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Canada

Anaerobic - Aerobic Treatment of Chemical Industrial Effluents

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ABSTRACT

Several chemical industries in Canada discharge untreated effluents containing substantial amounts of organic pollutants. Environmental concern regarding the pollution of water bodies has lead the authorities to issue stringent regulations with respect to the quality and quantity of wastewater that can be discharged. Chemical characterization and biotreatability of some waste streams generated by a chemical industry in Québec was therefore undertaken. The study showed that two highly concentrated effluents were amenable to biological treatment. The first effluent, "plastifiant", was generated from the production of plastics, while the second, "colonne", was the product of a resin distillation column. Batch assay tests, including biochemical methane potential (BMP) and anaerobic toxicity assay (ATA), showed a moderate degree of anaerobic treatability with soluble COD removals of 45 to 61% and 11 to 67% for the colonne and plastifiant, respectively. Percentage COD removal was found to vary depending on the source of seed sludge. A mixture of biomasses from different sources was shown to be preferable for the anaerobic degradation of both effluents. The colonne effluent did not exhibit any toxicity to methanogenic bacteria. Inhibition of anaerobic microorganisms from the plastifiant effluent was found to be directly proportional to the increase in concentration, indicating that this effluent should be diluted. Continuous flow studies revealed that the selected effluents could be treated by anaerobic, aerobic or sequential anaerobic-aerobic techniques with soluble COD removals of 58, 80 and 89%, respectively. A significant impact of the type of anaerobic sludge and operating parameters with respect to the extent of biological treatment was noted, suggesting that the treatment efficiencies can be further improved. The one-step anaerobic or aerobic process was found to be applicable as a pre-treatment, while for a full treatment and direct discharge into receiving water bodies, a two-step sequential anaerobic-aerobic process should be implemented.

SOMMAIRE

Plusieurs industries chimiques au Canada rejettent des effluents riches en matières organiques et ce, sans aucun traitement. L'impact négatif de ces rejets sur l'environnement a poussé les autorités à établir des normes strictes quant à la qualité et la quantité des eaux usées déchargées. Dans cette perspective, une caractérisation ainsi qu'une étude de biotraitabilité de quelques effluents générées par une industrie chimique au Québec ont été entreprises. L'étude a démontré que deux effluents forts concentrés peuvent être soumis au traitement biologique. Le premier effluent, "plastifiant", est généré à partir de la production de plastique, alors que le second, "colonne", provient d'une colonne à distillation de résines. Des tests en batch, incluant le potentiel biochimique en méthane (BMP) et les tests de toxicité anaérobie (ATA), ont montré un degré de traitabilité anaérobie modéré avec une efficacité d'enlèvement de la DCO soluble de 45 à 61% et de 11 à 67% pour la colonne et le plastifiant, respectivement. Le pourcentage d'enlèvement de la DCO s'est avéré dépendant de la source de l'inoculum. Un mélange de biomasses de différentes sources s'est montré supérieur pour la dégradation anaérobie des deux effluents. L'effluent colonne n'a entraîné aucune toxicité pour les bactéries méthanogènes. L'inhibition des bactéries anaérobies par l'effluent plastifiant s'est avéré proportionnel à la concentration de l'effluent, indiquant que cet effluent doit être dilué. Des études en réacteurs continus ont démontré la faisabilité de traitement des effluents sélectionnés par les techniques anaérobie, aérobie et séquentielle anaérobie/aérobie avec une efficacité d'enlèvement de la DCO soluble de 58, 80 et 89%, respectivement. Le type de boue anaérobie ainsi que les conditions d'opération des réacteurs se sont révélés avoir un impact significatif sur la qualité du biotraitement. Ceci suggère qu'une optimisation du procédé sera nécessaire pour améliorer l'efficacité du traitement. Le procédé à une seule étape anaérobie ou aérobie s'est révélé applicable comme un pré-traitement. Cependant pour un traitement complet permettant de décharger ces effluents dans les corps récepteurs, le procédé séquentiel anaérobie/aérobie doit être exécuté.

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TABLE OF CONTENTS

ABSTRACT i

SOMMAIRE ii

ACKNOWLEDGMENTS iii

TABLE OF CONTENTS iv

LIST OF TABLES vii

LIST OF FIGURES viii

GLOSSARY OF TERMS X

1. INTRODUCTION 1
   1.1. BACKGROUND 1
   1.2. ANAEROBIC DIGESTION 2
   1.3. STATUS OF THE CHEMICAL INDUSTRY 3
   1.4. THE INDUSTRY COVERED BY THE PRESENT STUDY . . 5
   1.5. OBJECTIVES OF THE RESEARCH 6
   1.6. THESIS ORGANIZATION 6

2. LITERATURE REVIEW 8
   2.1. ANAEROBIC DIGESTION 8
      2.1.1. History: Past and Present Applications 8
      2.1.2. Process Description 12
      2.1.3. Sensitivity of Methanogenesis 14
      2.1.4. Factors Affecting Treatment Performance 15
      2.1.5. Treatment Processes 18
      2.1.6. The Upflow Anaerobic Sludge Blanket Reactor and its Derivatives 19
   2.2. AEROBIC TREATMENT 21
      2.2.1. History 21
      2.2.2. Common Process Types 22
      2.2.3. Principle of Activated Sludge Processes 23

2.2.4. Factors Affecting the Performance of Activated Sludge Processes 23
2.3. ANAEROBIC VERSUS AEROBIC PROCESS 24
2.4. ANAEROBIC / AEROBIC SEQUENCING 28
2.5. BIODEGRADABILITY AND TOXICITY OF INDUSTRIAL EFFLUENTS 31
2.6. RESEARCH NEEDS FOR COMPLEX WASTEWATERS 33

3. MATERIALS AND METHODS 35
3.1. EXPERIMENTAL DESIGN 35
3.2. SOURCES OF SLUDGE 35
3.3. ANAEROBIC TREATABILITY BATCH STUDIES 37
3.3.1. Experimental Procedures 37
3.3.2. Measurement of Gas Production 40
3.4. CONTINUOUS FLOW STUDIES 41
3.4.1. Design of the Reactors 41
3.4.2. Start-up Procedures and Operating Conditions 46
3.4.3. Feed Composition 46
3.4.2. Monitoring of the Reactors 48
3.5. ANALYTICAL METHODS 48
3.5.1. General 48
3.5.2. Biogas Composition 50
3.5.3. Volatile Fatty Acids and Alcohols 50
3.5.4. Gas Chromatography/Mass Spectrophotometry 50
3.5.5. Heavy Metals 51
3.5.4. Anions and Cations 51

4. RESULTS AND DISCUSSION 52
4.1. WASTEWATER CHARACTERIZATION 52
4.1.1 Selection of Effluents 52
4.1.2. Characteristics of the Selected Effluents 55
Effluent Strength 55
pH and Alkalinity 57
Cation and Anion Concentrations 58
Heavy Metal Concentrations 58
GC/MS and HPLC Analyses 60
4.1.3. Treatability of the Selected Effluents 62
4.2. BATCH ASSAY TESTS 62
4.2.1. Biochemical Methane Potential 62
Effect of Biomass on the Degradation of the Effluents . . . 64

Methane Production 66
COD Removal Efficiency 69
Specific Removal and Biomass Activity 72
4.2.2. Anaerobic Toxicity Assay 74
Effect of Storage 76
Toxicity of the Effluents 79
4.2.3. Anaerobic Treatability of the Selected Effluents 81
4.3. CONTINUOUS FLOW STUDIES 81
4.3.1. Anaerobic Digestion 83
Treatment Efficiency 85
Volatile Fatty Acid Production 88
pH and Alkalinity 90
Methane Production and Yield 93
Biomass Washout 96
Specific Removal Rate 98
Application of Anaerobic Digestion for Treatment of the Selected Effluents 99
4.3.2. Aerobic Treatment 101
Treatment Efficiency 102
Volatilization of Contaminants 103
Design and Operating Conditions 105
Applicability of an Aerobic Process for Treating the Selected Effluents 108
4.3.3. Sequential Anaerobic-Aerobic Treatment 109
Treatment Efficiency 110
Application of the Sequential Anaerobic-Aerobic Process for Treating the Selected Effluents 112

5. CONCLUSIONS AND RECOMMENDATIONS 114
Effluent Characterization 114
Batch Assay Tests 114
Continuous-Flow Studies 116
Recommendations for Future Research 117

6. REFERENCES 119

APPENDIX A A-1
APPENDIX B B-1
APPENDIX C C-1

LIST OF TABLES

Table 2.1.	Full-Scale Anaerobic Plants Treating Chemical Industrial Wastewaters	10
Table 2.2.	Comparison between Aerobic and Anaerobic Treatment	26
Table 2.3.	Comparison of Batch Assay and Continuous-Flow	33
Table 3.1.	Stock Solutions Used in Growth Medium	38
Table 3.2.	Composition of Growth Medium	38
Table 3.3.	Composition of Bicarbonate and Sulfide Solutions	39
Table 3.4.	Composition of Trace Metal Solution	47
Table 4.1.	Waste Streams Generated at the Monsanto Plant	53
Table 4.2.	Characteristics of the Various Waste Streams	53
Table 4.3.	Ratios of Selected Characteristics, Highlighting the Biological Degradability of the Various Waste Streams	54
Table 4.4.	Characteristics of the Selected Effluents	55
Table 4.5.	Ratios of Selected Characteristics, Highlighting the Biological Degradability of the Selected Waste Streams	56
Table 4.6.	pH and Alkalinity Measurements	57
Table 4.7.	Anion Concentrations in the Selected Effluents	58
Table 4.8.	Cation Concentrations in the Selected Effluents	59
Table 4.9.	Constituents of the Selected Effluents	60
Table 4.10.	Performance Results of BMP Tests for the Plastifiant and Colonne Effluents	63
Table 4.11.	Characteristics of the Influent to the Continuous-Flow Reactors	82
Table 4.12.	Performance of the UBF Anaerobic Reactor at Various Hydraulic Retention Times	84
Table 4.13.	Influent and Effluent pH as a Function of OLR	91
Table 4.14.	Performance of the Aerobic Activated Sludge Reactor at Steady State	101
Table 4.15.	Performance of the Aerobic Polishing Reactor at Steady State	110
Table A.1.	Constituents of the BMP Tests	A2
Table A.2.	Constituents of the ATA Tests	A2

LIST OF FIGURES

Figure 2.1. The Three Stages of Methane Fermentation 13
Figure 2.2. A Comparison between Anaerobic and Aerobic Processes 25
Figure 3.1. Schematic Layout of Anaerobic Reactor 42
Figure 3.2. Schematic Layout of Aerobic Reactor 44
Figure 3.3. Modified Layout of Aerobic Reactor 45
Figure 4.1. Average Cumulative Methane Production for 4,600 mg/L Bioassays of the Colonne Effluent 64
Figure 4.2. Average Cumulative Methane Production for 4,600 mg/L Bioassays of the Plastifiant Effluent 64
Figure 4.3. Cumulative Methane Production during BMP Bioassays of the Colonne with Mixed Biomass 67
Figure 4.4. Cumulative Methane Production during BMP Bioassays of the Colonne with Municipal Biomass 67
Figure 4.5. Cumulative Methane Production during BMP Bioassays of the Plastifiant with Mixed Biomass 67
Figure 4.6. Cumulative Methane Production during BMP Bioassays of the Plastifiant with Municipal Biomass 67
Figure 4.7. Net Methane Production as a Function of Concentration after 115 d Incubation of the Colonne Bioassays 69
Figure 4.8. Net Methane Production as a Function of Concentration after 115 d Incubation of the Plastifiant Bioassays 69
Figure 4.9. COD Removal Efficiency as a Function of Concentration during the BMP Bioassays of the Colonne Effluent 70
Figure 4.10. COD Removal Efficiency as a Function of Concentration during the BMP Bioassays of the Plastifiant Effluent 70
Figure 4.11. Specific Removal as a Function of Concentration during BMP Bioassays of the Colonne Effluent 72
Figure 4.12. Specific Removal as a Function of Concentration during BMP Bioassays of the Plastifiant Effluent 72
Figure 4.13. Cumulative Methane Production during ATA Bioassays of the Colonne with Municipal Biomass 74
Figure 4.14. Cumulative Methane Production during ATA Bioassays of the Plastifiant with Municipal Biomass 74
Figure 4.15. Cumulative Methane Production during ATA Bioassays of the

Colonne Effluent with Fresh Municipal Biomass 77
Figure 4.16. Cumulative Methane Production during ATA Bioassays of the Plastifiant Effluent with Fresh Municipal Biomass 77
Figure 4.17. Inhibition of Colonne Effluent Degradation as a Function of Concentration and Type of Municipal Biomass 79
Figure 4.18. Inhibition of the Plastifiant Effluent Degradation as a Function of Concentration and Type of Municipal Biomass 79
Figure 4.19. Influent and Effluent Soluble COD Concentrations during the Continuous-Flow Anaerobic Study 83
Figure 4.20. Effluent SS and VSS Concentrations during the Anaerobic Continuous-Flow Study 83
Figure 4.21. COD Removal Efficiency as a Function of OLR during the Anaerobic Continuous-Flow Study 85
Figure 4.22. Influent and Effluent VFA Concentrations as a Function of OLR during the Anaerobic Continuous-Flow Study 89
Figure 4.23. Influent and Effluent Alkalinity as a Function of OLR during the Continuous-Flow Anaerobic Study 92
Figure 4.24. Methane Production Rate as a Function of OLR during the Anaerobic Continuous-Flow Study 93
Figure 4.25. Biogas Composition as a Function of OLR during the Anaerobic Continuous-Flow Study 94
Figure 4.26. Methane Yield at Various OLRs during the Anaerobic Continuous-Flow Study 95
Figure 4.27. Biomass Washout Rate at Various OLRs during the Anaerobic Continuous-Flow Study 97
Figure 4.28. Biomass Specific Removal Rate at Various OLRs during the Anaerobic Continuous-Flow Study 98
Figure 4.29. Influent and Effluent Soluble COD Concentrations during the Aerobic Continuous-Flow Experiment 102
Figure 4.30. Effect of Stripping on SCOD Concentration 104
Figure 4.31. Distribution of Influent Soluble COD Removal Potential 105
Figure 4.32. Effluent Suspended and Volatile Solids Concentrations during the Aerobic Continuous-Flow Experiment 107
Figure 4.33. Influent and Effluent Soluble COD Concentrations during the Sequential Anaerobic-Aerobic Study 111
Figure 4.34. Summary of the Removal of Soluble COD by the Sequential Anaerobic-Aerobic Process 113
Figure B.1. Chromatogram of the Colonne Effluent B-2
Figure B.2. Chromatogram of the Plastifiant Effluent B-3
Figure C.1. Influent Alkalinity Titration Curve Using 0.1 N HCl as Titrant . . C-1

GLOSSARY OF TERMS

Anaerobic Toxicity Assay	ATA
Biochemical Methane Potential	BMP
Biochemical Oxygen Demand	BOD
Chemical Oxygen Demand	COD
Dissolved Oxygen	DO
Food to Microorganism	F:M
Gas Chromatography	GC
Gas Chromatography/Mass Spectrophotometry	GC/MS
High Performance Liquid Chromatography	HPLC
Hydraulic Retention Time	HRT
Methane Production Rate	MPR
Mixed Liquor Suspended Solids	MLSS
Mixed Liquor Volatile Suspended Solids	MLVSS
Organic Loading Rate	OLR
Specific Removal Rate	SRR
Soluble Biochemical Oxygen Demand	SBOD
Soluble Chemical Oxygen Demand	SCOD
Suspended Solids	SS
Total Biochemical Oxygen Demand	TBOD
Total Chemical Oxygen Demand	TCOD
Total Organic Carbon	TOC
Upflow Sludge and Bed Filter	UBF
Volatile Fatty Acid	VFA
Volatile Suspended Solids	VSS

1. INTRODUCTION

1.1 BACKGROUND

Environmental concern regarding the pollution of water bodies from the discharge of contaminated industrial wastewater has lead several countries to issue stringent regulations concerning the quality and quantity of wastewater that can be discharged. Alternatively, industries could channel the wastewater through the sewerage network to a municipal treatment plant. However, the authorities will often impose a charge for the treatment and may insist on partial or full onsite treatment, prior to accepting the wastewater for treatment and disposal.

One of the most efficient and cost-productive treatment technologies available to industrial wastewaters is biological treatment. However, highly concentrated waste streams as well as toxic and recalcitrant contaminants warrant the use of a more sophisticated approach as an alternative to the commonly used technology of employing well aerated tanks with acclimated mixed biomass. Such alternatives may include anaerobic digestion or a sequential anaerobic/aerobic treatment process.

1.2 ANAEROBIC DIGESTION

Anaerobic biological processes have been a successful solution to the treatment of waste streams resulting from food processing (beverage, vegetable, dairy, distillery), pulp and paper industries, landfill leachates, as well as municipal wastewaters (Lee *et al.*, 1989; Lettinga and Hulshoff Pol, 1991; Young, 1991). Although it has failed, in some cases, to fulfil the requirements for the treatment of industrial wastewaters from the chemical industry (Gledhill *et al.*, 1988), anaerobic treatment has been regarded, more recently, as a good alternative for the treatment of some chemical/petrochemical industries (Borghans and Van Driel, 1988; Henry and Varaldo, 1988; Macarie *et al.*, 1992).

Anaerobic treatment is nowadays considered to be a well established technology for wastewater treatment and sometimes a better alternative to aerobic treatment, especially for high strength effluents, i.e. with COD $\geq$ 5,000 mg/L (Young and McCarty, 1969; Hobson *et al.*, 1974; Speece, 1974; Witt *et al.*, 1979). At present, there are at least 420 anaerobic full-scale treatment facilities operating internationally (Huss, 1981; Camilleri, 1988 a and b; Bonastre and Paris, 1989; Heijnen *et al.*, 1989; Craveiro, 1991; Lettinga and Hulshoff Pol, 1991; Young, 1991; Habets, 1993; Safety, 1994).

The success of anaerobic treatment is due to its low cost (compared to other technologies, essentially physico-chemical and aerobic biological treatments) which is generally associated with the reduction in energy consumption resulting from the production of methane as a by-product on the one hand, and the lack of aeration on the other. There are several advantages offered by anaerobic technology over its aerobic counterpart: (1) greatly reduced energy requirements, anaerobic treatment being often considered as a net energy producer; (2) greatly reduced biomass, generally in the order of 20% that of activated sludge; (3) freedom from constraints of F/M control, which has become a severe problem when COD $\geq$ 10 g/L; (4) lower sensitivity towards heavy metal poisoning, which is a serious problem in aerobic systems even at as little as 2

mg/L for certain heavy metal concentrations; and (5) greatly reduced nutrient requirements, which is an important economic factor (Witt *et al.*, 1979).

However, the main drawback of anaerobic treatment is that anaerobically treated wastewaters must receive a post-treatment (which is generally aerobic, such as activated sludge, trickling filter, aerobic fluidized bed reactor or aerobic lagoon processes) before being discharged to the environment. This arises from the fact that anaerobic treatment produces an effluent that is rarely, if ever, of sufficient quality to be discharged without further treatment (Huss, 1981; Odegaard, 1988).

On the other hand, the combination of aerobic and anaerobic treatments is gaining popularity for the complete mineralization of toxic compounds which cannot be degraded by one single process, but rather are initially mineralized, aerobically or anaerobically, into products finally amenable to the opposite treatment (Zitomer and Speece, 1993).

1.3 STATUS OF THE CHEMICAL INDUSTRY

The chemical industry generates significant quantities of wastewaters and contaminated solids. The contaminants produced from this industry generally include oil and grease, phenols, ketones, volatile acids, and heavy metals (Samson and Guiot, 1990).

In Canada, the member companies of the Canadian Chemical Producer's Association (CCPA) produce over 90% of industrial chemicals manufactured in Canada. Member companies, with over 200 sites across the country, directly employ more than 31,000 people in Canada and an additional 100,000 indirectly. The chemical industry is the fifth largest in Canada in terms of value of shipments (CCPA, 1992) and the seventh largest in Québec (MICTQ, 1993).

In 1990, the value of goods delivery sales reached $ 3.7 million, distributed as follows: industrial products (30.8%), plastics and resins (21.1%), toilet products (10.5%), paint (8.5%), soaps and detergents (4.4%), fertilizers (2.6%), ink (1.6. %), and others (20.0%) (CCPA, 1992).

Reported emissions from member companies arise from several sources: discharges to air and water from process operations; accidental releases to air, water and land; emissions to air from leaks in valves and pumps; emissions to air as a result of storage and handling of chemicals; and emissions to land as part of the landfilling or landfarming of wastes. It was reported that almost all emissions to water were from Québec, where two facilities discharging sulphuric acid accounted for 85% of such emissions. These emissions are targeted to be virtually eliminated in 1995 (CCPA, 1992; PASL, 1992). While most of the emissions to water occurred in Québec, emissions to air were highest in Ontario, and underground injection was practised exclusively in Alberta due to the unique geological conditions in that province (CCPA, 1992).

