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HYDRAULIC OVERLOAD OF UPFLOW ANAEROBIC SLUDGE BED REACTOR TREATING LANDFILL LEACHATE

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All praise is due to Allah (God), yet
The one who does not show gratitude to creation has not shown gratitude to their creator.

ABSTRACT

The impact of hydraulic shockloads on UASB reactors operating at mesophilic conditions (T = 35°C) was studied. The wastewater, landfill leachate, was pretreated by filtering it through peat moss. The reactor was ½ filled with sludge previously acclimated from a pulp mill wastewater treatment facility.

The shockloads imposed on the reactor were hydraulic where the flowrate of the influent wastewater was increased by 2 - 3 times the initial flow rate at quasi steady-state (corresponding to a change of HRT from 2.5 - 3 to 1 - 1.5 d) where the influent concentration was maintained around 10 g COD/L. Two modes of shock-loading were compared: continuous versus intermittent for a total duration of 3 hours, where the intermittent operation distributed the flowrate increase over 9 hours to make a total of 3 hours.

The results showed that a UASB reactor can endure a single shockload of OLR close to 9.6 ± 1.8 g COD/L.d and recover to pre-shock conditions in a period not exceeding 30 hours. Intermittent shock feeding resulted in better effluent quality; nonetheless, it took a longer time to recover, and was more prone to solids washout.

When a UASB was subjected to two hydraulic shockloads within 2 days, it was found that the effluent quality in the second shock was worse than the previous one and took a longer period of time to recover to pre-shock conditions.

However, UASB reactors showed less endurance to organic shockloads even if the OLR was equivalent to hydraulic shockloads of comparable OLR which may be due to mass transfer limitations.

An attempt to quantitatively measure rate of return (recovery) to pre-shock conditions as a result of a shock was made by linear regression, and the term 'rate of recovery' (RC) was introduced.

Nickel was found to exist in the feed of runs where there was a relatively better effluent quality and faster recovery periods compared to runs where nickel was not detected in the feed. However, some exceptions were found, and thus it requires more in-depth study for verification.

Gas production showed no significant difference in production in intermittent or continuous shock modes.

ABRÉGÉ

L'impact de chargements hydrauliques chocs sur des réacteurs anaérobies à écoulement ascendant et à lit de boues (*UASB*) opérés dans des conditions mésophiles (T = 35°C) fut étudié. L'eau de lixiviat d'un site d'enfouissement fut pré-traitée par filtration à travers un lit de tourbe. Le réacteur fut à moitié rempli de biomasse, préalablement acclimatée, provenant d'une usine de traitement de pâte.

Les chargements chocs imposés sur le réacteur étaient de nature hydraulique, où le taux d'écoulement de l'affluent d'eau usée était de 2 à 3 fois supérieur au taux initial d'écoulement en conditions fixes (correspondant à une variation de TRH de 2.5 – 3 jours à 1 –1.5 j), et où la concentration de l'affluent fut maintenue approximativement à 10 g DCO/L. Deux modes de chargements-chocs furent comparés: continu par opposition à intermittent pour une durée totale de 3 heures, où l'augmentation du taux d'écoulement du mode d'opération intermittent fut étaler sur 9 heures pour totaliser 3 heures.

Les résultats démontrent qu'un réacteur de type *UASB* peut supporter un seul chargement-choc de TCO d'environ 9.6 +/- 1.8 g DCO/L.d et retrouver ses conditions d'avant choc dans un délai de moins de 30 heures. Le mode d'alimentation intermittent à produit un effluent de meilleure qualité sauf qu'il a pris plus de temps à récupérer et il était plus prédisposé à perdre des matières solides.

Quand le réacteur *UASB* fut soumis à deux chargements hydrauliques chocs en 2 jours, la qualité de l'effluent au cours du second choc était inférieure à celle du précédent et à pris une longue période de temps pour retrouver son état d'avant choc.

Toutefois, les réacteurs UASB ont démontré moins de tolérance aux chargements organiques chocs même pour un TCO équivalent aux chargements hydrauliques chocs de TCO comparables, ce qui peut être causé par des restrictions de transfert de masse.

Afin d'essayer de quantifier le taux de rétablissement (récupération), résultant d'un choc, régression linéaire et l'expression 'taux de récupération' (TC) fut introduite.

Du nickel était présent dans l'eau usée d'alimentation d'essais expérimentaux où la qualité de l'effluent était relativement supérieure et où la période de récupération était plus rapide comparativement aux essais où le nickel n'était pas détecter dans l'eau d'alimentation. Il y avait toutefois quelques exceptions et celles-ci exigeraient une étude plus approfondie pour des fins de vérification.

La production de gaz n'à pas démontrer de différences significatives entre celle obtenue par mode intermittent ou continu de chargement choc.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure **Page**

ABBREVIATIONS

AAT	Acetoclastic activity test
ABR	Anaerobic baffled reactor
AF	Anaerobic filter
b	VSS decay rate coefficient (d^{-1})
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
COD_{rem}	Chemical oxygen demand concentration removed
CM	Completely mixed
dS/dt	Rate of substrate utilization (g COD/L.d)
DSFF	Downflow stationary fixed film
EB/FB	Expanded bed/fluidized bed
FAS	Ferrous ammonium sulfate
FS	Fixed solids
FSS	Fixed suspended solids (g/L)
GC	Gas chromatograph
H	Height (cm)
HRT	Hydraulic retention time (d)
HVFA	Higher volatile fatty acids (propionic and butyric)
ICP	Inductively coupled plasma
k	Maximum specific rate of COD removal by biomass per day (g COD/g VSS.d)
k_{rec}	Maximum specific rate of COD removal by biomass per day (g COD/g VSS.d) during recovery from shockload
K_s	Half-velocity constant (g COD/L)
L	Litre
N/D	Not detectable
OLR	Organic loading rate (g COD/L.d)
PF	Plug flow
POTW	Publicly owned treatment works
Pr/Ac	Propionate to acetate ratio
Q	Flow rate (L/d)
RC	Rate of recovery (mg Ac/L.h)
R^2	Coefficient rate of determination
RMOC	Regional Municipality of Ottawa-Carleton
SE	Standard error
S_o	Substrate concentration in influent (mg/L)
S_{de}	Substrate concentration in effluent (mg/L)
σ	Standard deviation
SLR	Specific organic loading rate (g COD/g VSS.d)
SRT	Solids retention time (d)
SS	Suspended solids (mg/L)
TKN	Total kjeldhal nitrogen
TOC	Total organic carbon
TSS	Total suspended solids (mg/L)
U	Specific substrate utilization rate, specific removal rate (g COD/g VSS.d)
UASB	Upflow anaerobic sludge blanket
USFF	Upflow stationary fixed film
V	Volume of empty bed in reactor (L)
VFA	Volatile fatty acid
VSS	Volatile suspended solids
X_v	Average concentration of VSS in the reactor (g/L)
X_e	Average concentration of VSS in effluent (g/L)
y	Concentration of Acetic acid as a function of time (mg Ac/L)
Y	Biomass yield coefficient (g VSS formed/g COD consumed)

CHAPTER 1
INTRODUCTION

1.1 Introduction

Landfill is a land space specifically allocated and designed for the purpose of solid waste disposal. Sanitary landfills play an important role in solid waste management, as they are engineered to control contamination produced at the site and minimize effects on the environment. Two main wastes or byproducts produced in a landfill are gaseous methane produced as a result of the anaerobic decomposition of organics, and a liquid waste called 'landfill leachate'. Both wastes have to be managed, and the focus of this study deals with the treatment of landfill leachate. Landfill leachate is a highly polluted wastewater that needs to be treated to satisfy provincial discharge limits before it is sent for final treatment in the regional publicly owned treatment works (POTW).

Anaerobic treatment offers several advantages in treating wastewater with high organic content, leachate in our case. Progress has been made on techniques and kinetics of anaerobic digestion, resulting in development of high performance digesters with increased stability that can successfully treat wastewater when operated at short hydraulic residence times (HRTs) of 18 - 48 hours. Various anaerobic high performance reactors have been reported to successfully treat leachate: anaerobic filters; fixed film reactors; and upflow anaerobic sludge bed reactors (Senior et al., 1995). The upflow anaerobic sludge bed (UASB) reactor was chosen for this study since it had been shown by Savard (2001) to be an excellent option for removal of organic matter from the leachate at the Carp Road landfill site in Ottawa.

Stable, consistent operation and good treatment performance in terms of organic removal are critical factors in evaluating anaerobic systems for industrial feasibility (Tay and Zhang, 2000). Process failure necessitates extended periods of recovery and start-up that can take a few to several weeks.

Nevertheless, with high rate anaerobic reactors, the risk of operational failure becomes more frequent, especially at the short HRT and high organic loading rates (OLRs) used in high rate reactors (Mathiot et al., 1992). Disruptions in performance could be the result of several types and sources of operational events, but the focus of this thesis is on the impact of transient conditions that impose an '***organic overload***' on the anaerobic digestion system. When an organic waste load exceeds the potential treatment capacity of the microbial population (biomass) in the reactor to break down the incoming organic waste, the system is considered overloaded. When an organic overload is exerted for a period of time, and then returned to its normal state, it is called a ***'transient shockload'***.

In general, causes of overloading due to reactor feed characteristics can be classified into three categories: hydraulic; organic; and toxic overloading. Hydraulic overloading, as defined in this thesis, refers to the increase of the organic load by increasing the influent flowrate while keeping the chemical oxygen demand (COD) concentration of the wastewater constant (i.e., decreasing the HRT of the system).

"Stability studies on the effect of organic and hydraulic overloading on the performance of anaerobic reactors are required since organic and/or hydraulic overloading are difficult to avoid in wastewater treatment" (Canovas-Diaz and Howell, 1988). Furthermore, stability studies provide valuable information to guide process design and operational procedures for anaerobic reactors.

Several studies have been reported in the literature assessing the effect of hydraulic and organic shock loads on anaerobic digestion in general. High rate anaerobic digesters are of specific interest, since they are the norm for treating low-moderate strength (1500 - 15,000 mg COD/L) industrial wastewater.

1.2 Scope of research

To date, no study has investigated the response of UASB reactors treating landfill leachate when subjected to transient hydraulic shockloads. Organic and hydraulic shockloads are common as a result of the changing production volume and concentration of landfill leachate produced throughout the year due to precipitation and landfill aging.

As a result, the objective of this study was to study the impact of (2-3) fold hydraulic shocks for 3 hours at different modes and frequencies on the performance of UASB reactors. Performance of the UASB reactors was determined by monitoring parameters such as volatile fatty acids (VFA), COD removal efficiency, suspended solids (SS), metal composition of feed and effluent, and specific biomass activity.

To minimize inert solids accumulation in the reactor, leachate pre-treatment was undertaken by filtering leachate through a column of peat moss. Peat was chosen because of its filtration properties, affordability, and availability in Canada (Savard, 2001).

CHAPTER 2
THEORETICAL ASPECTS

This chapter aims to introduce the necessary concepts to understand the purpose of this study. First, a definition of the wastewater (leachate) and its characteristics is provided. Then, the technical background to understand anaerobic digestion, along with the factors influencing bioconversion is explained. An emphasis is put on both the UASB reactor used in this study, and different design parameters. Finally, a brief review is presented of the performance of a laboratory UASB reactor treating the wastewater at hand.

2.1 Definition of leachate

A major concern that is associated with landfills is the production of 'leachate'. Leachate is the liquid formed within a landfill site that is comprised of water entering the site (including snow and rain water) that is contaminated by the municipal waste as the infiltrating liquid percolates downwards through the waste. "Landfill leachate is a high-strength wastewater, characterized by low pH, high biochemical oxygen demand (BOD), COD, and by the presence of toxic inorganic and organic chemicals. In addition, the leachate quality is variable from landfill to landfill, and over time as a particular landfill ages." (Qasim and Chiang, 1994).

Leachate poses a potential problem due to the fact that it migrates laterally and/or vertically depending on the characteristics of the surrounding material. Leachate pollutes surface or ground water, which can result in fish kill, loss of aesthetic value and degradation of the water quality.

Most engineered landfills are sealed at their bases, where leachate is being collected on a regular basis. There are existing techniques for the dissipation of leachate by re-pumping it to the upper layer of the landfill, or by wetland spraying. Inevitably, there will be excess leachate that has to be treated.

The high concentrations of organic and inorganic constituents in leachate have to be treated. Generally, the objective of treatment is to release relatively low effluent concentrations in organics, ammonia, halogenated hydrocarbons, heavy metals, and fish toxicity (Kenneth, 1995). Co-treatment of leachate and sewage is the current process used in the local (Ottawa-Carleton) region.

2.1.1 Chemical and biological characteristics of landfill leachate

The chemical composition of leachate depends on several parameters.

1. Waste composition: "The nature of the deposited waste material will affect gas and leachate production and composition by virtue of the relative proportions of degradable and non-degradable components, the moisture content, and the specific nature of the biodegradable element." (Kenneth, 1995).
2. Landfill age (stage of waste stabilization): Variation in leachate composition and in quantity of pollutants removed from waste is often attributed to landfill age, defined as time measured from the deposition of waste or time measured from the first appearance of leachate. It should be emphasized that variations in composition of leachate do not depend exclusively on landfill age but on the degree of waste stabilization and volume of water that infiltrates into the landfill. The pollutant load in leachate generally reaches maximum values during the first years of operation of a landfill (2-3 years) and then gradually decreases over the following years. This trend is generally applicable to organic components, main indicators of organic pollution

[COD, BOD, total organic carbon (TOC)], and to main inorganic ions (heavy metals, Cl^-, SO_4^{-2}).

Leachate characteristics (Keith and Tchobanoglous, 1994) for new (less than 2 years) and old (more than 10 years) landfills are described in Table 2.1.

Table 2.1: Typical composition of leachate from new and mature landfills.

	Value (mg/L)		
	New landfill (less than 2 years)	**Mature landfill (greater than 10 years)**	
Constituent	**Range**	**Typical**	**Range**
BOD_5	2000-30,000	10,000	100-200
TOC	1,500-20,000	6,000	80-160
COD	3,000-60,000	18,000	100-500
TSS (total suspended solids)	200-2,000	500	100-400
Organic nitrogen	10-800	200	80-120
Nitrate	5-40	25	5-10
Total phosphorus	5-100	30	5-10
pH	4.5-7.5	6	6.6-7.5
Calcium	200-3,000	1,000	100-400
Magnesium	50-1500	250	50-200
Potassium	200-1,000	300	50-400
Sodium	200-2,500	500	100-200
Chloride	200-3,000	500	100-400
Sulfate	50-1,000	300	20-50
Total Iron	50-1,200	60	20-200

2.2 Leachate collection and production

Leachate used in this study was obtained from the industrial Carp Road landfill located in the eastern part of the Regional Municipality of Ottawa-Carleton (RMOC), ON, Canada. Leachate produced in this landfill was collected from two locations: groundwater purge wells and the leachate collection system cells. The original 0.243 km^2 of natural attenuation cells have contaminated surrounding groundwater by lateral migration of pollutants. This contaminated groundwater is collected by 11 purge wells and fed into the municipal sewage system collection network at a flow rate of 44,300 L/h. The waste containment cell produces leachate at 2840 L/h over a surface area of 103.195 km^2. Total leachate production is approximately 47,000 L/h or 1,000,000 L/d (Savard, 2001).

The amount of leachate generated is dependent upon a number of factors that may be summarized as follows (Kenneth, 1995):

- Water availability: amount of precipitation; irrigation; liquid waste disposal
- Landfill surface conditions: surface topography (hydrologic properties of cover and waste materials) and local meteorological conditions.
- Refuse state: affects the 'field capacity' of the waste, defined as the maximum moisture content which a solid area can retain in a gravitational field without producing continuous downward percolation.

2.3 Anaerobic digestion

Anaerobic digestion is a natural process where micro-organisms, in the absence of oxygen, break down organics in a nurturing environment to produce methane and carbon dioxide as major products. Anaerobic treatment processes are accomplished by providing an environment where a complex, diverse and closely dependent group of bacteria are present (Speece, 1996).

2.3.1 Anaerobic bioconversion process

Anaerobic degradation of complex pollutants in wastewater involves three phases: hydrolysis/acidification; acetogenesis; and methanogenesis. This process requires the presence of at least three groups of bacteria, and involves several intermediate steps.

Hydrolysis/Acidification: In this process, complex pollutants or substrate polymers, such as carbohydrates, fat, and proteins are hydrolysed to simple soluble compounds by acidogenic bacteria (also referred to as fermentative bacteria) forming volatile fatty acids (VFAs). Extracellular enzymes are involved in performing this task. For wastewaters that contain a large fraction of suspended particles, the hydrolysis rate can be limiting for the overall rate of anaerobic digestion (Van Haandel and Lettinga, 1994; Droste, 1997).

Acetogenesis: VFAs longer than two carbons (e.g., propionate and butyrate) formed in acidogenesis are converted by acetogenic bacteria to the final products for methane production: acetate; hydrogen; and carbon dioxide as described in the following equations:

$$CH_3CH_2COOH + 2\ H_2O \longrightarrow CH_3COOH + 3H_2 + CO_2$$

$$CH_3CH_2CH_2COOH + 2\ H_2O \longrightarrow 2\ CH_3COOH + 2H_2$$

However, degradation of propionate and butyrate to acetate is thermodynamically unfavourable unless the other product, hydrogen, can be readily removed. In the case of propionate degradation, the hydrogen partial pressure must be kept under 10^{-4} atmosphere (Droste, 1997). Under low hydrogen partial pressure ($pH_2 < 10^{-6}$ bar), nearly all substrate carbon goes exclusively to acetic acid, CO_2 and hydrogen (McCarty, 1981).

Methanogenesis: Acetate and H_2 gas are converted to CH_4. Methane production occurs by two major routes. The primary route is the fermentation of acetic acid produced in the acetogenic phase to methane and carbon dioxide according to the following equation:

$$CH_3COOH \longrightarrow CH_4 + CO_2$$

The bacteria that execute this reaction are called *acetoclastic* or acetotrophic methanogens. The other reaction route is performed by hydrogenophilic methanogenic bacteria that reduce carbon dioxide by hydrogen to methane with an overall reaction of

$$4H_2 + CO_2 \longrightarrow CH_4 + 2H_2O$$

Each route represents 72% and 28% of methane production in anaerobic reactors respectively (Droste, 1997). Methanogenesis is often the rate-limiting step in the overall digestion process, particularly for soluble wastes and high loading rates, resulting in an accumulation of VFA. However, at lower temperatures, the rate-limiting step may be hydrolysis when complex substrates are present. The bioconversion scheme in anaerobic digestion is shown in Figure 2.1.

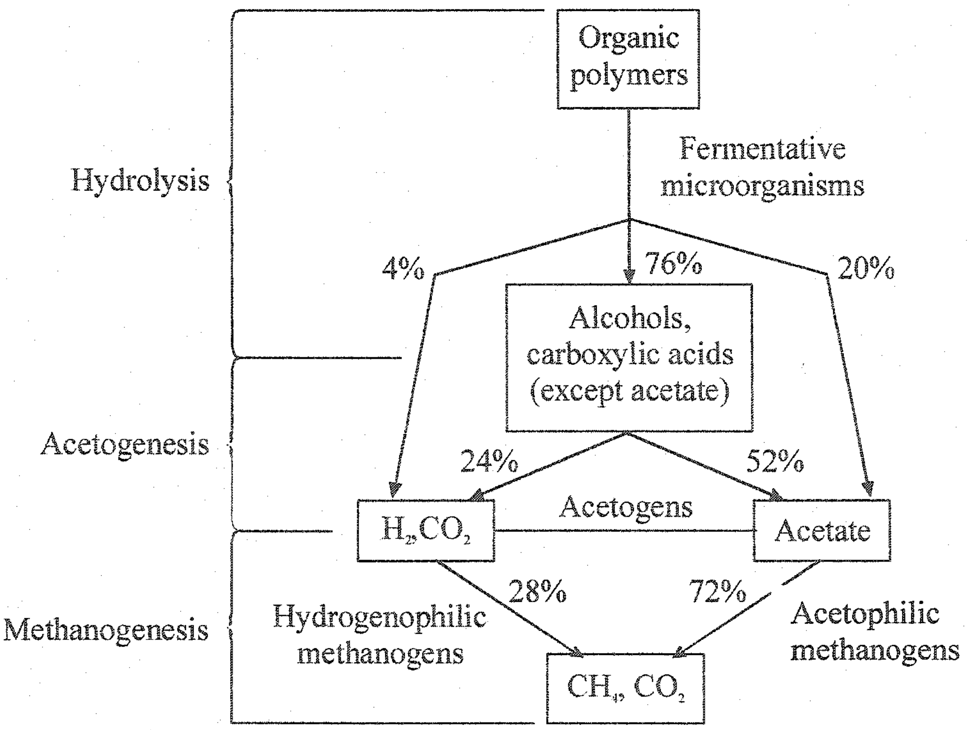

Figure 2.1: Bioconversion scheme of anaerobic digestion of organic waste.
(Adapted from Droste, 1997)

2.4 Advantages of anaerobic digestion

Speece (1996) summarized the positive features in using an anaerobic digester as follows:

- Greater capacity to achieve efficient pollutant reduction of high strength wastewaters compared to aerobic processes which are limited by their oxygen transfer coefficients.
- Reduction of waste biomass disposal costs because of less biomass production.
- Less nutritional requirement (nitrogen and phosphorous) for operation compared to aerobic processes.
- Energy conserved with concomitant ecological and economical benefits: biogas released in digestion can be an energy source for operations, and offset costs.
- Surfactant foaming avoided and substances that are non-degradable under aerobic conditions are successfully processed. Wastewaters from pharmaceuticals, brewery and alcohol industries result in severe foaming when treated aerobically caused by the bubbling of air. However, non-foaming biodegradation is possible anaerobically.
- Chlorinated organic toxicity levels reduced: aerobic technology is incapable to biodegrade chlorinated organics, while they can be biotransformed anaerobically.

2.5 Disadvantages of anaerobic digestion

For a better assessment of anaerobic digestion, possible disadvantages of anaerobic digestion, in general, are presented (Speece, 1996):

- Long start-up period is required for development of biomass because of low kinetic growth rates of biomass (on the order of weeks/months).

- Insufficient inherent alkalinity generation in dilute or carbohydrate wastewaters. Alkalinity capacity is important to maintain pH in the reactor in a range suitable for methanogenic activity (around 6.5 - 7.5).
- Effluent quality below surface water discharge criteria.
- Low kinetic rates at low temperatures.
- Sensitive to process disturbances, and requires tight control of operating conditions.
- Sulfide and odour generation from sulphate feed stocks.
- Nitrification is not possible.

2.6 Operational considerations affecting anaerobic digestion performance

In this section, factors that enhance the removal efficiency of wastewater in anaerobic digestion are addressed including temperature, pH, intermediates concentrations, presence of essential nutrients, and absence of toxicants/inhibitors.

2.6.1 Temperature

Anaerobic processes are more sensitive to temperature changes than aerobic systems. Anaerobic micro-organisms are classified according to the temperature range where they are most active as follows: psychrophilic (15-20°C); mesophilic (30-40°C); or thermophilic (50-60°C). The mesophilic range is the most common range used in anaerobic digesters (Savard, 2001). Significant reductions in loading rates must be made for low temperature operations for the treatment of landfill leachate as illustrated by Kettunen and Rintala (1998).

2.6.2 pH

The value and stability of pH in an anaerobic reactor are crucial for optimum activity of methanogens. The optimum pH range for methanogenic activity is around neutral pH (6.3-7.8). Acidogenic populations are less sensitive to low or high pH values (Van Haandel and Lettinga, 1994). To maintain pH near neutrality, use of carbonate-buffered solutions such as bicarbonates helps maintain pH at a constant value. Monitoring alkalinity gives an indication of the wastewater system buffering capacity.

2.6.3 VFA intermediates

Since acetate is a major precursor for methane production, a well functioning anaerobic system must process acetate efficiently and remove it to low concentrations in the effluent. Low concentrations of propionate are indicative of a well functioning anaerobic process. Elevated propionate concentrations may indicate difficulties in any one or more of the bioconversion steps described earlier on Page 8.

2.6.4 Nutrient requirements

Nitrogen and phosphorous are essential nutrients for microbial growth. The work of Chian and Dewalle (1977) showed that COD: N: P ratio of 100:207:0.2 was adequate for successful treatment of landfill leachate. Van Haandel and Lettinga (1994), and Droste (1997) reported a ratio of COD: N: P in anaerobic digesters of 500:5:1. Hawkes et al. (1992) used a ratio COD: N: P 100:2:1. However, unionized toxic ammonia is toxic to methanogenic bacteria.

For other trace nutrients, the necessary quantities have not been clearly established for a stable anaerobic operation. However, four elements -iron, cobalt, nickel and sulphide– have been shown to be obligatory nutrient requirements for methanogens to convert acetate to methane (Speece, 1983).

2.6.5 Toxicity

Apart from the hydrogen ion concentration previously mentioned in Section 2.2.1.2, several compounds, such as heavy metals and chloro-organic compounds affect the rate of anaerobic digestion, even at very low concentrations (Van Haandel and Lettinga, 1994). However, research has shown that the anaerobic bacteria can accommodate and break down a wide variety of toxic materials (Speece, 1996).

2.7 Methane theoretical production

Methane theoretical production can be determined using the following redox stoichiometry at 35°C. The COD equivalent of methane is as follows (Speece, 1996):

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

The equation above shows that for each mole (16 g or 22.4 L) of methane consumed at standard temperature and pressure, two moles (64 g) of COD equivalent are destroyed. From the above stoichiometry, it is calculated that a ratio of 0.35 L of CH_4 is produced per gram of COD removed (22.4 L/64 g). To compensate for a higher temperature, CH_4 equivalence is 0.395 L at 35°C and one atmosphere. Taking into consideration that CH_4 produced typically accounts for 60-70% of total biogas production, then the theoretical total gas yielded for COD utilized is around 550 to 650 L biogas/kg COD.

2.8 Design parameters for anaerobic digesters

Some of the important design parameters of an anaerobic digester that are used for computations in this thesis, are presented in this section: HRT, solids retention time (SRT), OLR, and specific-organic loading rate (SLR).

