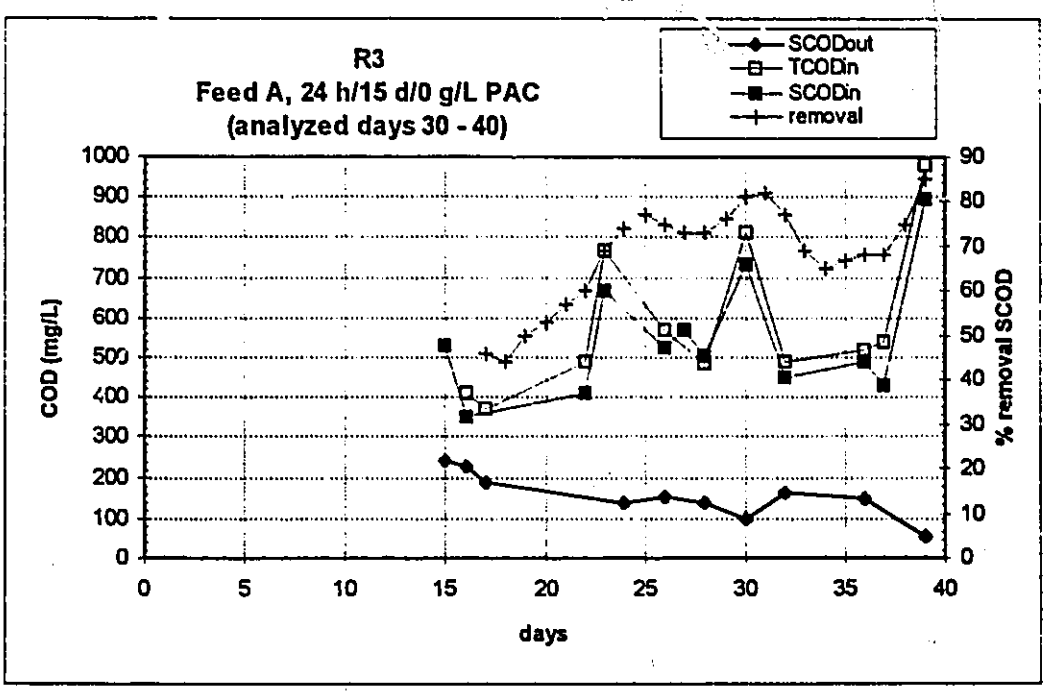


(B)

Figure C-2 Reactor performance (A) solids, (B) COD removal.

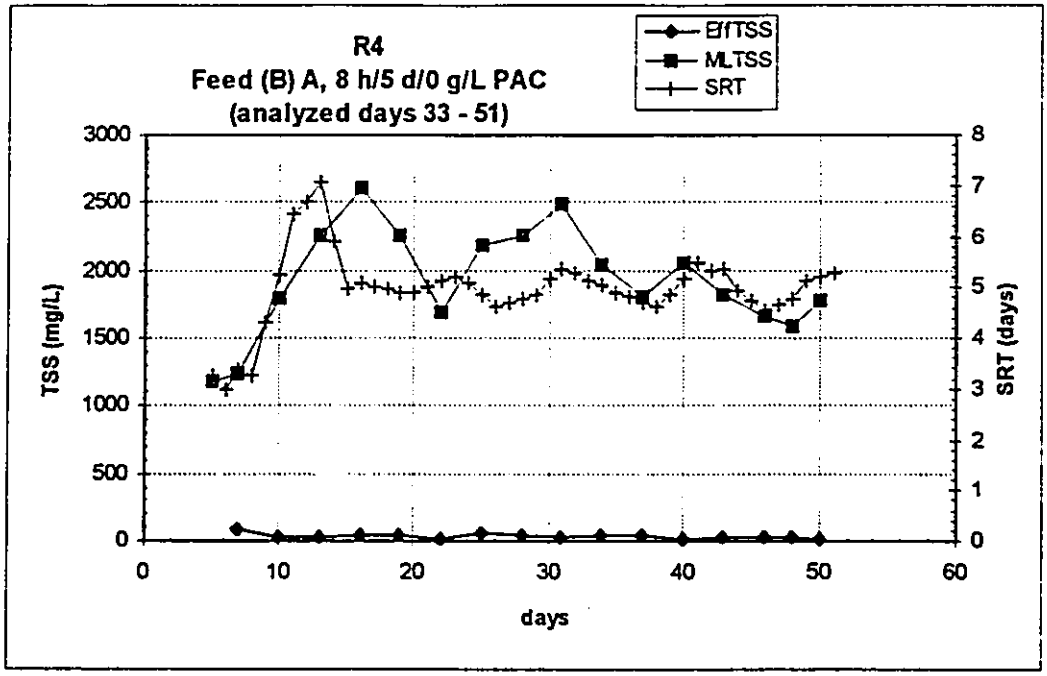


(A)

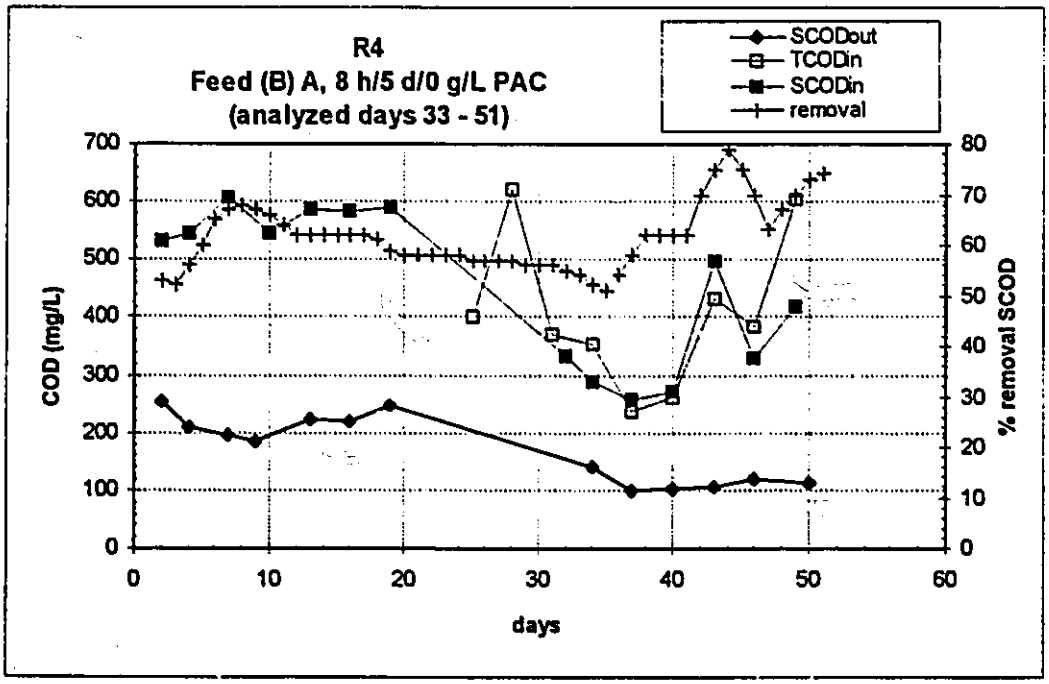


(B)

Figure C-3 Reactor performance (A) solids, (B) COD removal.

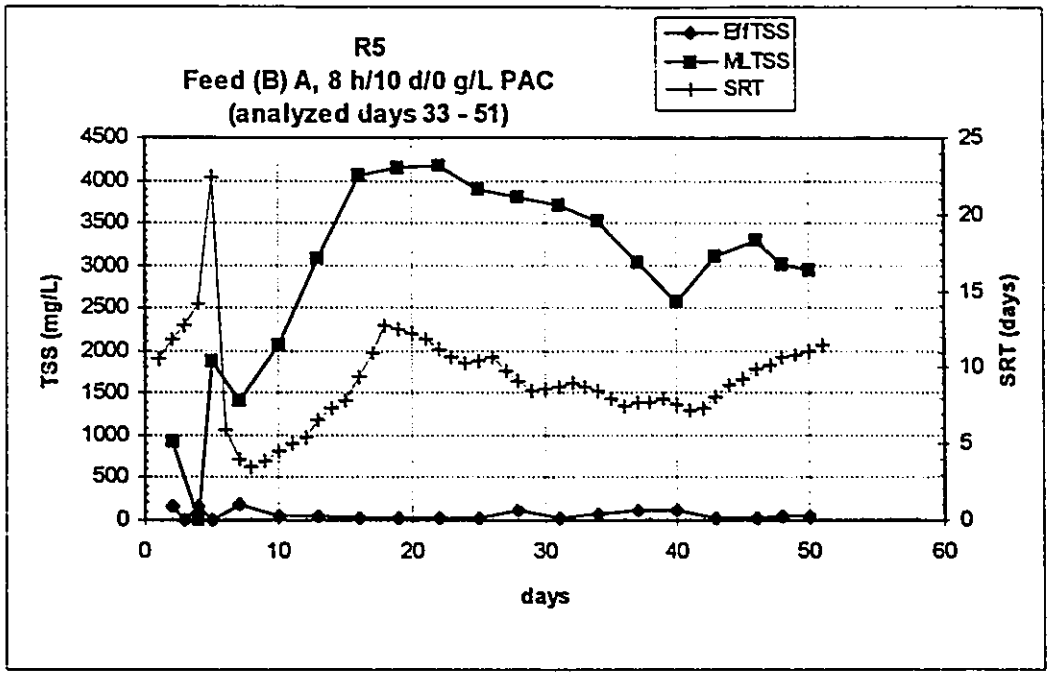


(A)