Industrial wastewaters from the chemical industry are often complex and among the most difficult effluents to be treated by biological processes generally, and by anaerobic systems specifically. The complexity of treating such effluents arises from the fact that effluents from the chemical industries: (1) contain a wide variety of organics unrelated to the carbohydrate structures found in municipal and food processing industrial wastes; (2) are highly variable in quality from one industry to another, and generally contain more than a single troublesome chemical compound; (3) generally have very high strength; (4) lack a balanced source of nutrients, especially nitrogen and phosphorous; and (5) are often characterized by the presence of complex process intermediates, polymers and toxicants which defy any biological treatment.

In Québec, in view of the need for a general reduction in pollutant emissions which has already resulted in major contamination of the St-Lawrence River, the Plan d'Action St-

Laurent (PASL) has targeted the 50 most critical industries, requiring them to install proper treatment units in order to be able to meet certain regulatory criteria. These priority industries include 17 chemical industries, two of which are currently out of operation. Among the 15 operating chemical industries, three use aerobic biological treatment, seven employ physico-chemical treatment, while the remaining five resort only to neutralization (PASL, 1992).

1.4 THE INDUSTRY COVERED BY THE PRESENT STUDY

The wastewater under study herein is produced by Monsanto Canada Inc. The plant, located in Lasalle adjacent to the Lachine Canal (Montreal, Quebec), is a chemical industry which produces a variety of chemical products such as plastics, resins, synthetic fibre and polymers. Although the plant also produces and manufactures one herbicide, this process contributes no wastewater to the final effluent, since it is carried out in a closed circuit. The average wastewater flow discharged by the industry is 1,600 m^3/d, with a chemical oxygen demand (COD) of around 4,500 mg/L (Andrew, 1993). Wastewater treatment at Monsanto is currently limited to settlement and pH neutralization. Following these operations, the wastewater flows to the municipal stormwater collector sewer in St. Patrick street and is discharged to the St. Lawrence river.

According to the PASL, which ranks Monsanto 17th among the 50 priority industries, the plant will be connected to the Montreal Urban Community (MUC) Wastewater Treatment Plant by 1995. However, the industry will have to meet certain criteria, namely limited COD, styrene, xylene and formaldehyde concentrations in the effluent. In addition, the effluent discharged to the MUC should not be toxic. In order to fulfil these requirements, Monsanto will have to investigate alternative treatment processes. These may be physical/chemical (such as filtration, chemical oxidation, coagulation, adsorption,

and photochemical degradation), or biological (including aerobic and/or anaerobic treatment processes, or trickling filters). The selection of any treatment alternative should be based on the type of wastewater and must be: (1) capable of producing a treated product which is less toxic than the original product, (2) economically feasible to build and operate, (3) technically appropriate for the operator, and (4) in compliance with applicable regulatory requirements.

1.5 OBJECTIVES OF THE RESEARCH

While the general target of this study leans towards evaluation of the anaerobic/ aerobic treatability of the various waste streams generated by the Monsanto Lasalle Plant, the more specific objectives are:

1. To characterize the various waste streams generated at Monsanto.

2. To assess their potential for aerobic and anaerobic treatment.

3. To select the most suitable effluent(s) for biological treatment.

4. To compare anaerobic treatment to aerobic treatment as well as the sequential anaerobic-aerobic process.

1.6 THESIS ORGANIZATION

Chapter 1: Introduction

This chapter introduces the problem and states the objectives of the present study.

Chapter 2: Literature Review

This chapter reviews the anaerobic and aerobic biological treatment processes, their advantages/disadvantages and how these processes complement each other, as well as the available techniques for evaluating the biodegradability and assessing the toxicity of effluents.

Chapter 3: Materials and Methods

This chapter enumerates the various sources of sludge used, presents the treatability batch study as well as the continuous flow studies which include the anaerobic, aerobic and sequential anaerobic/aerobic process systems, and finally reviews the analytical techniques involved in the present study.

Chapter 4: Results and Discussion

This chapter addresses the results and discussion in three different sections: Section 1 presents a general evaluation of the characteristics of most waste streams generated at the industry; Section 2 presents the anaerobic degradation potential of the two most concentrated waste streams, along with their potential toxicity to anaerobic microorganisms; Section 3 evaluates and compares the anaerobic, aerobic and sequential anaerobic-aerobic treatments for the two concentrated effluents.

Chapter 5: Conclusions and Recommendations

This chapter draws general conclusions and suggests recommendations for further research.

2. LITERATURE REVIEW

2.1 ANAEROBIC DIGESTION

Anaerobic digestion is the breakdown of organic matter by a consortium of symbiotic microorganisms in the absence of oxygen. The organic matter is converted to methane and other end products including carbon dioxide and ammonia (McCarty, 1981; Ditchfield, 1986).

2.1.1 History: Past and Present Applications

The formation of methane from anaerobic digestion has been recognized, since the seventeenth century, as a means for producing combustible gas (Environment Canada, 1988). Indeed, the microbiological formation of methane has been occurring naturally for ages in streams and ponds and in such diverse habitats as rice paddies, marshes, benthic deposits, deep ocean trenches, hot springs, trees, cattle, pigs, iguanas, termites, and human beings (Steggerda and Dimmick, 1966; Balch *et al.*, 1979; Mah and Smith, 1981).

Around 1881, anaerobic treatment was reported to be a useful method for reducing the mass of suspended organic material removed from municipal wastewaters. As a matter

of fact, it was in France that the first significant contribution towards anaerobic treatment of wastewaters took place, when Louis Mouras developed an airtight chamber in which suspended organic material was liquified (Vochten *et al.*, 1988). However, it was not until World War I, when the demand for solvents stimulated the large-scale development of fermentation, that North America started intensifying its scientific study of anaerobics. In the early seventies, North American interest in anaerobic biotechnology began to rise and is continuing to grow considerably, both in the harnessing of the process for industrial wastewater treatment and in the bioconversion of crop-grown biomass to methane (Chynoweth and Srivastavs, 1980; Sheridan, 1982). Vochten *et al.* (1988) reported that "anaerobic treatment has been re-discovered in the last decade, mainly as a result of the energy crisis".

Compared to other developing and industrialized countries, North America has been slower to adopt large-scale anaerobic technology (Environment Canada, 1988). In developing countries, low technology digesters are used to produce methane gas for home heating and cooking. In India, for example, more than one million family digesters existed in 1985 (Environment Canada, 1988), while more than seven million were used in the rural areas of China (National Academy of Sciences, 1977). Nyns *et al.* (1983) reported the existence, in 1983, of 550 biogas digesters in Switzerland and the European Community (EC). By 1988, 743 biogas plants had been built in the twelve EC member states (Pauss and Nyns, 1993).

The application of anaerobic technology was primarily associated with the treatment of primary and secondary sewage sludges (Environment Canada, 1988). Today, anaerobic treatment technologies are in use for many types of chemical industrial effluents. At present, at least 17 full-scale anaerobic treatment plants are in operation at chemical industries in 11 countries. The increase in number of full-scale plants treating chemical effluents since 1981 is illustrated in Table 2.1. A noteworthy increase in the construction of plants is evident after 1991, reflecting the recent increased popularity of anaerobic treatment for this specific type of effluent.

Table 2.1: Full Scale Anaerobic Plants Treating Chemical Industrial Wastewaters

Constructor Name	Company Name and Location	Type of Watewater	Year Constructed	Type of Reactor	Reactor Volume (cu.m)	Influent COD (g/L)	Hydraulic Retention Time (Hrs)	Organic Loading (kg/m^3-d)	Percent Removal	Reference
Celanese	Pampa, Texas, U.S.A	Chemical Processing	1981	Upflow Filter	6 400	14	22 - 30	12 - 15	80 - 90	Young, C. J. (1991)
Celanese	Bishop, Texas, U.S.A	Chemical Processing	1981	Upflow Filter	6 400	12	24 - 36	8 - 12	75 - 85	Young, C. J. (1991)
N. A.	Augusta Manufacturing Plant, Georgia, U.S.A	Aspartame Production	1985	Two Stage Upflow Hybrid Reactor	3 800	12	72 - 96 36 - 48	3 - 4 6 - 8	93 - 95 85 - 90	Young, C. J and Young, H. W (1991)
Biothane	DSM Chemicals, Rotterdam, Netherlands	Phenol Production	1986	Upflow Anaerobic Sludge Blanket	1 250	18 - 30	60 - 80	7 - 12	95	Borghans and Van Driels (1988)
Biothane	Shell Chemicals, Netherlands	Methylstyrene propene-oxide (MSPO)	1987	Upflow Anaerobic Sludge Blanket	1 350	20 - 45	22 - 62	10 - 20	80 - 95	Frankin *et al.* (1991) and Frankin *et al.* (1994)
Amoco Co.	China American Petrochemical Co. (Capco), Taiwan	Terephthalic Acid	1989	Downflow Fixed Film Reactor	10 000	N.A	N.A	N.A	85	Shelley, S. (1991)
SGN	Hoechst Chemical Plant, Cuise-Lamotte, France	Chemical Processing	1988 - 1989	Downflow Fixed Film Reactor	1 900	45 - 48	127 - 138	45 - 47	90	Henry, M. and Varnldo, C. (1988)
N.A	Chemical Industry in China	Terephthalic Acid	1990	Upflow Hybrid Reactor	N.A	6 - 8	21	8	70	Macarie *et al.* (1992)

N.A: Not Available

Table 2.1: Cont'd

Constructor Name	Company Name and Location	Type of Wastewater	Year Constructed	Type of Reactor	Reactor Volume (cu.m)	Influent COD (g/L)	Hydraulic Retention Time (Hrs)	Organic Loading (kg/m^3-d)	Percent Removal	Reference
Biothane	Kelco Biospecialities, U.K	Chemical fermentation	1991	Upflow Anaerobic Sludge Blanket	750	N.A	N.A	N.A	N.A	Safley, M. (1994)
Paques	Bombay Dyeing Manufacturing Co. Patalanga, India	Dimethyltere-Phthalate Production	1992	Upflow Anaerobic Sludge Blanket	1 500	20	. 60	8	70	Habets, L.H.A. (1993)
Paques	Tonen Chemical Kawasaki, Japan	Maleic Acid Production	1992	Upflow Anaerobic Sludge Blanket	100	13.6	18 - 19	18	90	Habets, L.H.A. (1993)
Biothane	Samyang Co., Seoul	Plastics	1992	Upflow Anaerobic Sludge Blanket	840	15	36	9.9	N.A	Safley, M. (1994)
Biothane	Dae Han, Ulsan, Korea	Diethylene Glycol	1992	Upflow Anaerobic Sludge Blanket	160	3.6	11.5	7.5	N.A	Safley, M. (1994)
N.A	Chemical Industry in Italy	Terephthalic Acid	1992	Fixed Bed Reactor	15 200	N.A	108	3.8	80	Vanduffel, J. (1993 and Pereboom *et al.* (1994).
Biothane	Caldic Europoort, Rozemberg, Netherlands	Fiberglass Production	1993	Upflow Fluidized Bed	275	20	48	10	N.A	DeSanto, N. J. (1994)
Biothane	NutraSweet Comp., Univ. Park, IL, USA	Aspartame Production	1993	Upflow Anaerobic Sludge Blanket	1 200	22.05	68	7.8	N.A	DeSanto, N. J. (1994)
Grontmij	Tuntex Petrochemical Inc. (TPI), Taiwan	Terephthalic Acid	1993	Upflow Anaerobic Sludge Blanket	7 000	4.4 - 7.5	30	10	55	Pereboom *et al.* (1994)

The loading rates achieved for chemical effluents in full scale plants range from 3 to 45 Kg COD/m^3-d (Table 2.1). The reported efficiencies are relatively high but do vary, depending mostly on the biodegradability of the particular wastewater being treated. Based on the present status, it can be fairly stated that anaerobic treatment systems are viable technologies for wastewater pollution control in the chemical industry.

2.1.2 Process Description

Methane producing bacteria use a limited range of substrates for growth and energy production. Methanogenesis cannot directly convert complex organic matter into methane. Thus, the combined action of physiologically distinct microorganisms is required to breakdown bio-polymers to methane and carbon dioxide (Zehnder *et al.*, 1980). The substrate flow in an anaerobic system (where carbon dioxide and protons are the only inorganic electron acceptors available) is illustrated in Figure 2.1.

As shown in Figure 2.1, the anaerobic conversion of organic materials into methane and carbon dioxide requires the presence of at least three entirely different physiological groups of active bacteria. Hence, in the anaerobic degradation of organic material, three basic phases are involved in such a way that a particular group of bacteria is associated with each phase (McCarty, 1981; Environment Canada, 1988).

The first group of hydrolytic bacteria converts complex organic compounds (e.g. carbohydrates, proteins and lipids) into individual monomers, which in turn are fermented to various intermediates (e.g., alcohols, fatty acids, carbon dioxide, ammonia and some hydrogen). The intermediates formed during the first phase will be metabolized in the second phase by acetogenic bacteria (obligate proton reducers) to produce hydrogen, carbon dioxide and acetic acid. It is important to note that the obligate proton reducers can only function if the partial pressure of hydrogen is kept low by hydrogen consuming organisms (Zehnder *et al.*, 1981); this would ensure favourable

thermodynamic conditions for the conversion of volatile acids and alcohols to acetate (Speece, 1983). Finally, in the third phase (methanogenesis), two physiologically different groups of methanogenic bacteria are active. One group converts the previously formed hydrogen and carbon dioxide to methane, and the other forms methane from decarboxylation of acetate (McCarty, 1981; Environment Canada, 1988).

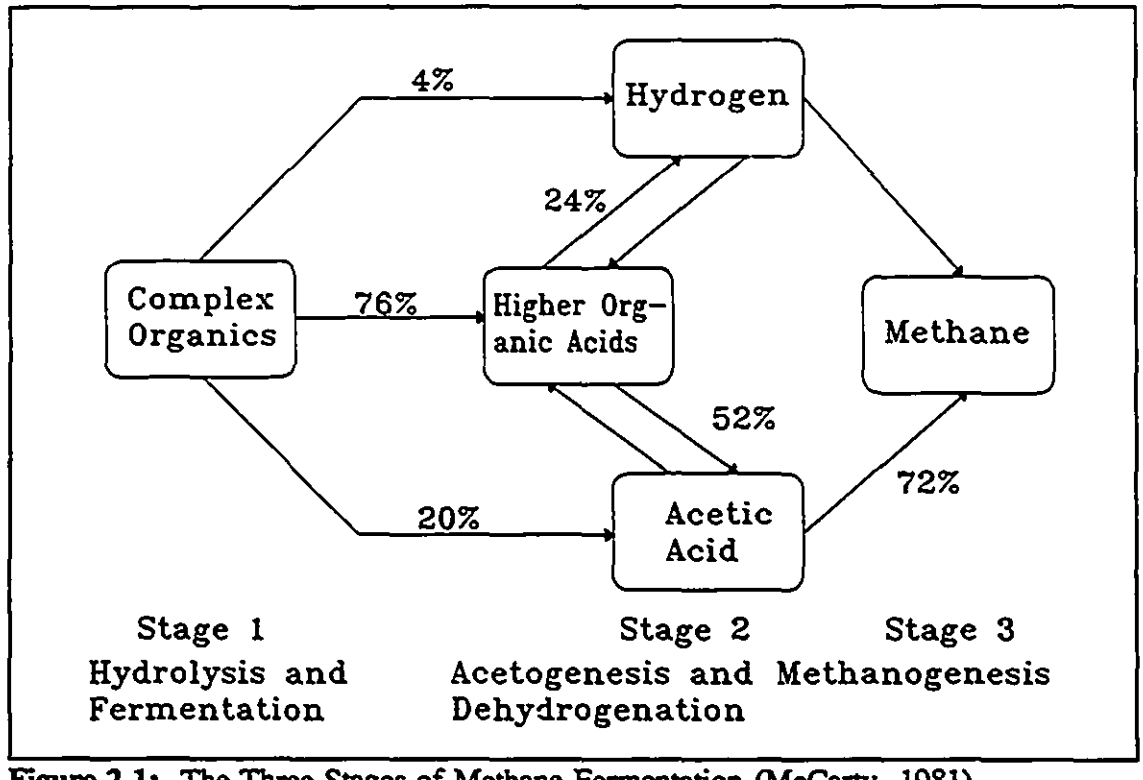

Figure 2.1: The Three Stages of Methane Fermentation (McCarty, 1981).

Ditchfield (1986) reported that the three types of bacteria (i.e. hydrolytic, acetogenic, and methanogenic) depend on each other for the supply of appropriate nutrient substrates and maintenance of a suitable environment (e.g. correct redox potential, ionic balance, and extremely low hydrogen ion concentration).

The fermentation pattern shown in Figure 2.1 may be substantially altered in the presence of electron acceptors such as metal oxides, nitrogen oxides, and oxidized sulfur compounds including elemental sulfur. In such a case, the intermediates formed during the first phase will be oxidized almost entirely to carbon dioxide and the electrons will be transferred to one of the above-mentioned inorganic electron acceptors. Methanogenesis will usually occur only after all these alternative electron acceptors are depleted (McCarty, 1981; Zehnder *et al.*, 1981).

2.1.3 Sensitivity of Methanogenesis

In an anaerobic environment, the acid forming bacteria are relatively tolerant to changes in pH and temperature. Moreover, those bacteria have a much higher rate of growth than the methane forming bacteria. As a result, it is generally assumed that methanogenesis is the rate-controlling step in anaerobic waste treatment processes (Benefield and Randall, 1985).

Parkin *et al.* (1983) and Yang and Speece (1985) reported that methanogens are the most sensitive microorganisms in the anaerobic chain process. Some compounds commonly found in wastewaters, e.g. NH_3, O_2, SO_3^{2-}, SO_4^{2-}, and H_2S, can be inhibiting towards methane forming bacteria while having no interference with aerobic treatment. Moreover, Benjamin *et al.* (1984) reported that methane forming bacteria were sensitive to chemicals such as aldehydes, halogenated compounds, double bonded molecules, and aromatic structures. Nevertheless, Parkin *et al.* (1983) have found that the toxicity can, in most cases, be reversed when a significant acclimation period is provided.

2.1.4 Factors Affecting Treatment Performance

The anaerobic conversion process depends on several parameters, including temperature, pH, alkalinity, nutrient requirements, sulfate concentration, retention time, and loading rate. Some of these factors are discussed below.

Temperature: Temperature is known to influence the rate of anaerobic metabolism. Although earlier literature identifies an optimum temperature of 30 to 37°C, Buhr and Andrews (1977), and Duff and Kennedy (1984) found satisfactory anaerobic conversion within the mesophilic (20 to 45°C) and thermophilic (above 45°C) temperature ranges. Moreover, Zehnder *et al.* (1981) reported that microbial methane formation occurs over a wide temperature range; namely, from about 0°C to 97°C. To achieve efficient/optimum anaerobic treatment, temperature ranges of 35 to 40°C and 55 to 65°C for mesophilic and thermophilic organisms, respectively, are recommended (Archer, 1983).

pH and alkalinity: The generation of methane in anaerobic digestion is adversely affected when the pH is below 6. Hence, for digestion to proceed, the pH has to be kept near neutrality, between 6 and 8 (Zehnder *et al.*, 1981; Samson and Guiot, 1990). Actually, the optimal pH in an anaerobic system ranges from 6.6 to 7.6 (Environment Canada, 1988). However, an exception is found in acid bogs where the pH can be as low as 3, yet active methane production is still observed (Zehnder *et al.*, 1981). A decrease in the digester pH is caused by the accumulation of volatile acids when these are produced by the acetogenic bacteria at a rate higher than their conversion by the methanogenic bacteria (Ditchfield, 1986). In such a case, the alkalinity of the wastewater plays an important role in buffering the depression in pH, thus maintaining the digester's pH and performance at an optimum level (Environment Canada, 1988).

Nutrient requirements: Carbon (C), nitrogen (N) and phosphorous (P) are the major nutrients required to sustain anaerobes. A balanced substrate of N, P and C (N/P around

5 and C/N between 10 and 15) provides a stable functioning of the reactor. Nitrate concentrations greater than 50 mg/L considerably reduce the methanogenesis process. Moreover, several heavy metals such as Fe, Co, Ni, Cu, and Mo are components of the essential enzymes which drive several anaerobic reactions. The presence of nutritive elements (e.g. Fe at 30 to 50 mg/L) and micronutrients (e.g. Ni, Co, Mo) has been shown to have a positive effect on methane production (Oleszkiewicz and Sharma, 1990; Samson and Guiot, 1990). Bivalent ions (e.g. Ca and Ba) were also reported to play an important role (Kosaric *et al.*, 1987; Mahoney *et al.*, 1987).

Sulfate concentration: Zehnder *et al.* (1981) presented three different mechanisms that have been reported to explain methanogenesis inhibition by sulfate.

1- Bacterial sulfate reduction forms sulfide which is poisonous to methane formers.
2- The formed sulfide limits the accessibility of trace metals (e.g. Fe, Ni, Co, Mo) to microorganisms by precipitating them as metal sulfides.
3- Electrons released from the oxidation of organic matter are almost entirely used for sulfate reduction, since this process is thermodynamically more favourable than methane formation. However, Zehnder and Brock (1980) found in their studies that both processes (i.e. sulfate reduction and methanogenesis) can occur simultaneously and at relatively high (10 mM) sulfate concentrations. On the other hand, sulfate reduction and sulfated protein biodegradation produce hydrogen sulfide gas (H_2S). This gas, which is in equilibrium with HS^- and dissociates depending on pH, is considered to be toxic for methanogenesis at concentrations greater than 50 mg/L (Samson and Guiot, 1990).