Hydraulic Retention Time:

HRT is a measure of the time it takes the influent to leave the reactor, computed using the following equation:

$$\text{HRT (d)} = V/Q \qquad \text{Equation 2.1}$$

where Q is the flow rate of influent wastewater (L/d), and V is the volume (L) of the empty bed reactor.

Solids Retention Time:

SRT is a parameter that measures the average time solids reside in the reactor. Maximal SRT is desirable for process stability and minimal sludge production. It is computed using equation 2.2 as follows:

$$\text{SRT(d)} = \frac{X_v V}{X_e Q} \qquad \text{Equation 2.2}$$

where X_v is the average concentration of VSS in the reactor (g/L) and X_e is the average concentration of VSS in effluent (g/L).

Organic loading rate (OLR) and specific organic loading rate (SLR) or (F/M):

OLR indicates the COD exerted by the influent wastewater per unit reactor volume, while the SLR expresses the COD load per unit of biomass, sometimes also referred to as Food: Micro-organism ratio. The parameters are expressed in equations 2.3 and 2.4 as follows:

$$\mathrm{OLR}(\mathrm{g\ COD/L.d}) = \frac{QS_o}{V} \qquad \text{Equation 2.3}$$

$$\mathrm{SLR}\ (\mathrm{g\ COD/g\ VSS.d}) = \mathrm{OLR}/X_v \qquad \text{Equation 2.4}$$

where S_o is the influent COD concentration.

2.8.1 Substrate balance in anaerobic digestion

A typical substrate mass balance in anaerobic digestion (Droste, 1997) is expressed as:

$$QS_o - QS_{de} - \frac{kX_{VSS}S_{de}}{K_s + S_{de}}V = \frac{dS_e}{dt}V \qquad \text{Equation 2.5}$$

where S_{de} is the substrate concentration in the effluent (mg/L), k is the maximum specific rate of substrate removal by active biomass per day (g COD/g VSS.d), and K_s is the half velocity constant (g/L).

The Monod expression could be replaced by any suitable rate expression that best fits the substrate degradation rate data.

2.9 High rate anaerobic reactors: Focus on UASB reactor

High rate anaerobic reactors are characterized by having a mechanism for increasing SRT in an attempt to attain the best possible organic waste removal at the shortest possible HRTs.

Two mechanisms of sludge retention are applied:

1) Active biomass is retained/immobilised. Reactors such as upflow anaerobic filters (AF), fluidised bed reactor (FB), and downflow stationary fixed filter (DSFF) are included under this category.

2) A liquid-solid separation device is incorporated to return separated solids to the reactor. This category includes anaerobic contact process, and the conventional UASB reactor which uses an internal solid/gas separation. (Van Haandel and Lettinga, 1994).

Lettinga and co-workers at the University of Wageningen in the Netherlands developed the UASB reactor in the 1970s. There are many studies reporting the success of UASB reactors treating industrial waste at high loads (e.g., dairy wastewater, slaughterhouses, landfill leachate) (Kettunen and Rintala, 1998; Nadais, 2001; Savard, 2001). UASB reactors have gained popularity in recent years with over 200 installations worldwide (Lettinga and Hulshoff Pol, 1991). The basic set-up of an UASB is presented in Figure 2.2.

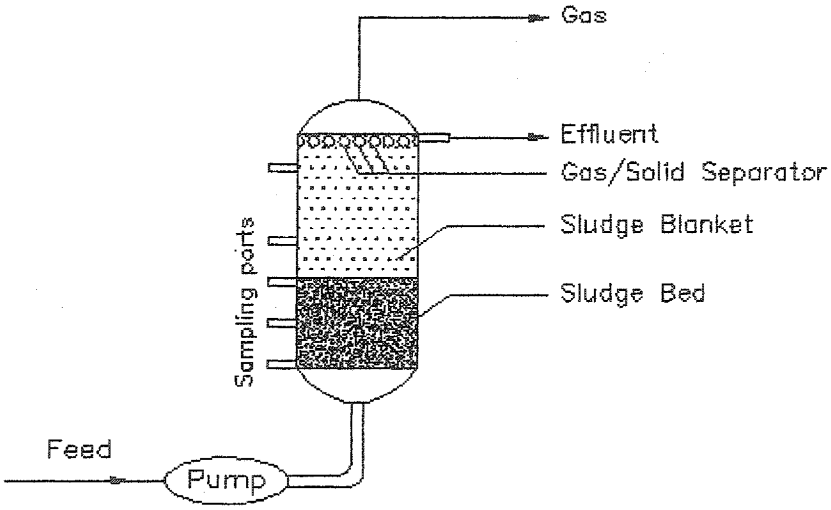

Figure 2.2: UASB reactor set-up

The UASB reactor has 3 distinct zones: *sludge bed*, *sludge blanket*, *gas/solid/liquid separation*. Wastewater is introduced as uniformly as possible over the bottom of the reactor and passes through the sludge bed, which contains high concentrations of active micro-organisms. The biomass is present in compact grains or granules, which are developed by some as yet undefined mechanism, under continuous upflow conditions. Dense granules have a high settling velocity. Development of granules avoids the costly packing in other reactor configurations and provides quiescent conditions for efficient biomass retention in the UASB. The sludge concentration of the bed is about 40-70 g VSS/L (Van Haandel and Lettinga, 1994).

The *sludge blanket* develops above the sludge bed. The microbial population in the blanket is retained by separation (bio-rings in this thesis experimental set-up) while gas and liquid escape from the top of the reactor. The blanket consists of smaller grains, flocs, gas bubbles, and ranges from dense and granular particles with high settling velocities near the base to lighter, less dense grains higher in the blanket. COD removal occurs throughout the bed and blanket. As the sludge concentration in the blanket is in the region of 10-30 g VSS/L, the average reactor sludge concentration is about 20-40 g VSS/L. The SRT of the bacteria is long enough to allow the growth of the methanogenic micro-organisms, even though the HRTs are low (Van Haandel and Lettinga, 1994).

2.9.1 Two-phase UASB reactor

Anaerobic treatment can take place in single or two-phase configurations. Single phase incorporates both acid formation (acetogenisis), and methane production in the same reactor, while two-phase operation attempts to separate acid formation from methane production, usually by providing two reactors. Many research papers have shown that a two-phase anaerobic operation performs better than a single phase (Speece, 1996), and has better stability to shockload (Bull et al., 1984). The existence of two reactors provides suitable environmental conditions for each bioconversion phase separately, and reduces inhibitions.

2.9.2 Flow pattern in UASB

The hydrodynamic regime in a UASB reactor is intermediate between the two extreme patterns: plug flow (PF) and completely mixed (CM). In a PF system there is no mixing and all particles will have exactly the same retention time in the reactor. In a CM system, mixing of the influent with the reactor contents is complete and immediate. As a result of mixing, some of the incoming liquid will leave the reactor immediately after entering, whereas some will remain for longer periods. To establish the hydrodynamic properties, tracer tests have been conducted (van Haandel and Lettinga, 1994). Sludge bed and blanket have been shown to be CM regions with both flow bypass and back flow (Paula and Foresti, 1992).

2.10 Definition of overload/shockload

When the organic waste load exceeds the potential capacity of the microbial population (biomass) in the reactor, to break down the incoming organic waste, the system is overloaded. Overload may be due to an excessive increase in the influent organic load, or due to a decrease of the activities of the micro-organisms (biomass) responsible for the elimination of organic waste (Mathiot et al. 1992). When this overload is exerted for a period of time, and then returned to its normal state, it is called a '***shockload***'.

Mathiot et al. (1992), and Speece (1996) listed a number of factors, either due to the feed characteristics or other conditions affecting biomass activity that could result in an overload to anaerobic system operating at steady-state. Some of these factors are:

1- Feed characteristics:

- Increase of influent COD concentrations
- Increase of feed flow rate
- Change in the characteristics of influent: a change in the nature of organic matter, in terms of its ease and complexity of degradation by biomass, or changing concentrations of nutrients
- Variation of pH
- Presence of toxic elements (organic, heavy metals, minerals)

2- Operational and biomass conditions:

- Excessive temperature fluctuations (usually a decrease from the optimum temperature range)
- Loss of biomass from the system
- Change in mass transfer between incoming wastewater and biomass, related to mixing or contact efficiency.

In general, causes of overloading due to feed characteristics can be classified into three categories: hydraulic, organic, and toxic overloading.

Hydraulic overloading, as defined in this paper, refers to the increase of the influent organic load by increasing the influent flowrate while keeping the COD concentration constant, i.e., decreasing the HRT of the system. Some researchers (Tay and Zhang, 2000) define hydraulic overload as an increase in feed flowrate and organic concentration proportionately, so as not to increase the OLR of the system at steady state.

Organic overloading refers to the increase in feed COD concentration while maintaining flowrate, or HRT constant. Toxic overloads can be caused by injecting substances known to be inhibitory to microbial activity.

2.10.1 Maximum load tolerated by anaerobic reactors

Overload may raise the question: What is the maximum organic load per unit of biomass that anaerobic reactors can treat? Quantifying the maximum COD loading is of concern to researchers conducting kinetic modelling, as well as engineers developing reactor design. The loading rate of anaerobic processes is limited by the quantity of the active biomass that can be retained in the reactor and effective contact between the biomass and the substrate. This question may be difficult to answer when one considers the variability of different parameters (Fang and Chui, 1995). For example, waste composition and characteristics (simple vs. complex substrate), and whether it has elements that may inhibit the activity of biomass. The variability may also stem from the difference of biomass activity/acclimatization to waste, start-up method, availability of a well-buffered system and sufficient nutrient requirements.

Henze and Harremoes (1983) estimated maximum COD removal rate per unit biomass as about 2 g COD/g VSS in fixed film reactors. Their estimate was based on a thorough review of literature on experimental and operational data followed by modelling analysis for a combined culture of methanogenic and acetogenic micro-organisms.

Fang and Chui (1995) did a similar study to determine maximum COD loading capacity in UASB reactors at 37°C. A synthetic feed (composed of milk and sucrose) of high strength COD (6,000 – 20,000 mg/L) was used at different HRTs. The highest loading achieved in this experiment was 100 g COD/L.d, corresponding to a SLR of 3 g COD/g VSS.d. The UASB was well buffered and supplied with all the essential nutrients to sustain microbial growth and activity. On the other hand, the waste was 70% soluble and easy to degrade (sucrose). Therefore, the maximum SLR values reported is not an estimate that could be compared to systems treating complex wastewater.

CHAPTER 3
LITERATURE REVIEW

In this chapter, a brief review of landfill leachate treatment using physical/chemical/biological methods is presented followed by a review of UASB reactor treatment of leachate as an example of anaerobic biological treatment. A survey of papers investigating the effect of overload (real and synthetic wastewater) on anaerobic reactors at mesophilic conditions is also presented, with emphasis on UASB reactor performance.

3.1 Leachate treatment

The goal of leachate treatment is to reduce the concentration of pollutants to allowed limits for discharge to surface water or for off-site treatment. Most leachates cannot be adequately treated using one method, and therefore a combination of processes is generally recommended.

3.1.1 Physical and chemical treatment

Options for physical/chemical treatment are briefly described below.

Chemical evaporation: Satisfactory results can be obtained with a two-stage treatment process of leachate consisting of high pH followed by an acid step. However, chemical evaporation is an expensive option.

Chemical oxidation: The purpose is to oxidize organics and metals by adding oxidants.

Chemical precipitation: Chemicals are added to precipitate heavy metals, and a portion of the organic matter. Chemical precipitation is accomplished by adding alum, lime, and iron salts. A major disadvantage of precipitation is the prohibitive operating expense.

Activated carbon: Activated carbon is a well-established sorption treatment method for many organics, but ineffective for highly soluble low-molecular weight organics such as acetone and methanol. Best results have been reported for low total solids concentration in influent when combined with biological methods (Shuckrow et al., 1982).

Membrane processes (reverse osmosis): Senior et al. (1994) reported that reverse osmosis (RO) could efficiently remove refractory organics, total solids and metals in leachate. However, a problem that arose was membrane fouling, which was partially overcome with a pretreatment step for removal of suspended and colloidal solids. The type of membrane, pH, pressure, and pretreatment are important factors in determining the effectiveness of the RO treatment process. However, Senior et al. (1994) indicated that the concentrate still required further treatment, or sometimes it was recycled to the landfill site.

Ammonia stripping: Old leachates have high concentrations of ammonia-nitrogen. Removal of ammonia has been achieved by raising pH above 9 with lime and bubbling air through the system, to release NH_3 gas. However, release of NH_3 gas raises environmental concerns that need to be addressed, and the process was deemed too expensive to setup and operate (Senior et al., 1994).

3.1.2 Biological treatment of landfill leachate

Biological treatment offers an effective approach for removal of biodegradable organic matter measured as BOD and suspended solids. Biological processes are generally characterised as aerobic and anaerobic.

Aerobic systems: Aerobic biological systems depend on micro-organisms grown in an oxygen-rich environment to oxidize organics to carbon dioxide, water, and cellular material (Senior et al., 1994). Aerobic processes, compared to anaerobic processes, tend to predominate over anaerobic reactors in countries such as the UK and Australia because of their effectiveness in removing ammonia (Kenneth, 1995). Disadvantages of aerobic processes are discussed in Chapter 2 when compared to anaerobic digestion. Some of the common aerobic processes employed to treat landfill leachate include activated sludge, rotating biological contactors (RBC), lagoons/reed beds, and sequencing batch reactors (SBR).

Anaerobic systems: Anaerobic treatment depends on a microbial consortium grown in the absence of oxygen with concomitant conversion of organic compounds to methane as detailed in Section 2.3. Anaerobic digestion presents several advantages to landfill leachate treatment versus aerobic treatment. Some of the advantages are less sludge production (around 85-90% of organic matter is transformed into methane thus favouring the energetics balance), pathogenic organisms are destroyed, and a much lower ratio of N:P:BOD is required. In contrast, however, anaerobic digestion has a lower biomass growth rate than aerobic bio-oxidation processes (Lema et al., 1988). The result is long start-up periods or long restarts after process upset or biomass washout. Some of the common high rate anaerobic reactors used to treat leachate include AF, fixed film reactors, and UASB reactors (focus in this thesis).

3.1.3 Application of UASB reactors in the treatment of landfill leachate

Savard (2001) presented a review of landfill leachate treatment using UASB reactors. A summary of operating conditions and performances is presented in Table 3.1.

Table 3.1: Performance of UASB reactor treatment of landfill leachate.

Reactor type	Temp. (°C)	OLR* (kg COD/m^3.d)	HRT (d)	COD removal (%)	References
UASB	18-23	3.3	0.96	57-60	Kettunen and Rintala (1998)
UASB	19-23	3.2	0.54	71-77	Kettunen and Rintala (1998)
UASB	12-14	1.5	1.3	49-55	Kettunen and Rintala (1998)
UASB	37	0.44-1.47	10-3	44-58	Mendez et al. (1989)
UASB	35	0.31-1.92	10.67-1.85	55.8-64.5	Mendez et al. (1989)
UASB-AF	35	1.43-21.79	7.67-2.68	67.9-92.8	Chang (1989)
UASB-AF	35	21.65-29.0	1	84.5-95	Myburg and Britz (1993)
UASB-AF	37	9.15-12.99	2-1.4	91-93	Britz et al. (1990)
UASB-AF	37	14.53-20.54	1.2-0.9	82-89	Britz et al. (1990)
UASB	35	9.4	2.3	87	Rumpf and Ferguson (1990)
UA Hybrid	35	21.65-29.0	1	80-95	Myburg and Britz (1993)
UASB	35	6.8	2.4	88	Berueta and Castrillon (1992)
UASB	35	1.3-8.2	2.4 –2	75-90	Inanc et al. (2000)

*OLR: Organic loading rate

Even though the upflow anaerobic (UA) hybrid reactor in Table 3.1 showed a high percentage of COD removal, propionic acid accumulation was noted at OLR of 29 g COD/L.d and appeared to be an indication of digester overloading and impending digester failure.

Berueta and Castrillon (1992) anaerobicaly treated leachate containing high concentrations of ammonia, at organic loadings of 6.8 g COD/L.d and HRT of 2.4 days, and obtained 88% COD removal. However, it was necessary to acidify continuously for buffering, and the test was reported to be an economic drawback in large-scale operations.

Inanc et al. (2000) reported that anaerobic attached growth processes such as the anaerobic filter and hybrid sludge bed reactor were more resistant to ammonia inhibition than UASB reactors. Since ammonia concentrations can be high in leachate, the selection of a UASB reactor was not recommended. To avoid inert solids or particulate accumulation in the lower part of UASB and hybrid sludge bed reactors, influent pre-treatment was recommended if the leachate feed had a high-suspended solids content.

When an accumulation of inert material occurs in UASB reactors, specific biomass activity decreases and granule calcification occurs. Rumpf and Ferguson (1990) suggested pre-treating landfill to remove iron and calcium prior to treatment in a UASB reactor. They recycled a portion of the reactor's effluent to a mixing tank with raw leachate so that the effluent's higher pH and alkalinity would precipitate Fe and Ca out of the leachate.

Savard (2001) concluded the following regarding the performance of UASB reactors treating landfill leachate based on her work:

- Maximum specific removal rate of biomass was 0.42 g COD/g VSS.d.
- OLRs over 10 g COD/L.d were considered to be a risk zone.
- For different seasons, the proposed HRT and OLR values where UASB reactors stabilise the wastewater best were:
    - Spring: HRT (0.95 d) and OLR (6.5 g COD/L)
    - Fall: HRT (1.4 d) and OLR (4.7 g COD/L)
    - Summer: HRT (1.6 d) and maximum OLR (10 g COD/L).

In the spring, a higher flow of leachate was experienced because of increased precipitation and snowmelt. The leachate concentration was diluted, and thus explained why the reactor could handle increased flow rates and lower HRT. On the other hand, leachate produced in the summer was more concentrated. More time was required to break down the increased influent concentration, which explains a need for increased HRT.

Based on this analysis, one would expect that in the fall the UASB reactor would operate with a lower HRT and higher OLR than in the summer, as influent concentration was lower then. This result was not demonstrated in Savard's conclusions because of her definition of best treatment. Savard's (2001) determination of best treatment operating conditions was based on the highest percentage removal (98%) that occurred at an OLR of 4.6 g COD/L.d and concentration of (~ 5 g COD/L). OLR higher than 4.6 g COD/L.d (~ 5 g COD/L.d) were also treated with high COD removal efficiency; however, there was no record of removal efficiency at higher feed concentration than 5 g COD/L.d. Savard's conclusions were thus limited to the range studied (at least for the fall situation) and not a comprehensive assessment.

Combined, peat moss pre filtration and UASB reactor treatment resulted in decreased solids displacement compared to operation without pretreatment. Despite pretreatment, solids accumulation was noticed and Savard (2001) recommended investigation of other pretreatment methods. In terms of metals removed in the process, efficient removal of Al, B, Ba, Mn, Zn, and Fe was observed.

3.2 Parameters indicating failure in anaerobic digestion

The methanogenic digestion process has been found to be sensitive to changes in hydraulic and organic loading and only recovers slowly once it has been upset (Marchaim, and Krause, 1993). Several parameters have been suggested in the literature to monitor the process performance in an attempt to detect process inhibition or failure as a result of overload. Some of these parameters were agreed upon to indicate impending failure, and others were doubtful or required more research to assess their role in governing reactor behavior. The parameters discussed are:

Volatile fatty acids (VFA) The most common on-line analysis technique is the total concentration of VFAs in the reactor. Low VFA concentrations (<100 mg/L) indicate that methanogenesis is not the rate limiting step. Furthermore, propionic acid has been shown to have the lowest tolerance level among the VFAs for the anaerobic bacteria. Propionic acid accumulated in anaerobic digesters during overloading and was difficult to remove during recovery (Fang et al., 1995). Speece (1996) stated that elevated VFA concentrations should be considered to be a result of trace metal deficiency in the acetogens or hydrogen-utilizing methanogens, unless proven otherwise. VFA concentrations should normally range between 50-100 mg/L. Stronach and Lester (1986) note that methanogenic populations were inhibited at propionate concentrations in excess of 300 mg/L, although this effect could be overcome by acclimation.

Alkalinity A direct relationship exists between alkalinity variation and VFA accumulation in anaerobic digestion. A more sensitive parameter for monitoring digestion is the ratio of VFA/alkalinity (Zickefoose and Hayes, 1976). These researchers recommended a ratio between 0.1-0.35 for a healthy digester.

Ratio of propionate/acetate (Pr/Ac) Marchaim and Krause (1993) suggested using the ratio of propionate/acetate, as this ratio was observed to increase prior to changes in biogas composition. However, there was no definite ratio where it indicated process failure. Besides, the mere accumulation of propionate, regardless of its ratio with acetate, indicates limitation in methanogenesis.

Hydrogen/ carbon monoxide monitoring Hydrogen is an important intermediate for methanogenesis (Figure 2.1, page 9). Hydrogen is produced during the fermentation of carbohydrates and the subsequent degradation of higher weight VFA such as propionate and butyrate. Degradation of propionate and butyrate to acetate is thermodynamically unfavourable unless hydrogen is readily removed. Investigation of hydrogen inhibition has been reported and some efforts have been made to use hydrogen concentration as a parameter to control anaerobic treatment to indicate overload conditions (Hickey and Switzenbaum, 1991).

Carbon monoxide (CO) has been hypothesized to be an intermediate in the pathways of methanogens and acetogens, and was first reported by Conrad and Thauer (1983). CO also demonstrated a characteristic response to heavy metal and inhibition induced by organic toxicant (Speece, 1996). Hickey and Switzenbaum (1991) studied the response of hydrogen and carbon monoxide as process indicators of anaerobic digesters subject to organic and hydraulic overloads. They asserted the relevance of hydrogen and carbon monoxide concentrations to indicate overload conditions along with other measures, but not as stand-alone indicators. In anaerobic digesters with high HRTs, gaseous parameters are not as quick to detect overload conditions as other conventional monitoring strategies.

It is possible that CO and H_2 monitoring is a better indicator of stress conditions in high rate anaerobic treatment systems, but this premise needs to be further assessed. H_2 monitoring has not been shown to provide any indication of the level of stress being exerted on the acetoclastic methanogen population, which accounts for almost 70% of methane production. Acetoclastic methanogens can be more easily overloaded than hydrogenphilic methanogenic bacteria, which produce about 28% of the methane in biogas. Application of H_2 and CO monitoring may be more successful in predicting impending digester failure in systems that are not well buffered. Decrease of pH below 6.0 would decrease the efficiency of hydrogenphilic methanogens, resulting in an increased H_2 concentration. Some researchers discarded the use of CO due to inconsistency of response with different substrates under the same operating conditions (Bae and McCarty, 1993).

Other common indicators include rate of biogas production, biogas composition, and reactor pH. However, these indicators are often the result of an imbalance rather than a warning of it.

3.3 General parameter responses to shockloads

Generally, anaerobic processes respond to shockloads in the following ways: an increase in VFA concentrations; a decrease in COD/BOD removal efficiency; a decrease in methane fraction of the biogas, but an increased methane production; higher effluent suspended solids; and increased or decreased pH depending on the buffer capacity of influent and system (Mathiot et al., 1992).

Tay and Zhang (2000) explained that the drop in percentage of CH_4 in biogas during overload was due to increased VFA concentrations. The excess VFA consumed alkalinity in the reactor and induced more CO_2 production, and thus the percentage CH_4 in biogas decreased. Factors causing overload are detailed in Section 2.10.

3.4 Effect of overload on high rate anaerobic reactors

It is important to conduct stability studies on the effect of organic and hydraulic overloading on the performance of anaerobic reactors treating wastewaters since upsets to feed flow rates and concentrations can occur frequently (Canovas-Diaz and Howell, 1988). Furthermore, stability studies can provide valuable information to guide process and operational design of anaerobic reactors.

The effective loading rate for an anaerobic process is limited by the amount of active biomass that can be retained in the reactor and the effective contact between the biomass and the substrate (Fang and Chui, 1995).

During hydraulic overloading, Kennedy and Van den Berg (1982) attributed anaerobic digestion failure performance to the loss of the slow growing methanogenic bacteria from the reactor. However, anaerobic reactors that immobilize bacteria, especially the methanogenic bacteria, onto support surfaces were shown to be less susceptible to washout and could be operated at short HRT, i.e. less than 12 hours.

Murray and Van Den Berg (1981) presented a different view and reported that overloadings were a good way to improve a reactor's performance at steady state. The authors argued that excessive substrate feeding stimulated the activity of inactive biofilm that did not support good microbial growth before overloading. On the other hand, Canovas-Diaz and Howell (1988) argued that the reactor performance improvement could be the result of stronger associations between H_2-producing acetogenic and methanogenic bacteria and not due to increased loading rates.

Effects of waste composition and strength, nutrient requirements, temperature, reactor height and width, and robustness under adverse operation conditions (hydraulic and organic overloadings), intermittent loadings and change in waste composition on downflow suspended fixed film (DSFF) reactors were studied by Kennedy and Van den Berg (1982). In their study, a DSFF reactor (690 cm^3 liquid volume) was found to tolerate sudden changes in the organic loading up to 10 times normal loading (hydraulically loaded) to 94 g COD/L.d imposed in 1 day, and recover their normal performance 12-48 hours after overloading. They found that the pH of mixed liquors was observed to be more important than the VFA concentrations in determining whether DSFF reactors would recover in a reasonable period of time after overloading.

It was noteworthy that most experiments of organic and hydraulic overloadings seemed to be conducted on mature digesters and used either well-buffered wastes or reactors with pH control (Kennedy and Van den Berg, 1982).

Mathiot et al. (1992) studied control parameters' variation following hydraulic and organic shockloads exerted on an upflow fluidised bed reactor (total capacity of 22 L, working volume equal to 8.6 L) using wine distillery wastewater as a substrate. The feed pH was adjusted to neutrality by the addition of buffers, and supplemented with nitrogen in the form of NH_4Cl (530 mg/L), 50 mg/L of KH_2PO_4, nickel (10 g/L) and cobalt (10 g/L). The reactor operated under standard conditions of 4 days HRT; influent COD concentration of 20 g/L corresponded to OLR of 12.8 g COD/L.d. The reactor was subjected to short intense organic shockloads twenty times greater than standard experimental loadings for 15 minutes, and long organic/hydraulic shockloads for 8 hours, followed by 4 hours of feed cessation, then returned to standard pre-shock conditions. Gas and liquid parameters showed a response to the overload conditions about 1 hour after the initiation of the shockload. In the short shockload, it took propionate a longer time to recover to its pre-shock conditions than other control parameters (gas composition and pH). It took a much longer time for the VFA and COD to recover after the organic shockload than it took in the hydraulic shockload scenario (increase flowrate to 22 L/d, corresponding to OLR of 51.2 g COD/L.d) due to the higher organic load exerted in the organic shockload (75.6 g COD/L.d).