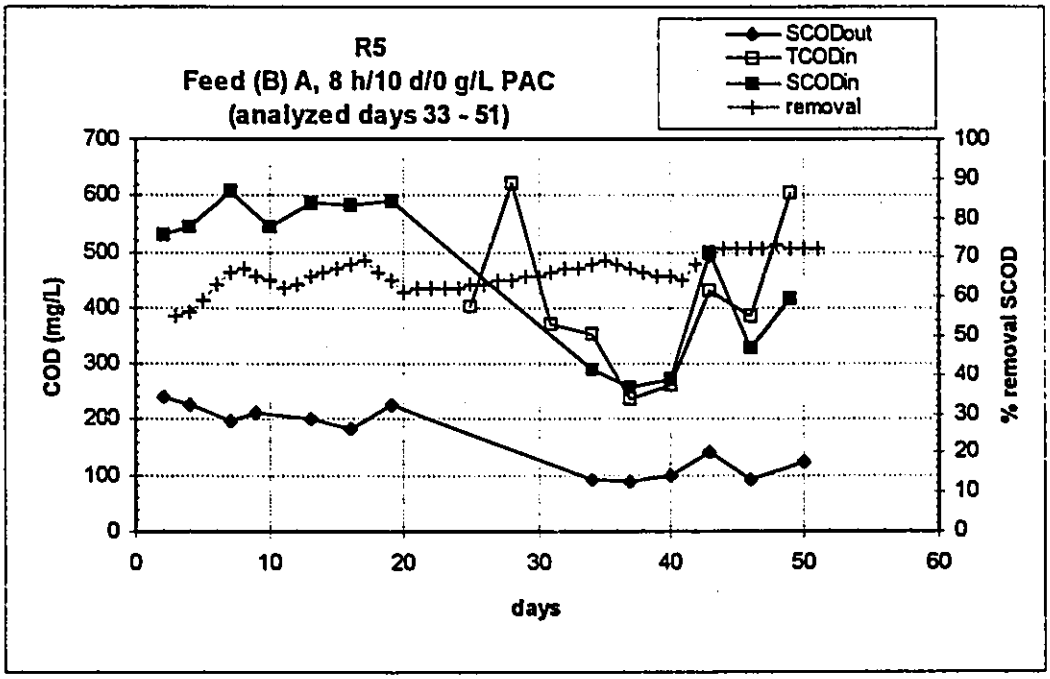


(B)

Figure C-4 Reactor performance (A) solids, (B) COD removal.

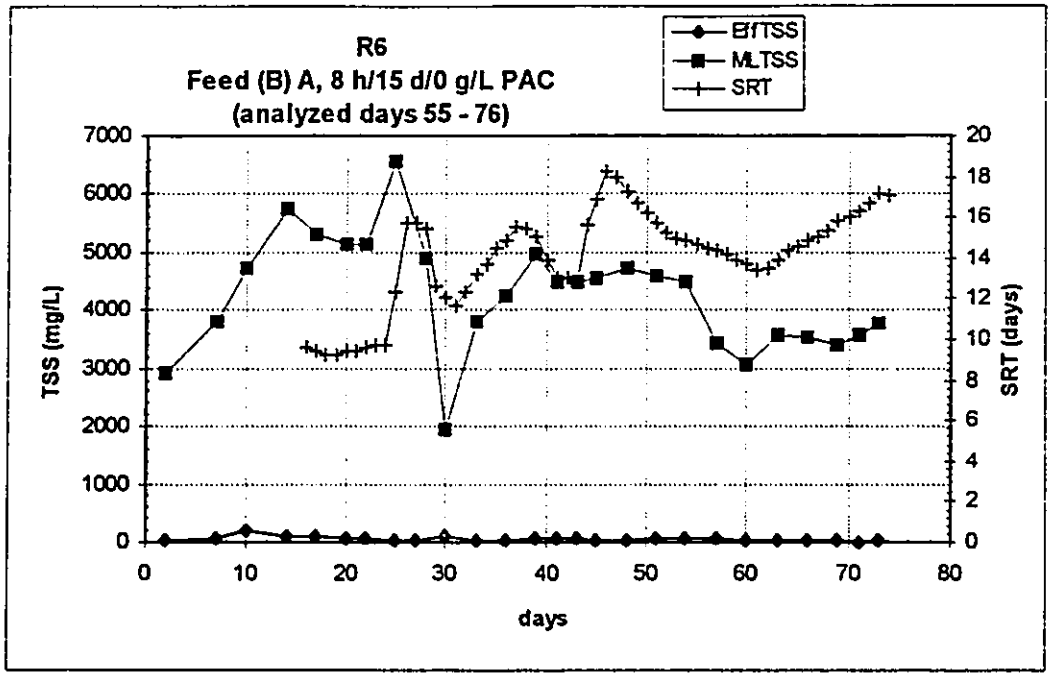


(A)

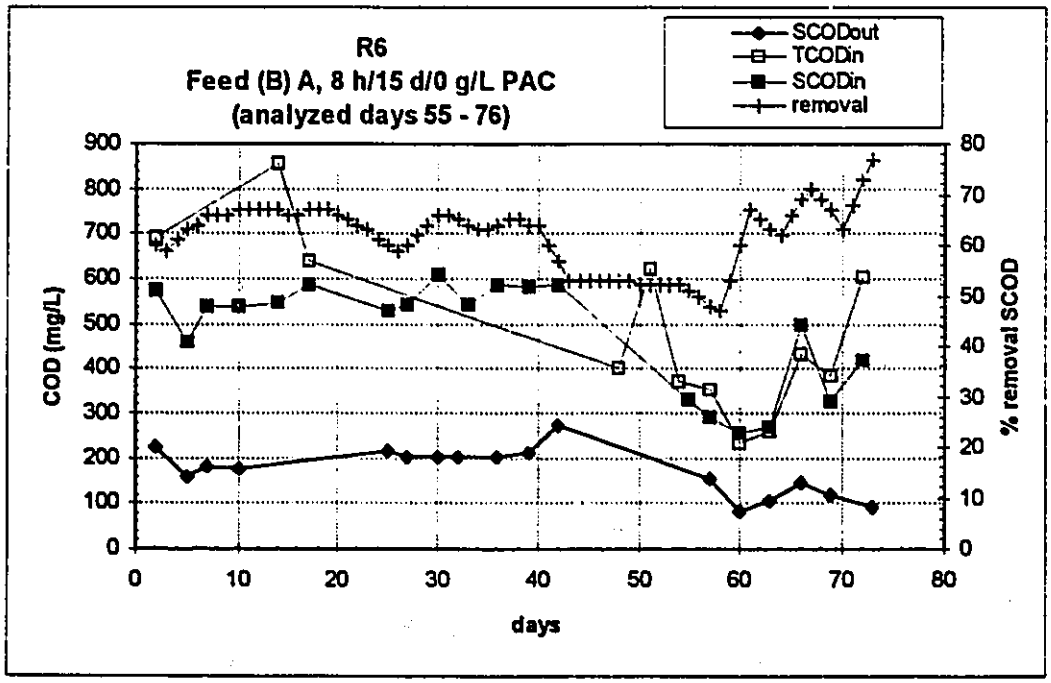


(B)

Figure C-5 Reactor performance (A) solids, (B) COD removal.

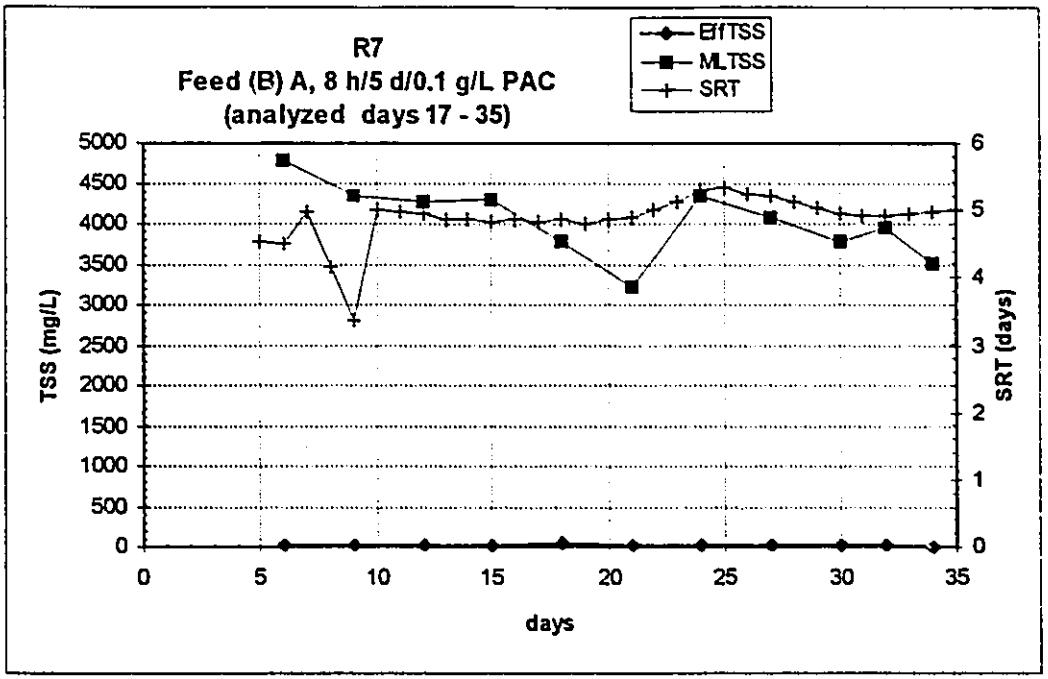


(A)