In addition to the above mentioned factors, the performance of an anaerobic treatment process is affected not only by the type of the wastewater (e.g. complex insoluble and non-complex soluble), but also by its quality (e.g. characteristics and concentrations of suspended matter) (Lettinga and Hulshoff Pol, 1991).

The presence of suspended matter or potentially precipitating matter in a wastewater may adversely affect the anaerobic treatment process performance. The adversity of the effect depends both on the characteristics of the suspended matter (e.g. biodegradability, size, surface area, density, and tendency of the suspended matter to coalesce and adsorb to the sludge), and on its concentration. For example, the accumulation in the sludge bed of a poorly or non-biodegradable suspended matter may reduce the specific methanogenic activity of the sludge. On the other hand, the presence of suspended fats and lipids will promote the tendency for sludge flotation and scum layer formation which may result in a significant washout of active biomass (Lettinga and Hulshoff Pol, 1991).

Kugelman and McCarty (1965) found that the rate of methane formation is affected by cation concentration which, when relatively low, has a stimulatory effect on the system. An optimum concentration exists however, and when exceeded, a decrease in the rate of methane fermentation will result. Moreover, the concentration of ammonia has a similar effect on the rate of methane fermentation. In this case, the fermentation pH determines the percentage distribution between the ammonium ion and ammonia. The free ammonia, which is the toxic form, is favoured by high pH values (Benefield and Randall, 1985).

Lettinga *et al.* (1991) have also presented an extensive review concerning the limitations of anaerobic treatment in the presence of organic compounds and sulfur.

Therefore, the satisfactory application of a certain anaerobic treatment type to complex industrial wastewaters (i.e. industrial wastewaters containing insoluble or potentially insoluble pollutants, and compounds which give rise to inhibition or toxicity, foaming, and/or sludge flotation) requires (1) a proper understanding of the fundamentals of the anaerobic digestion process; (2) a sufficient understanding of the problems that may develop; (3) a proper layout of the process and design of the reactor system; and (4) a proper operation and control of the process (Lettinga and Hulshoff Pol, 1991).

2.1.5 Treatment Processes

Successful exploitation of an anaerobic reactor consists, among other considerations, of maintaining excellent hydraulic conditions and avoiding short circuiting. This fact has been clearly demonstrated by several research studies conducted by Hall (1983), Samson and van den Berg (1984), Samson and Guiot (1985), Samson and Kennedy (1985), and Samson *et al.* (1985). Moreover, Samson and Kennedy (1985) reported the advantage of having a high rather than wide reactor, since the former makes use of the turbulence caused by the ascending gas bubbles.

Over the last forty-five years, there have been many process developments for the advancement of anaerobic treatment both for municipal sludges, and industrial wastewaters (McCarty, 1981).

The first continuous anaerobic digestion systems used to have extremely long hydraulic retention times (HRT; 30 to 60 days) which were associated with the same solids retention time (SRT). However, since biomass retention, independent of HRT, is the primary reason for improvements in process efficiency and stability of anaerobic reactors (Droste *et al.*, 1987), subsequent developments have focused on separating these two residence times by (a) recycling the biomass, (b) immobilizing the biomass on fixed or rotative supports, or on micro-supports in suspension, and (c) by auto-immobilization (i.e. organisms adhering to each other to form granules with proper settling characteristics) (Samson and Guiot, 1990).

Because of the slow growth of methanogenic bacteria, biomass retention is important to the performance of high-rate anaerobic reactors. The retention of biomass permits a substantial reduction of the HRT while maintaining a long SRT (Stander, 1966; van den Berg, 1977; van den Berg and Kennedy, 1983). Actually, the method of biomass retention is the factor that differentiates the various high rates reactors from one another (Droste *et al.*, 1987; Environment Canada, 1988), since it affects the start-up procedure,

the process limitations, the type and strength of wastewater that can be treated, as well as other reactor characteristics (van den Berg and Kennedy, 1983).

Several types of high rate anaerobic reactors have been developed and are extensively covered in the literature. They include: 1) the anaerobic contact process (Schroepfer *et al.*, 1955; Huss, 1981; Morfaux *et al.*, 1982; Wheatley, 1990; Nahle, 1991), 2) the anaerobic filter (Young and McCarty, 1967; Witt *et al.*, 1979; Young and Dahab, 1982; Wheatley, 1990), 3) the downflow stationary fixed film (van den Berg and Lentz, 1980; Camilleri, 1988 a and b; Verrier *et al.*, 1988; Henry and Varaldo, 1988), 4) the anaerobic attached film expanded bed (Switzenbaum and Jewell, 1980; Switzenbaum, 1983; Hall, 1987; Wheatley, 1990), and 5) the upflow anaerobic sludge blanket (UASB) reactor (Lettinga *et al.*, 1979, 1980 and 1983; Lettinga and Hulshoff Pol, 1990).

2.1.6 The Upflow Anaerobic Sludge Blanket Reactor and its Derivatives

Lettinga *et al.* (1979) developed the "Upflow Anaerobic Sludge Blanket" (UASB) reactor which is similar to that developed by Stander (1966). One of the major advantages of this reactor is the incorporation of a large surface area separating the gas from the liquid and keeping the floating solids from clogging the gas ports.

Another major advantage of the UASB reactor is its capacity to retain the biomass in a granular form. However, in order to minimize the biomass wash-out of the reactor, this system requires the development of granules (granular particles containing bacteria) with proper settleability characteristics that can be well mixed by the circulating gas. Moreover, the close cell packing improves the metabolic interspecies transfer, and hence, the granule overall activity (Guiot *et al.*, 1992). In addition, the construction of such a reactor is extremely simple and it can operate at HRTs as low as 4 hours.

Granulation of the sludge is generally regarded as the major factor affecting the starting

of a UASB system. Availability of nutrients, pH range as well as the composition of the wastewater can play an important role in the formation of granules. Biomass granulation has been extensively studied by several authors (Lettinga *et al.*, 1980, 1983; Guiot *et al.* 1988, 1992).

Moreover as with any other process, many potential problems have been identified in UASB reactors. These include: (1) progressive accumulation in the lower part of the reactor of inactive solids in the biomass (e.g. insoluble salts); (2) loss of biomass due to flotation, granule splitting, and excessive bed expansion; and (3) presence of dead zones and creation of preferential paths by compaction of the biomass due to hydrostatic pressure, uneven distribution of the influent, or simply a low influent upflow velocity (Lettinga and Hulshoff Pol, 1991).

Many modifications of the UASB reactors have given rise to other anaerobic reactor configurations. For example, combining the principles of biological solids attachment on a filter medium with the sludge blanket of a UASB, Bachmann *et al.* (1982) introduced, in a laboratory-scale investigation, the baffled sludge blanket, the performance of which has been evaluated by Guiot and van den Berg (1985) and Gorur *et al.* (1986). Following the same line of thought of Bachmann *et al.* (1982), Guiot *et al.* (1984 a and b) developed the upflow sludge blanket filter (UBF) which promotes the advantages of its predecessors while minimizing their limitations. Indeed, in their studies, Guiot *et al.* (1984 a; b) have reported efficient retention of biomass with little or no short-circuiting. Some other UASB derivatives include: internal-circulation reactor (Vellinga *et al.*, 1986); gas-lift reactor (Beeftink and van den Hewel, 1987); baffled-hybrid reactor (Tilche and Yang, 1988); and multiplate reactor (El-Mamouni *et al.*, 1991).

Nowadays, the UASB technology is widely utilized for a large variety of wastewaters (Samson and Guiot, 1990).

2.2 AEROBIC TREATMENT

2.2.1 History

Landspraying, which was a common sewage treatment practice, was first mentioned and put into practice in the United Kingdom in 1885. Based on this technique, the trickling filter method of treatment was developed and was placed into operation for the first time in England in 1893 (Verstraete and van Vaerenbergh, 1986; Metcalf and Eddy, 1991).

Verstraete and van Vaerenbergh (1986) reported that the year 1882 witnessed the first tests leading to the development of the activated sludge process in Europe and that the principle of sludge recycle came into existence around the year 1912. The "activated sludge process" was created when Ardern and Lockett (1914) described the sludge as being activated. Therefore, the use of aerobic biological treatment can be traced back to the late nineteenth century, and by the 1930s, it became a standard method of wastewater treatment (Rittmann, 1987).

Initial research regarding the activated sludge process dealt with oxygen requirements. Since the oxygen requirement had been noted in early studies to diminish rapidly as treatment progresses, the oxygen supply can be adjusted in such a way that oxygenation capacity is decreased towards the outlet end of the aeration tank, where the oxygen demand is lower than that required at the inlet. This practice, called "tapered aeration", permitted a considerable saving in power (Verstraete and van Vaerenbergh, 1986).

Such "step aeration" or "step loading" was introduced by Gould (1942), and has been applied widely since it turned out to produce well-settling sludges. When further research studies started to focus on increasing the volumetric loading rates and therefore the oxygen requirements, high capacity aeration devices were developed and the treatment process was termed "high-rate activated sludge process". It was not until the 1970s that research on activated sludge started focusing on nitrification, denitrification,

and biological phosphorous removal (Vestraete and van Vaerenbergh, 1986).

2.2.2 Common Process Types

Aerobic biological treatment processes can be divided into two major categories, namely suspended- and attached-growth processes. Although both processes perform the same oxidation reactions and accumulate similar microorganisms, they differ in the manner in which cells are retained.

The principal suspended-growth biological treatment processes include: (1) activated-sludge processes such as tapered aeration, step aeration, completely mixed, contact process, oxidation ditch, and pure oxygen, (2) aerated lagoons, (3) sequential batch reactors, and (4) the aerobic digestion process.

On the other hand, attached-growth or biofilm process include (1) the trickling filter, (2) the biological tower, (3) the rotating biological contactor, (4) the activated biofilter, and (5) the expanded or fluidized bed filter (Rittmann, 1987). Of all these, activated sludge and trickling filter systems are the most commonly used among the suspended- and attached-growth biological treatment processes, respectively (Rittmann, 1987; Metcalf and Eddy, 1991).

In the basic activated sludge process, three fundamental aspects can be varied independently, namely the layout (completely mixed, gradient in substrate or aeration supply), the loading rate (high rate, low rate, and very low or extended aeration), and the aeration system (surface or submerged aeration).

Since the activated sludge process has been used in this study for treating the wastewater and polishing the anaerobic effluent, it is of interest to present a brief description of the principle behind this treatment.

2.2.3 Principle of Activated Sludge Processes

The activated sludge process proceeds according to the following steps (Verstraete and van Vaerenbergh, 1986):

1- Sorption of soluble, colloidal, and suspended organics in and on the sludge flocs.
2- Biodegradation of the sorbed organics resulting in the production of CO_2, H_2O, minerals, and new microbial mass.
3- Ingestion of bacteria and possibly of other suspended matter by protozoa or other predators.
4- Oxidation of ammonium (NH_4^+) to nitrite (NO_2^-) and further to nitrate (NO_3^-) by the nitrifying bacteria.
5- Oxidation of cell reserves, which results in sludge digestion and lysis, when the supply of feed is insufficient.

2.2.4. Factors Affecting the Performance of Activated Sludge Processes

The major factors affecting the performance of an activated sludge process include: (1) reactor type; (2) hydraulic retention time; (3) hydraulic loading; (4) organic loading; (5) aeration capacity; (6) solids retention time; (7) food/microorganism ratio; (8) sludge recirculation rate; (9) nutrients; and (10) environmental factors (e.g. temperature and pH). Some of these environmental factors are discussed below.

Temperature: This is an important consideration because of its effects on microbial activity. The microbial activity increases with temperature up to a point beyond which it starts decreasing. In activated sludge processes, the majority of microorganisms are psychrophiles (0 to 10°C) and mesophiles (10 to 45°C) (Reynolds, 1982). In fact, temperature changes will affect the values of the biokinetic coefficients used in process design as well as the settling characteristics of the sludge (Benefield and Randall, 1985).

pH: The microorganisms utilized in the activated sludge process thrive best within a pH range of 6.5 to 9.0 (Reynolds, 1982). Since carbon dioxide is one of the end-products from aerobic bio-oxidation, the buffering system of the incoming wastewater is of utmost importance to maintain a neutral pH. Hence, for some industrial wastewaters with a very low or high pH, neutralization is required prior to treatment.

Nutrient Requirements: The organic removal in activated sludge processes is accomplished by aerobic heterotrophic microorganisms which utilize a portion of the organic material as carbon and energy source for synthesis and maintenance of new biomass. However, in order for the synthesis function to proceed, an adequate supply of all the elements that are found in the cytoplasmic material of a cell should be provided by the wastewater. In contrast with municipal wastewaters, this nutrient requirement is often not met with industrial wastewaters which are generally found to be deficient in nitrogen and/or phosphorous (Benefield and Randall, 1985).

In addition to the previously discussed factors, the activated sludge process is adversely affected by the presence of some chemical agents and compounds, depending primarily on the concentration, temperature, and contact time. These chemicals and compounds include 1) acids and bases (e.g. benzoic acid and ammonium hydroxide); 2) oxidizing and reducing agents; 3) heavy metals (e.g. mercury, arsenic and lead); and 4) industrial chemicals (e.g. organic acids, alcohols, ethers, aldehydes, phenols, chlorophenols, cresols, dyes, as well as antibiotics produced by pharmaceutical fermentations) (Reynolds, 1982).

2.3 ANAEROBIC VERSUS AEROBIC PROCESS

One of the main differences between aerobic and anaerobic treatment processes is that the former produces principally solid end products, while the latter produces mainly gases. Thus, with the anaerobic option, there are savings associated with the net

production of combustible by-product gas (i.e. methane) and the reduction in sludge disposal costs. In addition, there is a reduction in energy requirements, since, unlike aerobic treatment which requires an oxygen supply, anaerobic processes function in the absence of oxygen (Ditchfield, 1986; Speece, 1983).

Although the value of the methane produced from the anaerobic treatment of industrial wastewaters is substantial, it is rarely sufficient to be the sole justification for selecting anaerobic biotechnology. Rather, the contributing factors that favour the adoption of anaerobic technology are the reduction in electricity consumption and the reduction in the disposal cost of the excess microbial cell production (Speece, 1983). A comparison between anaerobic and aerobic processes is illustrated in Figure 2.2.

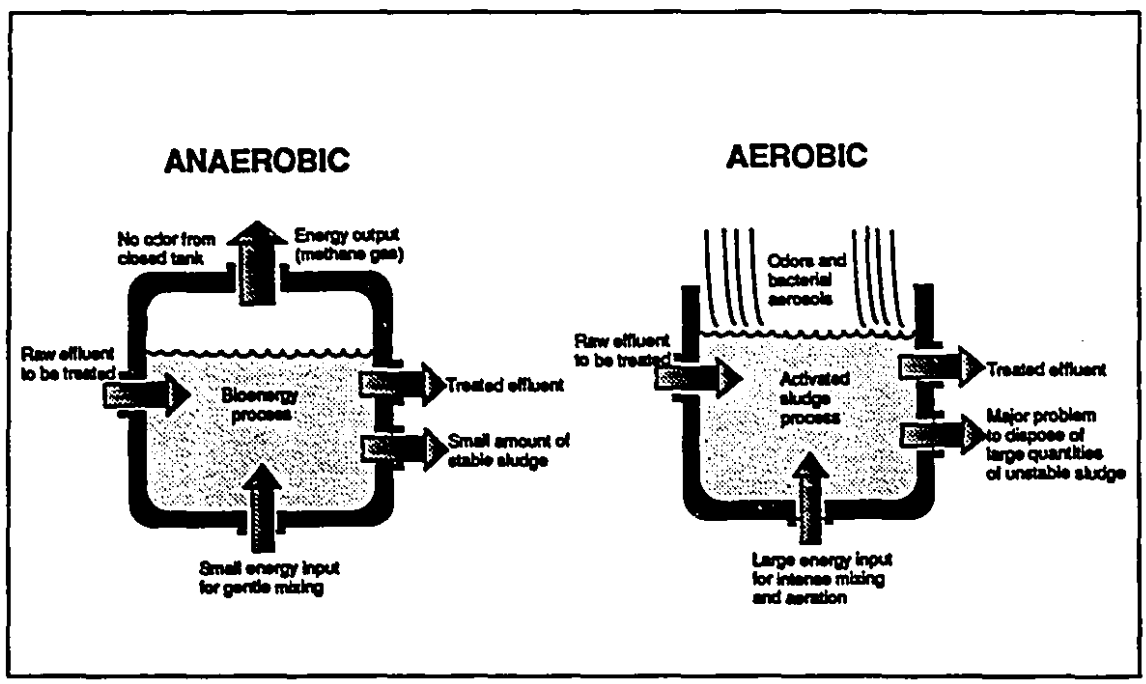

Figure 2.2: A Comparison Between Anaerobic and Aerobic Processes (Ditchfield, 1986).

A comparison between the technological features of both treatment processes is presented in Table 2.2

Table 2.2: Comparison between Aerobic and Anaerobic Treatment (Eckenfelder *et al.*, 1988).

Parameter	Anaerobic	Aerobic
REQUIREMENTS:		
Energy requirements	Low	High
Reactor volume	Small	Large
Mechanical equipment	Little	Much
Maintenance	Not very frequent	Frequent
Experience	Little	Much
Nutrient requirements	Low	High for certain wastes
Alkalinity requirements	High for certain wastes	Low
DESIGN PARAMETERS:		
Solids concentration (kg VSS/m^3)	10 - 30	3 - 5
Organic loading (kg COD/m^3-d)	5 - 30	0.8 - 2.0
Sludge loading (kg COD/kg VSS-d)	0.5 - 1	0.2 - 0.5
Hydraulic retention time	Hours	Hours to days
Sludge retention time (d)	> 20	5 - 10
Sludge production (kg/kg COD)	0.1	0.4
Sludge stabilization	Not necessary	Necessary
PERFORMANCE:		
Degree of treatment	Moderate (60 to 90%)	High (95%+)
Sludge production	Low	High
Process stability (to toxic compounds and load changes)	Low to moderate	Moderate to high
Startup	Slow, complex	Fast, simple
Startup time	2 to 4 months	2 to 4 weeks
Energy production	Biogas	None
BOD removal (%)	80	95
COD removal (%)	60 - 70	85
TOC removal (%)	50 - 70	85-95

The advantages of aerobic treatment over anaerobic treatment include (Vochten *et al.*, 1988):

1. A wider range of waters, with variable composition, can be successfully treated.
2. Better process stability and control.
3. A higher degree of BOD, N and P removal.

Indeed, since the aerobic microbial communities have large free energy potentials, they can trigger the operation of a variety of biochemical mechanisms. Hence they are capable of coping with (a) low substrate levels, (b) variable environmental conditions, and (c) a wide array of chemicals.

However, although aerobic treatment can cope with a wide range of wastewaters, for as much as 20% of the time, the quality of effluents leaving well attended aerobic treatment plants that face no major toxic pulses or shocks do not meet their discharge standards (Berthouex and Fan, 1986). Furthermore, the food to microorganism ratio and the sludge age are two major parameters that can adversely affect treatment performance if not properly designed and closely monitored. Also, the main disadvantages of aerobic treatment include low volumetric loading rates, high power input, and substantial sludge production. In contrast, the respective opposite of these are known to be the advantages of anaerobic treatment. Moreover, the anaerobic microbial communities are specifically suited to high temperatures and high concentrations of both soluble and insoluble organic matter (Vochten *et al.*, 1988).

The main disadvantages associated with anaerobic treatment include the following (Olthof and Oleszkiewicz, 1982; Benefield and Randall, 1985; Vochten *et al.*, 1988):

1. Elevated temperatures required to maintain microbial activity at a reasonable rate.
2. Slow recovery after a toxic shock (days to weeks) due to biomass washout.

3. Production of a low quality effluent (high residual BOD and COD) requiring further treatment. In other words, organic stabilization is incomplete at economical treatment times.
4. Significant removal of ammonium or phosphate species from the wastewater is not achieved.

Another major drawback of anaerobic treatment is its incapacity to produce a final quality effluent, i.e. an effluent that can be discharged directly into the environment (high COD, suspended solids, nitrogen, phosphorous and sulfides concentrations, and no dissolved oxygen). Thus, as a consequence, in many cases where anaerobic treatment is employed, a sequential anaerobic/aerobic system is the overall process to be considered (Huss, 1981; Odegaard, 1988; Zitomer and Speece, 1993). Consequently, the anaerobic process is often referred to as a pretreatment step.

Since the anaerobic process lacks several of the benefits of the aerobic process, and vice versa, the two processes should be appropriately looked upon as complementary to one another rather than as competitors.

2.4 ANAEROBIC / AEROBIC SEQUENCING

Since anaerobic treatment of high strength industrial wastewaters cannot produce a final quality effluent, it needs to be followed by a polishing treatment, which is generally an aerobic process. The potential of a sequential two-step anaerobic/aerobic treatment to produce high quality effluents has been indicated by several researchers (DiGeronimo *et al.* 1979; Suflita *et al.* 1982; Chaudhry *et al.*, 1991; Armenante *et al.*, 1992; Zitomer and Speece, 1993; Guiot *et al.*, 1993, 1994).