Nachaiyasit and Stuckey (1997) reported on studies performed to assess stability of anaerobic fluidised bed (FB), AF, and anaerobic baffled reactors (ABR). They concluded that both transient and step changes in HRT, and the concomitant increase in OLR, had a substantial impact on biomass retention and COD removal. While both organic shocks at constant HRTs and hydraulic shocks at constant feed COD can result in the same OLR, their influence on reactor performance and intermediate behaviour are different. Mass transfer changes during the overloads were believed to have caused the different responses. The authors indicated that more research was needed on ABR's response to transient and step load changes, and that was the reason for their choice of exploring ABR performance in shock conditions. Using a feed COD of 4 g/L and HRT of 20 hours, the reactor was exposed to hydraulic and organic shockloads for 3 hours. ABR performance was found to deteriorate more severely as a result of decreasing HRT with a substantial loss of biomass than from organic shockload. Nonetheless, the ABR recovered its pre-shock performance conditions in 9 hours.

Tay and Zhang (2000) reviewed previous papers dealing with high rate reactors under shocks and observed that AF and expanded/fluidised Bed (EB/FB) have a significant amount of literature to substantiate the claim about their ability to resist organic, hydraulic, or toxic shocks. However, they were in doubt about the effectiveness of granulation in UASB to provide it stability in resisting shocks.

3.4.1 Literature review of effect of organic and hydraulic shockloads on single-phase UASB reactors

Yang and Anderson (1993) reported that anaerobic granulation provided UASB reactors with high stability that maximized their ability to treat higher loading rates. Their study indicated that changes in the characteristics of the granular sludge could be induced either by overloading or by changes in the carbon source in the wastewater, although the rate of such changes was found to be rather slow.

Most overload studies conducted on UASB reactors were organic overloads. Investigating the effect of hydraulic shockloads was preferred as they are more prone to occur and less researched compared to organic shockloads.

Hawkes and co-workers (1993) also investigated the impact of shockloads on two-phase UASB digestion, and found that it displayed a greater stability manifested by quicker return to VFA base line values, despite higher maximum VFA values than observed in single stage UASB. Fang et al. (1995) also reported similar work that reached the same conclusion. However, operating two-phase reactors adds operating costs that not many wastewater treatment plants are willing to bear. For this reason, a single-phase reactor was studied in this thesis.

Paula and Foresti (1992) studied the effect of organic overloads on the kinetic parameters of UASB reactors subjected to organic overloads. A 10.5 L UASB reactor treated synthetic wastewater at different initial COD concentrations corresponding to OLR of 2.07 - 14.8 g COD/L.d at overall COD removal efficiencies varying from 98 to

80%. Overall kinetic parameters were possibly affected by the step increase of influent COD concentrations manifested by the different results of k and K (previously defined in Section 2.8.1) at different OLRs. However, the authors did not supply any statistical significance testing to verify the extent of change of k and K values at different OLRs.

Jawed and Tare (1996) correlated the methanogenic activity with the performance of bench-scale models of UASB, downflow stationary fixed film (DSFF), and upflow stationary film (USFF) reactors at varying organic loading with an empty-bed HRT of 0.8 to 1.10 d. The reactors performed similarly at lower organic loading. However, at higher loading, the performance of DSFF and USFF reactors was reasonably stable, whereas the UASB reactor did not perform well.

Speece (1996) recommended that UASB processes should not operate with less than 1-3 hour HRT. UASB mode was found to be more prone to biomass washout than was an attached growth system.

Lay and Cheng (1998) examined the effect of changing recirculation ratio on the stability of an UASB reactor treating phenolic wastewater. The HRT and feed concentration were maintained constant, and thus the hydraulic loading rate (HLR) - measured as [m/h]- was varied. Using the Haldane relationship, the phenol biodegradation half-saturation constant (K_s) was determined and was found to decrease with a decrease in the recirculation ratio, indicating that the granules had higher substrate affinity under a low HLR than at a high HLR.

3.4.2 Performance of UASB reactors subjected to organic/hydraulic shockloads

Below are 4 cases that study UASB reactors' stability undergoing shockloads compared to other reactors or at different modes and frequencies.

Case 1:

Hawkes et al. (1992) studied the stability of three anaerobic digesting processes treating food processing wastewater subject to step overloads (shock) under different conditions. They observed that metal-supplemented feeds (Fe, Mn, Ni, dosed at 0.02 mg/L feed wastewater) to UASB reactors may be conducive to lessen the instability of operation when hit by an organic shockload. Nonetheless, under steady-state operation, there was no apparent effect of metal supplementation on performance. Although all 3 reactors recovered to pre-shock levels in all cases 16 hours after the initiation of an 8-hour shock, the unsupplemented UASB reactor showed a greater sensitivity to increased overloads exhibited by a higher maximum value of VFA, especially propionic acid. This paper presented more evidence for the importance of nickel in anaerobic digestion reactors.

Murray and Van Den Berg (1981) showed that trace nutrients' addition allowed accumulation of a thicker methanogenic fixed film. On the other hand, Cheu-Lin (1992) showed that Ni addition caused 50% inhibition of VFA degradation batch tests when dosed at 100 mg/L; nevertheless Ni was the least toxic element compared to chromium, cadmium, lead, copper, and zinc. In this work however, there was no metal addition, except phosphorus, to leachate being fed.

Case 2:

Dudley and co-researchers (1993) studied the efficacy of UASB digesters of 5.1 L operating liquid volume to treat increased hydraulic loads. Brewery wastewater (4500 mg COD/L) was the substrate of choice and the temperature was 32°C. No improvement was observed in obviating the negative effects accompanying overloading, such as lowered

COD removal rates, lowered pH and bicarbonate alkalinity, by the inclusion of a conditioning tank and partial recycle. However, in a full-scale plant, the provision of a conditioning tank and recycling were required to maintain physical integrity of digester sludge and minimize washout.

Case 3:

Tay and Zhang (2000) performed a comparison of three high rate digesters subjected to several types of shockloads, where UASB was one of the reactors used. From the seven scenarios that were carried out, three were of relevance to this thesis.

The first scenario was a two-fold organic shockload wherein the influent COD was doubled (5,000 to 10,000 mg/L) while HRT was maintained constant (12 h), corresponding to an OLR of 20 g COD/L.d, for a period of 6 hours. The second scenario represented a two-fold hydraulic shockload corresponding to an OLR of 20 g COD/L.d for a period of 6 hours. The third scenario was a four-fold organic shockload corresponded to an OLR of 40 g COD/L.d for a period of 3 hours. The VFA build-up was minimal in the first two scenarios; however, in the second scenario a slight decrease in pH was reported. The third scenario had a higher VFA accumulation reaching a maximum of 250 mg/L an hour after the shockload period ended.

These results indicated that UASB was more sensitive to organic shockloads but did not provide a clear comparison to the other scenarios of hydraulic shock since the OLR was not equivalent in both scenarios. The authors were more concerned with comparing the performance of several reactors than assessing how a single anaerobic reactor reacted to shockloads of different types, but of similar OLRs.

Case 4:

Nadais, and co-workers (2001) concluded that UASB reactors operated in an *intermittent* mode- 48 hour feed followed by a feedless period of 48 hours and had very good performance and stability in response to 75% fat shockload and 100% organic and hydraulic shockloads. The scope of this thesis brought a comparison of a UASB reactor fed on intermittent and continuous feeding that experienced comparable HRT changes, and thus OLR magnitudes.

The reactors had a working volume of 6 L. The feed rate used before the shock corresponded to an OLR of 12 g COD/L.day and an HRT of 12 hours. COD removal during the organic load dropped from 93 to 85%, while in the hydraulic shock, COD removal dropped to values between 69 - 74%. The results for 100% hydraulic shock were not as good as the organic shockload, even though the OLR on the reactors was the same. The authors attributed the difference in response to mass transfer limitations. At shorter HRTs there were increased mass transfer limitations and decreased contact time between substrate and biomass. In addition, low pH was a probable reason for the poor results of hydraulic shockloads compared to organic shockloads. The maximum VFA at the end of the feedless period of the organic and hydraulic shockloads were 600 and 1000 mg/L respectively, while VFA was not detected before the overload indicating a healthy reactor with stable treatment efficiency.

From the case studies, it has been shown that UASB reactors responded differently to organic vs. hydraulic shockloads manifested in changing measures of impact. The work of this thesis attempts to investigate the effect of landfill leachate hydraulic shockload at different feeding modes to the performance of UASB.

CHAPTER 4
EXPERIMENTAL METHODOLGY

4.1 Experimental setup

4.1.1 UASB reactor setup

The UASB reactor setup used is schematically shown in Figure 4.1. The UASB reactor was made of glass with an approximate total volume of 7 L and an effective volume (liquid capacity) of 5.75 L +/- 0.5 L. The reactor was housed in a room with the temperature controlled at 35 +/- 1°C. The reactor was 13 cm in diameter and 60 cm in height. The influent inlet was placed at the bottom through a T-shaped connector. The vertical orientation of the tubing often caused a clogging problem in the influent tubing due to the falling of granules from the reactor, which required regular clean up of tubing. Sample ports were installed at uniform intervals up the walls of the reactor, for biomass samples' analysis for TSS and VSS. At a height of 50 cm, a recycle line was installed which led back to the influent line. Effluent recycling dilutes the incoming COD, and precludes substrate toxicity.

The biogas volume was measured using a pre-calibrated Wet Tip Meter (Wet Tip Inc.) calibrated using a Fisher Scientific Lab-Crest flow meter (cat. no. 448-118) with a stainless steel float. The rate of biogas production was measured by dividing the measured gas volume (as calibrated by the number of flips recorded by the Wet-tip meter) by time. Sometimes the rate of biogas production was calculated by connecting the wet-tip meter to a chart recorder that plotted a peak whenever the wet-tip tip meter flipped.

The effluent tubing, exiting from the reactor at a height of 55 cm, passed through a glass U-tube to prevent gas leakage from the reactor, and to prevent atmospheric oxygen entering the reactor and deactivating bacteria active in anaerobic conditions. The level difference displayed in the U-tube provided information about the reactor pressure and whether gas production was occurring or not. The existence of a positive pressure difference also confirmed that there was no gas leakage from the reactor.

The reactor top was sealed with a glass lid having two openings to access the inside of the reactor, and a gas exit to allow biogas passage to the Wet-tip meters. On top of the sludge blanket, Koch™ bio-rings were placed to act as a gas/solid separator, and to prevent excessive biomass washout by detaching gas bubbles from granules when floating granules hit the bio-rings. Feed was pumped from the refrigerator maintained at 4°C.

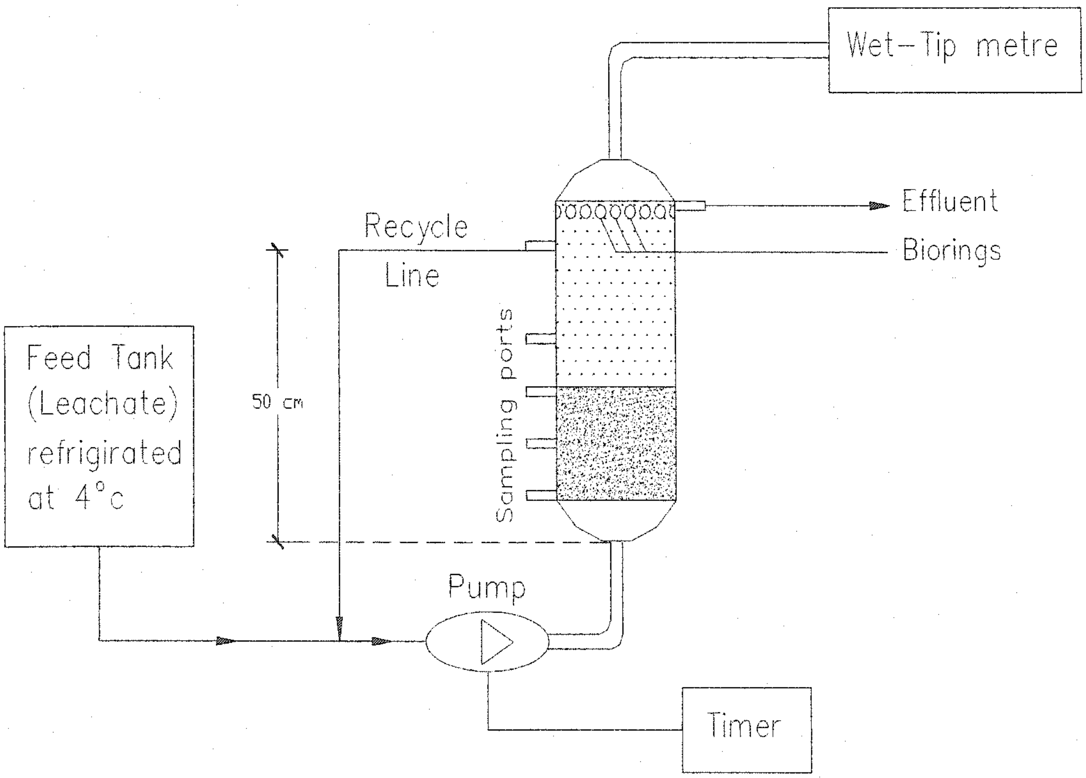

Figure 4.1: Laboratory set-up of UASB reactor.

4.1.2 Pumping system

Masterflex double head pumps were used for feed and recycle pumping to the UASB reactor. The design of the pump allowed for simultaneous pumping of feed and recycle lines at the same rate. The recycle to feed ratio is calculated from the ratio of the square of the inner diameter of tubing used for each line. The tubing used for the recycling line had an inner diameter of 0.794 cm (5/16 in.), whereas the feed tubing had an inner diameter of 0.318 cm (1/8 in.). The recycle to feed ratio was (6.25:1). Since the Masterflex pumps had speed settings that far exceeded the desired feed rate, a timer was connected to the pump allowing intermittent feeding to be set by the operator. The timer had 48 buttons when if all were turned on, then the pump would be operating all day long. Each button accounts for 20-25 minutes of feeding, on average, and the volume being pumped per button turned ON ranged between 60 – 100 mL. The flow rate was adjusted by turning the ON/OFF buttons until the reactor reached the desired flowrate/HRT.

The tubing used for pumping were specially designed tubings from Masterflex, whereas the rest of the tubings connecting from the pump to the reactor were clear Nalgene® Tygon®. The use of clear tubing was based on the recommendation of Savard (2001), to quickly detect any potential clogging problems. Clearance of solids in the tubing was necessary once a week to remove fine solids depositing, particularly in the feeding line and plastic connectors.

4.1.3 Peat moss filter

The filter was a column, one meter high having a square section of 18 cm by 18 cm, made of Plexiglas divided into two layers. The bottom layer was filled with 1 L of

1.2 cm glass marbles and 2 L of sand to provide support for the layer above. The top layer was peat moss saturated with water for 24 hours to decrease dry peat flotation and dust problems. The peat moss used was commercially available from a gardening store under the trademark "Planters Pride". The dry peat looked like fine brown soil which contained small wood pieces and a few tree branches.

The peat moss was first immersed in a pail of water for 24 hours before being placed in the filter to increase density of peat moss and thus enhance stability in the filter. The peat slurry was poured inside the container and allowed to settle for 24 hours. Successive addition and settling of slurry were made until 40 cm of packed peat had accumulated. Small stones were placed on top of the peat to prevent cavity formation when pouring leachate onto the filter.

Raw landfill leachate was poured directly onto the top of the peat column that acted as a filter for solids removal. A port was installed at the bottom of the column where the filtered leachate exited, collected in pails and was kept in a refrigerator next to the hot room where the UASB was housed. The filtered leachate was tested for metals and COD concentration. Peat filters were kept wet since serious channelling problems would occur if the peat was left to dry.

Peat moss was changed whenever the filtered leachate colour was found to be close to the original leachate, indicating weak filtration. Filtered leachate looks yellowish at the beginning of filtration. As the peat moss becomes more saturated with repeated filtration, the colour of filtered leachate darkens and the rate of leachate flow decreases. Savard (2001) reported that the flow rate of leachate through fresh peat filters started at a rate of 1.3 L/h, and decreased with repeated filtrations.

4.2 Materials: leachate, and granular sludge

4.2.1 Landfill leachate

Landfill leachate was obtained from the Carp Road Landfill, an industrial landfill site, and kept in a freezer (–20°C) in room A-013 in the basement of the engineering building in the University of Ottawa. Whenever additional feed leachate was needed, a barrel would be moved to an adjacent refrigerator allowing the leachate to thaw in 4°C. Raw leachate had a pungent smell with an orange-brownish colour, which indicated a considerable amount of colloids and fine solids.

Leachate was then transported to the laboratory where it was filtered through the peat moss column and ready for storage until additional feeding was required. At this stage, COD concentration was measured, and necessary phosphorus amounts were added accordingly. The raw Carp Road leachate available as stock feed had sufficient nitrogen (470 mg/L) in the form of total Kjeldhal nitrogen (TKN) which is a sufficient quantity to sustain anaerobic microbial growth according to the COD:N ratio (100:1). However, phosphorus concentration in the leachate was low and did not satisfy the minimum ratio to sustain microbial growth. Thus, phosphorus was added in the form of potassium phosphate, dibasic (K_2HPO_4) at a concentration of 2 mg/g COD.L. No pH or buffering capacity adjustment was necessary; the raw leachate was found to have high buffering capacity. During the experimental runs, the pH range was well within average safe zone of UASB treatment (6.5-7.5), with no addition of buffering salts confirming Savard's (2001) observation.

4.2.2 Granular sludge (biomass)

Anaerobic granular sludge was provided from the Lake Utopia Pulp and Paper Mill in New Brunswick, Canada, which has a UASB reactor for the treatment of their Chemical Thermal Mechanical Pulp (CTMP) wastewater. These granules were used to inoculate the UASB reactor before the startup. Granules were light brown and had approximate diameters ranging from 0.5 - 4 mm. Solid profiles and specific acetoclastic activity tests were performed on samples of the sludge during the reactor operation to assess the sludge characteristics and how it related to the reactor performance. Specific activity of seed sludge was found to be in the range of 0.32-0.37 g Ac/g VSS.d.

4.3 Tests and analysis of influent and effluent samples

4.3.1 COD

The methodology followed in conducting COD was the closed reflux, titrimetric method described in Standard Methods (1992) Section 5220 C. Digestion vessels were 20 x 150 mm. Therefore, according to Table 5220:I of Standard Methods, 5.0 mL samples were analysed and corresponding reagent volumes used. Ferrous ammonium sulphate (FAS) concentration was measured with every set of samples. The FAS bottle was kept in a cupboard so as to minimize its degradation as a result of exposure to light.

Total COD of the samples was investigated and thus, samples were not filtered. Soluble COD was not measured, as it was thought to present redundant results. Generally, soluble COD accounts for about 90% of total COD of leachate, indicating that organics in the suspended form are relatively low (Kennedy et al., 1988).

4.3.2 pH

Sample pHs were measured with a Fisher pH meter (model 320). Standard VWR Scientific pH 10.0 and 4.0 buffer solutions were used to calibrate the pH meter before each use. Caution was used to cap the samples before measuring the pH, and measurement took place immediately after sampling to prevent loss of CO_2 (Speece, 1996).

4.3.3 Metals composition and concentration

Dr. Nima De Silva, a chemistry professor from Carleton University, measured metals concentrations by using the inductively coupled plasma (ICP) method.

4.3.4 Suspended solids/volatile solids

Standard Methods (1992) Methods 2540D and 2540E were used. TSS and VSS were measured by filtering samples with glass-microfibre filters from Whatman (Cat.No. 1822 070); each was 7.0 cm in diameter.

A known volume of sample, usually 250 mL, was kept at 4°C before filtration. The filtration apparatus was set on a vacuum pump, and solids sticking to the filter walls were washed with distilled water and added to the filter placed in an aluminum tray ready for drying. Samples were dried in a 105°C oven overnight, and cooled in a dessicator for at least 20 minutes before being weighed for TSS measurements. To calculate the volatile fraction, expressed as VSS, the trays carrying filters were then placed in a 550°C furnace for 20 minutes, and then placed in a dessicator for 20 minutes before being weighed.

4.3.5 VFA

VFAs were analyzed according to the method of Ackman (1972). Procedures used to calibrate and analyze VFAs were described by Elliot (1989). VFA concentrations were measured by a Hewlett Packard (HP) 5840A packed column gas chromatograph (GC), equipped with a flame ionization detector. The GC column temperature was set at 180°C, and the injector temperature was set at 400°C. The GC system was fitted with an auto-sampler (HP 7672A Automatic Sampler) and an integrator (5840A GC HP Terminal). The carrier gas was 99.9% pure helium, and formic acid was used to eliminate peak tailing in VFA readings. Samples for VFA analysis were taken from the recycle sample port reflecting the level of biomass activity in the sludge blanket and reactor operation in general.

A sample of 1.0 mL was centrifuged prior to analysis with an Eppendort 5415 Centrifuge, for a minimum of 2 minutes at 10 000 rpm. Samples, VFA mixture and internal standard volumes were taken using Eppendorf 4700 micropipette (0.5 mL). The GC was calibrated with a standard solution of a VFA mixture and internal standard. VFA standard mixture was composed of three organic acids of 0.20% concentration (2000 mg/L acetic, 2000 mg/L propionic and 2000 mg/L butyric acids). The internal standard was a solution of 2000 ± 50 mg/L of iso-butyric acid.

4.4 Tests and analyses

4.4.1 Acetoclastic activity test (AAT)

AAT aims to provide information on the rate of methanogenesis via acetate degradation by the biomass in the reactor with abundant quantities of the easily degradable substrate (acetic acid). AATs were conducted as described in Kennedy (1999). Ten millilitres of anaerobic sludge (biomass) were drawn from reactor ports at two different heights (10 and 30 cm) using a wide mouth syringe. Samples were transferred into a serum bottle with 40 mL of defined buffer reduced medium, also prepared according to the same reference. All bottles containing biomass and defined medium were purged with nitrogen prior to sealing with a rubber septum and an aluminium cap. Bottles were placed on a rotary shaker at 100 rpm, at 35°C for 24 hours.

The test was initiated by injecting samples with 100-200 mg of acetate from prepared acetate stock solutions. Every 60 or 90 minutes, a 1.0 mL sample of the defined medium was taken, centrifuged, and the acetate concentration was measured using the GC as described in Section 4.3.5.

4.4.2 Volatile/Fixed suspended solids

Biomass solids content were determined from the serum bottles used for AAT at the end of the test, rather than being sampled from the reactor, to reduce inconsistency of relating samples to rate of acetate degradation per unit of biomass. About 5 mL of biomass was filtered and weighed as described in Section 4.3.4.

4.4.3 Biogas

Biogas composition was measured by a Hewlett Packard 5710A GC fitted with a thermal conductivity detector. Column temperature was set at 150°C and the injector temperature was set at 100°C. The carrier gas used was helium. Biogas samples were taken with a gas-tight syringe in the sampling port of the gas tubing from the top of the reactor to the wet-tip meter. The samples were injected in the GC within seconds after sampling to avoid contamination and loss of gas sample. The GC was not used in all runs to measure gas composition as it encountered failure midway throughout the experiment.

4.5 Experimental method

The experimental set-up and objectives of this work were set based on findings of the literature review, Chapter 3, and previous results reported by Savard (2001). The UASB reactor was operated until the desired HRT was reached; COD removal had reached more than 90%; and total VFA levels in the effluent were less than 100 mg/L for 2 days.

The desired HRT at steady state was 2.5 - 3 d with an influent COD concentration of ~10 g/L, which corresponded to an OLR of (3.5 - 4 g COD/L.d). Actual influent concentrations were mostly decreasing from the expected values due to degradation of the aqueous organics in the feed tank, which could not be completely avoided. Every 1-2 days, measured amounts of filtered leachate concentrations/water were added to adjust feeding COD concentrations to the desired level.

4.5.1 Monitoring performance of the UASB reactor

The reactor was monitored daily for flowrate and gas production. At least twice a week, before the desired steady state was achieved, COD tests were carried out on influent and effluent samples. The acetoclastic activity test (AAT) was performed every

2-4 weeks, i.e. before and after a shockload scenario to determine differences in acetate degradation activity as a result of shockloads.

The solids test, VSS and TSS, and ICP metal analysis of influent and effluent samples were done before, during, and after the shockloads. Gas production during the shockload was monitored using the chart recorders; however, several leakage problems in the wet-tip meter rendered the calculations of gas production crude and approximate.

4.5.2 Shockloading strategy

As explained in Section 2.2, the quantity of landfill leachate generated varies throughout the year in proportion with the amount of precipitation that percolates through the landfill.

According to Statistics Canada website, climate normals from 1961-1990 provided by Environment Canada's climate information branch (http://www.statcan.ca/english/Pgdb/Land/Geography/phys08a.htm), Ottawa experiences 159 wet days per year on average, which corresponds to a wet day every 2.3 days. A wet day is a day in which total precipitation exceeds 2 mm.

A transient hydraulic shockload strategy was executed when the UASB reactor was operated at the 2.5-3 d HRT steady state. The reactor then experienced hydraulic shockloads in two different modes. After the shock, the flowrate was restored to pre-shock flowrate conditions.

In the first mode, flowrate was increased over a 3-hour period of continuous feeding so that the daily flowrate was increased by a factor of 2-2.5, and the HRT was halved (i.e., 1.25-1.5 d). The second shockload scenario spread the hydraulic shockload of 3-hour intensity over a 9-hour period. The feed was intermittent to the reactor during a

9-hour period, but would be equivalent to the increase of the flowrate executed in the first mode (3 hours of continuous feeding). Both shockload scenarios were also subjected to two hydraulic shockloads of the same intensity spread over a period of 2.3 days, which was the average period between wet day events in Ottawa, making up a total of 4 scenarios.