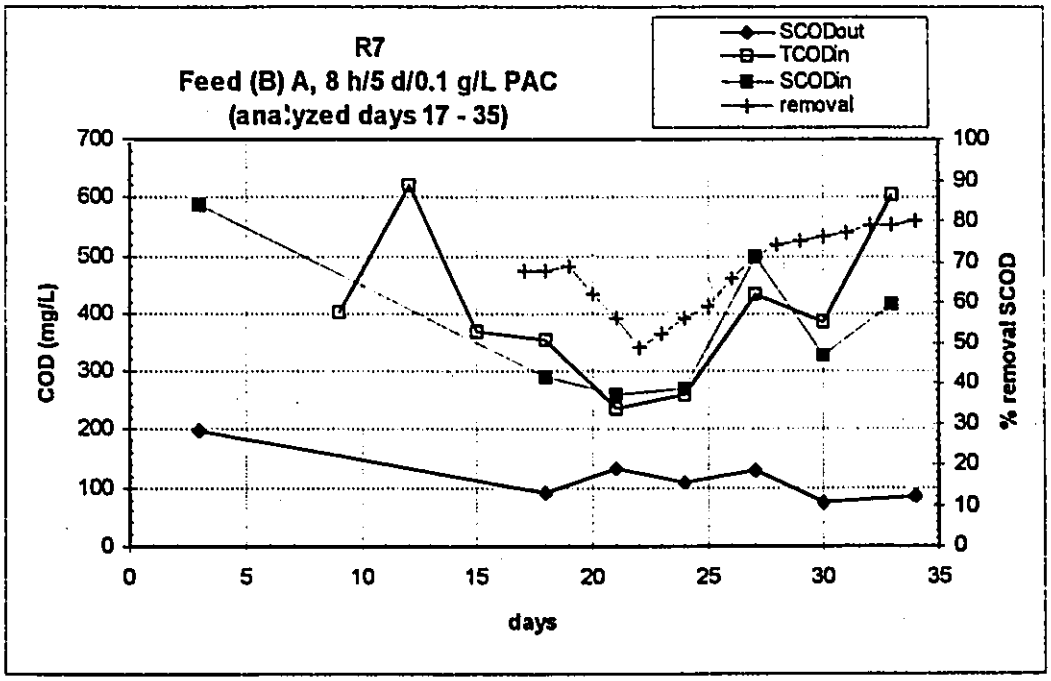


(B)

Figure C-6 Reactor performance (A) solids, (B) COD removal.

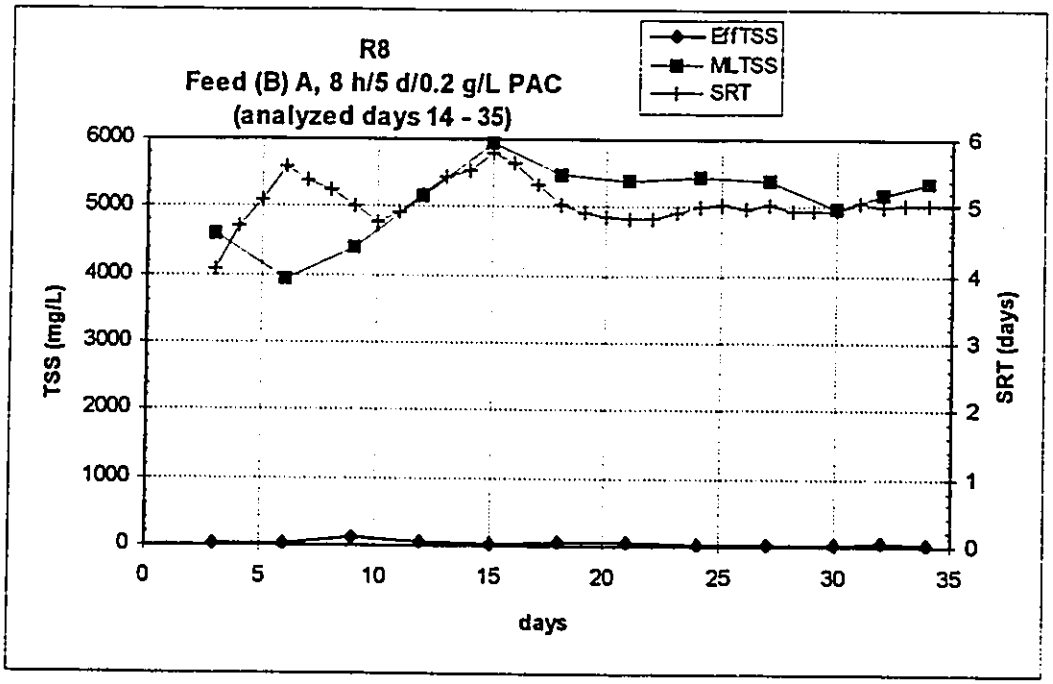


(A)

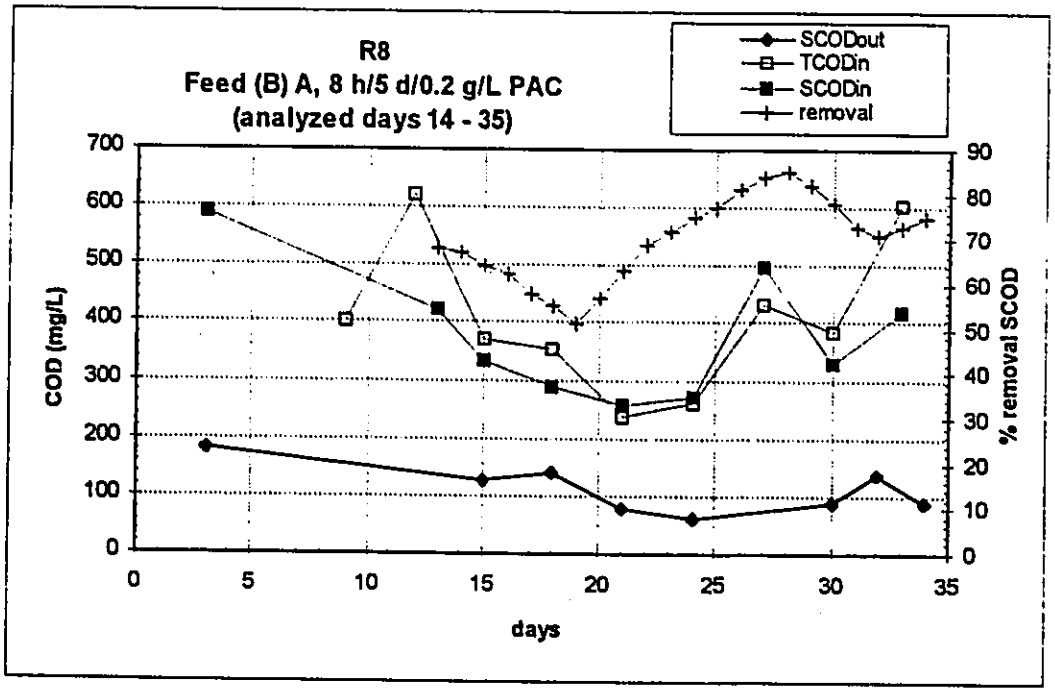


(B)

Figure C-7 Reactor performance (A) solids, (B) COD removal.

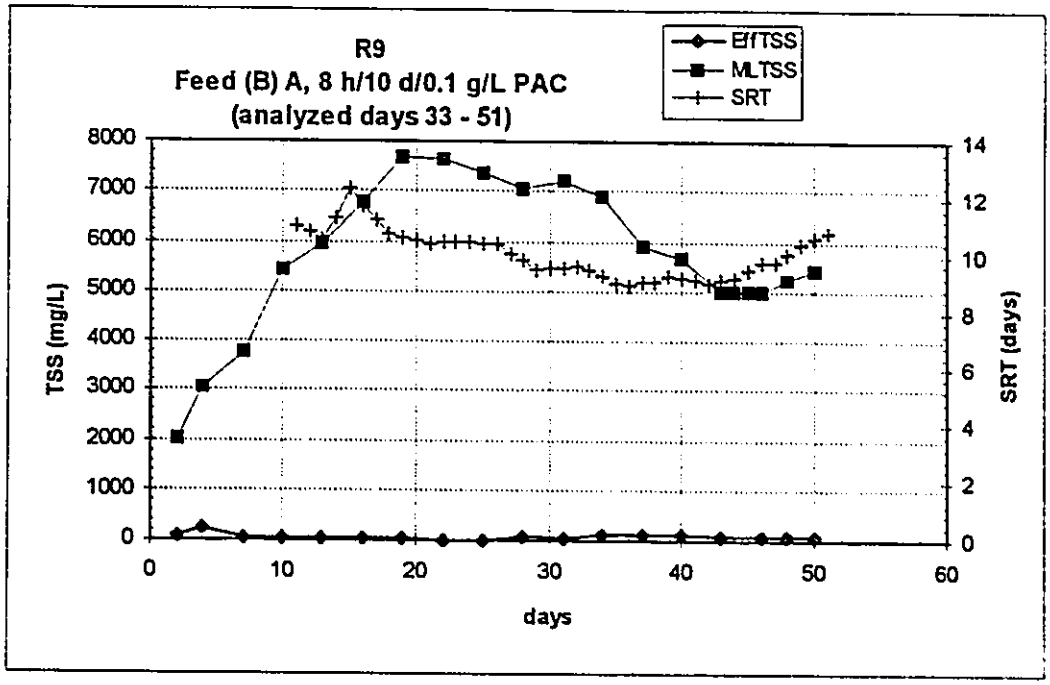


(A)