Anaerobic/aerobic sequencing is generally successful at reducing toxicity, and may be

used to mineralize otherwise recalcitrant and toxic compounds (Guiot *et al.*, 1994 and 1993; Zitomer and Speece, 1993). However, compared to a single process (anaerobic or aerobic), the sequential anaerobic/aerobic process may not be advantageous in terms of operation and maintenance (i.e. installation of two treatment units instead of one and the fact that more instrumentation is required for monitoring and control). Nevertheless, the advantages of the single process are not lost. In fact the treatment of pulp and paper effluents by a sequential anaerobic/aerobic process produced only 30% of the sludge generated by an aerobic process alone (Zitomer and Speece, 1993). Furthermore, annual savings of 2.5 million French Francs (around 0.5 million US$) have been reported from the use of a full-scale sequential anaerobic/aerobic process compared to the aerobic treatment of chemical industrial effluents (Henry and Varaldo, 1988).

The sequencing of anaerobic processes has been reported by many researchers to enhance (1) sludge settling; (2) nitrogen and phosphorous removal; (3) biodegradation of toxic and hazardous compounds (Zitomer and Speece, 1993).

In their study, Eckenfelder *et al.* (1988) indicated the need for (1) a treatability evaluation to confirm the technical feasibility of anaerobic pretreatment and (2) an economical feasibility study to indicate whether or not such a pretreatment is economically feasible. The results of their economic modelling indicated that the anaerobic pretreatment would not be economically feasible if the influent wastewater strength is below 1,000 mg/L BOD_5. It is important to note, however, that Eckenfelder *et al.* (1988) dealt with a readily biodegradable wastewater.

A major disadvantage of aerobic processes involves the recalcitrance of highly chlorinated chemicals, such as hexachlorobenzene, tetrachloroethylene, and carbon tetrachloride (Zitomer and Speece, 1993), or hetero-substituted aromatics, such as 4-chloro-2-nitrophenol (CNP) (Beunink and Rehm, 1990). These compounds (i.e. halogens, $-NO_2$), which have electron-withdrawing properties, deactivate ring-cleavage

reactions. However, in an anaerobic environment, such compounds are appreciably degraded (i.e. reduced). In fact, the halogenated compounds undergo an "anaerobic reductive dehalogenation" to produce less halogenated homologs that are less toxic and more amenable to degradation under conventional aerobic conditions. Hence, the anaerobic step allows the oxygenase enzyme system to be operative and to subsequently proceed to the oxidative ring-cleavage reaction (Guiot *et al.*, 1993 and 1994; Zitomer and Speece, 1993). An integrated anaerobic/aerobic process for the biodegradation of aromatic compounds has been successfully tested and operated by Armenante *et al.* (1992). It is interesting to note that the more halogenated a compound is, the faster the anaerobic dehalogenation reaction will be (Vogel *et al.*, 1987). On the other hand, aromatic compounds that are anaerobically recalcitrant are efficiently biodegraded, up to complete mineralization, by conventionally cultured aerobic bacteria (Zitomer and Speece, 1993).

Aerobic bacteria tend to polymerize haloaromatic compounds to make them rather resistant to further breakdown (Sahm *et al.*, 1986). However, these same haloaromatics have been amenable to biodegradation in an anaerobic process. Similarly, Vogel and McCarty (1985) reported the occurrence of anaerobic dehalogenation, while, thus far, no aerobic metabolization of chlorinated hydrocarbons (e.g., chloroform, trichloroethane, and tetrachloroethane) has been reported.

Another important aspect of anaerobic/aerobic sequencing is the achievement of a successful treatment of volatile compounds (e.g., chlorinated aliphatics, nitrobenzene, etc.) which would have otherwise been stripped by aeration in the conventional aerobic process before degradation occurs (Dickel *et al.*, 1993). Due to their high vapour pressure, the major part of these compounds is stripped during aerobic treatment resulting in air pollution and strong odour nuisance. In a two-stage process, the reduction of volatiles by anaerobic pretreatment drastically reduces emissions from stripping.

Henceforth, the anaerobic process is displayed as a first treatment step that conveys an effluent to the aerobic polishing unit with fewer toxic and recalcitrant compounds.

2.5 BIODEGRADABILITY AND TOXICITY OF INDUSTRIAL EFFLUENTS

In view of the complexity of many industrial effluents requiring treatment, there is a need to assess the degradation potential and possible toxicity of the wastewater towards the selected treatment process. It has been often difficult to explain system failure and distinguish between failures due to non- biodegradable or toxic materials and those due to inadequate design or operation.

Several tests for assessing aerobic biodegradability have been developed and some have been incorporated into legislation (Howard *et al.*, 1981, and Grady, 1985). Furthermore, a large number of short term screening tests which indicate the toxicity of a substance to activated sludge can be used. Among these are bacterial bioluminescence assays (Ribo and Kaiser, 1987), respirometric methods (Green *et al.*, 1975; Pagga and Gunthner, 1981), measurement of inhibition of growth (Alsop *et al.*, 1980; Dutka and Kwan, 1982; Slabbert and Grabow, 1986) and viability of bacterial cells (Dutka, 1986). However, relatively few methods for determining anaerobic biodegradability and toxicity have been published.

Anaerobic toxicity assays (ATA) and biological methane potential (BMP) tests, developed initially by Hungate (1969) and modified by Miller and Wolin (1974), Owen *et al.* (1979), Shelton and Tiedje (1984) and Cornacchio *et al.* (1988) can be used to screen effluents and generate treatability and toxicity information. These bioassays can also be used to determine the concentration at which the wastewater exhibits toxicity as well as the length of time required for the microorganisms to acclimate to it. The advantages of these methods are that they provide a quick, simple, and inexpensive evaluation of the

effluents to be treated. In addition, these techniques do not require a detailed knowledge of the wastewater constituents. However, the reported results can vary greatly depending on the selected microbial culture. In most cases, multiple populations of microorganisms are involved in the complete degradation of one compound and the toxicity effect may be different on each species (Benjamin *et al.*, 1984). Thus, to ensure accurate results it may be necessary to carry out the ATA and BMP tests with varying inocula from different sources. Furthermore, the biodegradation of several compounds by unacclimated sludge may require a period of weeks. Consequently, the assay tests should generally be run for at least eight weeks (Shelton and Tiedje 1984) and, in some cases, up to 15 weeks (Cornacchio *et al.*, 1988).

In the ATA batch procedure an active anaerobic culture is fed with various concentrations of the wastewater along with a nutrient supplement and some easily degradable compounds such as acetate/propionate. The presence of acetate as a substrate allows the sensitivity of the methanogenic bacteria to be evaluated while the use of propionate permits an estimation of the impact on hydrogen-forming acetogenic and hydrogen-utilizing methanogenic bacteria (Grady, 1985). Thus, a decrease in the rate of methane production with increasing wastewater concentration is indicative of toxicity to the methanogenic and/or acetogenic micro-organisms. In the BMP test, the extent of wastewater biodegradability can be obtained. The procedures are similar to those used for the ATA test. However, no easily degradable compound is added. Thus, the wastewater organics are the only sources of carbon for the production of methane which is interpreted as the biodegradation potential of the wastewater.

Alternatively, continuous-flow small-scale reactors can be used to generate treatability data. Table 2.3 compares the process technological features of batch assays and continuous-flow treatability studies.

The major disadvantages of continuous-flow testing are the length and cost of the

technique to achieve a complete treatability study during which several parameters are tested and evaluated. While batch assays cannot replace continuous-flow testing, they can provide a first screening of several parameters. Consequently, they can indicate whether anaerobic treatment is a possible alternative, which type of biomass has the greater potential to degrade the contaminants of the wastewater, and the most suitable operating conditions to be considered.

Table 2.3: Comparison of Batch Assay and Continuous-Flow.

Parameter	Batch Assay	Continuous Flow
- Wastewater volumes needed	Small	Large
- Equipment cost	Low	High
- Labour requirement	Minimal	High
- Monitoring and analytical cost	Low	High
- Parameters examined without extending program	Many	Few
- Assessment of biological acclimation	Low to moderate	Moderate to high
- Process conditions resemble full scale treatment conditions	No	Yes

2.6 RESEARCH NEEDS FOR COMPLEX WASTEWATERS

There is no doubt that anaerobic and aerobic treatment processes have been extensively covered in the literature. By now the mechanisms and control of both processes are well understood. The susceptibility of various compounds to degradation is well established

and a large literature is available on this subject. Furthermore, several operational problems (e.g. granulation, sludge bulking, short circuiting, etc) have been identified and different alternative solutions developed. However, both processes have inherent limitations and their success in the treatment of chemical industrial effluents cannot yet be guaranteed and may be site specific. In fact there is a remarkable lack of data regarding the performance of laboratory or pilot-scale reactors fed with actual chemical effluents. The application of a sequential anaerobic-aerobic process looks attractive, although even in that case insufficient insight is available and additional research is required.

In view of the uncertainties regarding the application of a one-step (anaerobic or aerobic) treatment process to specific chemical industrial effluents and considering the benefits of a sequential anaerobic-aerobic technique, a research study was initiated to evaluate the biotreatability of some waste streams generated by a chemical industry. The objectives of this study are presented in Chapter I. In the following chapters the experimental program and the collected data will be presented and analyzed.

3. MATERIALS AND METHODS

3.1 EXPERIMENTAL DESIGN

In June 1993, wastewater samples were obtained from the various waste streams generated by the Monsanto plant, LaSalle, Quebec. Samples were collected in 1 L polyethylene containers and analyzed for chemical oxygen demand (COD), biochemical oxygen demand (BOD), total organic carbon (TOC), suspended solids (SS), pH, and oil and grease. Based on these analyses, two effluents were selected for further studies which extended from July 1993 to January 1994 and included: (1) anaerobic treatability batch studies, (2) qualitative and quantitative analysis of the effluents' constituents by gas chromatography/mass spectrophotometry (GC/MS) and high performance liquid chromatography (HPLC), (3) determination of anions, cations and heavy metals, and (4) continuous flow reactors. Around 500 L of each effluent were collected in 20 L plastic containers and stored without any pretreatment at -20°C until needed for experimentation.

3.2 SOURCES OF SLUDGE

Anaerobic sludge samples were collected from 3 different treatment plants in air-tight polyethylene containers and held at 4°C until use. Sludges were obtained from the following locations:

- Primary and secondary digesters of the Vaudreuil Municipal Wastewater Treatment Plant, Vaudreuil, Quebec. The average sludge retention time (SRT) in the digesters was 20 to 30 d and the total solids approximately 30 g/L.

- Quesnel River Pulp Co. Quesnel, B.C. The plant treats pulp and paper effluents using two UASB reactors with a 3,500 m^3 capacity each. The hydraulic retention time (HRT) varies from 5 to 10 h at volumetric loading rates of 9 to 18.5 kg COD/m^3-d.

- Champlain industries, Cornwall, Ontario. The plant treats wastewater from autolysed yeast manufacturing using a 400 m^3 UASB reactor. The digester operates at 9 h HRT and an average organic loading of 10.7 kg COD/m^3-d.

Aerobic activated sludge was also obtained from three different treatment plants. The sludge was collected in polyethylene containers and used immediately. The sources of activated sludge included:

- Aeration basins of the Vaudreuil Municipal Wastewater Treatment Plant. The average (SRT) in the aeration basins was 3.4 d, the concentration of the mixed liquor suspended solids (MLSS) 2,500 mg/L and the influent COD around 150 mg/L.

- Aeration basin of Shell Products, Montreal-East Refinery, Montreal, Quebec. The HRT was 15 h, the MLSS 2,000 mg/L and the influent COD concentration around 150 mg/L.

- Laboratory scale sequential batch reactor (SBR), McGill University, Montreal, Quebec. The reactor was designed to treat leachate from a landfill site. The HRT was 4.6 d, the SRT 30 d, the MLSS 4,500 mg/L and the influent COD

around 1,200 mg/L.

3.3 ANAEROBIC TREATABILITY BATCH STUDIES

The batch anaerobic treatability studies included (i) biochemical methane potential (BMP) assays to indicate effluent biodegradability and corresponding methane yields, and (ii) anaerobic toxicity assay (ATA) to evaluate the toxicity of the effluents on methane production from a spike of readily degradable organic acid substrate. BMP and ATA assays were performed according to the method described by Owen *et al.* (1979) and Cornacchio *et al.* (1988). The assays were conducted in 160 mL serum bottles which were filled to a volume of 50.5 mL, flushed with a 30% CO_2/70% N_2 gas mixture and sealed with a thick butyl rubber stopper. The pH of the wastewater was adjusted to 6.9 $\pm$ 0.1 with concentrated sulfuric acid and various wastewater concentrations were tested. In view of the complex characteristics of the effluents and the absence of acclimated microorganisms, several tests were conducted using biomass from different sources. All assays were carried out in duplicate and are detailed in Appendix A.

3.3.1 Experimental Procedures

Stock solutions of inorganic salts, vitamins, resazurin (a redox indicator to detect oxygen contamination), 2 methyl-n-butyric acid, and sodium sulfide (to provide a reducing environment) used in the defined medium were prepared as outlined in Table 3.1. These were combined in the proportions given in Table 3.2 and were boiled for 5 minutes prior to the addition of 0.34 g $NaHCO_3$. The medium was allowed to cool while 30% CO_2/70% N_2 mixture was being bubbled through the liquid. A bicarbonate buffering solution and a sulfide solution were also prepared as described in Table 3.3.

Table 3.1: Stock Solutions Used in Growth Medium

Solution	Component	Concentration (g/L)
Mineral I	NaCl	50
	$CaCl_2.2H_2O$	10
	NH_4Cl	189.4
	$MgCl_2.6H_2O$	10
Mineral II	$(NH_4)_6Mo_7O_{24}.4H_2O$	10
	$ZnSO_4.7H_2O$	0.1
	H_3BO_3	0.3
	$FeCl_2.4H_2O$	1.5
	$CoCl_2.6H_2O$	10
	$MnCl_2.4H_2O$	0.03
	$NiCl_2.6H_2O$	0.03
	$AlK(SO_4)_2.12H_2O$	0.1
Vitamins B	Nicotinic acid	0.1
	Cyanocobalamin	0.1
	Thiamin	0.05
	p-aminobenzoic acid	0.05
	Pyridoxin	0.25
	pantothenic acid	0.025
Phosphates	KH_2PO_4	50
Resazurin		0.1
2-methyl-n-butyric acid		102

Table 3.2: Composition of Growth Medium

Solution	Volume Added (mL)
Distilled Water	900
Mineral I	10
Mineral II	1
Vitamins B	1
Phosphates	10
Resazurin	15
2-Methyl-n-Butyric acid	1

Table 3.3: Composition of Bicarbonate and Sulfide Solutions

Solution	Component	Concentration (g/L)
Bicarbonate	$NaHCO_3$	42.0
	$KHCO_3$	100.0
Sulfide	$Na_2S.9H_2O$	25.0

In the BMP test 10 mL of the growth medium, 0.9 to 15 mL of wastewater and 2 mL of bicarbonate buffer solution were anaerobically dispersed into the serum bottles which had been previously purged of oxygen. The wastewater volume was selected to produce final COD concentrations of 13,800, 6,900, 4,600, 1,600, and 800 mg/L. The deionized deoxygenated water was then added to bring the interim assay volume to 42 mL. Finally, a 0.5 mL aliquot of the sulfide solution was added as a reductant. A 30% CO_2/70% N_2 gas mixture was bubbled through the serum bottle contents until the redox indicator became colourless, thus indicating less than 10% oxygen in the headspace (Shelton and Tiedje, 1984). An 8 mL aliquot of sludge was added to the bottles which were then sealed and incubated in a Brunswick thermostated shaker at 35°C temperature and 100 RPM agitation. After equilibration for one hour at the incubation temperature, the test was initiated by zeroing the headspace gas pressure to 1.033 kg/cm^2 (1 atm). Controls were prepared in the same manner with the exception that the wastewater was replaced by an equivalent volume of deionized deoxygenated water.

The ATA procedure was similar to that described for the BMP. Based on the concentration of the wastewater, final assay volumes of 2% - 35% (v/v) were tested for inhibitory effects. In view of the elevated COD strength of the wastewater, bioassay concentration was limited to a maximum of 35% so that the final assay COD concentration did not exceed 12,000 mg/L (Cornacchio *et al.*, 1988). In addition to the serum bottle constituents listed above, ATA tests also contained a spike of acetate and propionate substrate. The concentrations of the acetate and propionate stock solutions

were 37.5 g/L and 13.25 g/L, respectively. Each bottle received a 10 mL aliquot of the acetate and propionate stock solutions. Blank controls were similar to those prepared for the BMP bioassays, whereas positive controls contained the defined medium, bicarbonate buffer, sulfide solution, inoculum, deionized deoxygenated water and a spike of acetate propionate.

3.3.2 Measurement of Gas Production

Gas measurements were made after 24 hrs incubation (day 1), on days 2, 4, 5, 7, 10, 12, 15, then every 5 days until methane production ceased. The volume of gas produced was measured by water displacement using a volumetric burette at 35°C. The volume of gas which accumulated in the headspace of the bottle displaced an equivalent volume of the acidified water from the volumetric burette into an erlenmeyer flask. After the atmospheric pressure between the burette and erlenmeyer was equilibrated, the volume of gas produced was measured. Determination of gas composition was made by injecting 0.3 mL of head space gas from the serum bottle into a gas chromatograph.

The methane yield resulting from the wastewater biodegradation was obtained as the difference between the total methane production during BMP testing and the background amount produced by the BMP control (without wastewater). The methane produced by the control was assumed to have resulted from organic matter associated with and/or from endogenous metabolism of the sludge inoculum (Schnell *et al.*, 1992).

ATA methane production data were used to calculate an inhibition index which quantified the degree of inhibition exerted by the wastewater. The percent inhibition was calculated using the following equation:

$$I = (1 - V_w/V_p) \times 100$$

where,

I = extent of inhibition (%)

V_p = volume of methane produced in the positive control without wastewater

V_w = volume of methane produced in presence of wastewater.

3.4 CONTINUOUS FLOW STUDIES

Continuous flow studies included: anaerobic, aerobic as well as sequential anaerobic-aerobic treatments. All experiments were carried out using glass reactors placed in a temperature controlled room at 35°C.

3.4.1 Design of the Reactors

The anaerobic continuous-flow study was conducted using an upflow sludge bed and filter (UBF) reactor as described by Guiot and van der Berg (1985) and shown in Figure 3.1. The reactor consisted of a cylindrical glass column with a 1 L working volume. The top quarter section was packed with polyethylene rings (Flexiring Koch Inc., Akron, OH) floating against a screen, for the purpose of improving the biomass retention and preventing the sludge from being washed out with the effluent. The wastewater was fed into the bottom of the reactor at the desired flow rate using a Harvard peristaltic pump (Model 1203, Southnatick, Mass.). The effluent flowed into a clarifier then to a U-tube after which it exited the reactor. Effluent recirculation was carried out from the bottom of the clarifier and pumped in, with the feed, by a Masterflex pump (Cole-Palmer model 7543-20 Chicago, Illinois). Effluent recirculation was selected to maintain a liquid upflow velocity of 2 m/h. This value was found to be the minimum velocity required to achieve fluidization of the sludge bed which results in an improvement of granular size and activities (Guiot *et al.*, 1992). The gas collected in the headspace of the reactor and clarifier flowed through a 0.64 mm Tygon tubing into a graduated burette filled with acidified water. Water displaced by the gas dripped into a calibrated cylinder and the

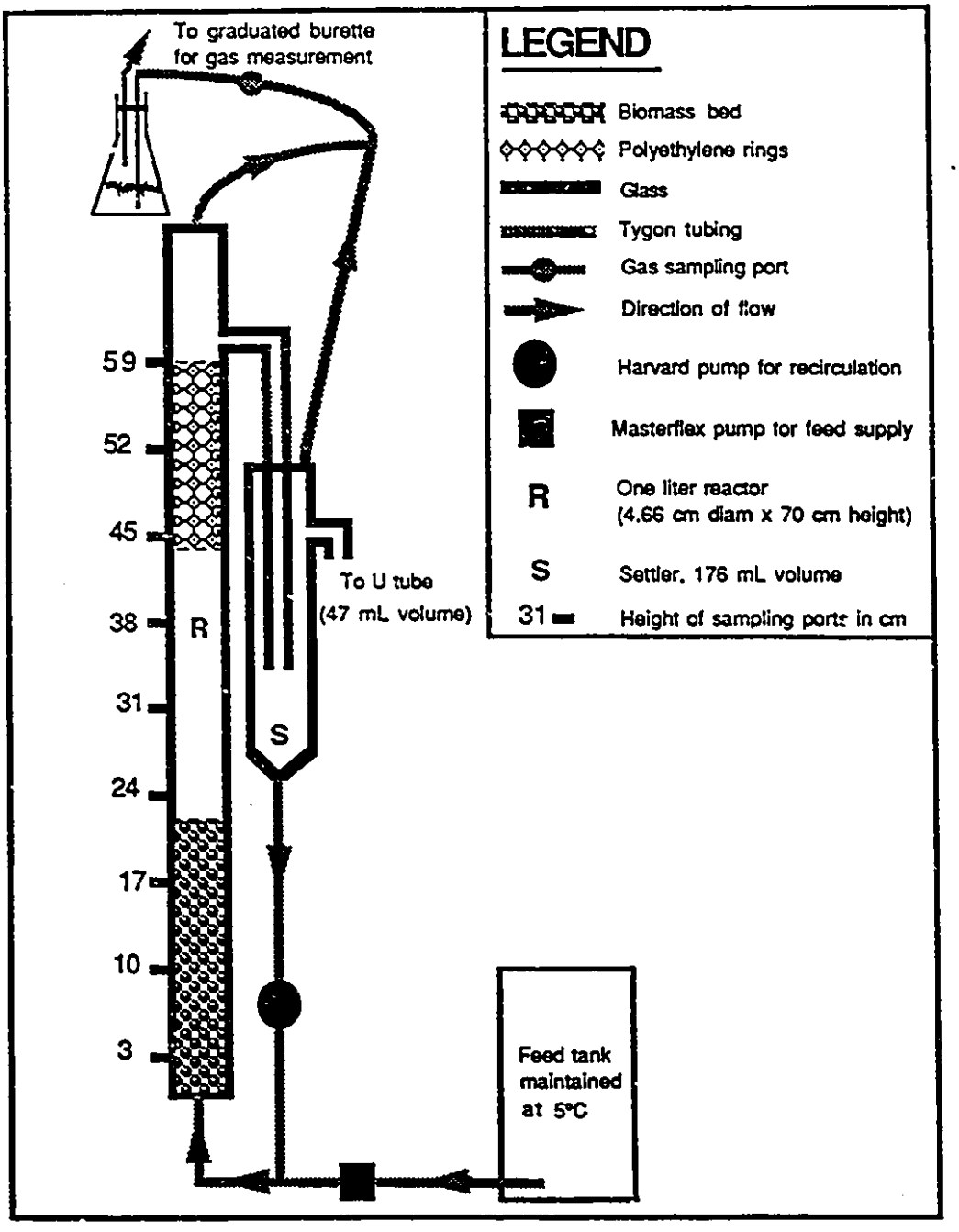

Figure 3.1: Schematic Layout of Anaerobic Reactor

volume was recorded to the nearest 10 mL. Gas samples were taken through a sampling port installed along the Tygon tube.