Each shockload scenario was duplicated whenever possible summing to a total of 7 runs, including replicates, where one scenario was not duplicated because of pumping failure to produce a continuous shockload. The Run # of each scenario is presented in Table 4.1. Each scenario was done over 1 or 2 days, and overloaded by a continuous or intermittent feeding mode. The Run # was given to each scenario for reference to it in the Results and Discussion section.

Table 4.1: Summary of 3-hour shockload scenarios performed.

Scenario			Run #
Feeding Mode	No. of Shocks	Duration (Days)	
Continuous	1	1	1
	1	1	2
	2	2	3
Intermittent	1	1	4
	1	1	5
	2	2	6
	2	2	7

The reactor performance was assessed by monitoring the VFAs and COD values during and following the shockload(s). Speed of recovery to pre-shock conditions were also observed as additional indicators on how fast the UASB reactors handled the sudden hydraulic shocks in quantitative terms.

4.5.3 Determination of kinetic parameters

The kinetic parameters of the biomass (yield coefficient, decay rate) were estimated by using the following equations:

$$\frac{1}{SRT} = YU - b \qquad \text{Equation 4.1}$$

where SRT (d) has been defined earlier in Section 2.8 (Equation 2.2), U is the specific rate of substrate utilization (g COD/g VSS.d), b is the VSS decay rate (d^{-1}), and Y is the biomass yield coefficient (g VSS formed/g COD consumed).

U can be expressed and rearranged as follows:

$$U = \frac{dS/dt}{X_v} \qquad \text{Equation 4.2}$$

$$U = \frac{1}{Y}\frac{1}{SRT} + \frac{b}{Y} \qquad \text{Equation 4.3}$$

where dS/dt is the rate of substrate utilization (g COD/L.d), and X_v is the average concentration of biomass (g VSS/L) in the reactor as defined earlier in Section 2.8.

To calculate Y and b, U was plotted vs. the reciprocal of SRT. According to equation 4.3, slope of the line gives 1/Y, while the intercept is b/Y.

CHAPTER 5
RESULTS AND DISCUSSIONS

5.1 Steady state operation

The reactor was operated to achieve a quasi-steady state and stable operation before the shockloads were applied. In starting up a run, a reactor was fed with diluted landfill leachate (~5,000 mg COD/L) in an intermittent feeding pattern, as explained in Section 4.12, at low flowrate rates. VFA concentrations were observed, and if they were not detected within 48 hours, the feed flowrate rate was increased by another 20 minute increment. Feed COD concentration was also increased, and the flowrate increased until the desired HRT and COD level in the feed (10,000 ± 1,500 mg COD/L) was achieved. The start-up period took about 5 weeks when the reactor was idle. Another start-up acclimatization operation (which took 28 days) was necessary after Run 4 to recover from the hydraulic shock to pre-shock conditions.

Savard (2001) observed that steady-state overall removal rates were strongly dependent on P addition. Low COD removal efficiencies in simulated spring conditions (influent soluble COD ~ 6000 mg/L at varying HRTs) were attributed to possibly P deficiency in feed or decreased HRT. In her work, peat filtration unexpectedly removed 50% of the original P from the raw leachate. Low HRT resulted in insufficient contact time between substrate and micro-organisms. Therefore, it was necessary to eliminate the chance of low P concentrations by adding measured amounts of P to the leachate feed and quicken attainment of the desired operating conditions.

5.2 Shockload magnitudes and scenarios

The procedure of this set of experiments was explained earlier in Section 4.5.2 and summarized in Table 4.1.

The hydraulic shockload scenario and magnitudes imposed on the reactor are shown in Table 5.1 and Figures 5.1 and 5.2 by recording the ratio of changes of flowrate and HRT during shockload scenarios compared to values 24 hours before the shockload. In Table 5.1, the scenario column are those previously identified in Section 4.5.2, Table 4.1. The column following the 'flowrates before the shockloads' and 'during the shockload' represents the sample standard deviation (σ). The Ratio column calculates the ratio of the flowrate during the shockload to the flowrate before the shock. In the double shockloads, as in Runs 3, 6, and 7, the first shock is designated with 'a', and the second shockload is designated with 'b'.

Table 5.1: Flow rate changes for shockload runs.

Run #	Date	Scenario	Flow before (L/d)	σ	Flow during (L/d)	σ	Ratio	σ
1	Sep.24	1 day / 3 h cont.	2.05	0.18	3.90	0.22	1.90	0.20
2	Sep.14	1 day / 3 h cont.	2.07	0.66	4.70	0.9	2.27	0.84
3a	Sep 8-10	2day / 3 h cont.	2.23	0.52	4.01	0.72	1.81	0.53
3b			1.83	0.56	3.95	1.18	2.16	0.92
4	Oct. 2	1 day / 3 h inter.	2.51	0.69	6.97	2.25	2.78	1.17
5	Nov. 14	1 day/ 3 h inter.	1.81	0.2	5.33	1.25	2.94	0.76
6a	Nov. 27-29	2 day/ 3 h inter.	2.00	N/A	5.04	0.42	2.52	0.21
6b			1.40	N/A	5.04	0.11	3.60	0.08
7a	Dec. 13-15	2 day/ 3 h inter.	1.79	0.55	5.28	0.78	2.94	1.00
7b			2.00	0.13	5.28	0.86	2.64	0.46

These shockload scenarios raised the OLR and F:M ratio to rates that were approximately 2-3 times preshock state values, as shown in Figures 5.3 and 5.4. Changes in OLR (g COD/L.d) before and during the overload as a result of the hydraulic shock is shown in Figure 5.3. In Figure 5.4, SLR changes during the overload provide a measure of the stress on micro-organisms. The error bars in all figures are ranges based on a 95% confidence interval (c.i).

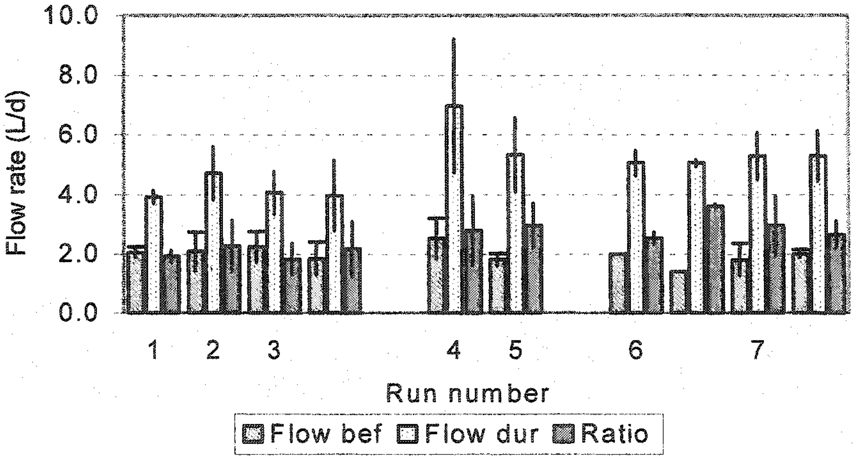

Figure 5.1: Flowrate fluctuations in overload scenarios.

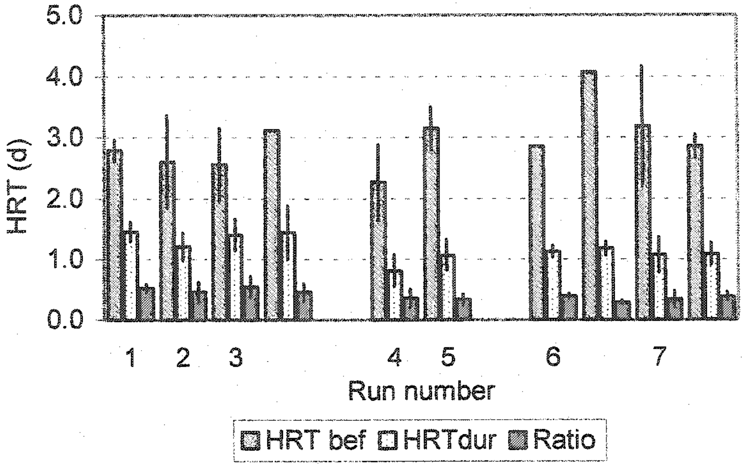

Figure 5.2: HRT fluctuations in overload scenarios.

In all shockloads, the COD of the effluent before the overload was low enough that the COD percentage removal was around 95%.

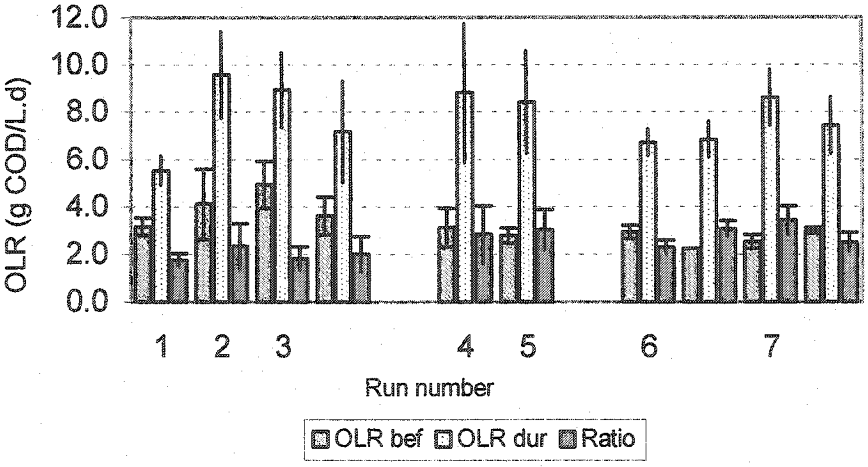

Figure 5.3: OLR fluctuations in overload scenarios.

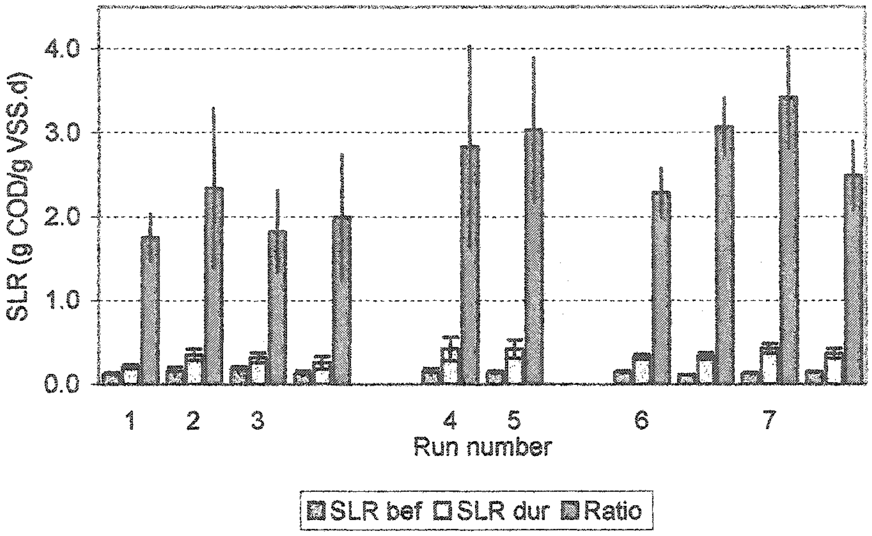

Figure 5.4: SLR fluctuations in overload scenarios.

5.3 Kinetics of anaerobic operation

The parameters Y and b were calculated using equation 4.3. The error margin for the kinetic coefficients were determined using the 95% confidence interval values computed using the linear regression tool in MS Excel 97.The data set used to find the kinetic coefficients is presented along with the results of the analysis in Table 5.2. The symbols A, and B in the table represent the period during which data were taken after (A), or before (B) a shockload run taking place. SRT was calculated using equation 2.2. Raw data values can be found in Appendix A. The specific removal rates (U) were calculated by multiplying the OLR before shockloads by the percentage COD removal (ranged between 95-97 %) achieved in pseudo steady-state at desired HRT magnitudes.

Table 5.2: Kinetic parameters at pseudo steady-state operation, and kinetic coefficients determined.

Date	1/SRT (d^{-1})	Spec. Org. Load (g COD/g VSS.d)	U, specific removal (g COD_{rem}/g VSS.d)
Sep-8B	0.0007	0.17	0.1666
Sep-10 B	0.00083	0.15	0.14131
Sep-14 B	0.0009	0.16	0.15426
Sep-23 B	0.0002	0.12	0.11626
Sep-28 B	0.00077	0.14	0.13462
Nov-13B	0.00097	0.13	0.12397
Nov-15A	0.00285	0.27	0.25171
Nov-24B	0.00065	0.17	0.16733
Dec-3 A	0.00045	0.12	0.06886
Dec-24 B	0.00069	0.15	0.14409

$Y = 0.02 \pm 0.01$ (g VSS /g COD_{rem}.d)

$b = 0.002 \pm 0.001\ d^{-1}$

$R^2 = 0.698$,

Standard error of regression = 0.027

The overall process rate coefficients Y fall closely within the typical range of coefficients (Y: 0.024-0.21), while the coefficient b was lower than the typical range (b: 0.01-0.04) reported by Droste (1997) which demonstrate the slow growth mechanism of biomass in anaerobic conditions.

5.4 Shockload scenarios:

In this section, a detailed description of each run and the impact it exerted on the UASB reactor is analysed.

5.4.1 Hydraulic shockload followed by recycling (Run 1)

The shock was produced by increasing the flowrate rate for 3 hours continuously to about 2-3 times the desired steady-state flowrate, thus increasing OLR equally (as shown in Figure 5.5), then followed by a recycle mode. The average OLR imposed on the reactor before, during, and after the run is indicated as a solid line in all the figures of this section, and its values can be read on Figure 5.3 with error ranges ± σ.

Table 5.1 decreased HRT from 2.79 d ± 0.17 d to 1.46 d ± 0.16 d for 3 hours. In calculating OLR, it must be emphasized that it is the average of the product of the concentration and the flow and not the product of the averages (Van Haandel and Lettinga, 1994). Prior to the shock, the total VFA (TVFA) concentration was negligible and not detected, and the COD concentration of the effluent was around 300 mg/L, equivalent to ~ 96% removal efficiency. After the shock, the TVFA increased gradually following the start of the shock to a maximum of 85 mg/L, and then decreased steeply to the baseline levels five hours after the shock ceased.

An increase of VFA concentration is a sign of excessive substrate concentration beyond the micro-organism's capacity of treatment. It is understood that the accumulation of VFA is a result of limitation of the activity of methanogenesis. The butyrate and propionate are not broken down to acetate as quickly as other VFAs that are produced in acetogenisis. The steep decrease of VFA concentrations is an indication of fast recovery, but the feed was terminated and the effluent was re-fed to the reactor. The reactor was operated in a recycling (batch) mode, which presented a dilute feed compared to the organic loading imposed during the overload and even before the overload.

The pH values in the reactor in all runs were in the range of 6.8-7.3 without any pH adjustment throughout the shockload. Values of effluent COD before and during the shockload can be seen in the experimental data section (Appendix A). COD percentage removal efficiencies are shown as a function of time in Figure 5.6. The influent concentration was not changed, while the effluent COD was gradually increasing, in a similar trend to VFA. Thus, the COD percentage removal decreases. A few hours after the cessation of the shock, bacterial activity increased to match the increasing load until it matched the rate of accumulation of VFA that resulted from the hydraulic overload.

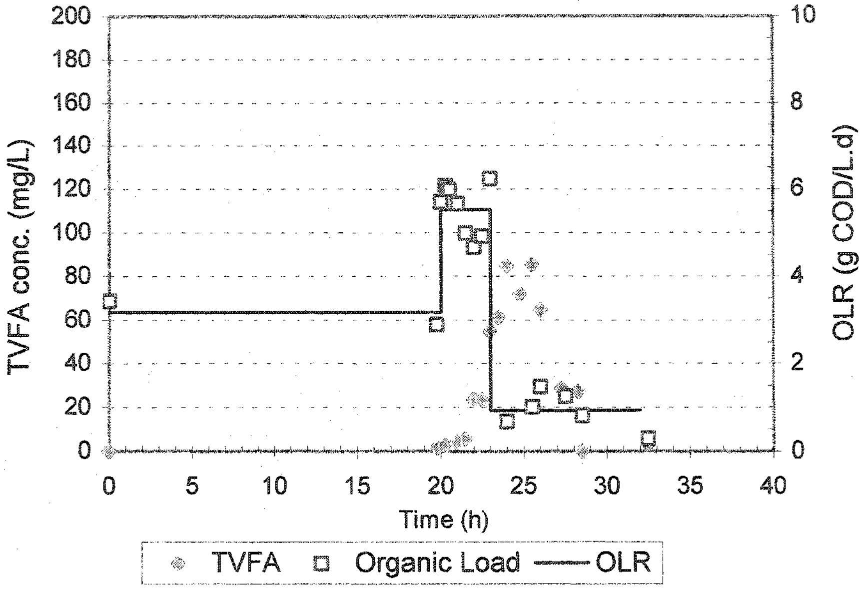

Figure 5.5: VFA response of reactor to a 3-hour continuous hydraulic shock followed by recycle mode operation (Run 1).

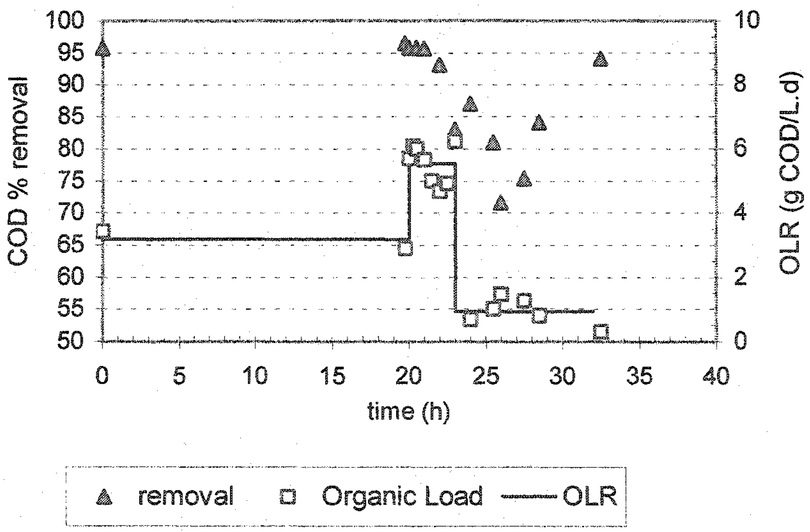

Figure 5.6: COD percentage removal during overload Run 1.

5.4.2 Shockload scenarios: single continuous hydraulic shockload (Run 2)

The shock was produced by increasing the flow rate for 3 hours continuously about 2.27 ± 0.84 times the pre-shock flowrate. Thus, increasing OLR 2.33 ± 0.86 times the pre-shock OLR, as shown in Figure 5.7, returns the feed rate to the values before the shockload. The higher values of OLR post-shock were unexpected since flowrate magnitudes after the shock was measured at 3.22 ± 0.31 L/d. Controlling OLR is a difficult task due to the changing COD concentrations that cannot be detected instantly.

OLR increased from 4.10 ± 1.49 g COD/L.d to 9.56 ± 1.84 g COD/L.d by decreasing HRT from 2.60 ± 0.75 d to 1.21 ± 0.23 d. COD percentage removal efficiencies are shown as a function of time in Figure 5.8. Prior to the shockload, 95% COD treatment efficiency was achieved. As the shock commenced, the COD effluent values kept increasing until 8 hours after the shock cessation, thus decreasing the removal efficiency to almost 60%. It took about 11 hours for the removal efficiency to return to its pre-shock values from the time the shock cessated. TVFA concentration increased gradually following the start of the shock to a maximum of 220 mg/L, and then decreased gradually over 11-19 hours after the shock despite operating at a higher OLR compared to loading before the shock. Studying the possibility of higher OLRs after hydraulic shocks may be a good subject to work on in a future set of experiments.

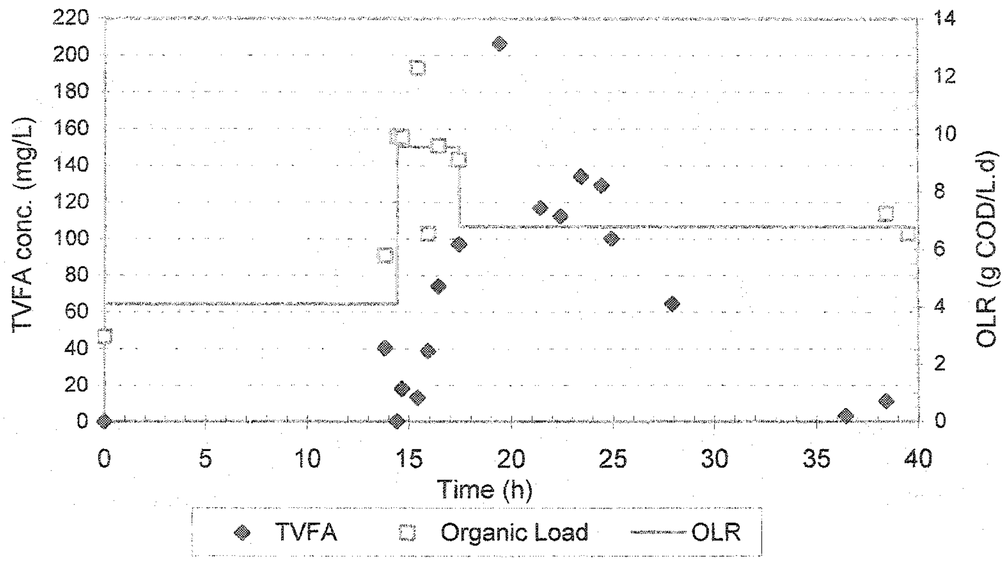

Figure 5.7: TVFA concentration changes during hydraulic overload Run 2.

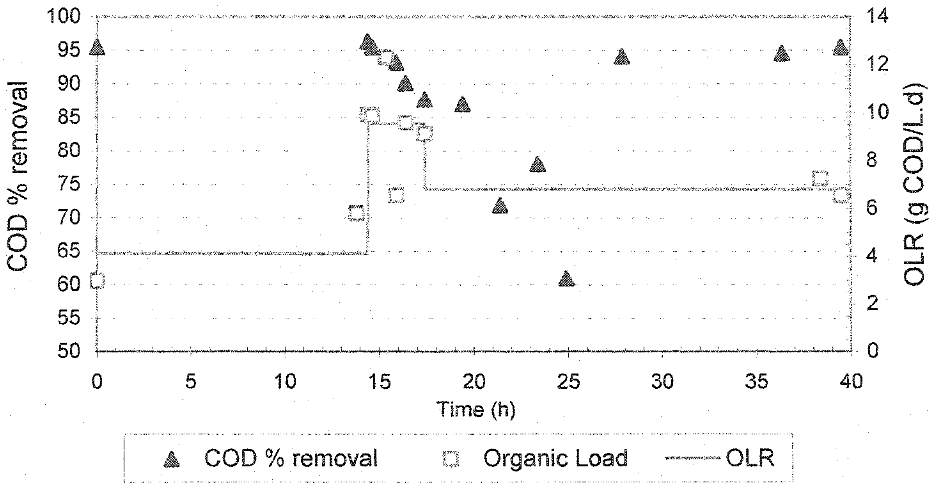

Figure 5.8: COD percentage removal during overload Run 2.

5.4.3 Shockload scenarios: double continuous shockload (Run 3)

In this run, two shockloads were imposed over 2 days. The 2 shocks were produced by increasing the flowrate rate for 3 hours in a continuous mode. As a result, OLR increased 1.82 ± 0.49, and 1.99 ± 0.75 times the OLR before the two shockloads

(3a, 3b) respectively, as shown in Figure 5.9. After each shockload, the reactor was fed at the pre-shock level. Twenty-four hours past the recovery of the first shock, the reactor was subjected to the second shockload. The pattern of VFA and COD percentage removal responding to the shockloads showed similarity to Runs 1 and 2.

The TVFA and percentage COD removal response in a double shockload within 60 hours (2.5 days), from the 20th to 80th h are shown in Figures 5.9 and 5.10. The maximum TVFA generated as a result of the shocks were comparable (519 mg/L in 3a, and 235 mg/L in 3b). However, the COD percentage removal was more severely affected in the second shockload (3b) compared to run 3a, resulting in a poorer effluent. It is possible that the micro-organisms breaking down the waste were partly washed out during the first shockload, and 24 hours for recovery was not sufficient time to compensate for the biomass lost. Again, it was noted that the TVFA concentrations were not indicative of the effluent quality, as observed in Runs 1 and 2.

A comparison in the performance of the UASB reactor in response to the different shock runs is displayed in Table 5.3. Runs 1 and 2 represent the single shock, and Run 3 represents the double shock mode.

Table 5.3: Summary of reactor's response to single and double continuous shock modes (Runs 1-3).

RUN	COD influent (mg/L)	OLR during (g COD/L.d)	SLR during (g COD/g VSS.d)	HRT (d)	Max. TVFA (mg/L)	Max. COD (mg/L)	Time to pre-shock (h)
1	8,600	5.53 ± 0.60	0.21 ± 0.02	1.46	85	2240	5
2	11,500	9.56 ± 1.84	0.35 ± 0.07	1.21	206	4538	11 – 19
3a	12,500	8.93 ± 1.57	0.32 ± 0.06	1.41	519	3857	25
3b	10,700	7.17 ± 2.16	0.25 ± 0.08	1.44	235	4628	15

Maximum COD concentrations of the effluent give an assessment of the effluent quality, which sometimes may not be observed clearly from the concentration of TVFA. The time to pre-shock column presents the time it took the VFA concentration to decrease to the baseline concentration prior to the shockload.