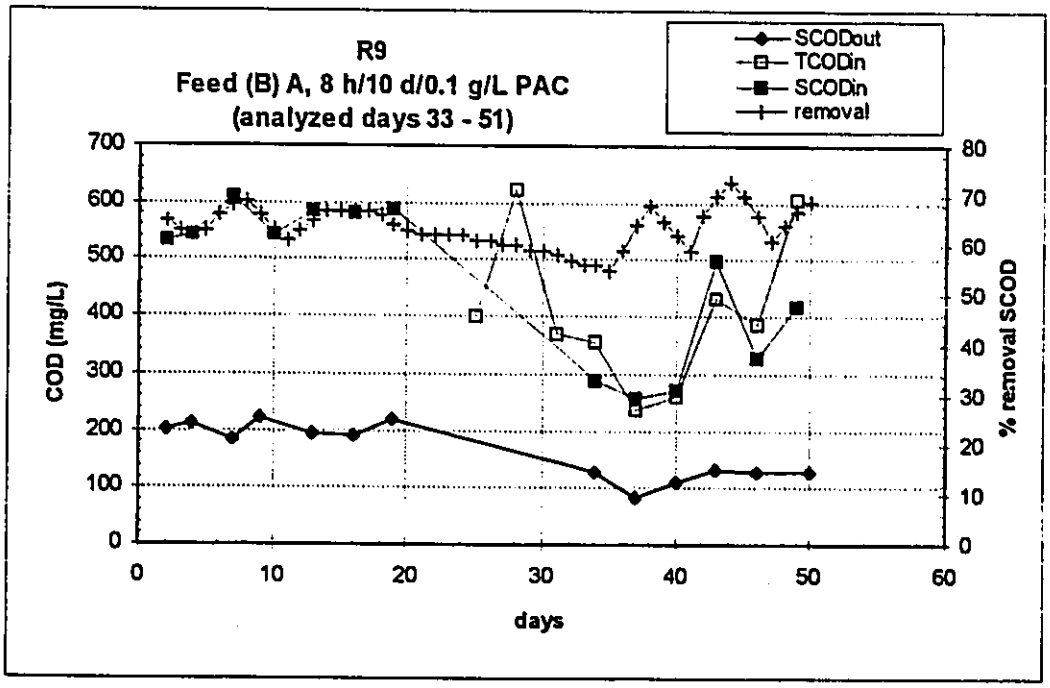


(B)

Figure C-8 Reactor performance (A) solids, (B) COD removal.

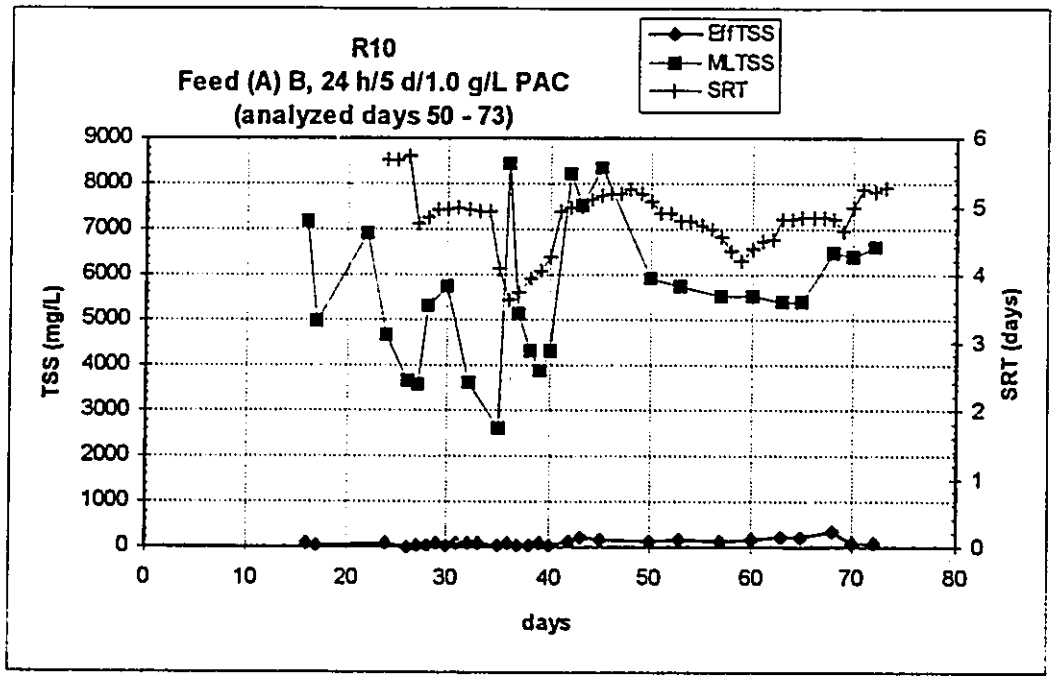


(A)

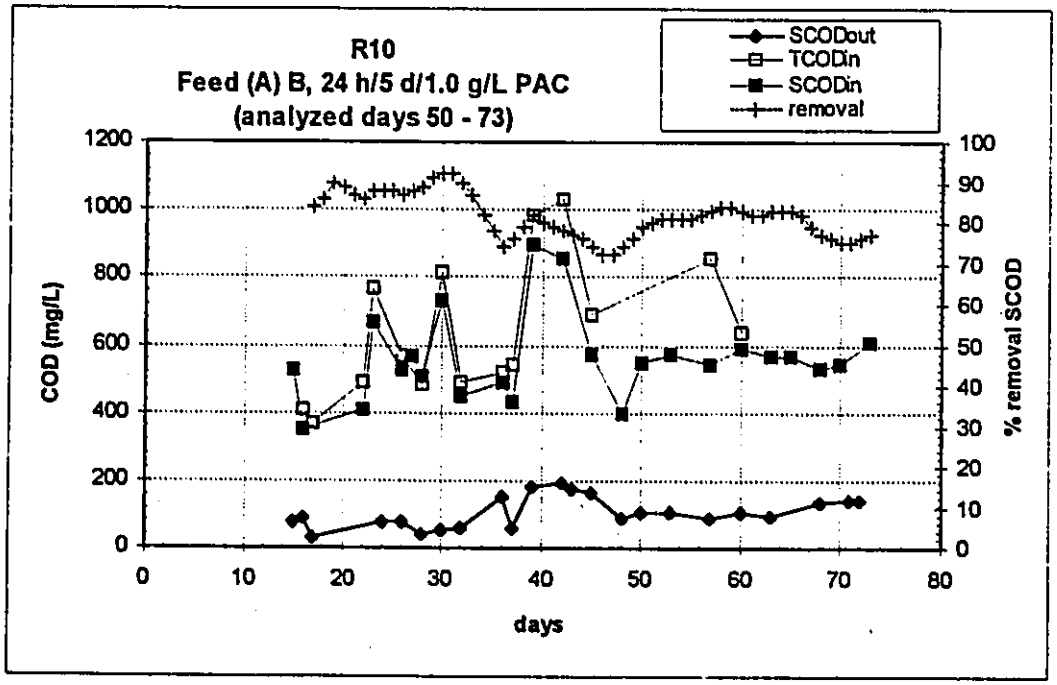


(B)

Figure C-9 Reactor performance (A) solids, (B) COD removal.