For the aerobic continuous-flow study, an integrated glass system consisting of an aeration column, a recirculation path and a settler was used and is shown in Figure 3.2. The wastewater was fed into the lower side of the reactor using a Harvard peristaltic pump (Model 1203, Southnatick, Mass.). Aeration and mixing of the activated sludge were performed by supplying air into the bottom of the reactor through a porous glass membrane. The system design was based on the assumption that aeration would be confined in the aeration column. The mixed liquor passes through an opening to the settler where the biomass settles by gravity, then flows back to the aeration column through the recirculation path. A clarified effluent, free of biomass, exits the settler at the top. However, it was noted that some air bubbles were passing from the aeration column to the settler, thus creating turbulence, hindering the proper settlement of the mixed liquor and leading to considerable losses of biomass in the effluent. Air supply was reduced so that fewer air bubbles would pass to the settler. However, this modification created yet more problems among which were: (1) very low recirculation rate and creation of anoxic conditions for the biomass in the circulation path, (2) poor mixing and clogging of the connection opening between the aeration column and the settler, (3) clogging of the porous membrane due to the low air pressure. Finally a separate settler was added to the system for the purpose of preventing sludge washout (Figure 3.3). This settler acted as a secondary clarifier to collect the biomass lost from the integrated system. Recirculation of the collected biomass was carried out from the bottom of the settler and pumped with the feed by a Masterflex pump (Cole-Palmer model 7543-20, Chicago, Illinois).

The sequential anaerobic-aerobic continuous flow study consisted of treating the wastewater by the anaerobic reactor and then polishing the anaerobic effluent in the aerobic reactor. The reactors used for this study were identical to the anaerobic and aerobic reactors described above and shown in Figures 3.1 and 3.3.

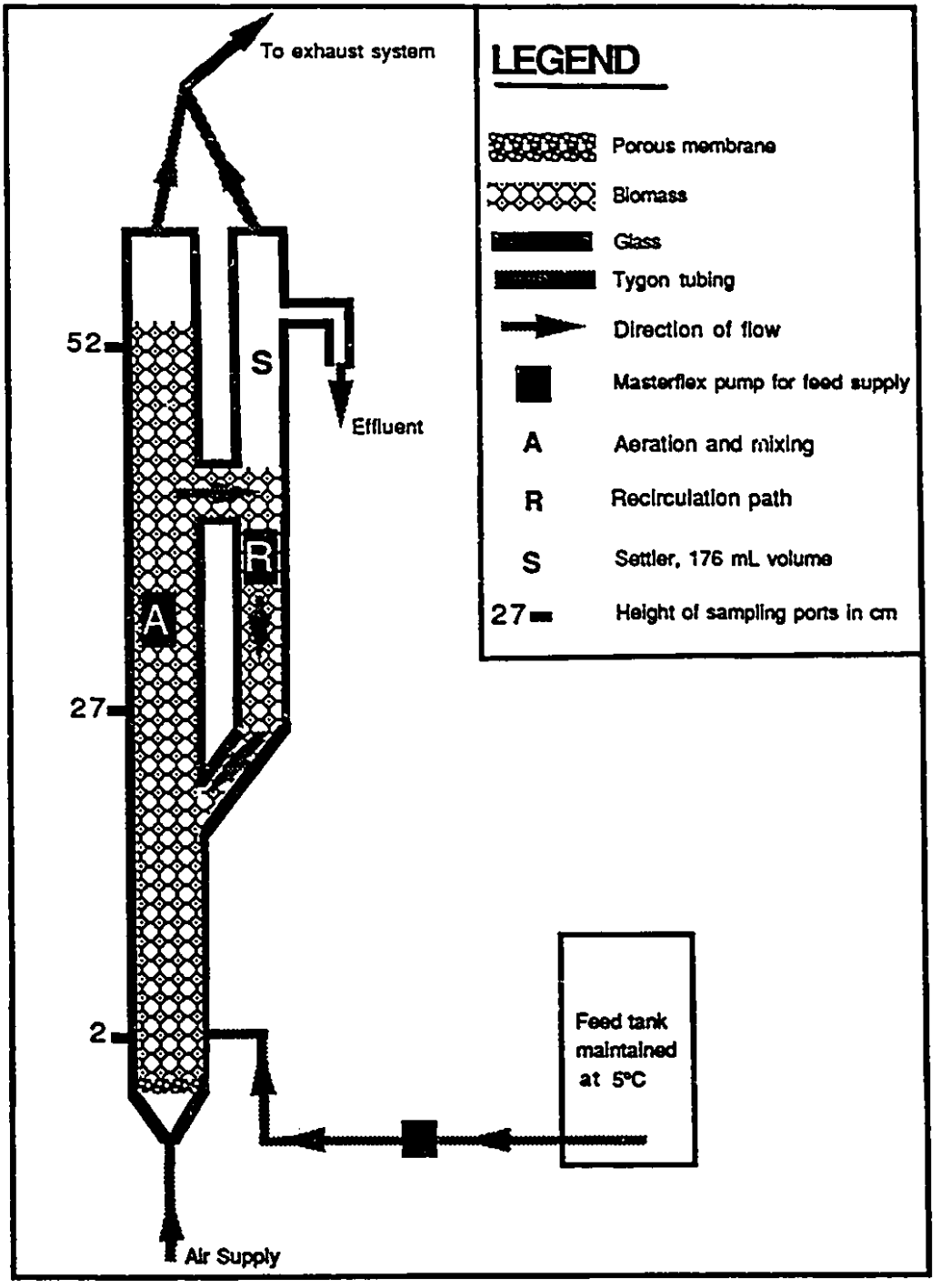

Figure 3.2: Schematic Layout of Aerobic Reactor

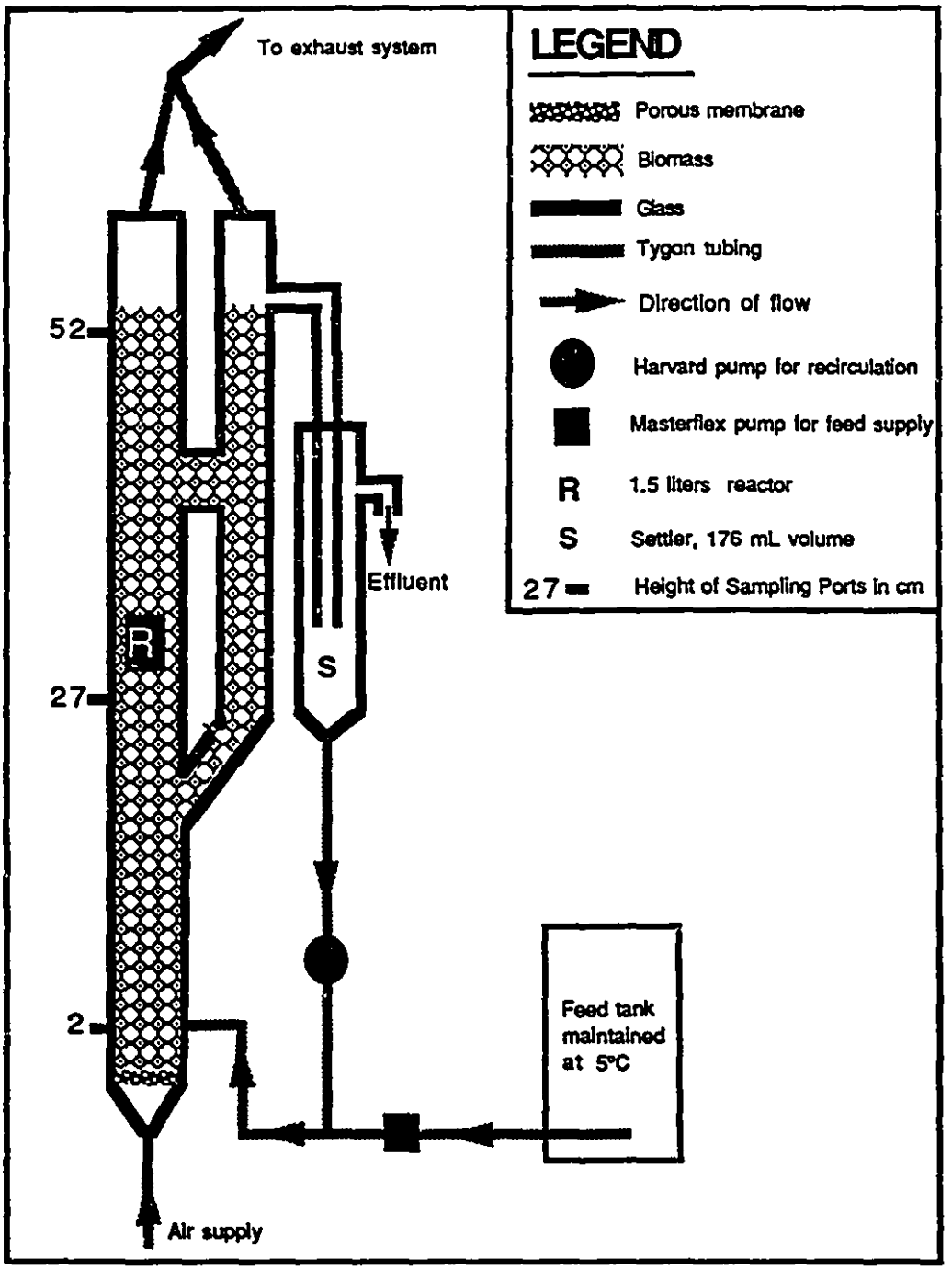

Figure 3.3: Modified Layout of Aerobic Reactor

3.4.2 Start-up Procedure and Operating Conditions

The anaerobic reactor was inoculated with 15 g VSS/L of municipal biomass obtained from the Vaudreuil treatment plant. The biomass was kept in the reactor for 12 h after which feeding started at an organic loading rate of 2.37 kg COD/m^3-d and an HRT of 7 d. The experimental protocol consisted of evaluating the performance of the reactor as a function of the organic loading rates in a series of pseudo-steady states (PSS) after a stable regime was established. The organic loading was increased by augmenting the flow rate, thus decreasing the HRT. Feed concentration was maintained constant throughout the study.

The aerobic reactor was inoculated several times with fresh activated sludge from the different sources mentioned previously in Section 3.2. The activated sludge obtained from the SBR treating leachate exhibited the best settling characteristics and responded well to the type of wastewater used. Consequently, this biomass was used to evaluate the performance of the aerobic continuous flow reactor. The MLSS concentration in the reactor was 7,050 mg/L. The experimental program consisted of operating the reactor at 7 d HRT which corresponded to an organic loading rate of 1.55 kg COD/m^3-d. The SRT was maintained at 30 d by wasting the necessary amount of mixed liquor.

In the sequential anaerobic-aerobic continuous flow study, the anaerobic effluent was fed to the aerobic reactor at a 4 d HRT and an organic loading of 1.24 kg COD/m^3-d. During this phase, the MLSS concentration and the SRT of the aerobic reactor were identical to the ones used in the aerobic study. Similarly, the design parameters of the anaerobic reactor were not modified.

3.4.3 Feed Composition

The influent to the reactors was prepared by mixing equal volumes of the two selected

effluents (see Section 4,1 below), resulting in a soluble COD of approximately 16,500 mg/L. To maintain good bacterial growth, essential nutrients were added to the feed. For the anaerobic reactor, a balanced COD/N/P/S ratio of approximately 100/2/0.4/0.2 was maintained, while for the aerobic reactor, a balanced COD/N/P ratio of 100/5/1 was used. Nitrogen was added in the form of urea, potassium in the form of potassium phosphate and sulfur as ammonium sulfate. The pH of the wastewater was adjusted to 7.4 $\pm$ 0.3 using hydrochloric acid. The feed was prepared every other day and stored in refrigerated containers at approximately 5°C.

At the beginning of the study, no trace metals were added to the feed of the anaerobic reactor. However, towards the end of the study, trace metals were added at the rate of 0.5 mL trace metal solution/ g COD. The composition of the trace metal solution is shown in Table 3.4.

Table 3.4: Composition of Trace Metal Solution (El-Mamouni *et al.*, 1991).

Component	Corresponding Element	Concentration (g/L)
$FeCl_2.4H_2O$	Fe^{2+}	2.00
H_3BO_3	B^{3+}	0.05
$ZnCl_2$	Zn^{2+}	0.05
$CuCl_2.2H_2O$	Cu^{2+}	0.04
$MnCl_2.4H_2O$	Mn^{2+}	0.50
$(NH_4)6Mo7O_{24}.4H_2O$	Mo^{6+}	0.05
$AlCl_3$	Al^{3+}	0.03
$CoCl_2.6H_2O$	Co^{2+}	0.15
$NiCl_2.6H_2O$	Ni^{2+}	0.10
$CaCl_2.2H_2O$	Ca^{2+}	15.00
Na_2WO_4	W^{6+}	0.075
$MgCl_2.6H_2O$	Mg^{2+}	10.00
Na_2SeO_3	Se^{4+}	0.05

3.4.4 Monitoring of the Reactors

The performance of the reactors was assessed daily by determining influent and effluent flow rates, gas production and composition, pH, temperature, as well as influent and effluent COD, volatile fatty acids (VFA), alkalinity, SS and volatile suspended solids (VSS). It should be noted that gas measurements and VFA analyses were carried out only for the anaerobic reactor. To estimate the total biomass concentration and its distribution through the reactors, the VSS concentration was determined at different heights in the reactors.

3.5 ANALYTICAL METHODS

3.5.1 General

COD, BOD, TOC, SS, VSS, pH, and alkalinity measurements were performed to characterize the various waste streams generated by the industry and to monitor the performance of the reactors. All analyses were carried out in accordance with *Standard Methods* (APHA-AWWA-WPCF, 1989), as noted below:

- COD : Section 5220C. The COD was determined using a Hach COD reactor Model 45600 (digestion at 150°C for 2 h) and a spectrophotometer (Hach DR/3000) at 620 nm wavelength.

- pH and Alkalinity: Sections 4500 H^+ and 2320 B, respectively. A Fisher Accumet pH meter model 825 MP with a glass combination electrode was used for all measurements. Based on the expected pH values, the pH meter was calibrated using

buffer solutions with pH values of 4 and 7, or 7 and 10. Alkalinity, measured as $CaCO_3$ was determined by titration with 0.2 N H_2SO_4. The end point of titration was at pH 4.5.

- SS and VSS: Sections 2540 D and 2540 E, respectively. The SS were determined by centrifugation (Beckman centrifuge J2-21M) for 10 minutes at 10 000 RPM and 4°C, followed by drying of the solids at 105°C for 18 to 20 h. The VSS were determined by incineration of the dried sample at 600°C for 1 h and computing the weight loss of the sample between 105 and 600°C.

- BOD: Section 5210B. Tests were carried out in 300 mL BOD bottles. Activated sludge from the Vaudreuil treatment plant and the SBR pilot units treating leachate were used as seeds. The bottles were incubated at 20°C in the dark for 5 d. Dissolved oxygen was measured using a dissolved oxygen probe (Orion Model 97-08) and an Orion SA 520 meter.

- TOC: Section 5310C. The TOC was measured using a Dohrmann DC-80 TOC analyser equipped with a reaction module, a detector/ electronics module and a printer. Prior to analysis, the samples were filtered through a 0.45 μm filter to remove suspended solids. Then both samples and standards were acidified with concentrated HNO_3 and sparged to remove inorganic carbon. Finally, a 200 μL volume was injected for analysis.

3.5.2 Biogas Composition

Biogas composition (CH_4, N_2, O_2, and CO_2) was determined by gas chromatography. The chromatograph was equipped with a thermal conductivity detector (Perkin-Elmer Sigma 2000, Norwalk, CT) and a Hewlett Packard integrator. The column was a 60/80 mesh Chromosorb 102, of 3.66 m length x 3.2 mm ID. The oven temperature was 40°C and the thermal conductivity detector was set at 105°C. Argon was used as the carrier gas at a flow rate of 20 mL/min. A 0.3 mL sample was injected into the stainless steel column. Percent biogas fractions were corrected to standard temperature and pressure (STP).

3.5.3 Volatile Fatty Acids and Alcohols

Volatile fatty acids (acetate, propionate and butyrate), formate and butanol were determined by HPLC (Model 590, Millipore Water Chromatography Division, Milford, Mass.). The HPLC was equipped with a refractive index detector (Model 410, Millipore), a programmable multiwavelength detector (Model 490, Millipore) and an autoinjector with a variable loop volume. The column was an interaction Ion-300 organic acid (300 mm x 7.8 mm). Sulphuric acid (0.0033 N) was used as the solvent at a flow rate of 0.4 mL/min. The temperature of the column was fixed at 30°C.

3.5.4 Gas Chromatography/Mass Spectrophotometry

GC/MS was carried out for the two selected effluents in order to identify the major constituents contributing to the COD. Prior to GC/MS analysis, the samples were acidified to pH 2 and extracted with methylene-chloride. Then, a 1 μL sample was analyzed by a Hewlett Packard GC (Model 5890) equipped with an automatic injector

(Model 7673A), a capillary column (J & W DB-5) of 30 m length x 0.25 mm ID, a mass selective detector (Model 5970), an MS chemstation (HP G1034B) for data analysis and a mass spectral data base (NIST Base, NIST/EPA/MSDC). Helium was used as the carrier gas at an 80 KPa head pressure. The oven temperature was set at 55°C for 3 minutes, and then raised gradually over 15 minutes until a temperature of 280°C was reached.

3.5.5 Heavy Metals

Heavy metals (Fe, Pb, Zn, Cd, Cr, Cu, K, Ca, Mg, Mn) were determined by atomic absorption spectrophotometer (Varian Techtron Pty., Model A 1275, Springale, Australia). Prior to analysis, the samples were digested with concentrated HNO_3 and HCl according to *Standard Methods* (APHA-AWWA-WPCF, 1989), Section 3030F. Atomic absorption analyses were carried out using single-element lamps. The wavelength for each element was set as specified in Section 3111 of *Standard Methods* (APHA-AWWA-WPCF, 1989).

3.5.6 Anions and Cations

Anions (Cl^-, NO_2^-, NO_3^-, HPO_4^-, SO_4^{2-}) and cations (Na^+, NH_4^+, K^+) were analyzed by high performance liquid chromatography (HPLC) Spectra-Physics Model SP 8800, San Jose, CA. The HPLC was equipped with a conductivity detector, and a Hamilton PRP-X 200 (250 mm x 41 mm) column. For the analysis of anions, the solvent was 7 mM p-hydroxybenzoic acid in 10% MeOH flowing at a rate of 1.75 mL/min. In the case of cations, 6 mM HNO_3 in 35 % MeOH was used as a solvent and the flow rate was maintained at 0.75 mL/min. All analyses were performed at a temperature of 40°C.

4. RESULTS AND DISCUSSION

4.1 WASTEWATER CHARACTERIZATION

4.1.1 Selection of Effluents

As mentioned earlier in Chapter 3 (Materials and Methods), wastewater samples were collected from the various waste streams generated at the Monsanto plant, Lasalle. The industry discharges approximately 1,650 m^3/d, 60% of which is generated from the different production processes and 40% from infiltration. Thus of the total flow of 1,650 m^3/d, only 1,000 m^3/d is polluted effluent and would require treatment.