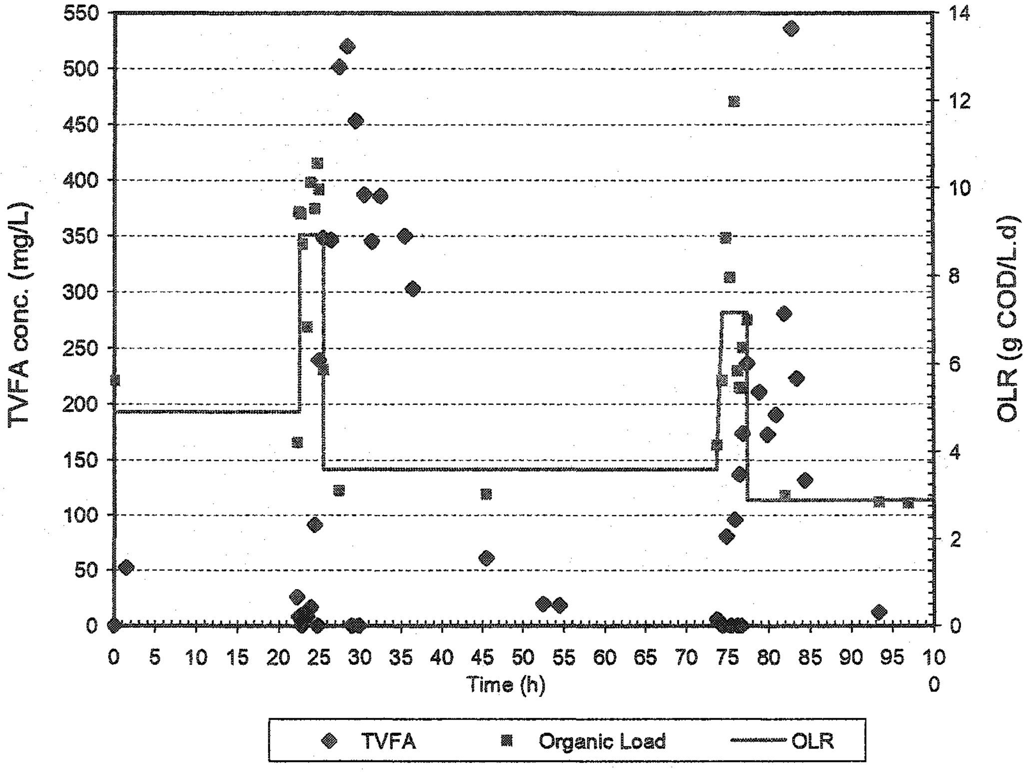

Figure 5.9: TVFA response to double shockload overload (Run 3).

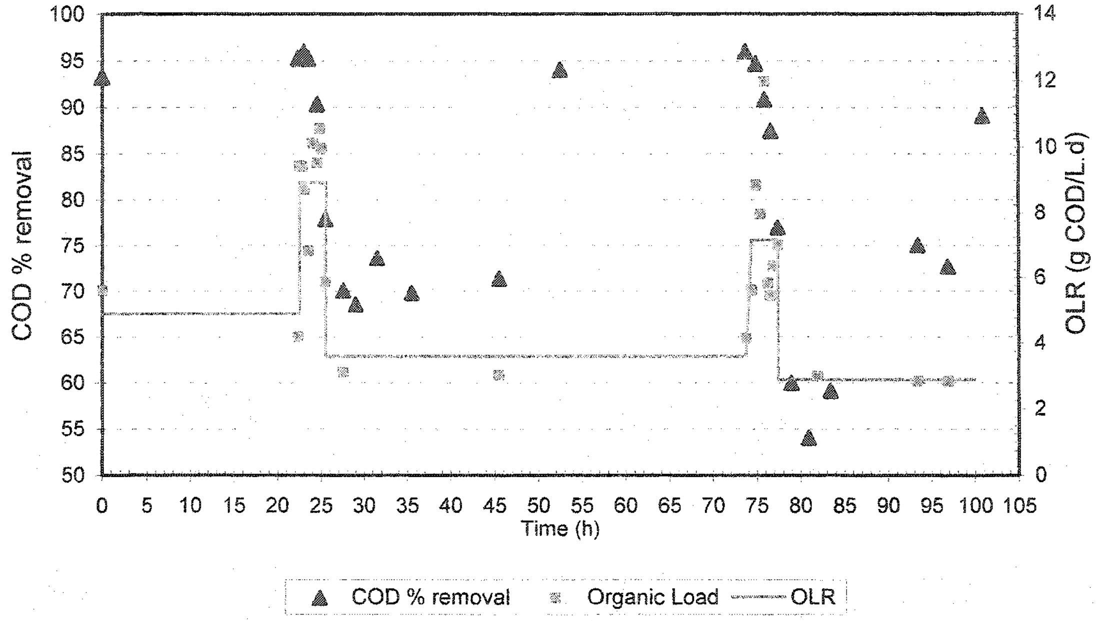

Figure 5.10: COD percentage removal of a reactor exposed to double shockload Run 3.

5.4.4 Shockload scenarios (intermittent overload): Runs 4 and 5

Runs 4 and 5 are duplicate runs employing an intermittent feeding mode to impose an overall 3-hour overload period to produce an equivalent increase in flowrate as the continuous mode. To attain a total of 3 hours overload, excessive feeding was switched 'ON' 7 times in 9 hours for a period of 25 minutes each, comprising a total of 175 minutes.

In Runs 4 and 5, the shocks were produced by increasing the flowrate rate about 2.78 ± 1.17 and 2.94 ± 0.76 times the steady state flowrate, and thus increasing OLR 2.83 ± 1.20 and 3.025 ± 0.851 times the steady state OLR, then fed at the steady state OLR before the overload in Runs 4 and 5, respectively.

In Run 4, OLR was increased from 3.12 ± 0.82 g COD/L.d to 8.81 ± 2.94 g COD/L.d, by decreasing HRT from 2.27 ± 0.62 d to 0.82 ± 0.26 d. In Run 5, OLR increased from 2.78 ± 0.31 g COD/L.d to 8.41 ± 2.17 g COD/L.d by decreasing HRT from 3.15 ± 0.35 d to 1.07 ± 0.25 d.

TVFA concentrations and COD percentage removal efficiencies of Run 4 are shown as a function of time in Figures 5.11 and 5.12, respectively. In Run 4, the reactor experienced a difficult time recovering from the shockload for more than 40 hours after the cessation of the shock. Higher VFA accumulated until it reached a peak ~ 3250 mg/L, and decreased to ~1500 mg/L after 40 hours, and low COD percentage removals ~ 65% after 40 hours from the cessation of the shock. Operation in a recycle mode was deemed necessary to prevent further poisoning of biomass, where the timing of its introduction is indicated in the figure as a vertical line. Start-up of the reactor to reach a steady state prior to the shock for this run took 28 days.

On the other hand, the reactor during Run 5 (a replicate of Run 4 in terms of feeding mode) has shown better tolerance to the shockload even though the SLR was equivalent to Run 4, as shown in Table 5.6: SLR = 0.33 ± 0.03; Run 5 SLR = 0.42 ± 0.11 g COD/g VSS.d. The reactor in Run 5 produced less TVFA, and better effluent quality than Run 4. Performance differences can be attributed to several reasons. A high flowrate was used in Run 4 for a short period (<20 minutes), reaching an HRT of 0.15 d, where washout of biomass occurred for 40 minutes. Washout was not observed in Run 5. Decrease of biomass concomitant with increased OLRs caused an excessive load on the micro-organisms' capability to breakdown incoming waste.

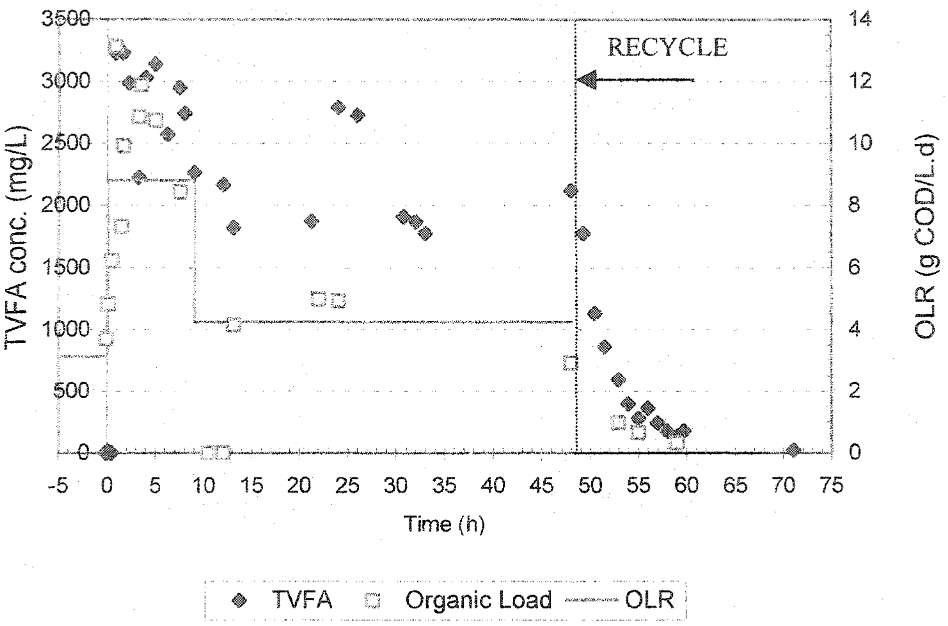

Figure 5.11: TVFA concentration changes during overload Run 4.

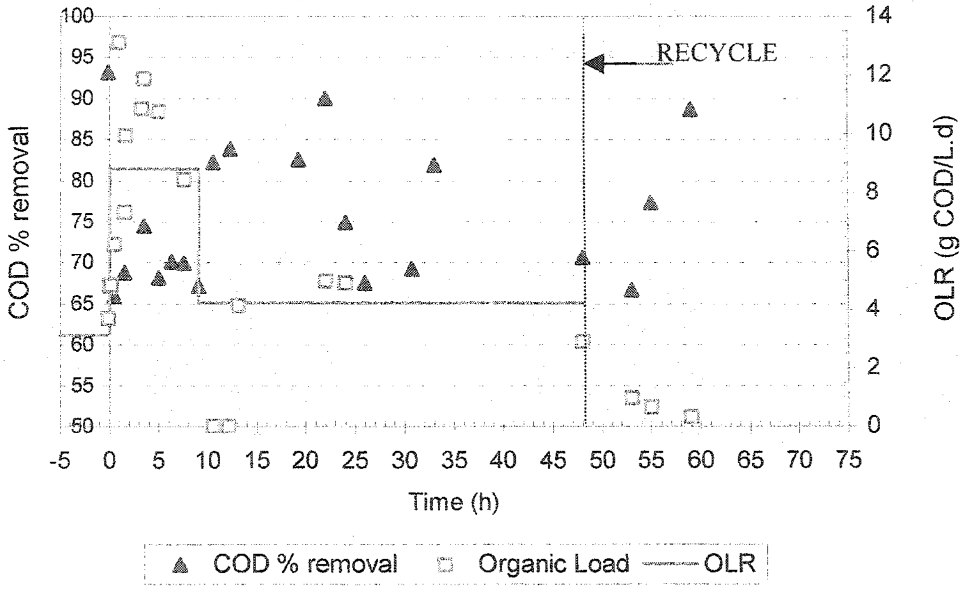

Figure 5.12: COD percentage removal during overload Run 4.

A summary of the reactor performance of Runs 4 and 5 is presented in Table 5.4. The VFA concentrations and COD percentage removal changes with respect to time are displayed in Figures 5.13 and 5.14. Changing feed characteristics and concentrations during the operation of the reactor, whether before, during or immediately after the shockload may account for the different reactor responses. Even if the filtered leachate added was of similar COD concentrations, it often happened that they would have different metal content, as can be seen in Appendix B. Varying feed characteristics could also explain changing response for a similar shockload type.

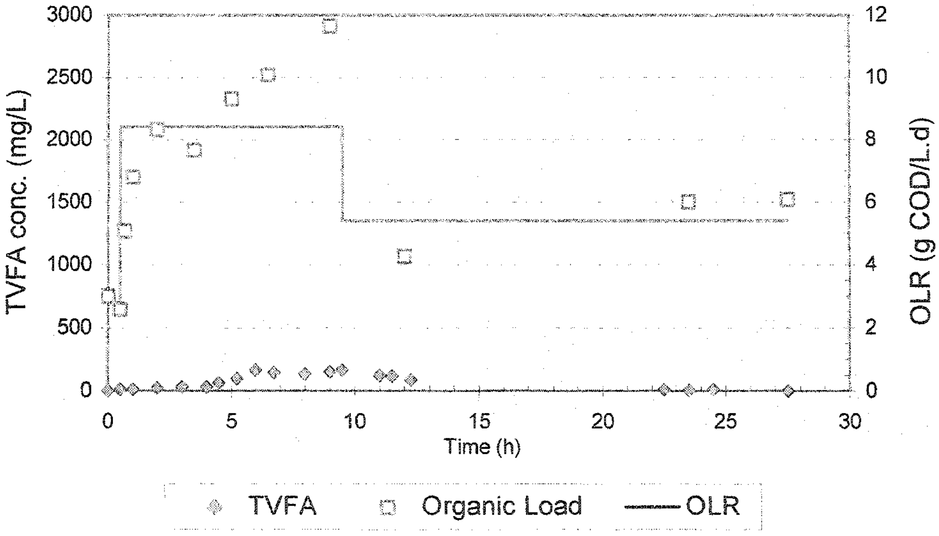

Figure 5.13: TVFA concentration changes during overload Run 5.

Another possible reason is noted when comparing the concentration of nickel (Ni) in the feed in the two runs. The concentration of Ni in Run 4 was less than 0.079 mg/L, while it was 0.280 mg/L in the feed used in Run 5. According to Speece (1993), nickel is a trace metal that aids growth of methanogens, which become rate limited during shockloads. However, this observation may not be conclusive or the only factor for such a discrepancy in the reactor's response to shocks 4 and 5. As shall be seen later in Section 5.10, the Ni concentrations in other runs were also not detected and the reactor withstood shockloads reasonably well.

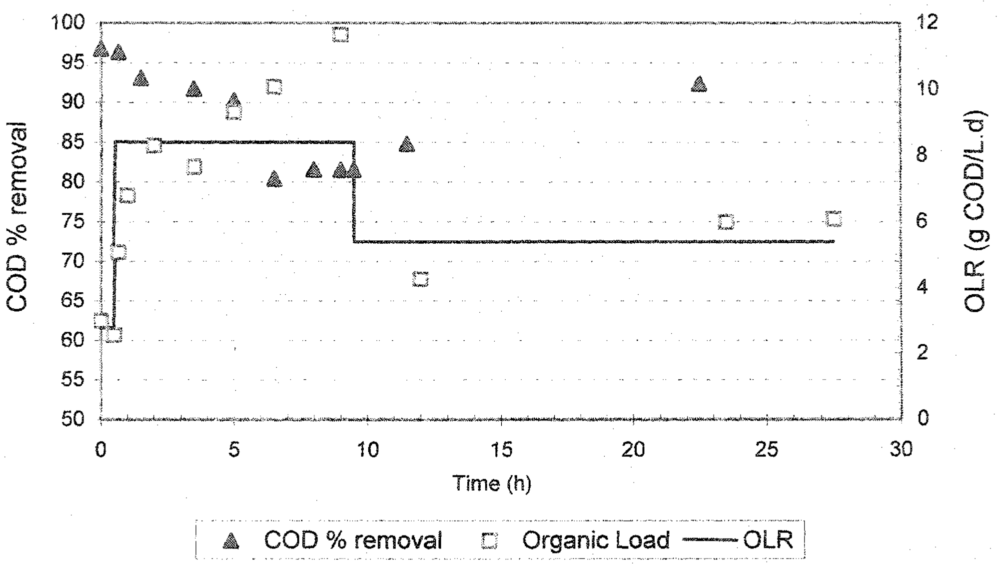

Figure 5.14: COD percentage removal efficiency in reactor during overload Run 5.

Table 5.4 : Summary of reactor performance in response to shockload Runs 4 and 5.

RUN	COD influent (mg/L)	OLR during (g COD/L.d)	SLR during (g COD/g VSS.d)	HRT (d)	Max. TVFA (mg/L)	Max. COD (mg/L)	Time to pre-shock (h)
4	7,200	8.8 ± 2.9	0.33 ± 0.03	1.13	3227	2436	40
5	8,762 -9,523	8.41 ± 2.17	0.42 ± 0.11	1.07	166	1752	13

5.4.5 Shockload scenarios: Runs 6 and 7 (double shockloads, intermittent overload feeding)

Runs 6 and 7 are replicates, and they resemble Runs 4 and 5 in terms of the overload feeding mode; however, the reactor was hydraulically shocked twice within 2 days in Runs 6 and 7 as opposed to a single shock in Runs 4 and 5. A summary of the loading rates imposed and performance of the UASB reactor to the shocks of Runs 6 and 7 are shown in Table 5.5. The VFA and COD percentage removal in Run 6 are shown in Figures 5.15 and 5.16 respectively. While the VFA and COD percentage removal changes during the shockload in Run 7 are plotted in Figures 5.17 and 5.18, respectively.

Table 5.5: Summary of reactor performance in response to shockload Runs 6 and 7.

RUN	COD influent (mg/L)	OLR during (g COD/L.d)	SLR during (g COD/g VSS.d)	HRT (d)	Max. TVFA (mg/L)	Max. COD (mg/L)	Time to pre-shock (h)
6a	7,600	6.7 ± 0.6	0.33 ± 0.03	1.13	50	1537	18
6b	8,000	6.8 ± 0.8	0.34 ± 0.04	1.18	2500	1963	20-30
7a	9,000	8.6 ± 1.2	0.43 ± 0.06	1.08	78	1180	12
7b	8,000	7.4 ± 1.2	0.34 ± 0.06	1.09	3850	1672	9

In both runs, it was noted that the reactor experienced a more difficult time in maintaining a low VFA level. The difficulty is manifest in the low COD removal in the second shockload compared to the first shockload, even though the SLR in both shocks were comparable in Run 6, or less than the first shock (see Run 7). It took the reactor in the second shock of Run 6 a few hours longer than the first shock to recover VFA and COD percentage removal to pre-shock conditions. The same behavior was noted in Run 7. This occurred although the reactor was impacted, in the second shock, by an equivalent

OLR and SLR to the first shock in the same run (time 0-9 h). The second shockload took place from time 51.5–60.5 h.

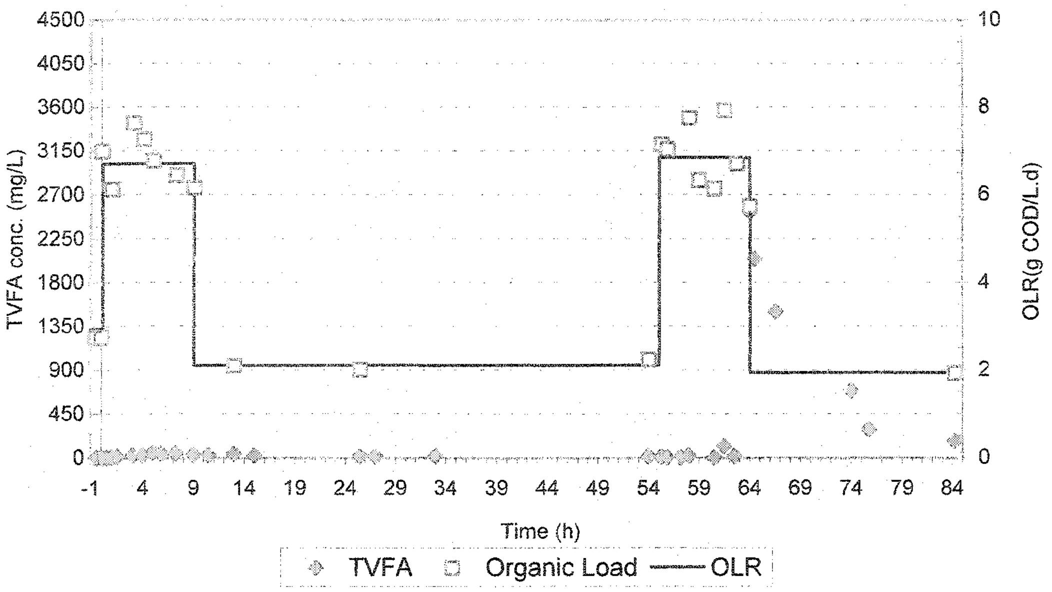

Figure 5.15: TVFA concentration changes during overload Run 6.

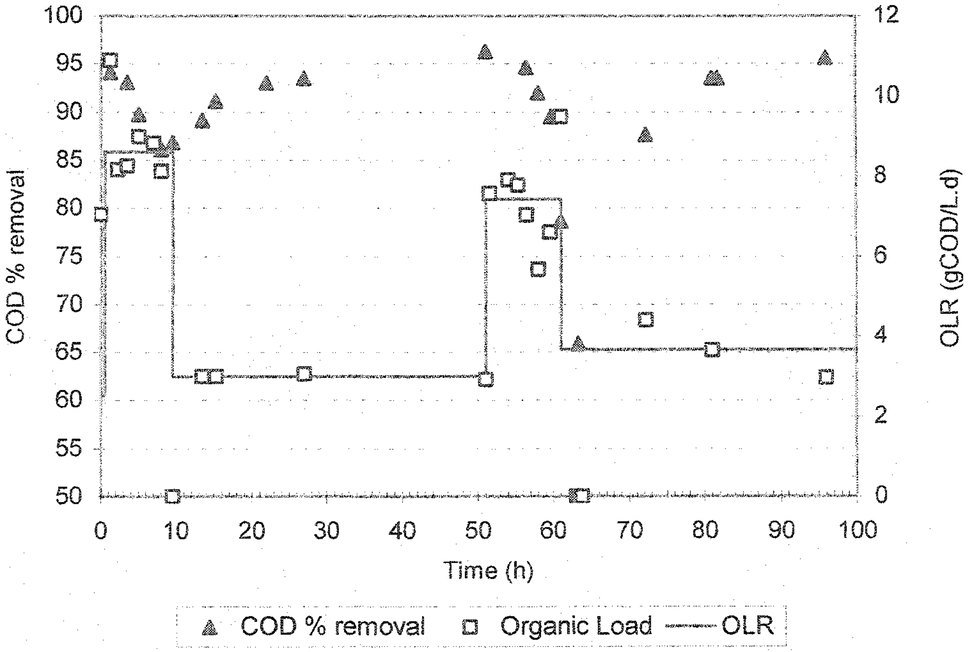

Figure 5.16: COD percentage removal in double intermittent shockloads (Run 6).

As the second shockload was ending (time 57-60 h), the TVFA and effluent COD concentrations declined (recovering to pre-shock conditions) during the shockload, which was unusual. In most cases of shockloads, the usual response was an increase in effluent COD and TVFA concentrations, which degraded a few hours after the cessation of a shock. In the second shockload of this run, the degradation happened during the shockload. Indeed, the elevated concentrations of VFA and COD in the effluent were higher than in the first shockload, yet the reactor appeared to accommodate the excessive influent substrate. Also, towards the end of the second shockload (at time = 60.75 to 61 h) in Run 7, and as the TVFA had showed consistent decrease to pre-shock levels, a mistake was made by reversing the feed and recycle line for 15 minutes. The reverse feeding resulted in incoming leachate entering the top of the reactor (sludge blanket) while the weaker concentration effluent was fed at the bottom to the sludge bed. The result of this mistake was another sharp increase of TVFA and COD concentration in the effluent. However, the COD effluent concentration recovered more quickly than what VFA values implied. Because of the intermittent mode, more time was allowed for the micro-organisms to break down wastewater between the feedings, which resulted in a better effluent concentration compared to continuous mode shockloads. Quicker recoveries to pre-shock concentrations were the manifestation of the enhancement of the micro-organisms' capacity to treat shockloads fed in an intermittent mode.

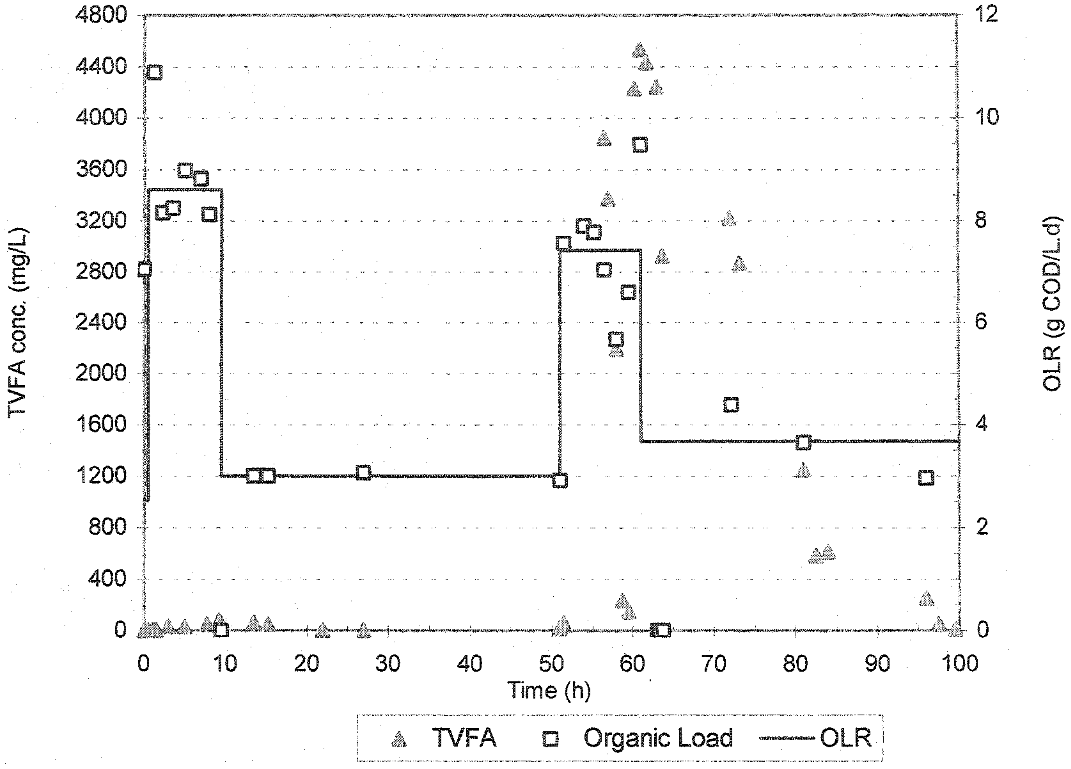

Figure 5.17: TVFA response to double shockload of intermittent feed mode (Run 7).