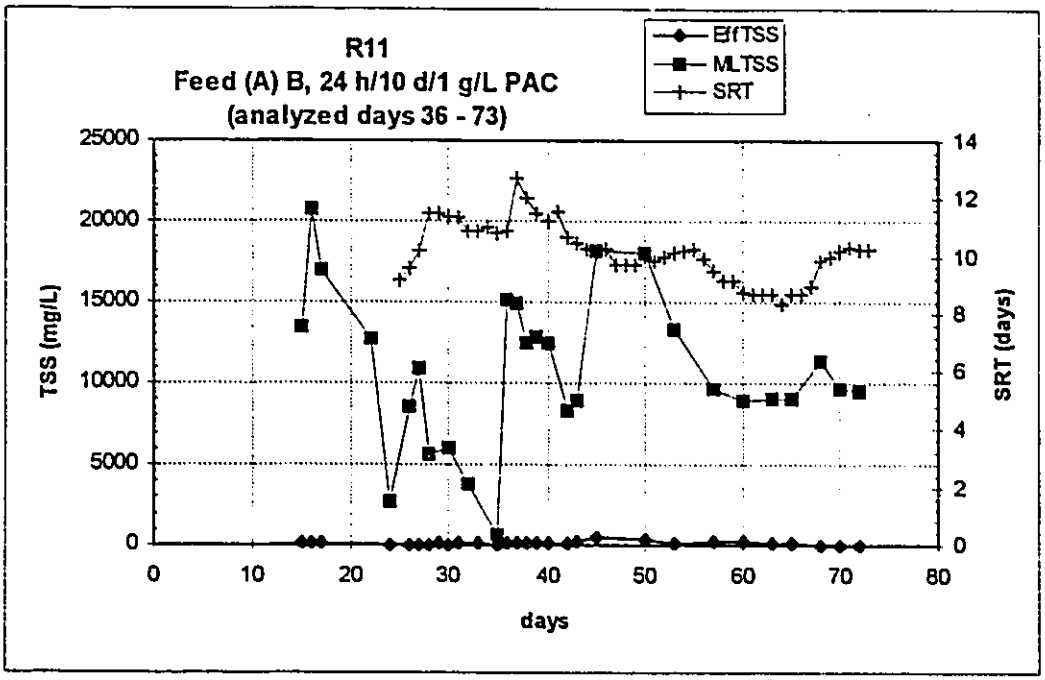


(A)

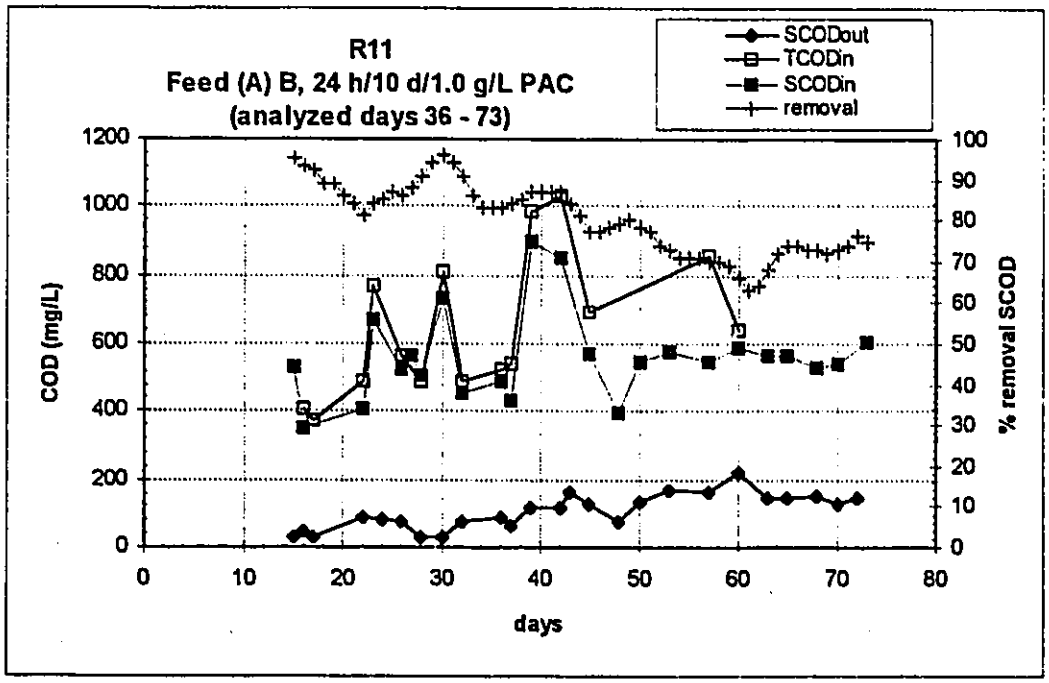


(B)

Figure C-10 Reactor performance (A) solids, (B) COD removal.

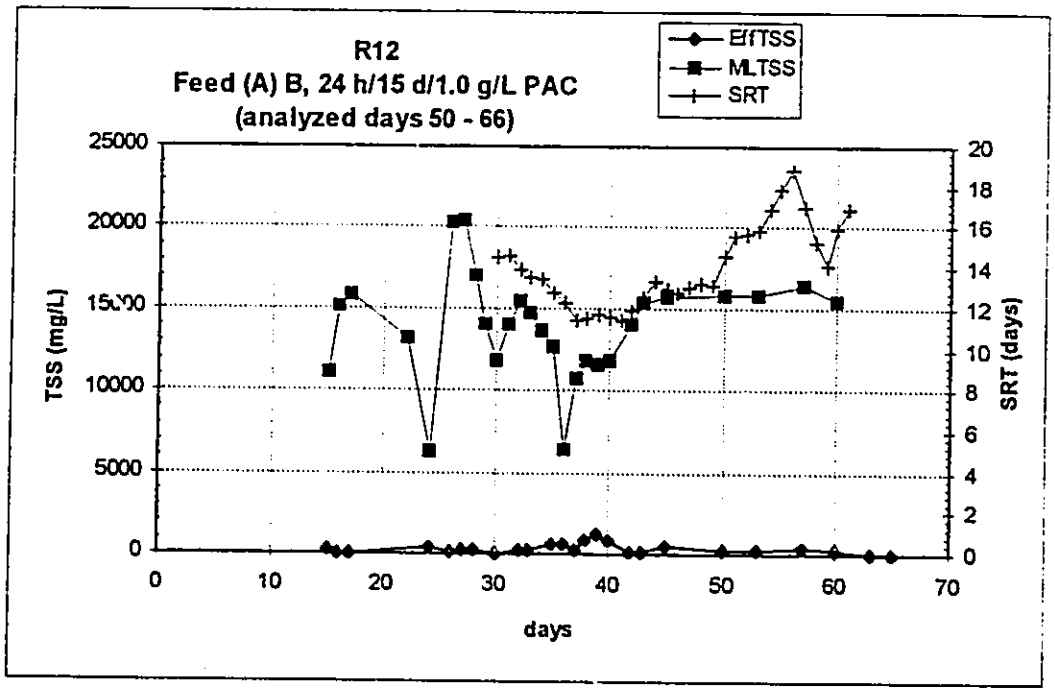


(A)

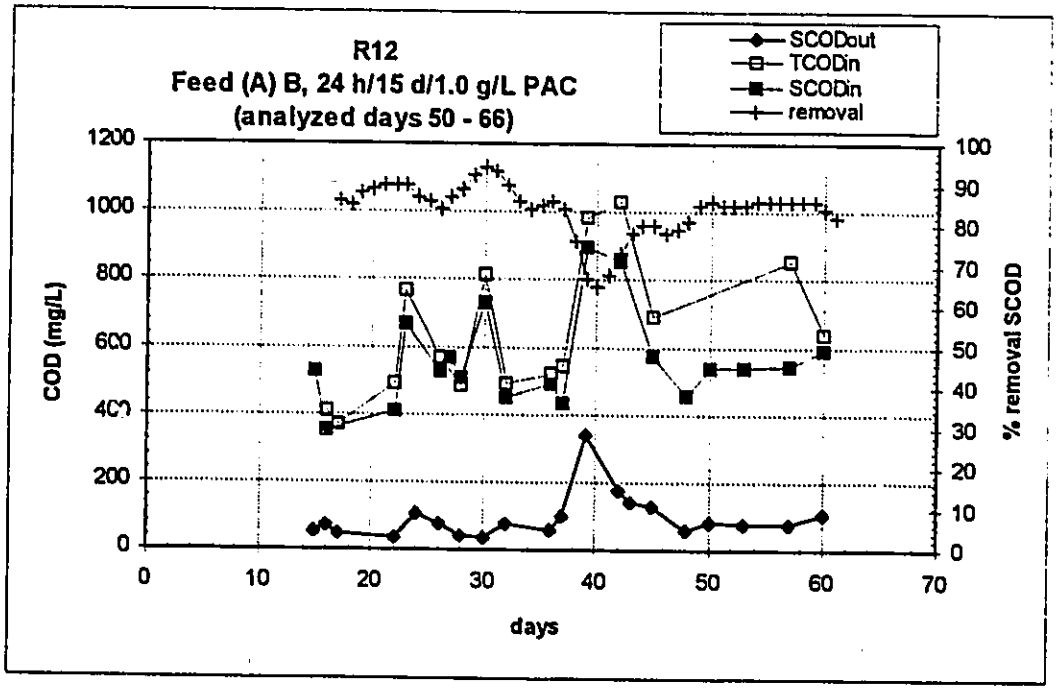


(B)

Figure C-11 Reactor performance (A) solids, (B) COD removal.