As shown in Table 4.1, five major waste steams are generated at the plant and account for approximately 75% of the polluted effluents. The COD analyses of these streams revealed that three effluents ("colonne", "plastifiant", and "polymerization") are highly concentrated and necessitate treatment. In fact these three waste streams constitute the majority of the COD discharged by the industry. Alternatively all the waste streams could be treated. However, it was speculated that an efficient treatment of the concentrated streams would yield a final effluent of acceptable quality. Furthermore, as the three effluents constitute only 50% of the polluted effluents flow, lower construction and operating costs would be required. If the polluted effluents prove to be toxic to the aerobic and/or anaerobic microorganisms, one or more of the other streams could be used for dilution purposes.

Table 4.1: Waste Streams Generated at the Monsanto Plant.

Waste Stream	Percent Flow of the Total Polluted Effluent Flow	Total COD (mg/L)
Colonne	20%	18,000
Plastifiant	15 to 20%	9,000
Resins	10%	115
Polymerization	15%	18,000
Compounding	15%	980
Others (laboratory, steam plant...)	20 to 25%	< 1,000

To assess whether the effluents are amenable to biological treatment, traditional tests including COD, BOD, TOC, as well as oil and grease were conducted. The results are presented in Table 4.2.

Table 4.2: Characteristics of the Various Waste Streams.

Waste Stream	Total COD (mg/L)	Soluble COD (mg/L)	Total BOD (mg/L)	Soluble TOC (mg/L)	Oil and grease[1] (mg/L)
Colonne	18,025	17,910	3,540	10,800	235
Plastifiant	9,010	8,975	5,600	3,200	147
Resins	115	75	26	40	23
Polymerization	18,350	4,380	430	1,010	-
Compounding	1,080	160	105	-	37
Final Effluent[2]	4,345	3,315	1,290	1,615	23

(1) Measured by Monsanto.

(2) Effluent discharged into the St. Lawrence River.

Selection of the effluents that could be biologically degraded was based upon the BOD to COD, soluble COD to total TOC and soluble COD (SCOD) to Total COD (TCOD) ratios (Table 4.3). Effluents with COD/TOC $\leq$ 4.0, BOD/COD $\geq$ 0.2, and SCOD/TCOD $\geq$ 0.70 were assumed to be suitable for biological treatment. Based on these criteria, the ratios presented in Table 4.3 reveal that the plastifiant, colonne and resin effluents are potentially amenable to biological treatment.

The colonne effluent is the product of the resin distillation column. These resins are composed of urea, formaldehyde, and alcohol such as butanol and methanol. Resins are used in the formulation of high quality enamels for cars and household appliances. On the other hand the plastifiant is generated from the esterification of acid with long chain alcohols. This process causes modification of polymers which are ultimately used in food packaging, electric cables, etc.

Table 4.3: Ratios of Selected Characteristics, Highlighting the Biological Degradability of the Various Waste Streams.

Waste Stream	COD/TOC (Soluble)	BOD/COD (Total)	SCOD/TCOD
Colonne	1.7	0.2	0.99
Plastifiant	2.8	0.6	0.99
Resins	1.9	0.2	0.65
Polymerization	4.3	0.02	0.24
Compounding	-	0.1	0.15
Final	2.1	0.3	0.76

The unsuitability of biological treatment for the polymerization effluent was most probably due to the very high content of solid fines and to the presence of polymers. This effluent is generated from the production of ABS (acrylonitrile-butadiene-styrene) which is a tough rigid plastic used for automobile parts and building materials. To

achieve successful biological treatment, physical and or chemical pretreatment might be required for this specific effluent. As this issue was outside the scope of this study, no further work was carried out regarding treatment of the polymerization effluent. Consequently and in conjunction with the results given in Table 4.1, the two other concentrated waste streams (colonne and plastifiant) were selected for further studies.

4.1.2 Characteristics of the Selected Effluents

Effluent Strength

It is well known that the strength of industrial effluents can vary greatly on a daily basis. For the design of a full-scale treatment, the degree of variation is assessed by daily monitoring over a long period of time. A stabilisation basin capable of damping the expected variations is then designed and constructed. As such a basin did not exist in this particular study, it was deemed more appropriate to collect one large batch of the selected effluents and store it at -20°C. This technique was adopted in order to avoid continual characterization of the collected samples and variations in the organic loading rate to the continuous-flow reactors.

Once samples of the two effluents (plastifiant and colonne) were obtained, BOD, COD, and TOC tests were carried out. Results of the analyses are shown in Table 4.4, while some ratios highlighting their potential biological degradability are given in Table 4.5.

Table 4.4: Characteristics of the Selected Effluents.

	Total COD (mg/L)	Soluble COD (mg/L)	Total BOD (mg/L)	Soluble TOC (mg/L)
Colonne	119,360	116,790	68,000	4,725
Plastifiant	13,230	13,160	7,400	39,500

Table 4.5: Ratios of Selected Characteristics Highlighting the Biological Degradability of the Selected Waste Streams.

Production Process	COD/TOC (Soluble)	BOD/COD (Total)	SCOD/TCOD
Colonne	2.96	0.58	0.98
Plastifiant	2.79	0.56	0.99

As expected with industrial effluents, the strengths of both effluents were considerably different from each other and from those originally tested. In the case of the plastifiant, the measured COD (13,230 mg/L) was approximately 32% higher than the value obtained during characterization of the various waste streams. This variation was considered to be within the average fluctuation of industrial effluents and was attributed to the type of product being produced at the time of sampling. However, a dramatic change was noted in the COD of the colonne effluent (119,360 mg/L; Table 4.4) which was over 6 times higher than the previously reported value (18,025 mg/L; Table 4.1). According to Andrew (1993), sudden increases in the colonne effluent strength do occur periodically. The reason for such variations is attributed to improper dosage of the various chemicals by the operators. At present, the industry is engaged in an optimization study in order to monitor and limit the unjustified fluctuations in the colonne effluent. A COD of approximately 18,000 mg/L is believed to be more representative of the actual situation in the industry.

Regardless of the variation in the strength of the selected effluents, previously set criteria (Section 4.1.1) for selecting the effluents amenable to biological treatment were still fulfilled (Table 4.5). Comparing the ratios presented in Tables 4.3 and 4.5, it can be noted that the only major reported difference was with respect to the biodegradability of the colonne effluent. The degradability of this effluent, evaluated by the BOD to COD

ratio, increased from 20% to 58%.

In view of the uncertainties regarding the strength of other batches that would be collected from the colonne effluent, and based on an average COD concentration of 18,000 mg/L, it was decided to proceed with the batch which had been collected (COD 119,360 mg/L). However, for the continuous-flow study, the colonne effluent will be diluted 6 times. This dilution would result in a COD concentration of approximately 20,000 mg/L) which is relatively close to the average value reported by the industry.

pH and Alkalinity

The pH and alkalinity of the two selected effluents were also measured to assess the need for neutralization and/or addition of buffer. As shown in Table 4.6 both effluents had very high pH values, outside the optimal range for biological treatment. Consequently it will be necessary to adjust the pH of both effluents prior to implementing any treatment process.

Table 4.6: pH and Alkalinity Measurements.

Production Process	pH	Alkalinity (mg/L as $CaCO_3$)
Colonne	13.3	32,400
Plastifiant	12.1	1,675

The alkalinity of the plastifiant effluent (1,675 mg/L) was within the recommended range for biological treatment (Benefield and Randall, 1985). On the other hand, the 32,400 mg/L alkalinity for the colonne effluent was excessively high. However, as acid will be added for pH adjustment, a considerable amount of alkalinity will be consumed.

Cation and Anion Concentrations

High concentrations of cations and anions can be toxic to microorganisms and inhibit their growth. Analyses reported in Tables 4.7 and 4.8 revealed that Na, Cl, and HCO_3 were present in the selected effluents in significant quantities. The presence of these elements can be attributed to the addition of sodium chloride and sodium bicarbonate as neutralizing agents prior to discharging the effluents. In the case of the colonne effluent, higher dosages are applied to enhance the polymerization and oxidation-reduction of formaldehyde into non-toxic components, which include essentially: a mixture of sugars (formose), formic acid and methanol. This explains the very high concentrations obtained for the colonne effluent.

Table 4.7: Anion Concentrations in the Selected Effluents (mg/L).

	Plastifiant	Colonne
F^-	N.D	N.D
HCO_3^-	81,000	518,300
Cl^-	90	978
NO_2^-	N.D	N.D
Br^-	N.D	N.D
NO_3^-	N.D	N.D
HPO_4^-	N.D	N.D
SO_4^-	N.D	N.D

N.D: Not detectable

Heavy Metal Concentrations

The concentrations of key heavy metals presented in Table 4.8 revealed that none of the analyzed elements was present in concentrations high enough to be toxic or inhibitory to aerobic microorganisms. In contrast, the presence of Fe in the colonne effluent would

be beneficial for anaerobic treatment as it is among the obligatory nutrients for methanogens to convert acetate to methane (Speece, 1983). Moreover, the availability of Ca and Mg in the plastifiant effluent might enhance granulation and the performance of methanogens. The positive effects of Ca and Mg have been observed in many systems. Hulsohoff Pol and Lettinga (1986) found that influent calcium ion concentrations up to 150 mg/L appeared to promote granulation, although no further improvement was observed at higher concentrations. Goodwin *et al.* (1990) also found that deficiencies in calcium and magnesium can adversely affect the performance of methanogens.

Table 4.8: Cation Concentrations in the Selected Effluents (mg/L).

	Plastifiant	Colonne
Na	2,700	40,000
NH_4	N.D	N.D
K	N.D	N.D
Fe	0.6	17.0
Pb	0.5	3.0
Zn	0.3	0.4
Cd	N.D	0.4
Cr	N.D	N.D
Cu	0.4	0.6
K	10.0	60.0
Ca	38.0	1.7
Mg	5.0	0.3
Mn	N.D	0.3

N.D: Not detectable

It should however be noted that other trace metals, such as nickel, cobalt and manganese can also improve the activity of anaerobic microorganisms. Due to the unavailability of the necessary equipment, nickel and cobalt contents of the selected effluents were not

measured. As for the manganese analyses, the results revealed that the plastifiant effluent did not contain any detectable quantities while the colonne effluent had only 0.3 mg/L. Hence, it would be necessary to test the effect of adding trace metals to the influent of the anaerobic continuous-flow reactor.

GC/MS and HPLC Analyses

In an attempt to identify the major constituents of the selected effluents, GC/MS and HPLC analyses were performed. Table 4.9 summarizes the results for the colonne and plastifiant. The chromatograms of the GC/MS analysis are included in Appendix B.

Table 4.9: Constituents of the Selected Effluents.

	Concentration (g/L)	Percent of Soluble COD	Method of Analysis
Colonne:			
- Acetate	1.23	1.1	HPLC
- Butanol	22.24	49.4	HPLC
- Formate	30.00	9.0	HPLC
- Formaldehyde	N.Q	N.Q	GC(1)
- Polymers	N.Q	N.Q	GC/MS
Plastifiant:			
- 2 Ethyl-1 Hexanol	N.Q	N.Q	GC/MS
- Methyl Hexanol	N.Q	N.Q	GC/MS
- Two Hexane Derivatives	N.Q	N.Q	GC/MS
- Styrene	N.Q	N.Q	GC(1)

(1) Analyzed by Monsanto
N.Q Not quantified

As shown in Table 4.9, approximately 60% of the COD of the colonne effluent was due

to substances (acetate, butanol and formate) that can be easily degraded by acclimated aerobic and anaerobic microorganisms (Speece, 1983). Moreover, the total amount of these substances, as a percentage of soluble COD, was very close to the reported BOD/COD ratio (0.58) for the colonne effluent. The presence of formaldehyde was associated with its incomplete transformation during production at the plant. Although formaldehyde is considered to be among the most toxic saturated aldehydes for anaerobic bacteria (Chou *et al.*, 1978), its complete degradation at a concentration of 7 g/L, was reported in a full-scale anaerobic treatment plant (Frankin *et al.*, 1994).

In addition to the above compounds, several polymers were also detected in the colonne effluent. Specific identification and quantification of these polymers was not attempted as it would have required detailed information regarding the specific products being used.

As for the plastifiant effluent, the GC/MS analysis showed that long chain alcohols were its main constituents, while the industry also reported the presence of styrene. Due to the unavailability of relevant standards, quantification of the identified compounds could not be conducted.

Alcohols are known to be biologically degradable. Yet they may exhibit severe toxicity to unacclimated biomass. In the case of an anaerobic microbial population, the toxicity would increase with a decrease in the chain length of hydrocarbons and/or the presence of double bonds between carbon atoms (Chou *et al.*,1978).

Studies conducted by Grbic-Galic *et al.* (1990) revealed that anaerobic degradation of styrene could be achieved depending on several factors such as presence of the necessary micro-organisms, elimination of other organic substrates which would otherwise interfere with styrene transformation, presence of toxic inhibitory compounds, etc. The oxidation and complete mineralization of styrene through an oxygenation path was also reported by Sielicki *et al.* (1978).

4.1.3 Treatability of the Selected Effluents

Compared to that of complex wastewaters, the biodegradation potential of the colonne and plastifiant effluents (BOD about 58% of COD) was relatively high. This result indicates that the selected effluents are good candidates for an aerobic treatment process.

The number of compounds that have proven to be amenable to anaerobic treatment is quite large, suggesting that effluents which are treatable aerobically will also be treatable anaerobically (Speece, 1983). However, there are some exceptions to this assumption and little is known regarding the interference of toxic or persistent compounds when present together in a complex wastewater.

In the present study, the selected effluents had a very high sodium content which might inhibit their anaerobic degradation. Moreover, the GC/MS and HPLC analyses revealed that both effluents do contain more than one compound which could be toxic to the anaerobic microbial population. To assess the anaerobic treatability of the selected effluents and to identify the most suitable biomass for their degradation, batch assay tests including biochemical methane potential (BMP) and anaerobic toxicity assay (ATA) were conducted. The results of these tests will be presented and discussed in the following section.

4.2 BATCH ASSAY TESTS

4.2.1 Biochemical Methane Potential

The biochemical methane potential (BMP) of both the colonne and plastifiant effluents were tested as described in Section 3.3, using two types of sludges. The first sludge was obtained from the primary and secondary digesters of the Vaudreuil municipal wastewater

treatment plant, while the second was a mixture of equal volumes of agro-food (Champlain), pulp and paper (Quesnel River), municipal (Vaudreuil), and aerobic activated sludge (Shell).

The results obtained for the two selected effluents are given in Table 4.10. Initial and final COD concentrations of the bioassay tests along with the removal efficiencies and methane production at 35°C are summarized for each BMP bioassay concentration.

Table 4.10: Performance Results of BMP Tests for the Plastifiant and Colonne Effluents.

BMP Bioassay Tests	Initial COD[1] (g/bottle)	Final COD (g/bottle)	Removal Efficiency (%)	Net Methane Production[1] (mL)	Specific Removal (g COD_{rem}/g VSS)	Methane Yield (L CH_4/g Initial COD)
COLONNE:						
Mixed Biomass						
- 13,800 mg/L	0.669	0.294	56.0	148.0	1.873	0.196
- 6,900 mg/L	0.334	0.129	61.5	81.1	1.080	0.215
- 4,600 mg/L	0.223	0.101	54.7	48.2	0.581	0.191
- 1,600 mg/L	0.078	0.037	52.3	16.1	0.215	0.183
Municipal Biomass						
- 13,800 mg/L	0.669	0.368	45.0	118.8	1.671	0.157
- 6,900 mg/L	0.334	0.149	55.4	73.1	1.027	0.194
- 4,600 mg/L	0.223	0.118	47.2	41.6	0.585	0.165
- 1,600 mg/L	0.078	0.042	46.2	14.2	0.190	0.162
PLASTIFIANT:						
Mixed Biomass						
- 4,600 mg/L	0.223	0.117	47.6	41.9	0.530	0.166
- 1,600 mg/L	0.078	0.035	55.6	17.1	0.217	0.195
- 800 mg/L	0.039	0.013	67.2	10.3	0.125	0.235
Municipal Biomass						
- 4,600 mg/L	0.223	0.199	10.8	9.6	0.115	0.038
- 1,600 mg/L	0.078	0.036	53.4	16.5	0.245	0.187
- 800 mg/L	0.039	0.190	51.3	7.9	0.125	0.179

(1) The COD of the aliquot extracted from each bioassay at the beginning of the test for the determination of VSS was subtracted from the initial COD.
(2) Calculated based on the inial COD and a conversion factor of 0.35 L CH_4/g COD at standard temperature and pressure (McCarty 1964).
(3) Computed by subtracting background methane production in control bottles from that in bioassays.

The results reported in Table 4.10 indicate that both effluents could be degraded anaerobically. However, the extent of degradation appears to be a function of the concentration and the type of inoculum, suggesting the presence of some toxic and/or persistent compounds. Nevertheless, the colonne effluent seems to be more easily degradable and less toxic than the plastifiant. The anaerobic biodegradability of the selected effluents is discussed in more detail below.

Effect of Biomass on the Degradation of the Effluents

The pattern of degradation as measured by the net methane produced during the first 6 weeks of incubation is illustrated in Figures 4.1 and 4.2 for the colonne and plastifiant effluents, respectively. As can be seen, both effluents exhibit better degradation with the municipal biomass.

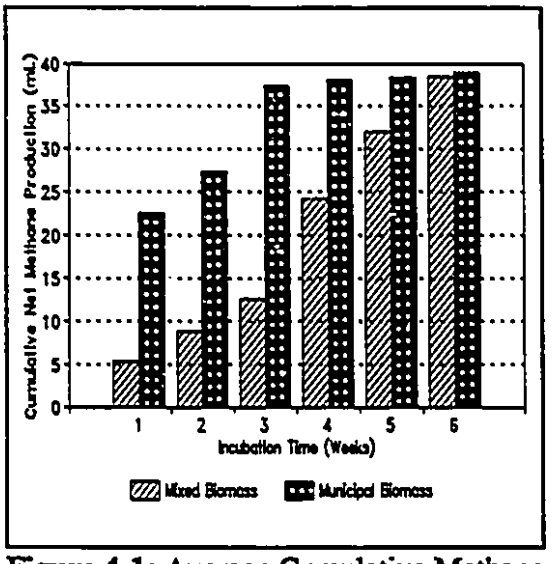

Figure 4.1: Average Cumulative Methane Production for 4,600 mg/L Bioassays of the Colonne Effluent.

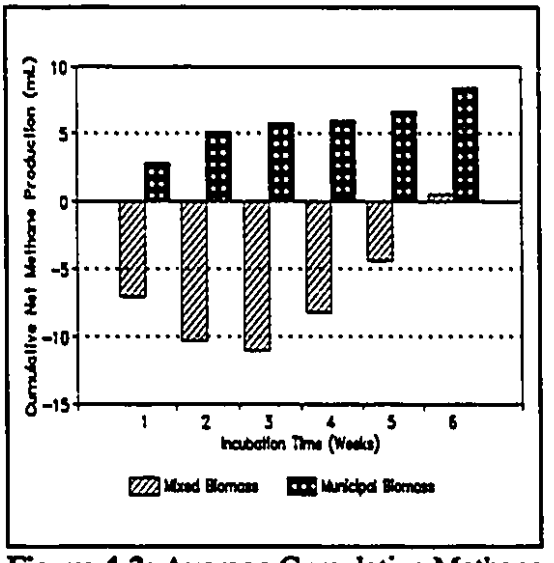

Figure 4.2: Average Cumulative Methane Production for 4,600 mg/L Bioassays of the Plastifiant Effluent.

In the case of the colonne effluent, methane production was observed after the first week

with both types of biomass. At all times, the rates reported with the municipal biomass were much higher than those observed with the mixed one. After 6 weeks of incubation, the difference between the two was negligible, indicating that both types of biomass might have a good potential to degrade this effluent.

The superiority of the municipal biomass was also revealed when degrading the plastifiant effluent. Although for the same concentration, a lower volume of methane was produced as compared to the colonne effluent, no lag period was observed. In contrast, with the mixed biomass, inhibition of the anaerobic process was observed at the beginning of the test. A lower methane production relative to the controls (indicated as negative values in Figure 4.2) was observed and may be attributed to the presence of toxicity. The inhibition increased during the first three weeks of incubation, after which it decreased slowly. By the 6 th week of incubation, methane production was observed, indicating that degradation of the effluent was starting. The reported toxicity at the beginning of the test may be explained by the fact that this microbial population was not adapted to the effluents constituents, hence the need for a long adaptation period. Indeed, it is well known that anaerobes have the capacity to adapt and toxicity can be reversible provided an adaptation period is allowed (Parkin and Speece, 1982).

The absence of a lag period and the better degradation achieved with the municipal biomass may be attributed to its partial acclimatization to a variety of inhibitory substances. Studies conducted by Benjamin *et al.* (1988) revealed that organisms acclimated to low concentrations of toxicant are better able to withstand a shock load of that toxicant than are unacclimated organisms. It is also worth noting that municipal biomass has been used in several research studies for assessing the degradation potential of organic chemicals (Shelton and Tiedje, 1984; Battersby and Wilson, 1988; Birch *et al.*, 1989).

The specific activity of the biomass may be another reason which might have led to the

observed differences between the two biomasses. In general, lag periods at the beginning of the assay tests are minimized by the use of anaerobic organisms which are in the log phase of growth or have a high specific activity (Cornacchio *et al.*, 1988). Hence, it might be speculated that the municipal biomass had a much higher activity than the mixed one.