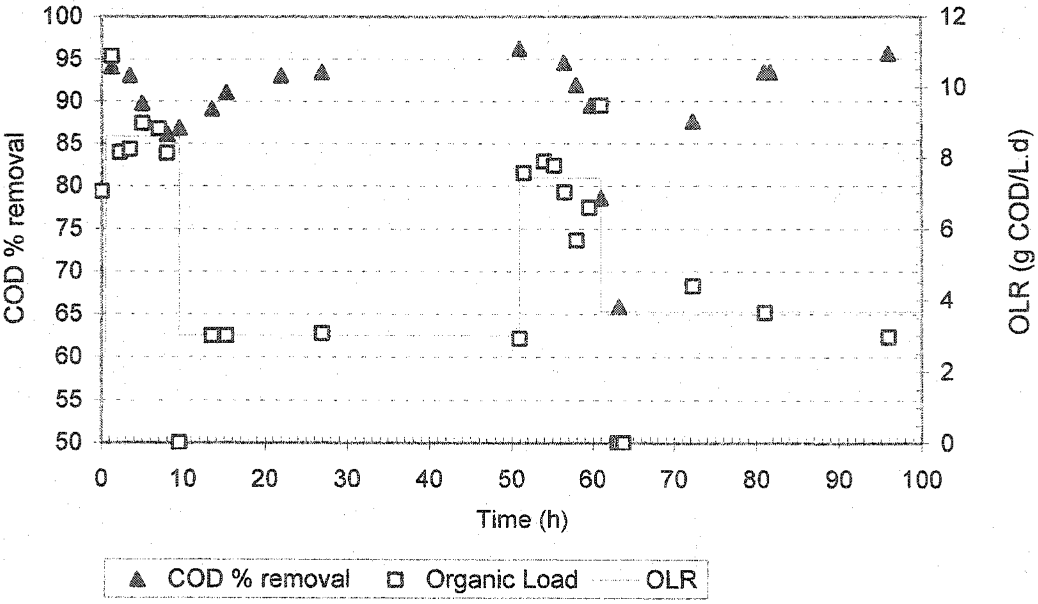

Figure 5.18: COD percentage removal when exposed to a double shockload (Run 7).

5.5 Ratio of propionic to acetic acids (Pr/Ac) during overloads

In Section 3.2.3, the suggestion of Marchaim and Krause (1993) was to consider the ratio of Pr/Ac as early indicators of overload. In this experiment, the increased ratio of propionate was inevitable since a condition of pseudo steady-state was assumed when there was minimal concentration of acetic acids, and needless to say, no propionate. Steady-state conditions were assumed, which indicated near complete conversion of acetate to CH_4 gas, or formation of biomass. However, it cannot be deduced from VFA values, ratio of Pr/Ac, or higher VFA (HVFA)/Acetate that a ratio above a particular value is sufficient to indicate that a system is overloaded. A few examples drawn from the data of the runs with comparable COD effluent values, Pr/Ac, HVFA/Ac ratios, and percentage COD removal, are presented in Table 5.6.

Table 5.6: Selection of VFA readings with respective Pr/Ac and COD values.

RUN	Ac, Pr, Bu (mg/L)	Pr/Ac, HVFA/Ac	COD_{eff} (mg/L)	COD (% removal)
2	32, 68, 0	2.12, 0	4500	60
	16, 47, 0	2.8, 0	700	94
3a	214,162, 124	0.75, 1.32	3685	70
	52, 229, 21.1	4.41, 4.81	~ 3500	~ 70
3b	45, 13, 22	0.295, 0	~ 4100	95
	45, 460, 27	10.1, 0	590	59
4	730, 1000, 1500	1.37, 3.43	2080	65
	42, 91.6, 0	2.15, 0	627	88
5	6, 2.9, 0	0.46, 0	~ 330	96
	57, 50, 55	0.88, 1.85	1752	80.4
	34, 6.8, 0	1.99, 0	933	92
6a	30, 10, 0	0.33, 0	1530	79.5
6b	47, 21, 47	0.44, 1.42	800	90
	885, 572, 1060	0.65, 1.85	1963	70
7a	25, 52	2.1, 0	1110	86.5
7b	1390, 875, 1582	0.63, 1.8	436	94.6
	55, 53, 41	0.97, 1.7	800	90
	1532, 1245, 1470	0.81, 1.77	4218	65
	26, 164, 62	6.3, 8.7	381	95.6

Values of acetate, propionate, and butyrate (Ac, Pr, and Bu) are indicative of the activity of the system, where low values tend to indicate a healthy reactor. Values for the ratio of (HVFA/Ac) were mentioned whenever observed after Pr/Ac ratios in the same column. As can be seen from the set of data in Table 5.6, the Pr/Ac and HVFA/Ac ratios are not always able to indicate stressed reactors. Ratios larger than 2.0 (considered high according to Marchaim and Krause (1993) and an early sign of process failure) were found in cases where the effluent COD values were lower accompanied by a high percentage removal (see for example, Runs 7a and 7b). On the other hand, lower ratios with high effluent concentration (indicating reduced removal efficiency) have been found in Runs 6b and 7b. Mere dependence on ratios of higher acids to acetic acid indicated misleading results in many cases, not making this ratio a reliable indicator of process failure.

5.6 Recovery rate calculations

The overload recovery rate (RC) with the unit (mg Ac/L.h) is used in an attempt to quantitatively assess the speed of reactor recovery as determined from acetic acid consumption and recovery to concentrations existing prior to overload, equation 5.1:

$$y = RC*t + e \qquad \text{Equation 5.1}$$

where y (mg Ac/L) represents the concentration of acetic acid as a function of time (t), and (e) corresponds to random error.

After the cessation of the shock, the VFA concentrations decline as the OLR is returned to pre-shock conditions. It is possible that as a result of the shock, the anaerobic consortia may be stimulated to treat the extra quantities of waste that have accumulated.

RC was calculated by finding the absolute value of the slope of decay of acetic acid from its peak concentration until it returned to pre-shock concentrations. The slope (RC), was calculated by using the linear regression tool in MS Excel 97, which employs the linear least squares estimation; thus a linear decay relationship was adopted.

It should be noted that since feed rate was returned to pre-shock HRT, the RC value accounts for removal of accumulated VFA (formed during the shock) as well as any VFA formed in the reactor during recovery period. The regression was repeated twice in Run 7b since the run experienced two shocks as explained earlier in Section 5.4.5.

It is important to note that only acetic acid was chosen for calculation of the breakdown rate despite the existence of other VFA. Acetate's decay indicates the activity of acetoclastic methanogens, while other VFAs indicate former stages of anaerobic bioconversions. In addition, higher VFA go through complex interactions as they are decomposed to acetic acid; thus making the analysis more complicated and beyond the scope of this thesis. COD values were not chosen for regression analysis for two reasons: less samples can be taken for analysis compared to VFA analysis; COD is non-specific and can include insoluble organics that are hard to treat anaerobically, let alone being indicative of reactor performance, as is the case with acetic acid.

The average RC and the 95% c.i. for the various hydraulic shockloads are presented in Table 5.7. R^2 values are the adjusted values of the coefficient of determination computed by the regression tool in MS Excel. Additionally, Table 5.7 contains the specific acetic acid recovery rate (k_{rec}) term, which was calculated by dividing RC by the mass of VSS in the reactor. The last column is the standard error (SE) of the linear regression estimation of the concentration of acetic acid at a particular time (y) after the cessation of a hydraulic shock.

Average RC values ranged from 0.9 to 478 mg Ac/L.h. It was difficult to determine a clear trend between overload conditions and RC values. The only trend noticed was the significant increase in RC values when acetic acid concentrations exceeded 800 mg Ac/L. RC values and reactor recovery to pre-steady state conditions were impacted on by the concentration and type of accumulated VFAs as well as the duration of the shock. In other words, it was difficult to predict recovery times for a given hydraulic shock based on RC values alone. Using RC value to give an indication of the speed of recovery in overloads without accounting for operator conditions should be avoided.

Table 5.7: Recovery rate calculations after shockloads.

Run	**Peak Acetic (mg/L)**	**RC (mg Ac/L.h)**	**R^2**	**k_{rec} (g Ac/g VSS.d)**	**# of points**	**SE**
1	28.0	1.5 < 5.2 < 8.9	0.61	0.001 < 0.005 < 0.008	8	7.53
2	87.8	1.9 < 4.2 < 6.6	0.68	0.002 <0.004 < 0.006	11	15.57
3a	160.9	15.5 <18.8 < 22.1	0.94	0.013 < 0.016 < 0.019	9	44.77
3b	159.3	3.1 < 4.4 < 5.7	0.89	0.003 < 0.004 <0.005	9	7.17
4	638.2	2.5 < 6.1< 14.7	0.14	0.003 < 0.007 < 0.017	11	160
5	33.63	6.8 < 9.5 < 12.2	0.93	0.008 < 0.011< 0.015	7	17.47
6a	16.3	0.3 < 0.9 < 1.5	0.69	0.00< 0.001 < 0.002	7	5.51
6b	885.3	12.2< 40.1<67.9	0.75	0.015 < 0.047 < 0.081	7	178
7a	25.7	1.7 < 4.4 < 7.0	0.94	0.002 < 0.005 < 0.008	4	5.3
7b:dur*	1389.5	292.1 < 478.6 < 665	0.94	0.342 < 0.561 < 0.779	5	144
7b: aft**	1588.3	33.7 < 47 < 60.3	0.86	0.034 < 0.048 < 0.071	11	247

* 7b:dur: Illustrating recovery occurring in the time period (51.5 - 60 h) in Run 7b.

** 7b:aft: Illustrating recovery occurring in the time period (60.75 - 98 h) after the end of Run 7b.

In comparison to maximum specific rates of substrate utilization (k) values determined for AAT tests (outlined in Section 5.10), the average k_{rec} values tend to be less. The average k_{rec} computed for 7b:dur (0.56 ± 0.22 g Ac/g VSS.d) was the only result that was comparable to k, determined in AAT (0.68 ± 0.1 g Ac/g VSS.d). All other k_{rec} values were significantly less and probably indicate that recovery was slower due to the added stress of degradation of influent during the recovery period (pre-shock HRT). In the run that was switched over to recycle mode following the overload (Run 1), k_{rec} (0.005 ± 0.003 g Ac/g VSS.d) was lower than the comparable AAT test. Unfortunately, the option of a recycle (batch) operation is not always possible.

SE serves as a useful single measure of the prediction capability of a model. The SE of the estimate is computed from the variance of the predicted value y, and SE indicates the precision with which the model estimates the value of the dependent variable (Berthouex and Brown, 1994). Berthouex and Brown (1994) list the values of R^2 required to establish statistical significance for a linear regression equation $y = ax + b$ and is presented in Table 5.8. This tabulation gives values at the 10, 5, and 1% significance level as a function of the number of observations used in the regression. These significance levels correspond, respectively, to the situation where one is ready to take 10, 5, and 1% chance of *incorrectly* concluding there is evidence of a statistically significant linear regression, when in fact x and y are unrelated. Comparing R^2 with the RC values allows one to reject the significance of RC values calculated for Run 4 and the organic overload, whereas Runs 6a and 6b were significant enough for a 5% risk (chosen as a criterion). The SE of Runs 6b and 7b would also recommend disregarding their designated RC values, even though their R^2 values may indicate significance according to

Table 5.8. However, an acceptable error margin in VFA concentration readings should not exceed 50 mg/L, the same error margin used to determine whether the GC needed calibration or not. The SE in Runs 6b and 7b during and after the shock far exceeded 50. Thus, it could be seen that RC estimations for acetic acid concentrations during recovery could only suggest significance for Runs 2, 3a, 3b, and 5 passing the 1% significance level, and Runs 6a and 7a for passing the 5% significance level.

Table 5.8: Values of R^2 required to establish statistical significance of linear regression for various sample sizes.

Sample Size	Statistical Significance Level		
	10%	5%	1%
3	0.9756	0.9938	0.998
4	0.81	0.903	0.98
5	0.65	0.77	0.92
7	0.45	0.57	0.77
9	0.34	0.44	0.64
11	0.27	0.36	0.54

5.7 Gas production changes

Biogas production is an indication of microbial activity. A portion of the VFA is converted by methanogens to methane. Therefore, it was expected that higher loading is associated with increased biogas production as a result of the excessive activity of breaking down acetate to biogas. Some papers (Tay and Zhang, 2000) reported that the percentage of methane during overloads was decreased. In this experiment, although measurements of percentage methane in biogas have only been done twice, it cannot be stated that percentage methane was decreased when a 95% c.i. test was conducted. There were also times during the overload where the percentage of methane was higher than the average percent before the overload. Also, no significant difference was observed in the production of biogas between intermittent and continuous feeding modes.

5.8 Comparison of intermittent and continuous shockloads

In the continuous shockload, the reactor was exposed to an increase in the flowrate for 3 hours (non-stop). This effect decreased the HRT, not providing adequate time for the micro-organisms to break down the waste. For this reason, low VFA concentrations were noticed, while COD concentrations of the effluent were much higher (check Figures 5.5, 5.6, 5.7, and 5.8). In the intermittent feeding operation, from Figures 5.11, 5.12, 5.13, and 5.14, the opposite was observed. VFA accumulation was observed since the excessive influent loading rate was allowed to undergo the bioconversion process for a lengthier period. The effluent COD was lower than the observed effluent VFA undergoing a continuous shock mode, indicating a better effluent quality. The VFA reading would not imply an effective treatment.

5.9 Comparison of single and double shockloads

Reactors have shown reasonable accommodation to a single shockload and returned to pre-shock conditions without serious repercussions. However, it seems that a 24-hour operation after recovery did not provide sufficient time for the micro-organisms to regain activity. Loss of biomass that occurred in the first shockload needed to be compensated; however, micro-organisms in the reactor were not given enough time to compensate. In Runs 6 and 7, shown in Figures 5.18, 5.19 and 5.20, and 5.21, it appeared evident from the reactor's deteriorating performance in the second shockload that it exerted a more severe effect on the methanogenic bacteria than the first shockload.

5.10 Biomass acetoclastic activity tests

Biomass activity was measured throughout the experiment. AAT tests were conducted before and after shockload runs to check for changes in bacterial capability of degrading organics. However, AAT is conducted in an ideal environment compared to the real environment of treatment. Substrate used in AAT is readily available and easily degradable (acetate) in a well buffered solution, which is not equivalent to the real wastewater characteristics. The test attempts to determine the maximum rate of degradation of methanogens (k) in treating acetate without any possible inhibitions, whether due to accumulation of higher VFAs or deficiency/presence of trace metals. The values of acetate degradation between the top and bottom samples, and the overall reactor capacity to treat acetate per day is shown in Table 5.9.

Duplicate samples were taken from two different ports in the reactor. From the data of substrate concentration vs. time, rate of substrate degradation was calculated with a 95% c.i. calculated by the regression tool in MS Excel97. Following the differential method (Fogler, 1992), the reaction rate was found to follow a zero-order model as illustrated in Figure 5.19 for AAT conducted for Runs 1 and 2.

Table 5.9: AAT rate results in reactor and average activity rate in the reactor.

	k (g Ac/g VSS.d)				whole reactor	
Run	**Bottom**	**± 95% c.i.**	**Top**	**± 95 % int.**	**total Ac/d**	**± 95% c.i.**
1,2	0.60	0.15	0.57	0.07	86.74	32.6198
3	0.37	0.08	0.32	0.06	55.26	22.5893
4	0.68	0.1	0.53	0.09	72.75	22.847
5,6	0.48	0.038	0.61	0.08	61.94	13.41
7	-	-	0.380	0.055	45.261	6.55098

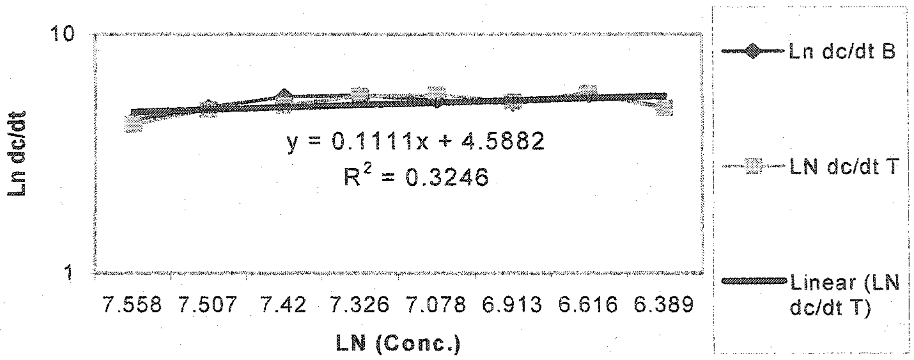

Figure 5.19: Determination of rate order of acetate degradation in batch test using differential method.

However, looking at the rate of substrate degradation during operation, and especially overload, is a more complex process. Complex feedstock with mixed VFAs and possible inhibitors, in addition to intermittent feedings, are to be considered and may require a dynamic model.

There is no evidence of decline or improvement of maximum degradation of acetate since values throughout the experimental period seem to coincide with each other when considering the 95% confidence intervals. Savard (2001) expected higher activity rate values in the bottom samples since the biomass is exposed to more substrate due to their proximity to the influent entrance. However, since the reactor has gone through weeks of acclimatization and operation in pseudo steady-state mode, it should not be unusual to expect a close rate of acetate degradation per gram VSS. One can predict that there is less VSS available for degradation in the bottom part of the reactor due to accumulation of fixed solids, which can affect substrate degradation throughout the reactor operation.

Some of the limitations faced during AAT measurements were the presence of propionate in some runs, which interfered with acetate biodegradation rate calculations; for example in the bottom sample calculations taken on Dec. 26. Also, it seems that the initial concentration of acetate injected influences rate of degradation. When higher concentrations were used (Runs 1, 4, and 7), maximum rate of decomposition values of Runs 1 and 4 are almost double those that started at a lower initial concentration, with one or two exceptions.

Pavlostathis and Giraldo-Gomez (1991) have reported from a survey of papers dealing with the kinetics of anaerobic digestion that typical half-velocity constants for mesophilic bacteria range from 11 to 421 mg COD/L. Half-velocity constant is a measure of the concentration of COD to achieve 50% of the maximum substrate utilization rate. Therefore, a range of 22-842 mg COD should be present at all data points to be reflective of the maximum utilization rate. This range only happened in the sample taken from the top port on Dec. 26. The bottom sample experienced formation of propionate which could be due to either overloading the capacity of methanogens, or contamination from the needle of the syringe sampling from the reactor.

5.11 Accumulation of inert solids in biomass throughout experimental period

VSS and FSS were measured from two sampling ports in the reactor. It was noticed during the operation of the treatment that inert solids accumulated throughout time, especially in the bottom part of the reactor. A consistent decrease of VSS content in the bottom part of the reactor (~10 cm height), from 53 to 39 g/L, along with an increase in FSS concentration, is shown in Table 5.10 and Figures 5.20 and 5.21.

On the other hand, the top port's (~30 cm height) VSS measurements did not experience a decrease equivalent to the bottom port and remained in the range of 48 - 50 g VSS/L. However, there was a noticeable increase in FSS concentrations in the top port of the reactor.

The bottom part of the sludge bed received the bulk of inert solids accumulation. This observation is consistent with information Savard (2001) and others reported in Chapter 3.

Calcium and magnesium precipitation is considered the main cause of inert deposit. Quality of landfill leachate being filtered throughout peat moss varied as the peat bed became more saturated, and was observed by the difference of colour of the effluent. When filtering through a fresh bed of peat moss, the filtered leachate colour looks like clear apple juice with a reduced odour compared to raw leachate.

Table 5.10: Solids concentration over the period of the experiment.

	Bottom VSS		**Top** VSS		**Bottom** FSS		**Top** FSS	
Date	**gVSS/L**	**stdev**	**gVSS/L**	**stdev**	**g FSS/L**	**stdev**	**g FSS/L**	**stdev**
Sep.7	53.52	0.18	50.16	0.18	44.52	0.18	29.2	0.18
Sep.20	46.66	0.18	49.062	0.18	74.27	0.18	44.92	0.18
Oct.6	40.22	0.18	48.744	0.18	57.37	0.18	38.62	0.18
Nov.13	49.22	0.18	40	0.18	117.90	0.18	67.01	0.18
Dec.26	38.60	0.18	49.512	0.18	78.16	0.18	51.61	0.18

Removal of calcium precipitates in the reactor is virtually impossible, and that could be the reason for the deterioration of reactor performance by Dec. 26 when treating organic shockloads. High bicarbonate in the feed, and perhaps phosphorus levels, may have favored calcium precipitation (Speece, 1996).

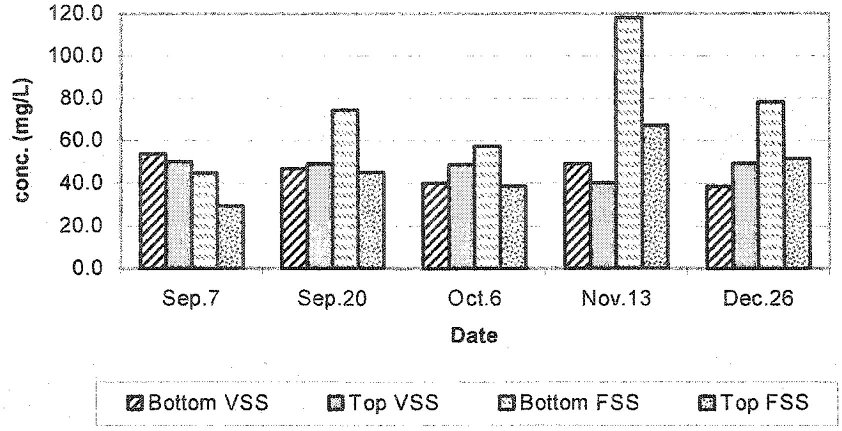

Figure 5.20: VSS and FSS concentration in reactor throughout the experimental period.

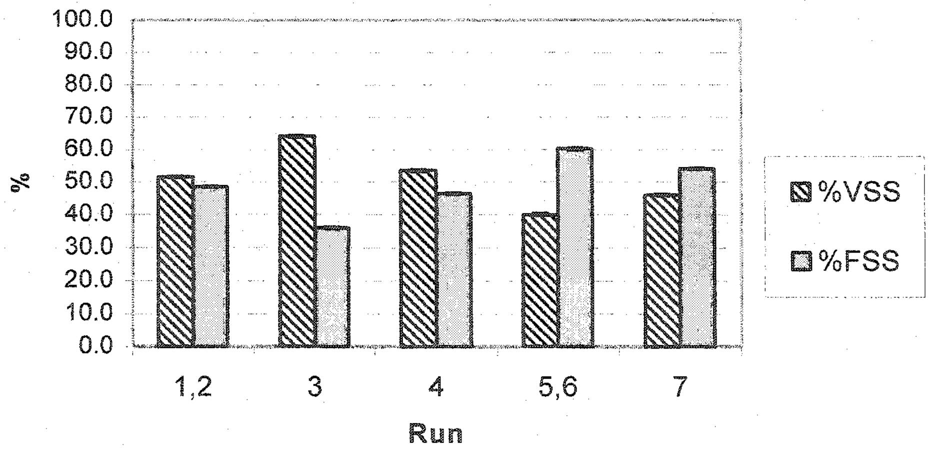

Figure 5.21: VSS and FSS percentage composition in UASB reactor during the experimental period.

5.12 Metal analysis results

Some evidence of Ni deficiency contributing to poor performance in shockload Run 4 and the second shockload of Runs 6 and 7 was noticed. Concentration of Ni present in the feed supplied during the shockload is displayed in Table 5.11. However, the impact is not conclusive since there is an exception in Run 1, and the second shockload of Run 3 (3b). On the other hand, one may argue that in Run 1, the reactor was subjected to a slightly low OLR (5.5 g COD/L.d), then followed by a batch (recycle) mode which diluted the incoming waste concentration.

Table 5.11: Concentration of nickel in feed and effluent of shockload runs.

Run	**1**	**2**	**3 (double)**	**4**	**5**	**6 (double)**	**7 (double)**
Ni (mg/L)	< 0.079	N/D	0.1609, <0.079	< 0.079	0.2801	0.49, < 0.079	0.1273, <0.079
Ni effluent	< 0.079	< 0.079	< 0.079, <0.079	0.1021	0.2503	< 0.079, < 0.079	< 0.079, < 0.079

Nickel was not added to the feed, but was sometimes present in the leachate wastewater. Savard (2001) has not recorded any removal of Ni by peat moss, thus Ni seems unlikely to be adsorbed during the peat moss filtration. One may need to check the Ni concentration before the start-up of operation, as the concentration may differ from one barrel of raw leachate to another.

5.13 Impact of organic shockloads on UASB reactor:

An organic shockload was imposed on the UASB reactor with OLR values close to hydraulic shockloads (6.5 ± 0.89 g COD/L.d) and equivalent to an SLR of 0.32 ± 0.04 g COD/g VSS.d.

Influent COD concentration was increased from an average of 10 g COD/L.d to ~ 19 g COD/L.d while maintaining the HRT at 2.86 ± 0.4 d. Feeding of the increased concentration was intermittent over 9 hours in the same way hydraulic shockloads in Runs 4-7 were fed. The VFA concentration changes and percentage COD removals are shown in Figures 5.22 and 5.23, respectively.

Despite the low OLR of the reactor compared to hydraulic shockload runs, the reactor showed greater sensitivity to the increase in OLR manifested in the large buildup of TVFA (reaching a maximum concentration of 10,579 mg/L), as shown in Figure 5.22.

On the other hand, COD effluent concentrations increased to levels comparable to other hydraulic shockloads (reaching a maximum of 3975 mg COD/L) previously experienced in this experiment.

Despite the high values of TVFA and COD in the effluent, the effluent COD removal efficiency did not decline below 78.6% during the overload. The recovery to pre-shock conditions was very slow, and was only possible after operation in a recycle mode for almost 48 hours.

One problem that blurred the judgement of the reactor's sensitivity to organic shockloads was the unexpected increase in VFA inside the reactor to magnitudes close to 3000 mg/L, and an effluent COD of approximately 2300 mg COD/L, which was discovered an hour before the start of the shockload. Nickel concentrations an hour before and during the shockload were not detected (Ni less than 0.079 mg/L). Potassium concentration before the shockload was measured at 3908 mg/L, which could explain the deterioration of waste treatment. McCarty (1964) reported the potassium concentrations between 2500 - 4500 mg/L were moderately inhibitory to anaerobic treatment.