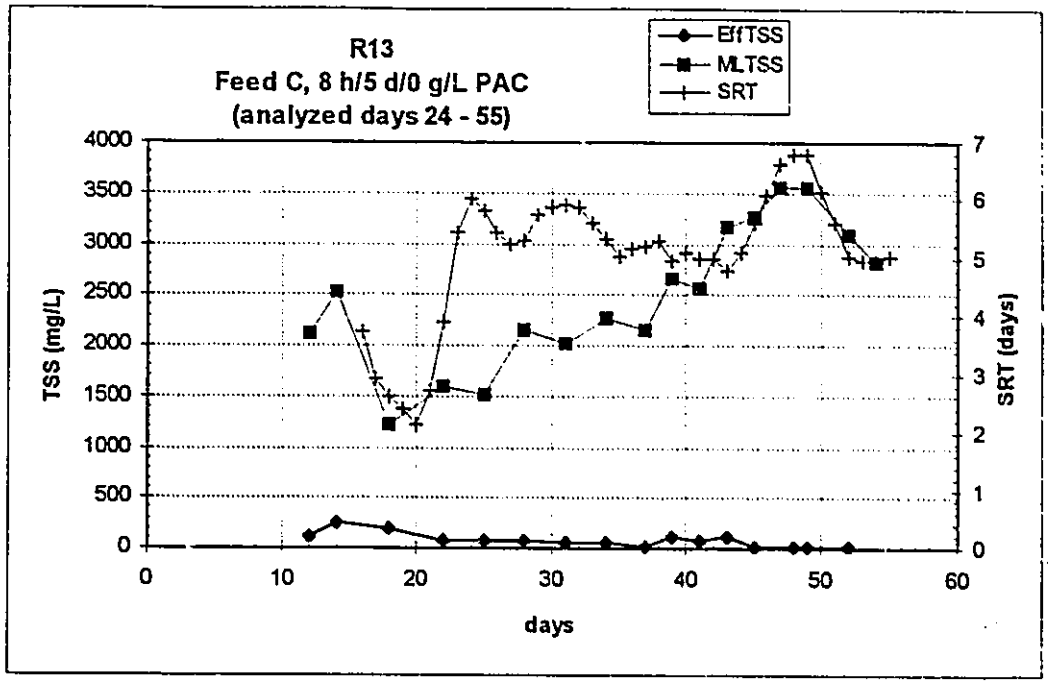


(A)

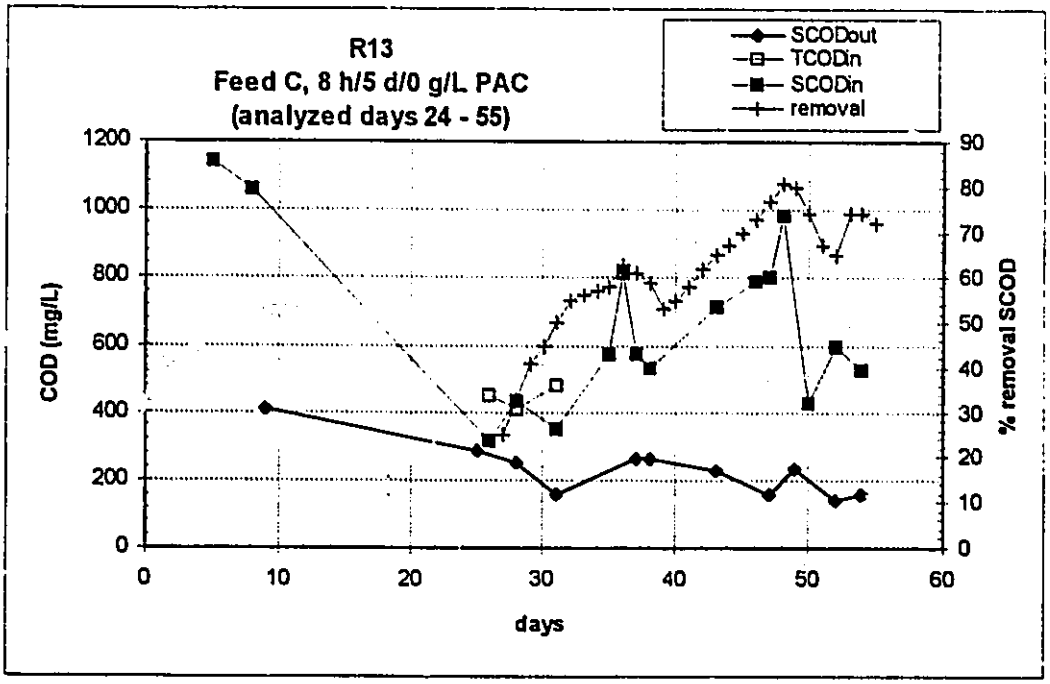


(B)

Figure C-12 Reactor performance (A) solids, (B) COD removal.

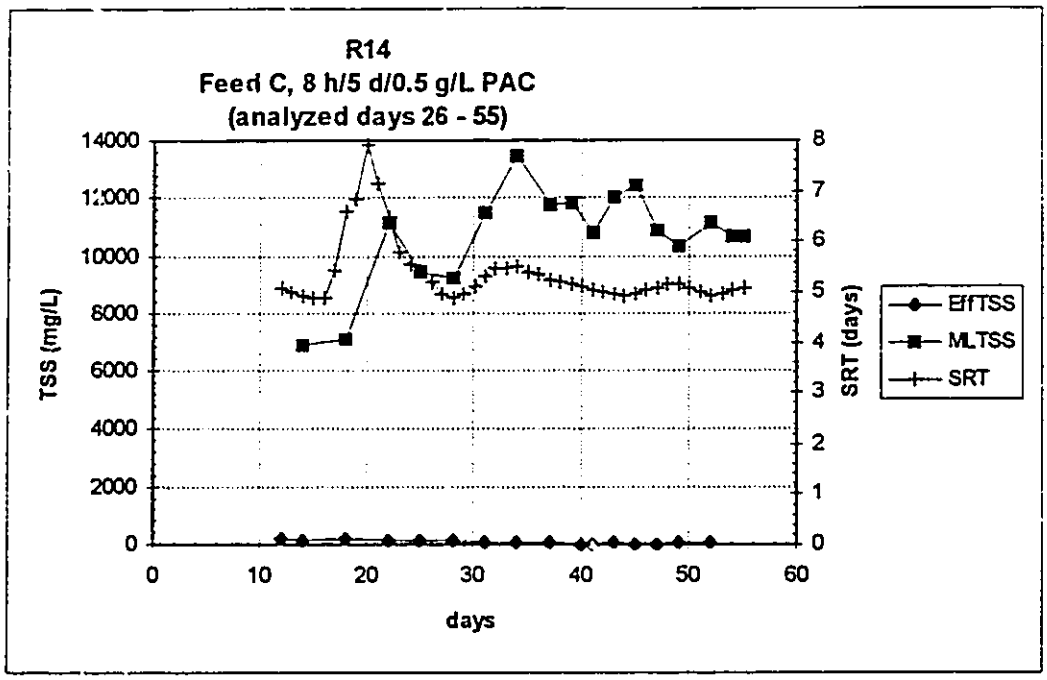


(A)

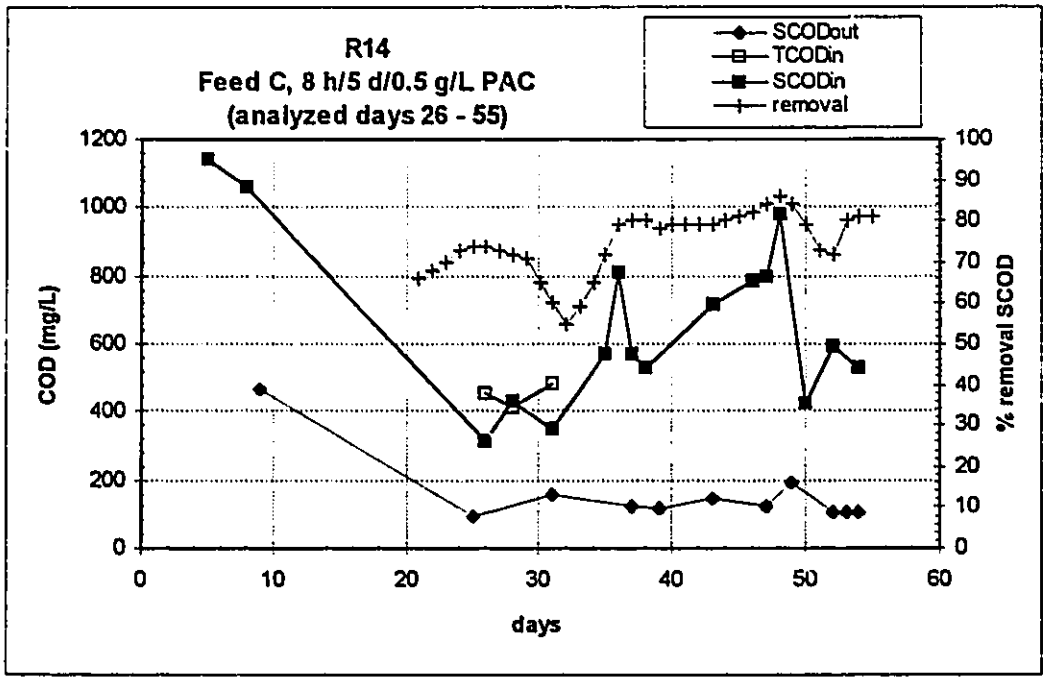


(B)

Figure C-13 Reactor performance (A) solids, (B) COD removal.