As methane production was still in progress at week 6, it was considered necessary to continue with the incubation until methane production was complete. This process would clarify the extent to which the particular sludges which were used can adapt and consequently degrade the colonne and plastifiant effluents. In addition, it would be possible at the end of the study to compare the results of the continuous-flow reactor with those of the batch assay and evaluate the reliability of the test method in predicting the treatability of complex effluents. Hence, incubation was continued and the results are presented in the following sections.

Methane Production

Monitoring of gas production was continued for a total period of 115 days. By the completion of incubation, methane production curves of all bioassays had reached a plateau, indicating that methane production had completely ceased. Cumulative methane production data during the various bioassay tests are illustrated in Figures 4.3 to 4.6.

Contrary to the previously observed trend, a much higher methane production was reported with the mixed biomass as compared to the municipal one. Some variability in the response of microbial populations from different sources would be expected, as observed by several researchers (Fedorak and Hrudey, 1984; Shelton and Tiedje, 1984). Hence, for an accurate assessment of the anaerobic degradation of an effluent, a mixture of microbial populations from diverse sources should be used.

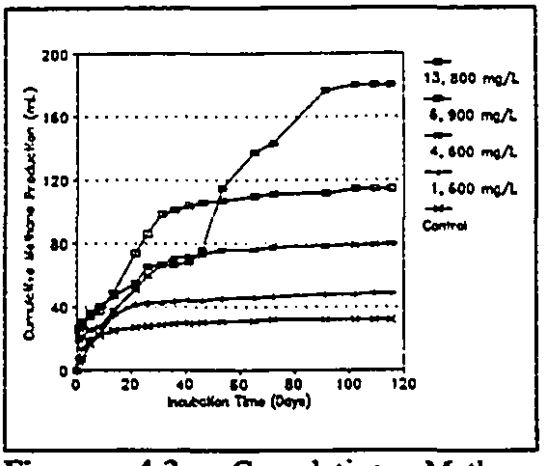

Figure 4.3: Cumulative Methane Production during BMP Bioassays of the Colonne with Mixed Biomass.

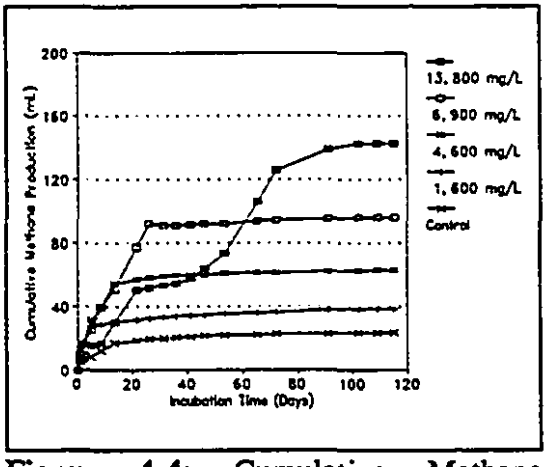

Figure 4.4: Cumulative Methane Production during BMP Bioassays of the Colonne with Municipal Biomass.

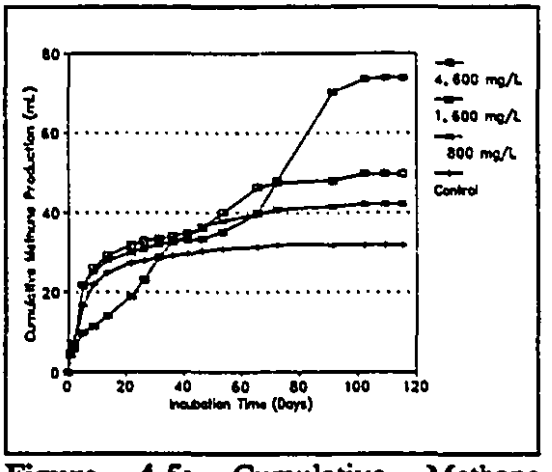

Figure 4.5: Cumulative Methane Production during BMP Bioassays of the Plastifiant with Mixed Biomass.

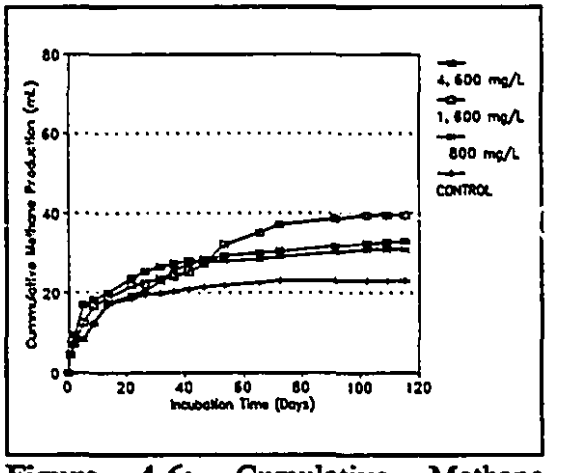

Figure 4.6: Cumulative Methane Production during BMP Bioassays of the Plastifiant with Municipal Biomass.

The lower degradation achieved with the municipal biomass, as compared to the mixed one, might be due to an inhibition of the acedogenic and/or methanogenic bacteria. At the beginning of the bioassay tests, the municipal biomass must have been acclimated to some of the constituents present in the effluents, as indicated by the absence of lag

periods and the immediate production of methane. Once these constituents were fermented to methane, either the acedogenic bacteria could not degrade the remaining compounds thus limiting the methanogens by the availability of substrate, or simply the methanogens were inhibited by some constituents of the effluents.

As shown in Figure 4.7, net methane production from the colonne effluent was not inhibited at high initial COD concentration. On the contrary, the volume of methane increased with an increase in the bioassay concentration, indicating that the microorganisms were not inhibited and that the effluent was fermented to methane. Hence this effluent did not contain toxic substances. Indeed, as reported in Section 4.1.2, around 60% of the COD of the colonne effluent was due to butanol, acetate and formate which are easily degradable substrates. On the other hand, regardless of the COD concentration, the net methane production reported with the mixed biomass was always higher than that obtained with the municipal biomass. The difference between the two biomasses was more noticeable with the increase in COD concentration. The difference increased from 11% at the lowest tested COD concentration (1,600 mg/L) to 20 % at a concentration of 13,800 mg/L.

The trends observed with the colonne bioassays regarding the difference between the two types of biomass were also observed with the plastifiant effluent (Figure 4.8). However, at the highest tested COD concentration (4,600 mg/L), the mixed biomass yielded 70% more methane than the municipal biomass. At that concentration, an inhibition of the municipal biomass was indicated by a decrease in cumulative methane production. The volume of methane produced by the municipal biomass (9.6 mL) at a bioassay concentration of 4,600 mg/L was 50 % less than the volume reported at a concentration of 1,600 mg/L (i.e. 16.5 mL). Hence, at high COD concentrations (4,600 mg/L) the municipal biomass was inhibited, while the mixed biomass was not affected and biodegradation of the effluent could hence be achieved.

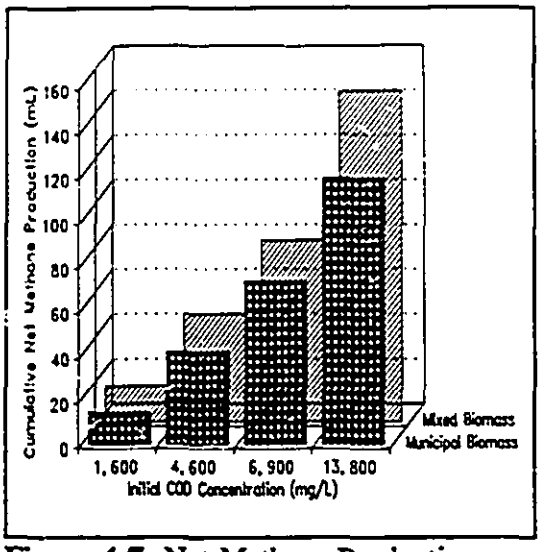

Figure 4.7: Net Methane Production as a Function of Concentration after 115 d Incubation of the Colonne Bioassays.

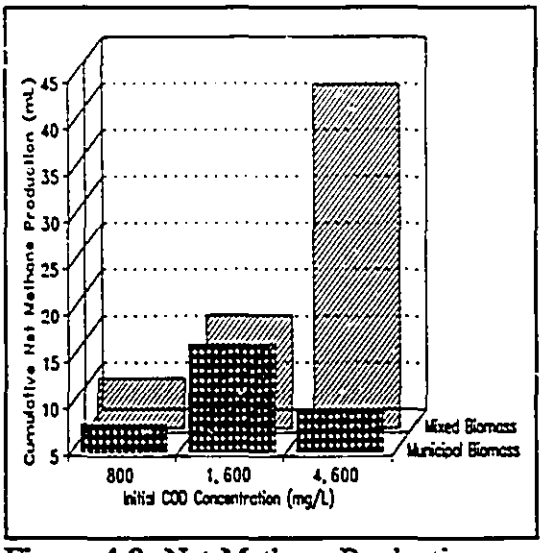

Figure 4.8: Net Methane Production as a Function of Concentration after 115 d Incubation of the Plastifiant Bioassays.

The superior degradation observed with the mixed biomass may be attributed to the presence of a wider variety of microbial populations. It appears that the mixed biomass contained one or more organisms capable of detoxifying the substances present in this effluent. Also, the complete mineralization of some compounds might have required the concerted activity of multiple species which were present in the mixed biomass but not in the municipal one. The advantages of using mixed microbial communities for degradation studies have been discussed by Grady (1985) who concluded that the degradation capacity of a community is much greater, both quantitatively and qualitatively, particularly when xenobiotic compounds are involved.

COD Removal Efficiency

The anaerobic degradation potential of the selected effluents was also evaluated based on the COD removal efficiency. The initial COD concentration and the cumulative volume

of methane production were used to compute the final COD concentration and the percentage removal. All methane data were automatically corrected for the moisture content through the GC software and converted to standard temperature and pressure. However, the methane dissolved in the aqueous phase and the fraction of methane used for cell growth were not considered. Hence, the calculated COD removal percentages may be slightly underestimated, especially in those bioassays where no inhibition or toxicity were noted. Nevertheless, it is unlikely that the observed trends would be affected by this underestimation. The results of the COD removal efficiency as a function of concentration and sludge type are presented graphically in Figures 4.9 and 4.10 for the colonne and plastifiant effluents, respectively.

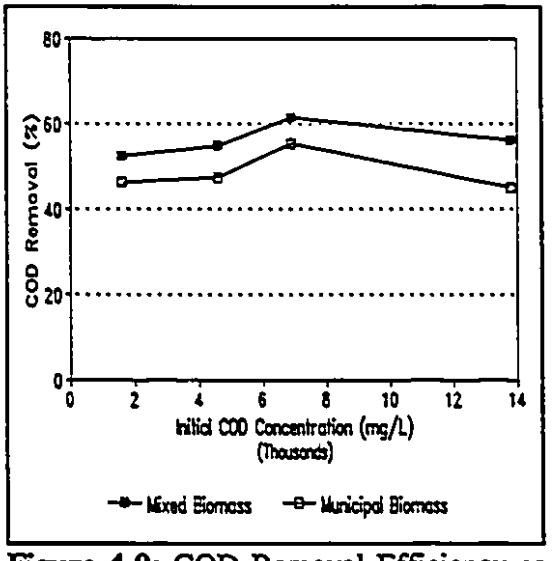

Figure 4.9: COD Removal Efficiency as a Function of Concentration during BMP Bioassays of the Colonne Effluent.

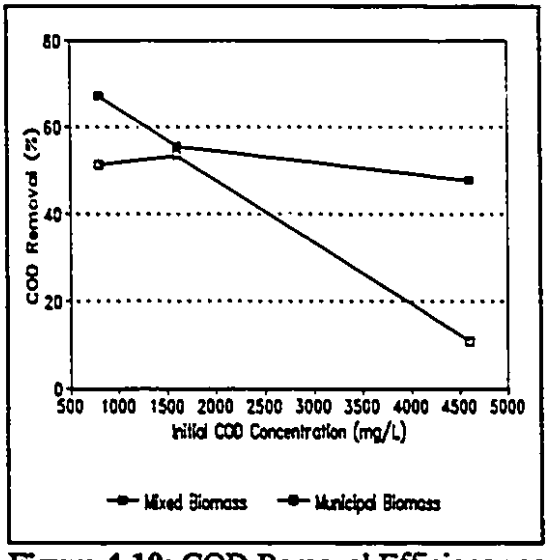

Figure 4.10: COD Removal Efficiency as a Function of Concentration during BMP Bioassays of the Plastifiant Effluent.

The COD removal efficiency of the colonne effluent varied between 45% and 61% (Figure 4.9). Regardless of the type of sludge, the COD removal efficiency first increased with increasing colonne effluent concentration, reaching a maximum value at a concentration of 6,900 mg/L. At this concentration, the removal percentages were

61% and 55% with the mixed and municipal biomass, respectively. It appears that increasing the concentration of the substrate increased the specific activity of the biomass with a consequently higher degradation being achieved. However, a further increase in the bioassay concentration from 6,900 mg/L to 13,800 mg/L decreased COD removal efficiency. The observed decrease was 19% and 9% with the municipal and mixed biomass. respectively. This reduction may be due to a decrease in the biomass activity and could indicate overloading. Another reason which might have caused the drop in the degradation percentages is the accuracy of the test method at high concentrations. The precision of the BMP tests has been evaluated by Battersby and Wilson (1988) who concluded that a test chemical concentration of 50 mg C/L represents a good compromise between precision and accuracy. Also Cornacchio *et al.* (1988) recommended that the BMP test be conducted at a maximum soluble COD concentration of 4,500 mg/L. Nevertheless it is evident that the mixed biomass had a better activity compared to the municipal biomass, as indicated by the lower percent reduction in the COD removal reported at high concentrations.

The plastifiant effluent exhibited a low to moderate degree of anaerobic treatability. Average COD removals of 48% to 67% and 11% to 53% were reported with the mixed and municipal biomass, respectively. Degradation percentages declined considerably with increasing bioassay concentrations (Figure 4.10). Extreme cases of low anaerobic treatability were observed at a COD concentration of 4,600 mg/L, as indicated by 14% and 80% reduction in COD removal compared to the values achieved at 1,600 mg/L by the mixed and municipal biomass, respectively. The adverse effect on the anaerobic microbial population was apparently caused by the toxicity of some constituents present in the plastifiant effluent.

The improved performance achieved during BMP testing at 800 mg/L and 1,600 mg/L concentrations suggests that anaerobic treatment of the plastifiant effluent may be suitable provided it is diluted or mixed with other biodegradable effluents. It is noteworthy that

actual dilution requirements could be somewhat lower in the case of a continuous-flow system where acclimation of the biomass may occur. Another factor which might improve the treatability of the plastifiant is the activity of the biomass used. Indeed, the importance of this parameter is well demonstrated by the differences observed between the mixed and municipal biomass.

Specific Removal and Biomass Activity

Sludge concentration in the BMP bottles and the amount of COD removed were used to compute the specific removal and consequently evaluate the biomass activity at the various tested concentrations. The amount of biomass was similar for all assays and varied between 0.17 and 0.20 g VSS per bottle. Figures 4.11 and 4.12 illustrate biomass activity as a function of concentration for the colonne and plastifiant effluents, respectively.

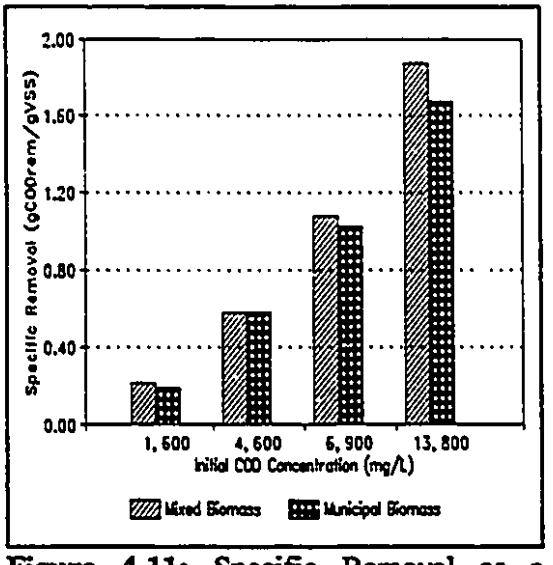

Figure 4.11: Specific Removal as a Function of Concentration during BMP Bioassays of the Colonne Effluent.

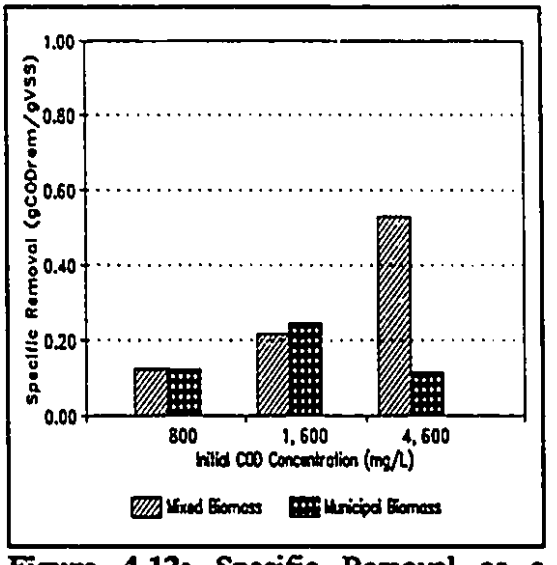

Figure 4.12: Specific Removal as a Function of Concentration during BMP Bioassays of the Plastifiant Effluent.

Specific removal was positively affected by the increase in concentration of the colonne effluent, indicating that the biomass was not inhibited by the effluent's constituents. At COD concentrations of 1,600 and 4,600 mg/L, no significant difference was noted between the two types of biomass. However, at concentrations of 6,900 and 13,800 mg/L, a reduction in the specific removal achieved by the municipal biomass, as compared to the mixed one, was observed. Therefore at high concentrations, the municipal biomass was either overloaded or slightly inhibited by the constituents of the effluent.

The plastifiant effluent had an inhibitory effect on biomass activity as indicated by the specific removal values reported at a BMP concentration of 4,600 mg/L. An increase in the plastifiant concentrations, from 1,600 mg/L to 4,600 mg/L, resulted in a dramatic drop in the specific removal of the municipal biomass and a non-linear increase with the mixed biomass. It appears that anaerobic microorganisms were inhibited in the presence of high levels of the effluent's constituents.

The observed reduction in biomass activity at high concentrations and the lower performance of municipal biomass as compared to the mixed one could be due to: (1) inhibition of methanogenic bacteria, (2) inhibition of acidogenic bacteria, thus reducing the VFA available for methane bacteria, (3) a combination of these two factors.

The effects of certain constituents present in the effluents on methanogens were determined by conducting anaerobic toxicity assay (ATA) tests as described in Section 3.3. By adding VFA such as acetate and propionate to the medium, the methanogens are then not dependent upon the non-methanogens for their source of substrate.

4.2.2 Anaerobic Toxicity Assay

Anaerobic Toxicity Assay (ATA) tests were conducted for the plastifiant and colonne effluents with the same municipal biomass used for BMP bioassays. The curves of average cumulative methane production as a function of incubation time at various tested concentrations (including the controls without effluent additions) are shown on Figures 4.13 and 4.14 for the colonne and plastifiant effluents, respectively.

Cumulative methane production curves for all ATA bioassays revealed a low methanogenic activity. Although methane was produced at each bioassay concentration, lengthy lag periods were observed, even with the controls, for which an incubation period of approximately 70 days was required prior to complete degradation of the acetate and propionate spikes. These lag periods may be due to several factors among which are origin of the biomass, inhibition of methanogens and effect of storage on the activity of the biomass.

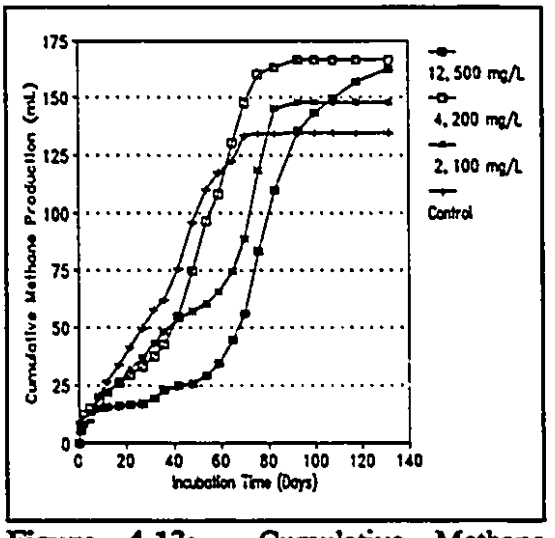

Figure 4.13: Cumulative Methane Production during ATA Bioassays of the Colonne with Municipal Biomass.