More tests need to be done using organic shockloads before affirming UASB reactor's sensitivity to organic shockloads compared to hydraulic ones.

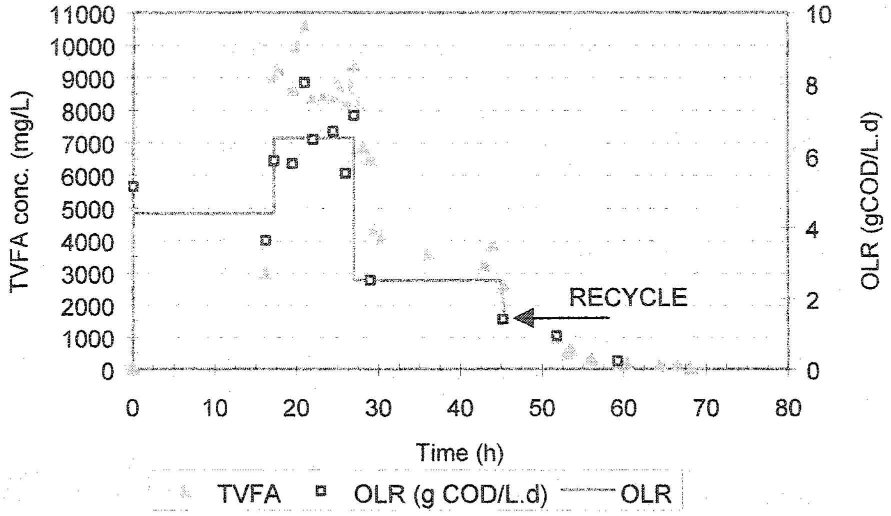

Figure 5.22: TVFA changes during an intermittent 3-hour two-fold-OLR organic shockload.

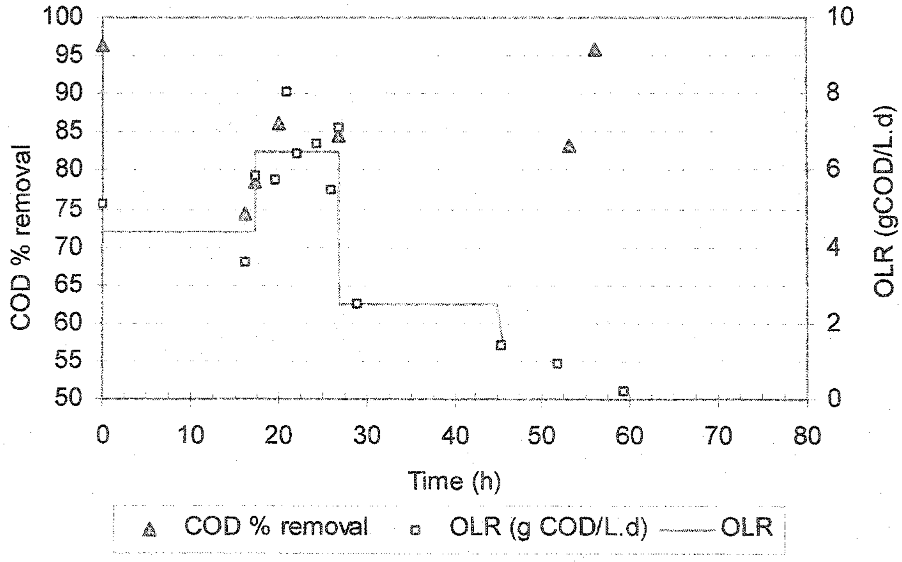

Figure 5.23: COD percentage removal in an intermittent 3-hour two-fold-OLR organic shockload.

If the organic overload was deemed after further testing to be damaging to the performance of UASB reactors treating landfill leachate, this damage could be due to mass transfer limitations in organic overloading. As more waste substrate is being fed, more biomass contact with the incoming waste is essential to handle the excess organics, which is not provided in organic shockloads. Organic overload increases the organic load but with the same feeding pattern and flowrate rate. There is no opportunity for more biomass coming into contact with the incoming waste.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Using peat moss as a filter and UASB reactor to investigate the effect of hydraulic shockloads of landfill leachate, the following conclusions and recommendations for further study are suggested.

6.1 Conclusions

- Under single shock scenarios, intermittent shocks had better effluent quality (in terms of COD concentration).
- Biomass was more prone to washout at HRT of 0.15 d or less.
- Double shocks had a more severe effect on UASB stability than single shocks, and impact on reactor performance became more evident in the second shock.
- Presence of nickel may be conducive to improving hydraulic shock tolerance.
- UASB reactor performance was more sensitive to an organic overload than by hydraulic overloads. Mass transfer limitations may be the reason.
- Inert solids accumulated in the biomass despite pretreatment.

6.2 Recommendations

To better characterize the response of UASB reactors to shockloads of landfill leachate feeds, the following aspects of analysis are suggested for further study:

- Study the effect of longer exposure to hydraulic shocks (continuous and intermittent).
- Investigate the possibility of operating at higher OLRs post shockloads.
- Further investigate the effects of nickel during shocks.
- Simulate the reactor's response to shocks using dynamic modeling.
- Study gas composition changes during overload, especially H_2 and CO_2.

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Appendix A

Raw data of UASB reactor response to shockload Runs (1 - 7), and organic shockload

Run 1 raw data and calculations

VFA (mg/L)

Day / time	Time	Q	S_o (COD)	S_e (COD)	COD %	OLR	Acetic	Propionic	Butyric		Gas Prd.	TVFA
	hr	L/d	mg/L	mg/L	removal	gCOD/gVSS.d				SRT	L/d	mg/L
Sep 18/12:50	-120.5	2.40	10758.62	620	94.24	4.53		-	-			0.00
Sep 19/11:50	-97	1.64	12413.79			3.56	-	-	-			0.00
Sep 20/12:50	-72	1.58	10,200.00	400	96.08	2.83						0.00
Sep 21/ 12:20	-48	1.12	8,800.00	380	95.68	1.73						0.00
Sep 23/12:45	0	2.17	9,000.00	380	95.78	3.43	0.00	0.00	0.00	5027.42		0.00
Sep 24/8:55	19.75	1.92	8,600.00	304	96.47	2.90	1.40	-	-			1.40
Sep 24/9:05	***20***	***3.78***	***8,600.00***	***360***	***95.81***	***5.70***			-		***15.12***	
Sep 24/9:20	***20.25***	***4.05***	***8,550.00***			***6.08***	***2.51***	-				***2.51***
Sep 24/9:35	***20.5***	***4.02***	***8,500.0***	***360***	***95.76***	***5.99***			-			
Sep 24/10:05	***21***	***3.84***	***8,400.0***	***360***	***95.71***	***5.66***	***4.26***	-	-		***20.40***	***4.26***
Sep 24/10:35	***21.5***	***3.42***	***8,300.0***	-	-	***4.98***	***4.11***	***1.54***			***30.60***	***5.65***
Sep24/ 11:05	***22***	***3.24***	***8,200.0***	***560***	***93.17***	***4.66***	***19.36***	***4.14***	-		***42.84***	***23.50***
Sep24/ 11:35	***22.5***	***3.48***	***8,050.0***			***4.91***	***15.31***	***8.31***			***36.72***	***23.61***
Sep24/ 12:05	***23***	***4.44***	***8,000.0***	***1360***	***83.00***	***6.23***	***26.21***	***28.31***				***54.52***
Sep 24/12:35	23.5	recycle			-		28.02	33.05	-			61.07
Sep 24/13:05	24	3.74	8,000.0	1040	87.00	0.68	27.91	31.49	25.12			84.52
Sep 24/13:50	24.75	recycle			-		30.60	41.21	-			71.81
Sep 24/14:35	25.5	3.74	8,000.0	1520	81.00	1.00	32.60	52.66	-			85.25
Sep 24/16:05	26	3.74	*7,900.0*	*2240*	71.65	1.47	28.45	35.81	-			64.26
Sep 24/17:20	27.25	recycle			-		8.06	20.45	-			28.51
Sep 24/17:35	27.5	3.74	7,800.0	1920	75.38	1.26			-			
Sep 24/18:20	28.25	recycle		-	-		15.74	11.50	-			27.24
Sep 24/18:35	28.5	3.74	7800	1240	84.10	0.81	-	-	-			0.00
Sep 24/22:35	32.5	3.74	7800	460	94.10	0.30	3.36	-	-	end of recycle		3.36
Sep 25/ 14:40	49.75	3.14	8190.48	323.81	96.05	4.51						
Sep 26/ 13:45		2.60	6476.19	380.95	94.12	2.95						
Sep 27/ 15:25		1.96	11047.62	419.05	96.21	3.80						

During shock		σ Q	**HRT error**
Average Q	3.78	**0.39**	**0.16**
Ratio	1.97		

During shock		σ OLR
Average OLR	**5.53**	0.60
Ratio of increase	1.91	

The data of reactor operation before, during and after Run 1 that have been recorded or calculated, are tabulated above.

Data values during the timeframe that are bolded, italicized and contained inside another table constitute the data collected in the duration of the 3-hour continuous feeding shockload. Average values of flowrates and OLR along with their sample σ are inserted in two smaller tables in the bottom.

Run 2: raw data and calculation

							VFA (mg/L)					
Day / time	**Time**	**Q**	**S_o (COD)**	**S_e (COD)**	**COD %**	**OLR**	**Acetic**	**Propionic**	**Butyric**		**Gas Prd.**	**TVFA**
	hr	L/d	mg/L	mg/L	removal	gCOD/gVSS.d				SRT	L/d	mg/L
Sep 12/12:30	-30.58	2.40	10400.00	620.00	94.04	4.38	6.48	-	-		8.05	6.48
Sep 13/10:30	-9.50	1.85	11000.00			3.56	-	-	-		7.64	0.00
Sep 13/19:00	0.00	1.55	11050.00	501.82	95.46	2.96					8.16	0.00
Sep 14/ 8:50	13.83	2.82	11781.80			5.78	34.68	5.53	-	1114.30	20.40	40.21
Sep 14/9:25	**14.42**	**4.80**	**11781.80**	**436.36**	**96.30**	**9.92**			-		**27.20**	**0.00**
Sep 14/9:40	**14.67**	**4.80**	**11745.44**	**534.50**	**95.45**	**9.88**	**15.06**	**2.81**	-			**17.87**
Sep 14/10:25	**15.42**	**6.02**	**11636.35**			**12.29**	**7.85**	**5.39**	-			**13.24**
Sep 14/10:55	**15.92**	**3.23**	**11563.63**	**785.45**	**93.21**	**6.55**	**25.42**	**13.25**			**48.96**	**38.67**
Sep 14/ 11:25	**16.42**	**4.76**	**11490.90**	**1134.54**	**90.13**	**9.60**	**47.98**	**26.05**	-		**33.77**	**74.03**
Sep 14/12:25	**17.42**	**4.58**	**11345.45**	**1396.39**	**87.69**	**9.12**	**58.21**	**38.92**	-			**97.12**
Sep 14/14:25	19.42		11422.46	1483.63	87.01		87.81	72.94	45.49			206.23
Sep 14/16:25	21.42		11499.46	3229.10	71.92		61.07	55.87	-		29.84	116.94
Sep 14/17:25	22.42		11537.96		-		48.88	63.48	-			112.36
Sep 14/18:25	23.42		*11576.47*	*2544.00*	*78.02*		54.64	79.24	-		29.84	133.88
Sep 14/19:25	24.42		11614.97		-		44.93	84.29	-			129.22
Sep 14/19:55	24.92		11634.22	4538.18	60.99		32.15	68.03	-		21.93	100.18
Sep 14/22:55	27.92		11749.73	698.20	94.06		16.94	47.52	-		16.74	64.45
Sep 15/7:25	36.42		**12000.00**	654.50	94.55		2.90	-	-			2.90
Sep 15/9:25	38.42	3.44	12000.00			7.24	7.41	3.79	-			11.20
Sep 16/10:30	39.50	3.00	12428.57	567.86	95.43	6.54						

During shock		σ Q	HRT error
Average Q	**4.70**	0.89	0.23
Ratio	2.26	1.21	

During shock		σ OLR
Average OLR	**9.56**	1.84
Ratio of increase	2.33	

The data of reactor operation before, during and after Run 2 that have been recorded or calculated, are tabulated above.

Data values during the timeframe that are bolded, italicized and contained inside another table constitute the data collected in the duration of the 3-hour continuous feeding shockload.

Average values of flowrates and OLR, along with their sample standard deviation are inserted in two smaller tables in the bottom.

Run 3a: raw data and calculation

Day / time	Time	Q	S_o (COD)	S_e (COD)	COD %	OLR	VFA (mg/L) Acetic	Propionic	Butyric		Gas Prd.	TVFA
	hr	L/d	mg/L	mg/L	removal	gCOD/gVSS.d				SRT	L/d	mg/L
Sep 7/ 9:30	0	2.60	12428.57	840.00	93.24	5.62					15.3	0
Sep 7/ 11:00	1.5						33.62	18.74			15.3	52.356
Sep 8/ 7:50	22.33	1.87	**12857.10**	608.60	95.27	4.21	21.46	4.53	0.00	1434.23	6.9	25.987
Sep 8/ 8:00	**22.5**	**4.20**	12828.44	**-**	**-**	**9.45**	**4.89**	**3.06**			**gas leak**	7.958
Sep 8/ 8:20	**22.83**	**4.20**	12771.31	**567.85**	**-**	**9.41**					**gas leak**	0
Sep 8/ 8:30	**23**	**3.90**	12742.75	**514.29**	**95.96**	**8.72**	**5.57**	**4.74**			**gas leak**	10.304
Sep 8/ 9:00	**23.5**	**3.08**	12657.07	**600.00**	**95.26**	**6.83**	**5.50**	**2.57**			**gas leak**	8.068
Sep 8/ 9:30	**24**	**4.59**	12571.38	**-**	**-**	**10.12**	**10.86**	**5.77**				16.621
Sep 8/ 10:00	**24.5**	**4.35**	12485.69	**1200.00**	**90.39**	**9.53**	**47.15**	**21.94**	**22.22**		**14.28**	91.306
Sep 8/ 10:20	**24.83**	**4.85**	**12428.57**	**-**	**-**	**10.56**						0
Sep 8/ 10:30	**25**	**4.58**	12421.43	**-**	**-**	**9.97**	**107.73**	**69.01**	**62.13**		**20.4**	238.874
Sep 8/ 11:00	**25.5**	**2.70**	12400.00	**2742.86**	**77.88**	**5.87**	**160.86**	**103.45**	**83.51**		**61.2**	347.814
Sep 8/ 12:00	26.5		12357.14	-	-		159.46	113.59	73.12		41.82	346.166
Sep 8/ 13:00	27.5	1.44	12314.28	3685.71	70.07	3.11	214.97	162.15	124.26		45.9	501.384
Sep 8/ 14:00	28.5		12271.42	-	-		197.83	187.96	134.01		45.9	519.794
Sep 8/ 14:30	29		12250.00	3857.14	68.51						40.8	0
Sep 8/ 15:00	29.5	1.44	12228.57	-	-		173.46	191.92	88.05		40.8	453.429
Sep 8/ 15:20	29.83		**12214.28**	-	-						39.78	0
Sep 8/ 16:00	30.5		12195.37	-	-		122.79	192.42	71.98			387.198
Sep 8/ 17:00	31.5		12167.01	3214.29	73.58		100.13	189.15	55.97			345.246
Sep 8/ 18:00	32.5		12138.65	-	-		94.63	230.44	60.75			385.822
Sep 8/ 21:00	35.5		12053.57	3642.85	69.78		70.61	252.47	26.82			349.894
Sep 8/ 22:00	36.5		12025.21	-	-		52.06	229.36	21.13		16.32	302.544
Sep 9/ 7:00	45.5	1.44	11982.67	3428.57	71.39	3.03	14.70	46.24			12.24	60.947
Sep 9/ 14:00	52.5		**11571.43**	685.70	94.07		10.76	8.86				19.618
Sep 9/ 16:00	54.5						8.87	9.45			18.386	18.319

During shock		σ Q	**HRT error**
Average Q	**4.05**	0.72	0.25
Ratio	1.81		

During shock		σ OLR
Average OLR	**8.94**	1.57
Ratio of increase	1.82	

Run 3b:raw data and calculations

Day / time	Time	Q	S_o (COD)	S_e (COD)	COD %	OLR	VFA (mg/L) Acetic	Propionic	Butyric		Gas Prd.	TVFA
	hr	L/d	mg/L	mg/L	removal	gCOD/gVSS.d				SRT	L/d	mg/L
Sep 10/11:15	73.75	2.23	**10714.29**	428.57	96.00	4.15	3.16	2.71	0.00	1200.55	8.30	5.87
Sep 10/11:55	**74.42**	**3.03**	10600.00	-	-	**5.63**					**19.58**	0.00
Sep 10/12:25	**74.92**	**4.80**	10514.29	**557.14**	**94.70**	**8.85**	**45.30**	**13.35**	**22.01**		**45.90**	80.66
Sep 10/ 12:55	**75.42**	**4.36**	10428.57			**7.97**						0.00
Sep 10/13:25	**75.92**	**6.60**	10342.85	**942.85**	**90.88**	**11.98**	**40.10**	**29.54**	**28.22**		**12.96**	95.86
Sep 10/13:45	**76.25**	**3.24**	**10285.71**	-	-	**5.85**					**12.96**	0.00
Sep 10/14:00	**76.50**	**3.03**	10274.43	-	-	**5.45**	**48.97**	**48.78**	**39.02**			136.77
Sep 10/14:10	**76.67**	**3.03**	10266.91	**1285.71**	**87.48**	**5.45**						0.00
Sep 10/14:25	**76.92**	**3.54**	10255.63	-	-	**6.38**	**72.44**	**62.14**	**39.01**			173.59
Sep 10/14:55	**77.42**	**3.90**	10233.08	**2357.14**	**76.97**	**7.00**	**76.58**	**97.31**	**62.02**	829.43	**20.40**	235.91
Sep 10/16:25	78.92		10165.41	4071.43	59.95		71.45	104.85	34.14			210.44
Sep 10/17:25	79.92		10120.30	-	-		50.93	90.84	30.88			172.65
Sep 10/18:25	80.92		10075.18	4628.57	54.06		54.24	109.14	26.69			190.07
Sep 10/19:25	81.92	1.70	10030.07	-	-	2.99	55.71	185.47	39.40		16.32	280.58
Sep 10/20:25	82.92		9984.96	-	-		45.77	462.57	27.73			536.07
Sep 10/20:55	83.42		9962.40	4071.43	59.13		44.68	157.30	20.60		30.24	222.57
Sep 10/23:55	84.42		9917.29	-	-		27.99	103.74	0.00			131.73
Sep 11/8:55	93.42	1.72	**9428.57**	2357.14	75.00	2.85	5.56	6.40	0.00			11.96
Sep 11/12:25	96.92	1.71	9400.00	2571.43	72.64	2.83					13.68	
Sep 11/18:25	100.92		9400.00	1026.00	89.09						28.56	

Average Q	Ratio	σ	HRT error
3.95	2.00	1.18	0.43

Average OLR	Ratio	σ OLR
7.17	1.73	2.16

The data of reactor operation before, during and after Runs 3a,3b that have been recorded or calculated, are tabulated above.

Data values inside the timeframe that are bolded, italicized constitutes values in the duration of two 3-hour continuos feeding shocks.

Average values of flowrates and OLR during shocks, along with sampel standard deviation (stdev) and ratio to preshock values are presented.

Run 4:raw data and calculations

Day / time	Time h	Q L/d	So (COD) mg/L	Se (COD) mg/L	COD % removal	OLR gCOD/gVSS.d	VFA (mg/L) Acetic	Propionic	Butyric	SRT	TVFA mg/L
Sep 28/		1.96	8625.00	375.00	95.65	2.97				1302.70	
Oct 1/3:00		2.03	**7125.00**	337.50	95.26	2.54	3.12	0.82			
Oct 2/10:40	-0.10	3.00	**7015.38**	480.00	93.16	3.69	-	-	-		0.00
Oct 2/10:50	**0.00**	**3.91**	7015.00			4.81					0.00
Oct 2/11:00	**0.17**	**3.96**	6947.96			4.82	7.40	4.12	-		11.52
Oct 2/11:20	**0.50**	**5.06**	7015.40	2392.60	65.90	6.23					0.00
Oct 2/11:45	**0.92**	**11.01**	6790.63			13.12	728.29	999.00	1500.35		3227.64
Oct 2/12:20	**1.50**	**6.25**	6678.26	2082.46	68.82	7.32					
Oct 2/12:30	**1.67**	**8.53**	6640.72			9.93	758.56	1018.71	1449.72		3226.99
Oct 2/13:05	**2.25**		6989.15				662.39	945.13	1378.98		2986.50
Oct 2/14:05	**3.25**	**7.79**	7938.40			10.85	443.74	756.12	1025.27		2225.13
Oct 2/14:20	**3.50**	**8.53**	**7938.46**	2030.77	74.42	11.87					
Oct 2/14:50	**4.00**		7876.45				861.85	864.03	1301.80		3027.68
Oct 2/15:50	**5.00**	**8.00**	7663.56	2436.92	68.20	10.76	986.30	868.01	1287.38		3141.69
Oct 2/17:05	**6.25**		7411.40	2215.38	70.11		750.29	740.74	1080.89		2571.92
Oct 2/18:20	**7.50**	**6.74**	7130.25	2141.54	69.97	8.43	906.20	822.73	1220.86		2949.79
Oct 2/18:50	**8.00**		7049.70				837.61	747.84	1156.71		2742.16
Oct 2/19:50	**9.00**		**6750.00**	2215.38	67.18		638.16	668.43	957.34	195.63	2263.93
Oct 2/21:20	10.50		6644.71	1181.54	82.22						
Oct 2/22:55	12.08		6528.89				596.63	728.21	839.62		2164.45
Oct 2/23:05	12.25		6644.71	1070.77	83.89						
Oct 2/23:55	13.08	4.00	**5907.69**			4.15	482.58	721.70	618.98		1823.26
Oct 3/6:05	19.25		4644.23	812.30	82.51						
Oct 3/8:05	21.25						542.82	618.26	712.37		1873.45
Oct 3/8:50	22.00	4.05	**7015.38**	701.54	90.00	4.98					
Oct 3/10:50	24.00	4.05	6921.10	1735.38	74.93	4.92	904.33	737.76	1148.57		2790.66
Oct 3/12:50	26.00		6826.82	2215.38	67.55		853.29	737.40	1138.03		2728.73
Oct 3/17:35	30.75		6602.91	2030.76	69.24		520.62	619.60	767.81		1908.03
Oct 3/19:50	32.00		6496.84				472.49	604.11	789.66		1866.26
Oct3/20:20	32.50		**5907.60**								
Oct 3/22:50	33.00		5907.60	1070.76	81.87		475.16	663.26	638.00		1776.42
Oct 4/10:50	48.00	3.00	**5538.46**	1624.60	70.67	2.91	412.96	638.69	1067.00		2118.65
Oct 4/12:05	49.25	recycle mode					351.20	589.62	836.75	201.10	1777.57
Oct 4/12:50	50.00	recycle	5538.46	2000 or more							
Oct 4/13:20	50.50	recycle mode					251.93	449.04	424.90		1125.87
Oct 4/14:20	51.50	recycle mode					233.62	388.59	239.60		861.81
Oct 4/15:50	53.00	3.00	5538.46	1846.15	66.67	0.97	166.64	336.24	90.91		593.79
Oct 4/16:50	54.00	recycle mode					109.76	241.74	45.43		396.93
Oct 4/17:50	55.00	3.00	5538.46	1255.38	77.33	0.66	71.67	207.15	0.00		278.82
Oct 4/18:50	56.00	recycle mode					75.26	236.28	47.66		359.20
Oct 4/19:50	57.00	recycle mode					48.92	168.18	25.53		242.63
Oct 4/20:50	58.00	recycle mode					42.93	132.11	0.00		175.03
Oct 4/21:50	59.00	3.00	5538.46	627.69	88.67	0.33	42.71	91.65	0.00		134.35
Oct 4/22:35	59.75	recycle mode					69.71	75.84	31.65		177.20
Oct 5/9:50	71.00	recycle mode		0.65			9.52	8.67	0.00		18.19

AVG Q	Ratio	σ	HRT err
6.98	2.77	2.25	0.26

Average OLR	σ OLR	Ratio
8.81	2.95	2.83

Run 5: After spiking 2.5 times the flowrate. for 9 hours.