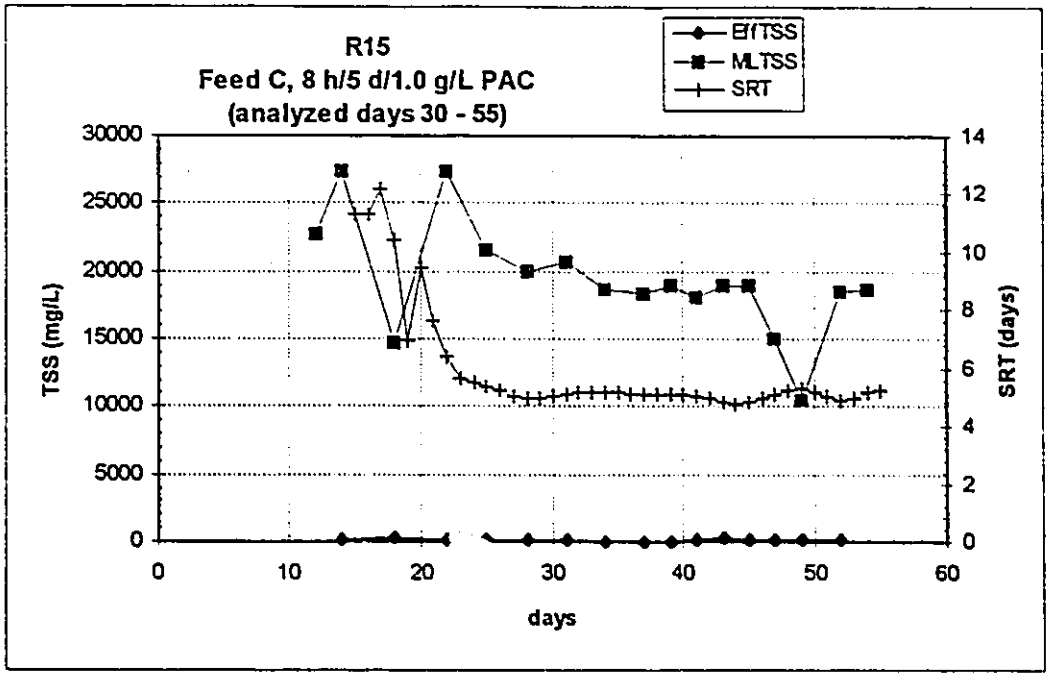


(A)

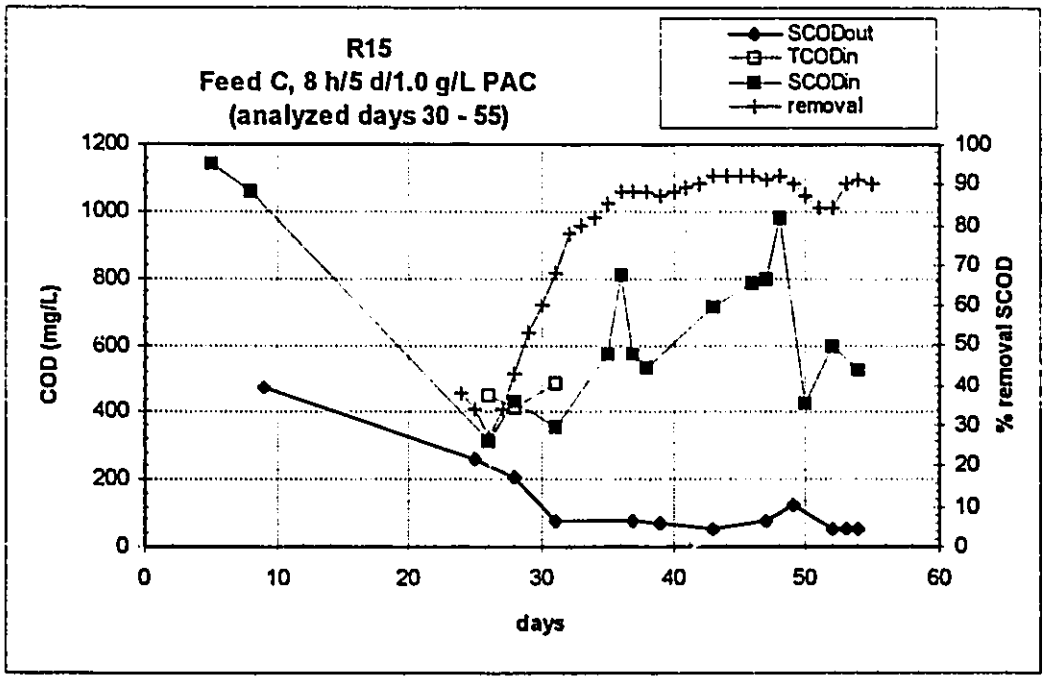


(B)

Figure C-14 Reactor performance (A) solids, (B) COD removal.

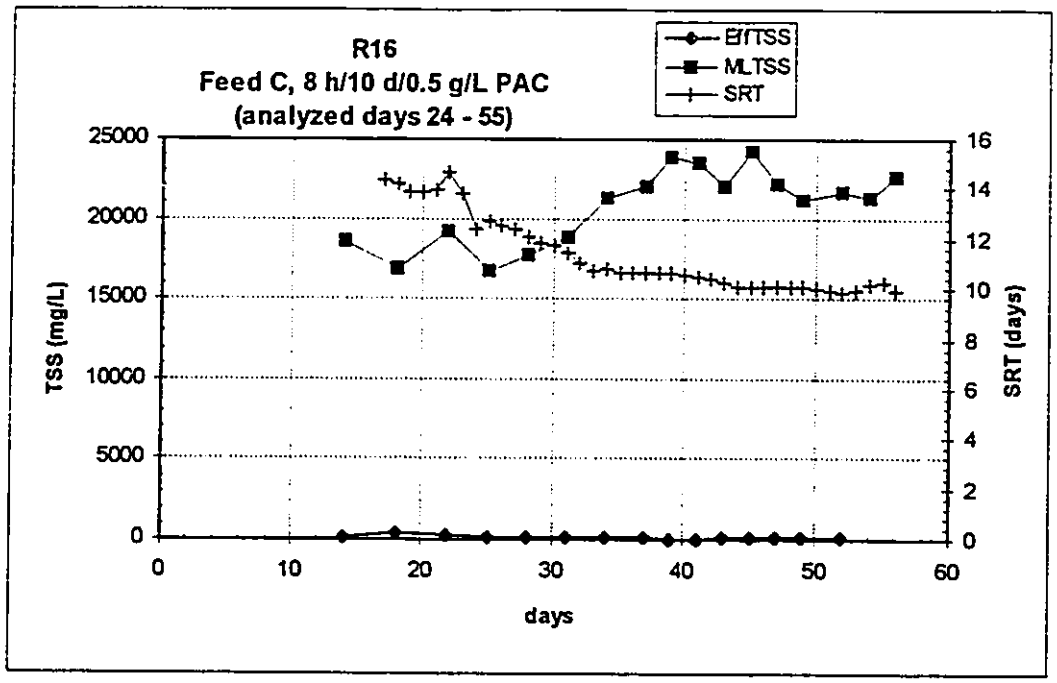


(A)

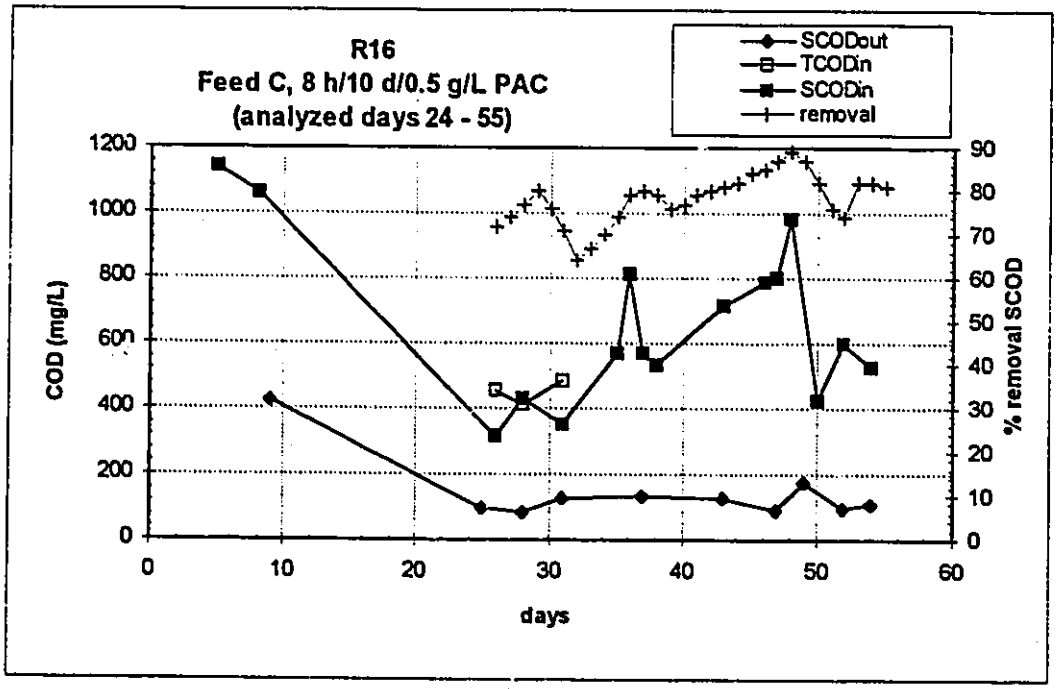


(B)

Figure C-15 Reactor performance (A) solids, (B) COD removal.

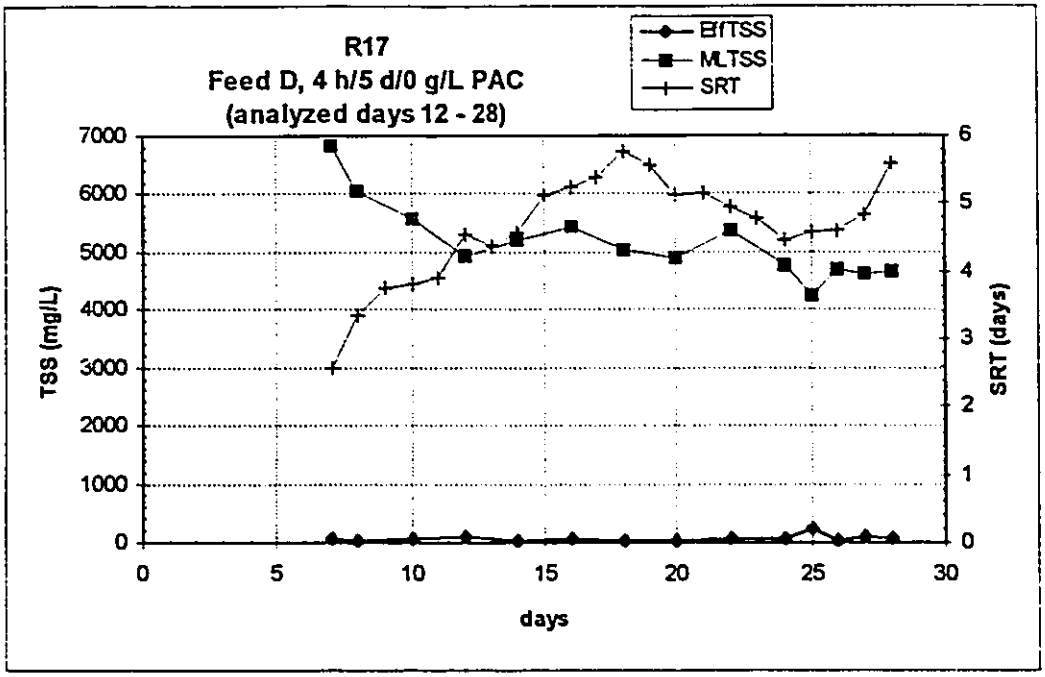


(A)

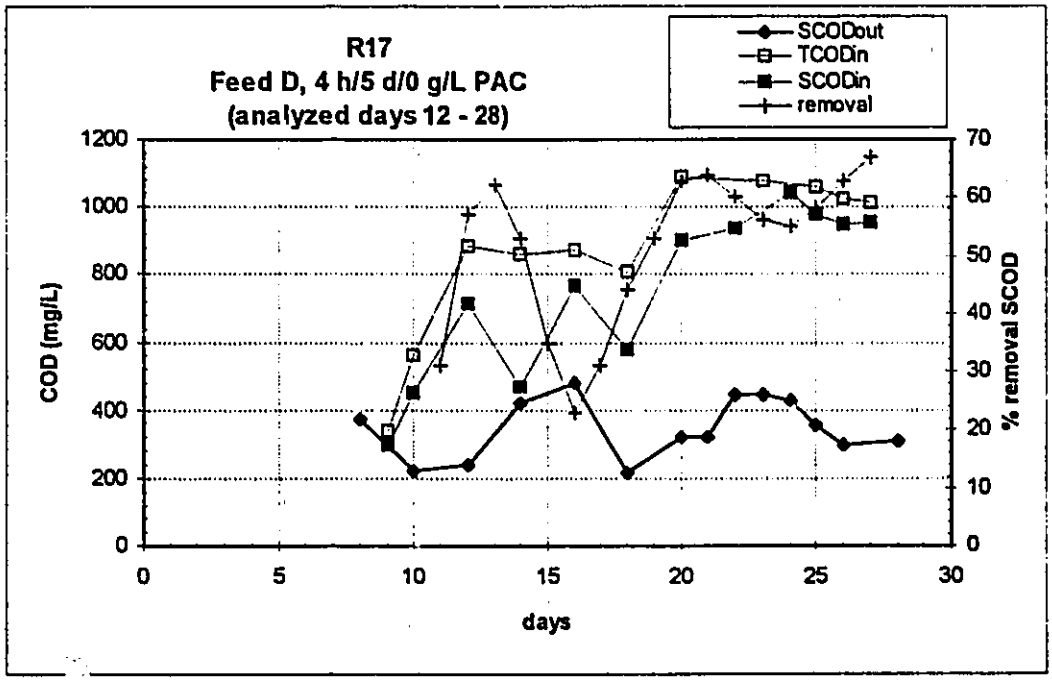


(B)

Figure C-16 Reactor performance (A) solids, (B) COD removal.

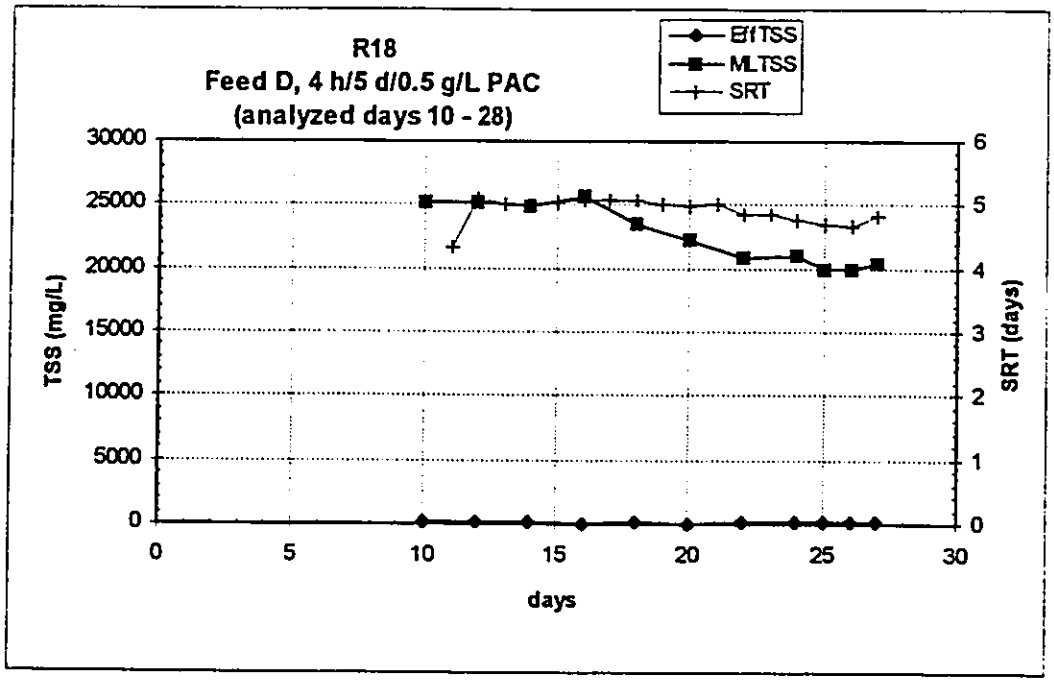


(A)

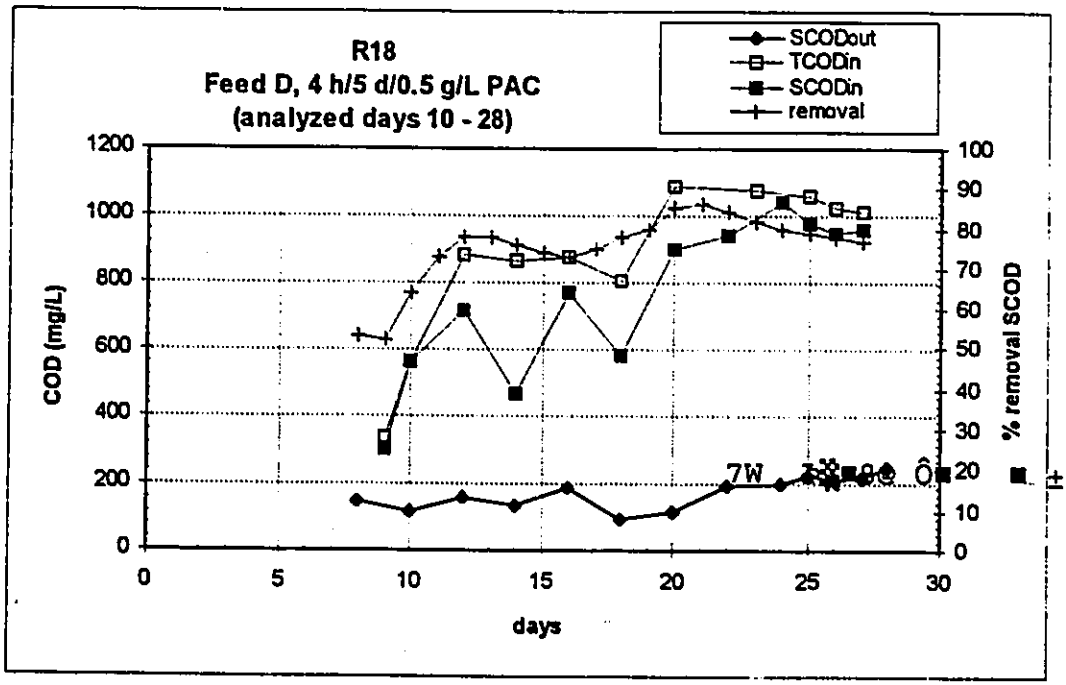


(B)

Figure C-17 Reactor performance (A) solids, (B) COD removal.



(A)



(B)

Figure C-18 Reactor performance (A) solids, (B) COD removal.

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