							VFA	(mg/L)			
Day / time	**Time**	**Q**	**So (COD)**	**Se (COD)**	**COD %**	**OLR**	**Acetic**	**Propionic**	**Butyric**		**TVFA**
	hr	**L/d**	**mg/L**	**mg/L**	**removal**	**gCOD/gVSS.d**				**SRT**	**mg/L**
Nov 13/ 16:00		1.95	8761.90	438.09	95.00	3.00				1030.67	
Nov 14/ 9:50	0	1.67	8761.90	285.70	96.74	2.56		2.17	-		2.169
Nov 14/ 10:21	***0.5***	3.30	8761.90			5.07	8.48	-	-		8.475
Nov 14/ 10:31	***0.667***	4.42	8761.90	323.80	96.30	6.79					
Nov 14/ 10:56	***1***		8761.90				6.34	2.92	-		9.254
Nov 14/ 11:21	***1.5***	5.40	8761.90	609.52	93.04	8.30			-		
Nov 14/ 11:56	***2***						13.61	6.39	-		20.002
Nov 14/ 12:56	***3***	4.88	8952.38			7.66	21.87	9.41	-		31.279
Nov 14/ 13:21	***3.5***		8952.38	742.85	91.70						
Nov 14/ 13:56	***4***						19.49	9.72	-		29.203
Nov 14/ 14:21	***4.5***	5.93	8952.38			9.31	32.80	28.12	-		60.913
Nov 14/ 14:56	***5***		8952.38	876.19	90.21						
Nov 14/ 15:06	***5.25***						30.19	29.38	36.13		95.698
Nov 14/ 15:56	***6***	6.41	8952.38			10.06	57.10	50.46	55.30		162.857
Nov 14/ 16:21	***6.5***		8952.38	1752.38	80.43						
Nov 14/ 16:36	***6.75***						35.91	64.06	41.52		141.483
Nov 14/ 17:51	***8***	6.98	9523.80	1752.38	81.60	11.65	38.59	52.92	40.28		131.792
Nov 14/ 18:56	***9***		9523.80	1752.38	81.60		33.62	68.30	45.31		147.23
Nov 14/ 19:21	***9.5***		9523.80	1752.38	81.60		33.63	100.36	32.24		166.223
Nov 14/ 20:51	11						30.69	57.67	33.48		121.834
Nov 14/ 21:21	11.5	2.55	9523.80	1447.62	84.80	4.26	26.50	63.40	26.44		116.333
Nov 14/ 21:50	12		12190.47								
Nov 14/ 22:06	12.25						29.66	59.04	-		88.693
Nov 14/ 22:31	12.67										
Nov 15/ 8:21	22.5	2.80	12190.47	933.33	92.34	5.99	3.43	6.84	-		10.274
Nov 15/ 9:21	23.5						-	4.26	-		4.255
Nov 15/ 10:21	24.5	2.84				6.07	4.87	3.84	-		8.707
Nov 15/ 13:21	27.5						-	-	-	350.50	0

Average Q	Ratio	stdev Q	HRT Error
5.33		1.25	0.25

Average OLR	Stdev	Ratio
8.41	2.17	3.02

Run 6: Raw data and calculations for double intermittent shocks

Run 6a: **VFA (mg/L)**

Day / time	**Time** h	**Q** **L/d**	**So (COD)** **mg/L**	**Se (COD)** **mg/L**	**COD %** **removal**	**OLR** **gCOD/gVSS.d**	**Acetic**	**Propionic**	**Butyric**	**SRT**	**TVFA** **mg/L**
Nov 27/10:00	-0.5	2.00	**7875.00**			2.74					
Nov 27/10:20	0	**2.00**	**7875.00**	206.25	97.38	2.74	-	3.02	-		3.015
Nov 27/10:26	***0.1***	**5.05**	7875.00			6.98	-	-	-		0.00
Nov 27/10:56	***0.5***		7819.50	300.00	96.16		-	-	-		0.00
Nov 27/11:26	***1***	**4.48**	7782.00			6.12	3.25	-	-		3.25
Nov 27/11:56	***1.5***		7744.50	328.13	95.76		7.20	4.36	-		11.56
Nov 27/13:26	***3***	**5.70**	7632.00	656.25	91.40	7.63	15.04	3.42	-		18.46
Nov 27/14:26	***4***	**5.47**	7557.00			7.26	15.63	6.31	-		21.94
Nov 27/15:26	***5***	**5.14**	**7500.00**	843.75	88.75	6.77	35.09	15.15	-		50.25
Nov 27/16:11	***5.75***						25.43	16.68	-		42.10
Nov 27/17:41	***7.25***	**4.89**	7500.00	1537.50	79.50	6.43	30.88	10.18	-		41.06
Nov 27/19:26	***9***	**4.67**	7500.00	900.00	88.00	6.15	16.28	13.20	-	155.40	29.49
Nov 27/20:56	10.5						12.78	12.58	-		25.36
Nov 27/21:11	10.75		**7500.00**	825.00	89.00						
Nov 27/23:26	13	1.60	7450.00	843.75	88.67	2.09	25.55	12.47	-		38.02
Nov 28/1:26	15						17.95	5.20	-		23.15
Nov 28/11:56	25.5	**1.60**	**7125.00**	375.00	94.74	2.00	9.03	5.41	-		14.44
Nov 28/13:26	27						12.63	-	-		12.63
Nov 28/19:56	33		7358.33	HRT error			11.59	-	-		11.59

Average Q	**Ratio**	σ	HRT error
5.06	**2.53**	0.43	0.10

Average OLR	σ	**Ratio**
6.76	0.57	2.47

Run 6b: Raw data and calculations: **VFA (mg/L)**

Day / time	**Time** h	**Q** **L/d**	**So (COD)** **mg/L**	**Se (COD)** **mg/L**	**COD %** **removal**	**OLR** **gCOD/gVSS.d**	**Acetic**	**Propionic**	**Butyric**	**SRT**	**TVFA** **mg/L**
Nov 29/16:26	54.00	1.40	**9090.90**	272.73	97.00	2.23	12.10	-	-		12.10
Nov 29/17:41	***55.25***	**4.58**	8881.11			7.13	7.58	-	-		7.58
Nov 29/18:18	***55.83***	**4.58**	8755.24	327.27	96.26	7.03					0.00
Nov 29/19:34	***57.13***						-	-	-		0.00
Nov 29/20:19	***58.00***	**5.24**	8419.58	436.36	94.82	7.74	19.04	-	-		19.04
Nov 29/ 21:19	***59.00***	**4.37**	8251.75			6.33					
Nov 29/22:50	***60.50***	**4.37**	**8000.00**	800.00	90.00	6.13	0.75	-	-		0.75
Nov 29/23:50	***61.50***	**5.65**	8000.00			7.92	47.77	21.02	46.89	269.32	115.68
Nov 30/00:50	***62.50***						6.35	6.35	0.00		12.70
Nov 30/1:05	***62.75***	**4.84**	7900.00	727.20	90.79	6.71					
Nov 30/2:20	***64.00***	**5.00**	6545.45	1963.63	70.00	5.74	885.27	572.99	1061.88		2520.13
Nov 30/2:50	64.50						640.93	647.98	750.07		2038.98
Nov 30/3:20	65.00		**6545.45**	727.73	88.88					added water	
Nov 30/4:56	66.60		**7636.36**	1818.18	76.19		485.05	388.02	624.85		1497.92
Nov 30/12:20	74.00			1090.90	85.71		107.16	405.52	174.27		686.94
Nov 30/14:05	75.75		7800.00				60.13	132.34	94.68		287.15
Nov 30/20:35	84.25	**1.50**	7327.27	1454.50	80.15	1.93	27.28	141.11	0.00		168.38
Dec 02/21							-	-	-		0.00
Dec 03/15:00		1.02	8000.00	218.18	97.27	1.43	-	-	-	2236.95	

Average Q	Ratio	HRT error
4.83	3.45	0.11

Average OLR	σ	Ratio
6.84	0.76	3.06

Run 7a: Raw data and calculations:

Day / time	Time hr	Q L/d	So (COD) mg/L	Se (COD) mg/L	COD % removal	OLR gCOD/gVSS.d	VFA (mg/L) Acetic	Propionic	Butyric	SRT	TVFA mg/L
Dec 12/12:55		2.18	7090.91	218.18	96.92	2.71				776.68	
Dec 13/ 10:20		**1.40**	**9454.54**	**400.00**	**95.77**	**2.32**	-	-	-		0.00
Dec 13/ 10:25	*0.00*	**4.25**	**9454.00**			**7.05**	-	-	-		0.00
Dec 13/ 10:55	*0.50*	**4.25**					-	-	-		0.00
Dec 13/ 11:25	*1.00*							-	-		0.00
Dec 13/ 11:40	*1.25*	**6.69**	9272.72	**545.45**	**94.12**	**10.88**	-	-	-		0.00
Dec 13/ 11:55	*1.50*						-	**3.00**	-		3.00
Dec 13/ 12:40p.m.	*2.25*	**5.09**	9127.27			**8.16**					
Dec 13/ 1:25p.m	*3.00*						**20.36**	**10.47**	-		30.83
Dec 13/ 1:55p.m	*3.50*	**5.26**	8945.45	**618.18**	**93.09**	**8.25**			-		
Dec 13/ 3:25p.m	*5.00*	**5.87**	**8727.27**	**890.90**	**89.79**	**8.98**	**16.60**	**12.97**	-		29.57
Dec 13/ 5:25	*7.00*	**5.85**	8598.78			**8.83**					
Dec 13/ 6:10p.m	*7.75*	5.00					**20.02**	**30.92**	-		50.94
Dec 13/ 6:20p.m	*8.00*	5.43	8534.53	**1181.80**	**86.15**	**8.13**			-		
Dec 13/ 7:40p.m	*9.25*						**25.47**	**52.70**	-		78.17
Dec 13/ 7:55p.m	*9.50*		8438.16	**1109.00**	**86.86**	**0.00**			-	175.71	
Dec 13/ 11:55p.m	13.50	**2.09**	8181.18	890.90	89.11	3.00	21.83	44.66	-		66.49
Dec 14/ 1:40 a.m	15.25	2.09	8181.18	727.27	91.11	3.00	24.82	26.56	-		51.39
Dec 14/ 7:25a.m	22.00	2.00	**8363.63**	581.80	93.04		-	2.91	-		2.91
Dec 14/ 13:25	27.00	2.09	8363.63	545.45	93.48	3.07	-	3.40	-		3.40

HRT error	0.29	
Average Q, σ Q	5.30	0.78
Ratio	**2.73**	

Average OLR	σ OLR	Ratio
8.61	1.18	3.21

Run 7b: Raw data and calculations:

Day / time	Time hr	Q L/d	So (COD) mg/L	Se (COD) mg/L	COD % removal	OLR gCOD/gVSS.d	VFA (mg/L) Acetic	Propionic	Butyric	SRT	TVFA mg/L
Dec 15/1:25 p.m	51.00	1.90	**8727.27**	327.27	96.25	2.91	12.59	6.33	-		18.92
Dec 15/1:55 p.m	*51.50*	**4.98**	8662.34			7.57	13.43	10.95	37.13		61.51
Dec 15/ 4:25	*54.00*	**5.40**	8337.66			7.90					
Dec 15/ 5:40	*55.25*	**5.40**	8207.79			7.78					
Dec 15/6:55 p.m	*56.50*	**4.96**	8077.92	436.36	94.60	7.03	1389.49	875.28	1582.58		3847.35
Dec 15/7:25 p.m	*57.00*		8662.34				1133.38	1011.46	1230.04		3374.88
Dec 15/8:25 p.m	*58.00*	**4.14**	**7818.18**	627.27	91.98	5.68	735.18	569.05	892.64		2196.87
Dec 15/9:10 p.m	*58.75*						92.00	62.46	78.76		233.22
Dec 15/9:55 p.m	*59.50*	**4.81**	7818.18			6.60	55.37	53.78	41.06		150.20
Dec 15/10:10 p.m	*59.75*		7818.18	818.18	89.53	**recycle and pump lines were reversed from (9:55-10:10)**					
Dec 15/10:40 p.m	*60.25*						1582.98	873.56	1772.11		4228.65
Dec 15/11:25 p.m	*61.00*	**6.92**	7818.18	1672.72	78.60	9.49	1588.33	1157.42	1790.07	169.44	4535.82
Dec 16/12:10 a.m	61.75						1663.34	908.56	1860.88		4432.78
Dec 16/1:25 a.m	63.00					0.00	1532.82	1245.85	1468.21		4246.88
Dec 16/1:40 a.m	63.25		**12363.30**	4218.18	65.88	0.00					
Dec 16/2:10 a.m	63.75					0.00	1088.23	707.12	1129.97		2925.32
Dec 16/10:30 a.m	72.00						931.64	973.77	1320.08		3225.49
Dec 16/10:40 a.m	72.25	**2.30**	10888.59	1345.45	87.64	4.39					
Dec 16/11:40 a.m	73.25						945.03	709.12	1213.61		2867.76
Dec 16/7:25 p.m	81.00		**9454.54**	618.18	93.46	0.00	204.54	746.35	297.03		1247.92
Dec 16/8:10 p.m	81.75		9454.54	618.18	93.46						
Dec 16/8:55 p.m	82.50						159.89	254.96	169.26		584.11
Dec 16/10:25 p.m	84.00						99.64	413.58	99.87		613.10
Dec 17/10:25	96.00	1.94	**8727.27**	381.80	95.63	2.97	26.16	164.85	62.64		253.65
Dec 17/11:55	97.50						26.61	25.14	-		51.76
Dec 17/13:55	99.50						-	8.52	-		8.52
Dec 17/14:40	100.25					0.00	12.37	10.33	-		22.70
Dec 17/15:55	101.50		10177.65				-	-	-		0.00

HRT error	0.18	
Average Q, σ Q	5.23	during shock
Ratio	2.21	

during shock

Average OLR	σ OLR	Ratio
7.43	1.19	2.56

ORGANIC OVERLOADING

Feeding for intermittent 175 minutes over 9 hours (double the organic load)

Day / Time	Q	So (COD)	Se (COD)	COD %	OLR	VFA mg/L				Solids (eff)	Time
	L/d	mg/L	mg/L	removal	gCOD/gVSS.d	acetic	propionic	butyric	TVFA	SRT	
Dec 23/7:50 p.m	2.60	7636.36	327.27	95.71	3.48	18.26	22.69	-	40.95		
Dec 24/3:00 p.m	1.80	9818.18	472.72	95.19	3.10	-	-	-	0.00	1447.71	
Dec 25/9:10 p.m	2.52	11612.90	416.13	96.42	5.13	2.63	-	41.04	43.67		0
Dec 26/ 1:05	2.28	9096.77	2322.58	74.47	3.64	1125.85	855.56	1001.03	2982.44		16.25
Dec 26/ 2:05	**1.80**	**18580.64**	**3975.00**	78.61	**5.87**	**3917.25**	**2258.71**	**2847.07**	9023.03		*17.25*
Dec 26/ 2:35		18530.87				4086.09	**2230.72**	**2958.19**	9275.00		*17.75*
Dec 26/ 4:20 p.m	**1.80**	18304.15			**5.78**	**3735.12**	**2075.23**	**2841.00**	8651.35		*19.5*
Dec 26/ 4:50	-	18248.85	**2550.00**	86.03		**4159.36**	**2745.62**	**3041.26**	9946.24		*20*
Dec 26/ 5:50	**2.52**	**18193.55**			**8.04**	**5292.29**	**2189.74**	**3096.97**	10579.00		*21*
Dec 26/ 6:50	**1.98**	**18580.65**			**6.45**	**3414.73**	**2361.61**	**2576.01**	8352.35		*22*
Dec 26/ 7:15	-					**3778.43**	**1985.20**	**2687.65**	8451.28		*23.416*
Dec 26/ 8:20	**2.05**	**18580.65**			**6.69**	**3362.22**	**2463.20**	**2558.27**	8383.69		*24.5*
Dec 26/ 8:50	-					**3916.80**	**2014.79**	**2821.25**	8752.84		*25*
Dec 26/ 9:50	**1.69**	18580.65			**5.52**	**3596.61**	**1924.16**	**2708.25**	8229.02		*26*
Dec 26/ 10:20	-					**3916.80**	**2021.45**	**2796.27**	8734.52		*26.5*
Dec 26/ 10:50	**2.10**	**19354.80**	**3000.00**	84.50	**7.13**	**3847.22**	**2683.83**	**2845.28**	9376.33		*27*
Dec 26/ 11:20	-	8709.67				3665.78	1931.22	2645.78	8242.78		27.5
Dec 26/ 11:55						3015.94	1599.18	2231.34	6846.46		28.08
Dec 27/ 12:50	1.65	8709.67			2.52	2569.76	1933.36	1983.08	6486.20		29
Dec 27/ 1:20	-					1846.08	1219.25	1268.10	4333.43		29.5
Dec 27/ 2:05	-	**9750.00**				1718.78	1034.56	1351.89	4105.23		30.25
Dec 27/ 7:50	1.65					1365.72	1102.75	1119.95	3588.42		36
Dec 27/14:50	-					1293.43	851.08	1108.30	3252.81		43
Dec 27/ 15:50	-	9056.45				1591.80	1103.71	1158.91	3854.42		44
Dec 27/ 17:05	recycle	3845.00			1.42	1036.46	734.53	828.00	2598.99		45.25
Dec 27/ 23:35	recycle	2598.00			0.96	208.39	644.30	138.87	991.56		51.75
Dec 28/ 12:50	recycle	9000.00	1500.00	83.33		97.33	321.23	72.17	490.73		53
Dec 28/ 1:20	recycle					139.08	377.83	87.49	604.39		53.5
Dec 28/ 3:50	recycle	8709.67	356.25	95.91		54.16	214.41	36.30	304.86		56
Dec 28/ 7:05	recycle	630.00			0.23	25.66	184.56	-	210.22		59.25
Dec 28/8:15	recycle					38.31	86.04	55.07	179.42		60.4167
Dec 28/ 12:17	recycle					23.28	59.40	35.21	117.89		64.45
Dec 28/ 14:20	recycle					36.10	38.00	53.00	127.09		66.5
Dec 28/ 16:00	recycle					15.96	19.68	-	35.64		68.167
Dec 29/ 6:00 p.m	recycle					33.64	21.61	60.54	115.79		94.167
Dec 29/ 8:15 p.m		8625.00				-	-	-	0.00		
Dec 29/ 9:35 p.m						-	-	-	0.00		
Dec 30/	0.25					48.04	337.43	37.75	423.23		
Dec 31/ 4:00 p.m	1.60					80.92	338.93	48.89	468.74		
Jan 1/ 5:30p.m	1.30					656.27	781.96	1069.35	2507.58		
Jan 1/ 6:00p.m	recycle										
Jan 2/ 12:45 a.m	recycle					1854.46	61.18	11.28	1926.92		
Jan 3/ 3:40 p.m	recycle					-	-	-	0.00		
Jan 4/ 2:40 p.m	1.00					187.58	581.89	661.68	1431.15		
Jan 5/ 6:45 p.m	0.22	6375.00	318.75	95.00	0.25	146.51	173.97	43.87	364.34		
Jan 6/ 5:45 p.m	0.23	6000.00	-		0.24	65.94	88.79	-	154.73		
Jan 7/	0.60	7125.00	337.50	95.26	0.75				0.00		
Jan 8/ 3:15 p.m	0.52	7125.00	300.00	95.79	0.65	164.92	115.26	61.43	341.60		
Jan 8/ 6:00 p.m		7125.00			55 ml in	19.88	18.33	-	38.20		
Jan 8/ 6:40 p.m		7125.00			22 min	47.39	92.06	-	139.45		
Jan 9/ 3:10 p.m	0.62	7000.00			0.76	186.29	62.14	100.08	348.51		
									0.00		

Average Q in shock	1.99
Stdev Q in shock	0.28
HRT during shock	2.861
error HRT	0.397

Average OLR	stdev OLR	Ratio
6.50	0.89	1.5

Appendix B

Metal analysis data for all runs (1-7)

	B	Ba	Ca	Fe	Mg	Mn	Ni	St	Z	K	Li	Na	P	S	Run
Limit of quantification (ppm)	**0.018**	**0.004**	**0.072**	**0.009**	**0.017**	**0.001**	**0.079**	**0.001**	**0.007**	**0.45**	**0.017**	**0.25**	**0.2625**	**0.408**	
Feed-Sep07	0.9575	0.4712	1038	0.2164	205.1	7.888	0.1609	36.81	0.0224	458	0.3231	772.3	5.202	275.1	3
R-SEP07	1.082	0.1259	87.79	0.1801	192.4	0.0045	<0.079	18.67	0.0115	464.8	0.3266	786	<2.625	41.79	
R-SEP08	1.077	0.1083	79.64	1.107	200.1	0.0016	<0.079	18.43	<0.007	483.5	0.335	797.1	<2.625	0.9251	
Feed-SEP10	1.129	0.1199	98.9	0.7051	195.4	0.0517	<0.079	17.51	0.0323	498.8	0.3401	808.4	<2.625	4.573	
R-SEP10	0.234	0.1104	102	0.7145	210.8	0.0078	<0.079	19.14	<.007	472.7	0.3218	827.2	<2.625	0.9251	
R-SEP14B	1.058	0.099	86.16	0.5097	211.4	0.0168	<0.079	18.53	0.0347	487.5	0.3282	828.1	<2.625	2.001	2
R-SEP14D	0.9863	0.1038	79.1	0.7828	214	<.001	<0.079	19.39	0.0132	500.2	0.3427	817.6	<2.625	1.472	
R-SEP23	0.6516	0.103	120	0.277	162.7	0.031	<0.079	19.05	0.0298	369.2	0.2379	661.6	6.18	1.993	1
R-SEP24	0.6909	0.0894	74.66	0.2404	147.1	<.001	<0.079	18.22	0.0072	363.8	0.2344	617.7	<2.625	0.6969	
R-SEP28	0.9624	0.0489	69.2	0.2102	164.4	0.0068	<0.079	16.06	0.0319	448.1	0.2688	696.2	<2.625	2.794	
R-OCT02	0.9434	0.07	91.75	0.2087	161.4	<.001	0.1021	19.41	0.0355	496.1	0.2874	728.7	<2.625	0.9538	4
R-OCT04	0.8891	0.0051	10.28	0.3577	149.8	<.001	0.0875	2.188	<.007	393.9	0.2272	678	<2.625	0.6473	
FEED-OCT02	0.9378	0.3442	510.6	0.2409	161.1	1.616	<0.079	29.56	0.0366	457.3	0.2681	688.3	3.638	0.7407	
NOV13_FEED	0.2528	0.3025	276.1	0.2396	94.97	0.8349	0.2801	10.63	0.0093	207.1	0.1495	323.5	5.276	4.314	5
R-NOV13B	0.6842	0.2819	25.09	0.1059	129.3	0.0029	0.2792	7.109	0.0134	362.3	0.2082	529.3	<2.625	3.798	
R-NOV14D	0.4965	0.29	40.1	0.1632	141.5	0.0025	0.2503	8.241	0.0072	349.1	0.1904	501.9	<2.625	2.204	
R-NOV15A	0.5587	0.2905	56.27	0.3023	142.7	0.0022	0.214	9.894	0.0117	451.9	0.2573	607.1	<2.625	4.696	
R-NOV24B	0.4169	0.4937	22.68	0.078	93.46	0.0012	0.4976	5.7	0.0084	309.4	0.1525	439.1	<2.625	2.389	6
R-NOV27A	0.6497	0.7757	21.4	0.1788	Overflow	0.0015	<0.079	11.12	<0.007	567.2	0.2761	638.7	<2.625	2.154	
R-NOV29D	0.4988	0.0674	136.4	0.1517	104.3	0.1246	<0.079	13.58	0.0122	206.6	0.1043	319.6	<2.625	1.735	
FEED-NOV29	0.4135	0.3011	35.67	0.1243	95.67	0.0027	0.3306	7.972	0.0077	314.5	0.1539	432.2	<2.625	0.892	
R-DEC03A	1.004	0.0752	87.63	0.1934	61.34	0.0567	<0.079	11.28	0.013	102.4	103.9	101.8	<2.625	10.08	
R-DEC12B	1.138	<0.004	25.68	0.3733	53.11	0.0318	<0.079	7.172	<.007	215.6	0.1207	349.9	<2.625	2.231	7
R-DEC13D	1.221	0.0188	21.62	0.267	69.92	0.0176	<0.079	6.179	<.007	279.9	0.1599	437.1	<2.625	2.224	
FEED-DEC13	2.271	0.1289	527.8	0.2367	101.9	0.0956	<0.079	32.16	<0.007	467.9	0.2816	608.7	<2.625	1.938	
FEED-DEC15	1.521	0.2276	252.6	0.5506	106.2	0.4065	0.1273	25.2	<0.007	538.8	0.2601	581.5	8.295	11.38	
R-DEC15D	0.3501	0.0324	19.67	0.1793	71.48	0.0143	<0.079	6.559	<0.007	214.4	0.118	342.4	<2.625	22.74	

Appendix C

Sample calculations

OLR with errors

From Section 2.7, p.15

OLR = QS_o/V using Raw data of Run 1, Sep.24 at 9:05 a.m-12:05 p.m./2001

OLR = (3.78L/d*8.600gCOD/L)/5.7L = 5.7(gCOD/L.d)

Average OLR from 9:05-12:05 p.m. = 5.53 (gCOD/L.d), where $\sigma = 0.60$

σ is the standard deviation computed by the function @STDEV in MS EXCEL.

SLR (F/M) with errors

From Section 2.7, p.15

SLR = OLR/X_v in reactor (gCOD/gVSS.d)

Calculating average SLR during shockload Run 1

Average X_v in reactor in Run 1 = 148.37 g VSS, where $\sigma_{X_v} = 0.0004$

SLR in run 1 = (5.53gCOD/L.d) / (148.37gVSS*5.7L) = 0.212 (gCOD/gVSS.d)

Since s (SLR) is a result of computing more than one variable with errors, it was calculated according to error propagation formula for multiplication/division numerical operations using σ as a measure of error in variables used to calculate SLR (Bertheoux, 1994).

$$\frac{\sigma_{SLR}}{SLR} = \left[\left(\frac{\sigma_{OLR}}{OLR}\right)^2 + \left(\frac{3.1(\sigma_{X_v})}{X_v}\right)^2\right]^{1/2}$$

where 3.1 is the bed height of biomass(L) in the reactor.

Substituting all the values gives,

$\sigma_{SLR} = 0.023$

HRT with errors

Defined in Section 2.7, p.14

HRT (day) = V/Q

Average Q in during shockload Run 1 = 3.9 L/d, $\sigma(Q) = 0.22$

Therefore, average HRT = (5.7L)/(3.9L/d) = 1.46d,

σ_{HRT}/HRT = 5.7 * σ_Q/Q, which gives $\sigma_{HRT} = 0.16$.

k from the AAT

Data are taken from test conducted on Sep.21/2001 for Run1 for the bottom sample

10 mL of biomass taken from the bottom of the reactor, and 40 mL of buffer was added.

Taking a 5ml sample of biomass for weight analysis X_v= 0.233g/0.005L = 46.66gVSS/L

Plotting the graph Acetate concentration versus time, and performing a linear regression analysis using MS Excel 97 yields a coefficient of regression = 234.326 (mgAc/hr).

employing the right unit conversions and dividing by X_v gives a value of

k = (234.326 gAc/hr*(24hr/d))/(46.66gVSS/L/50mL) = 0.6 gAc/gVSS.d

where division by 50mL provides the conversion to the size of flask which acted as the medium for acetate breakdown.

SRT

From equation 2 in Section 2.7, SRT is defined by the following equation:

$$SRT = \frac{X_v V_R}{X_e Q}$$

In Table 5.2, the SRT value calculated for Sep–8B at 7:50 a.m. as follows:

X_v= 51.48 g/L , V_R = 3.1 L , X_e = 0.06 g/L, Q = 1.865 L/d to yield SRT = 1434.227 d

Thus, 1/SRT = 0.0007 d^{-1}.