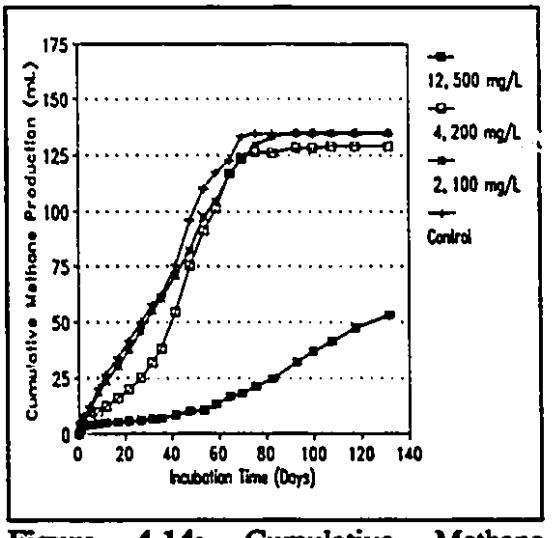

Figure 4.14: Cumulative Methane Production during ATA Bioassays of the Plastifiant with Municipal Biomass.

The specific activity of anaerobic digester sludge is not expected to be high. Hence, anaerobic treatment processes conducted with municipal biomass would necessitate a long start-up time since the growth rate of methanogens is relatively slow. Nonetheless, the incubation time (around 70 days) required for complete degradation of the acetate and propionate spikes in the controls was far above average values reported in the literature. In most research studies, complete degradation of the VFA spike in controls inoculated with digester sludge was achieved within 10 to 20 days incubation (Schnell *et al.*, 1992; Benjamin *et al*, 1984; Fedorak and Hrudey, 1984). Because the average retention time (20 to 30 d) and the organic matter content (3%) of the Vaudreuil sludge used for the ATA bioassays were within the range recommended by Shelton and Tiedje (1984), it is unlikely that the lengthy lag periods were due to the fact that a municipal sludge was used.

The amount of VFA (acetate and propionate) added to the ATA bioassays can be considered an important factor that may have caused long lag periods. As mentioned in Section 3.3 (Materials and Methods), a 10 mL aliquot of a solution containing 37.5 g/L acetate and 13 g/L propionate was added to each bioassay bottle. The resulting amounts of acetate and propionate (0.5 g/bottle) were relatively high compared to the values considered in several other studies. Average values reported in the literature vary between $5x10^{-3}$ and 0.1 g/bottle (Fedorak and Hrudey, 1984; Cornacchio *et al.*, 1988; Wang and Latchaw, 1990; Kudo *et al.*, 1991). Hence, it might be thought that a long adaptation of the microorganisms to the extremely high VFA spike was required. However, according to Cornacchio *et al.* (1988), it is the ratio of substrate to inoculum (g/g) which should dictate the amount of VFA to be added. In their modified test procedure for industrial wastewaters, the authors recommended a minimum ratio of 0.9:1 to ensure non-limiting substrate concentrations in the spiked controls and to eliminate short lag periods. Though the ratio adopted in this study (2.5:1) was higher than the one recommended by Cornacchio *et al.* (1988), it cannot be the only justification for the very long lags.

Effect of Storage

The storage of biomass was more likely to be the major reason for the observed lags. By the time the ATA bioassays were initiated, the municipal biomass had been stored at 4°C for 8 weeks. An attenuation of sludge activity may have occurred during this storage period. The effect of storage on the activity of the biomass has been evaluated by several researchers. Shelton and Tiedje (1984) have found that sludge storage had no significant effect on the extent of degradation but rather on the lag times required before degradation began. Consequently, the authors recommended the use of fresh sludge whenever possible. The preservation characteristics of anaerobic sludge was also evaluated by Shin *et al.* (1993) who reported a sharp decrease after one month storage at 4°C followed by a relatively constant level. After 10 months, the specific methanogenic activity was reduced by 80%.

To assess the effect of storage on the length of lag periods and on the toxicity of the effluents to methanogens, fresh sludge was collected from the same digesters and a new series of ATA was initiated. One possible drawback of this technique is that the collected sludge may not have the same characteristics as the one obtained five months earlier. Hence, some variations in the degradation and/or toxicity of the effluents may be observed. However, in their study, Shelton and Tiedje (1984) reported that no major discrepancies were obtained in the results with sludges from the same plant over a 2-year period.

Figures 4.15 and 4.16 illustrate the cumulative methane production curves of the colonne and plastifiant effluents, respectively, using fresh municipal biomass. As expected, the lag periods reported with all bioassays were much shorter than those observed with the stored biomass. The incubation time required for the complete degradation of acetate and propionate in the control was around 20 days compared to 70 days with the stored biomass.

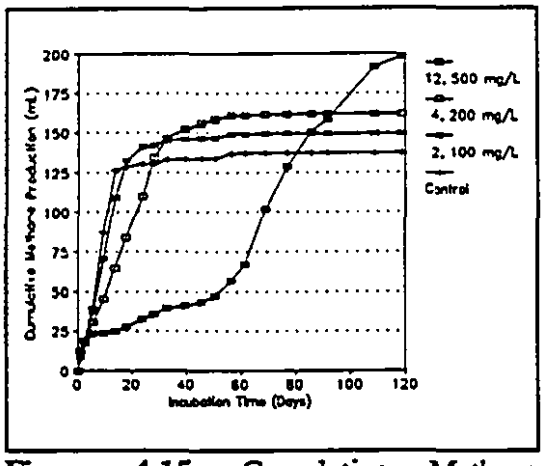

Figure 4.15: Cumulative Methane Production during ATA Bioassays of the Colonne with Fresh Municipal Biomass.

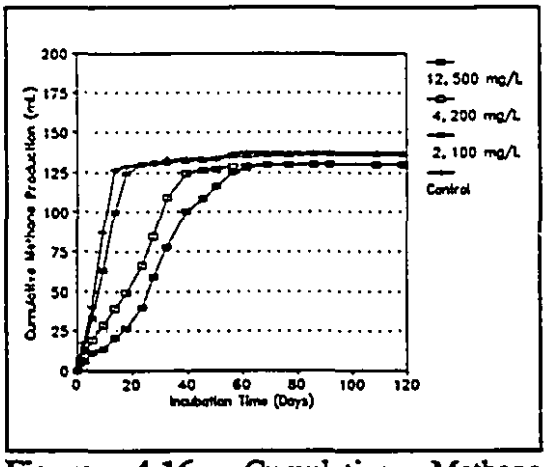

Figure 4.16: Cumulative Methane Production during ATA Bioassays of the Plastifiant with Fresh Municipal Biomass.

Comparing the methane production curves shown in Figures 4.13 and 4.15 for the colonne effluent, it can be seen that the final volumes of methane production were almost the same with the stored and fresh biomass. The slight difference reported at the highest tested concentration (12,500 mg/L) can be attributed to the fact that methane was still being produced at the time the tests were terminated. It is likely that, if the tests were continued until methane production ceased completely, the same amount of methane would have been reported. At the 12,500 mg/L concentration, lengthy lag periods were observed with the fresh and stored sludge and were attributed to the elevated ratio of substrate to inoculum (around 9:1). Hence, the lower methane production as compared to the control during the first 80 days of incubation is not the result of the effluent's toxicity but is rather due to the acclimation of the biomass to a very high COD load resulting from the VFA spike and the effluent.

The above results indicate that, at all tested concentrations, the colonne effluent was not toxic to the methanogenic bacteria. This is evidenced by the higher volumes of methane produced by the colonne effluent as compared to the control. On the other hand, it appears that acclimation times for methanogens in the presence of the colonne effluent

are concentration dependent with higher concentrations requiring longer acclimation periods.

The same trends were also observed with the plastifiant ATA bioassays conducted with the stored and fresh biomass. All ATA bioassays with 2,100 and 4,200 mg/L plastifiant produced the same amount of methane with both biomasses. At 12,500 mg/L concentration, methane was still being produced after 140 days incubation in the bioassays inoculated with the stored biomass (Figure 4.14), whereas in the bioassays prepared with the fresh biomass, methane production ceased completely after 60 days incubation. However, the volume of methane produced after 60 days incubation with the fresh biomass was much higher than that at the end of 140 days incubation with the stored biomass. Comparing the cumulative volume of methane (128 mL) obtained with the fresh biomass to that produced by the control (135 mL), it is evident that the effluent was toxic to the methanogens. Hence, the use of fresh biomass did not affect the toxicity, it only reduced the lag time.

Considering the present results regarding the type of biomass and the length of lag periods in the ATA bioassays, it is evident that a fresh biomass should be used in order to avoid long incubation periods. Although storage reduces the activity of the biomass hence requiring a long adaptation period, there was no evidence that the extent of degradation and/or toxicity would be affected. Reactivation of a stored sludge may be considered a possible solution for reducing incubation periods. However, there is insufficient insight whether this operation may induce some changes in the microbial population. Regardless of the type of biomass, lag periods at the beginning of ATA bioassays may be observed and could be due to toxicity of the effluent, high loading rates, and/or adaptation of the biomass. In order to obtain accurate results regarding the extent of degradation and toxicity, it is imperative to continue the bioassays until the methane production curves reach a plateau indicating that the maximum possible adaptation and degradation have been achieved. It is worth mentioning that in several

studies on the response and recovery of methanogens exposed to organic and inorganic toxicants, a decreased rate of gas production in some cases and a temporary total cessation of gas production in others were observed (Chou *et al.*, 1978; Parkin and Speece, 1982). The most interesting result is that in most cases the organisms eventually acclimate to the toxicant and gas production returns to its pre-exposure rate.

Toxicity of the Effluents

To evaluate the toxicity of the effluents, inhibition percentages were calculated for all ATA bioassay concentrations. Inhibition curves computed with the stored and fresh biomass as a function of concentration are illustrated on Figures 4.17 and 4.18 for the colonne and plastifiant effluents, respectively. Negative values indicate a stimulation of biogas production, while an increase in the positive values reflects a higher inhibition. As mentioned earlier, no major discrepancies regarding toxicity of the effluents were noticed with the stored and fresh biomass, especially for the lower two initial concentrations.

The colonne effluent exhibited no toxicity for any concentrations. In contrast, a stimulation of biogas production was reported indicating degradation of the effluent. These results are in agreement with those obtained during the BMP bioassay tests and reveal that the effluent is not inhibitory to the methanogenic bacteria. It is probable that the limited degradation achieved during BMP testing was due to the colonne-degrading organisms (i.e. non-methanagonens). The absence of some species required for degrading certain constituents present in the colonne, or toxicity of the effluent to some specific non-methanogens, are possible reasons which might have lead to a lower degradation as compared to the mixed biomass used in the BMP tests.

Toxic effects of the plastifiant effluent on methanogenic organisms are illustrated by the

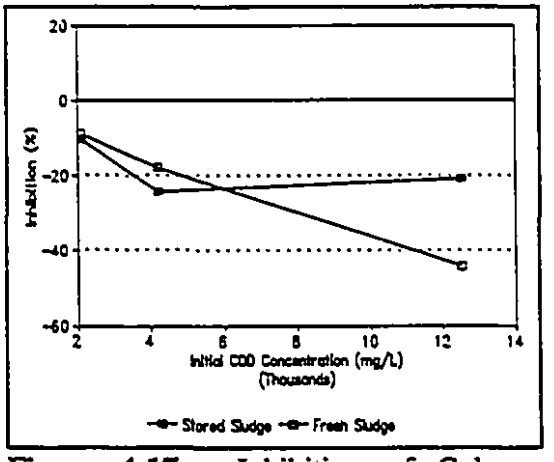

Figure 4.17: Inhibition of Colonne Effluent Degradation as a Function of Concentration and Type of Municipal Biomass.

inhibition percentages. The data in Figure 4.18 show that the bioassays containing 2,100 mg/L had no inhibitory effect, but the bioassays with higher concentrations were all inhibitory.

Comparing the results obtained during the BMP and ATA tests, there appears to be a threshold concentration below which the effluent was degradable and non-toxic, and above which a severe toxicity was observed. During BMP bioassays, a dramatic reduction in COD removal efficiency of the plastifiant was observed at a concentration higher than 1,500 mg/L. Also, ATA batch tests revealed that at a concentration of 2,100 mg/L, methane production was neither inhibited nor enhanced by the plastifiant. Hence, the highest degradable and non-toxic concentration lies between 1,500 and 2,100 mg/L.

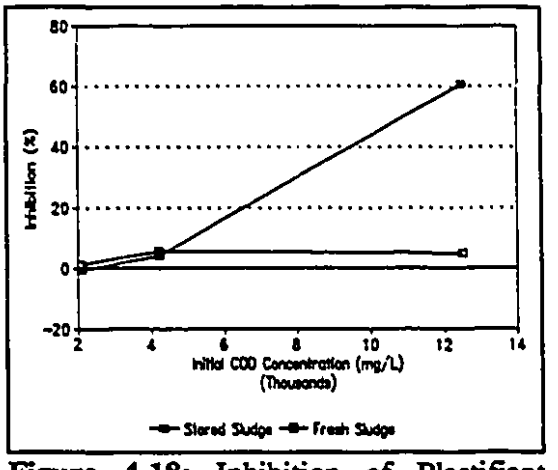

Figure 4.18: Inhibition of Plastifiant Effluent Degradation as a Function of Concentration and Type of Municipal Biomass.

Since acetate and propionate were added to the ATA bioassays, it can be reasonably stated that methanogenic bacteria were being inhibited at the high concentrations. Whether these elevated concentrations are also inhibitory to the non-methanogens or whether the plastifiant-degrading organisms are only a minor portion of the microbial population has not been determined. The adverse effect of the plastifiant on methanogenic activity and consequently on anaerobic treatment was presumably due to

the toxicity of its constituents. The combination of toxic compounds present in the plastifiant may have resulted in synergistic effects on the overall toxicity and hindered any possible acclimation of the biomass at high concentrations.

4.2.3 Anaerobic Treatability of the Selected Effluents

Considering the results obtained in the BMP and ATA batch assay tests, it can be stated that the selected effluents have a fairly good potential for anaerobic treatment provided that an adaptation period is allowed. However, contrary to the results of Battersby and Wilson (1989) which were obtained with organic compounds, the biodegradation potential of the selected effluents appears to vary depending on the type of sludge.

To assess the reliability of the BMP and ATA bioassays in predicting the anaerobic treatability of industrial effluents and to clarify the question of whether a better adaptation of the biomass in a continuous flow reactor will lead to a higher treatment efficiency, a continuous flow anaerobic reactor was inoculated with municipal biomass. The results of this study will be presented and discussed in Section 4.3.1.

4.3 CONTINUOUS - FLOW STUDIES

Continuous-flow experiments included anaerobic, aerobic as well as anaerobic-aerobic sequential reactors. The influent to the reactors was prepared by mixing the colonne and plastifiant effluents in equal volumes. This was done so that the influent to the reactors would resemble the actual situation on site: the two waste streams are indeed generated in equal proportions.

On the other hand, the results of the BMP and ATA assays indicate that the plastifiant

effluent should be diluted to enhance its biodegradation and to reduce its toxicity to the anaerobic microbial population. The highest degradable and non-toxic concentration was found to be about 1,800 ± 300 mg COD/L. This concentration corresponds to a 7 times dilution of the plastifiant effluent. However, it was thought that the dilution requirements might be lower in the case of a continuous flow reactor where adaptation might occur.

Moreover, the batch assay tests conducted with the colonne effluent revealed that this effluent could be degraded easily by the anaerobic microbial population. Hence, it was assumed that mixing the colonne and plastifiant effluents in equal proportions might be equivalent to diluting the plastifiant two fold.

As mentioned earlier, the pH values of the colonne and plastifiant effluents were above the recommended limits for biological treatment. Hydrochloric acid was used to adjust the pH of the influent to the reactors and essential nutrients (nitrogen and phosphorus) were added. Characteristics of the influent to the reactors are summarized in Table 4.11.

Table 4.11: Characteristics of the Influent to the Continuous-Flow Reactors.

Parameter	Average
Total Chemical Oxygen Demand (mg/L)	17,100 ± 450
Soluble Chemical Oxygen Demand (mg/L)	16,700 ± 400
pH	7.6 ± 0.3
Alkalinity (mg/L as $CaCO_3$)	1,500 ± 50
Suspended Solids (mg/L)	80 ± 20
Nitrogen (mg N/L):	
- Anaerobic Reactor	340 ± 20
- Aerobic Reactor	820 ± 30
Phosphorus (mg P/L):	
- Anaerobic Reactor	68 ± 4
- Aerobic Reactor	160 ± 10
Sodium (mg/L)	4,500 ± 300
Chloride (mg/L)	2,800 ± 200

4.3.1 Anaerobic Digestion

The results presented in this section cover a period of 105 days of continuous operation of the laboratory upflow sludge bed and filter (UBF) reactor. Unless otherwise indicated, the data presented in graphical and tabular forms were collected from day 21 to day 105. Days 0 to 21 were used for adaptation and equilibration of the sludge to the wastewater and to the hydraulics of the laboratory system.

The average hydraulic retention times (HRT) investigated were 7, 5, 3, and 1.5 d which correspond to organic loading rates (OLR) of 2.37, 3.16, 5.82, and 11.45 g COD/L-d, respectively. A given loading rate was maintained until pseudo-steady state (PSS) conditions were reached, as defined by a relatively constant effluent COD in all cases (Figure 4.19) and suspended solids values except for the 3 d HRT (Figure 4.20). The principal results of the pseudo-steady state condition at each tested HRT/OLR are summarized in Table 4.12. They indicate that the UBF reactor can handle a wide range of loading rates.

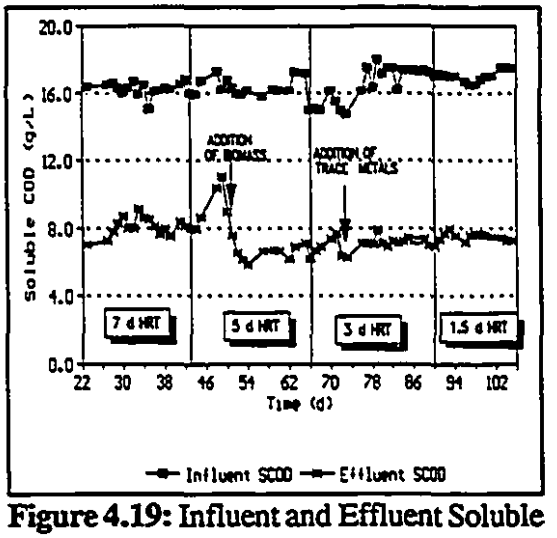

Figure 4.19: Influent and Effluent Soluble COD Concentrations during the Anaerobic Continuous-Flow Study.

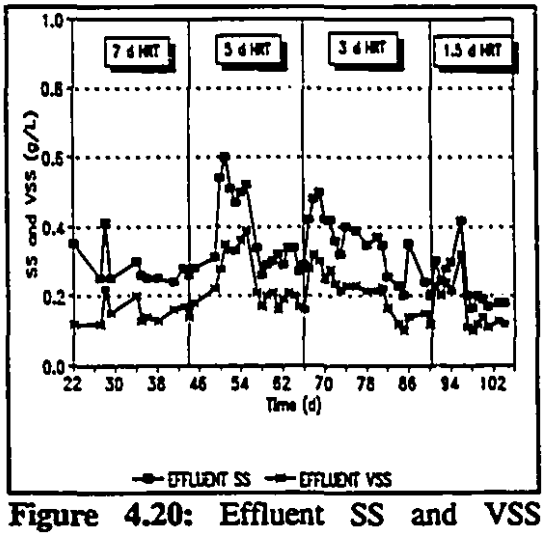

Figure 4.20: Effluent SS and VSS Concentrations during the Anaerobic Continuous-Flow Study.

Table 4.12: Performance of the UBF Anaerobic Reactor at Various Hydraulic Retention Times.

	ANAEROBIC REACTOR			
	7 d	5 d	3 d	1.5 d
Days of operation	0-43	44-65	66-90	91-105
Actual HRT	6.81	5.25	2.95	1.49
Influent soluble COD (mg/L)	16,270	16,650	17,160	17,055
Effluent soluble COD (mg/L)	7,930	6,890	7,120	7,460
% Removal	51.3	58.6	58.5	56.3
Influent pH	7.85	7.75	7.59	7.23
Effluent pH	8.47	8.60	8.39	8.33
Inf. alkalinity (mg/L as $CaCO_3$)	1,550	1,520	1,500	1,450
Eff. alkalinity (mg/L as $CaCO_3$)	4,600	5,740	5,500	5,200
Organic loading (g COD/L-d)	2.37	3.16	5.82	11.45
Specific loading (g COD/g VSS-d)	0.20	0.29	0.58	1.23
Specific removal rate (g COD removed/g VSS-d)	0.10	0.17	0.34	0.69
Methane yield (L CH_4/g COD removed)	0.27	0.31	0.29	0.29
Volumetric methane production rate (L CH_4/L reactor-d)	0.37	0.67	1.11	2.12
% Methane	74.2	78.4	78.0	79.4

Treatment Efficiency

Figure 4.21 illustrates soluble COD removal efficiency at the various tested OLRs. At the lowest tested OLR (2.37 g COD/L-d), i.e. the reactor was achieving 51.3% removal of soluble COD. When the OLR was increased to 3.16 g COD/L-d, the reactor achieved a slightly better COD removal efficiency than at 2.37 g COD/L-d. This was mainly due to better acclimatization of the biomass to the wastewater. The higher COD removal can also be attributed to the higher gas production which might have led to better sludge bed mixing and improved mass transfer. This conclusion is supported by previous studies conducted by Samson and Guiot (1985). The authors reported that biogas production can slightly improve mixing by a small reduction of the amount of dead space. The maximum COD removal efficiency of 58.6% in the present study was achieved at an OLR of 3.16 g COD/L-d.

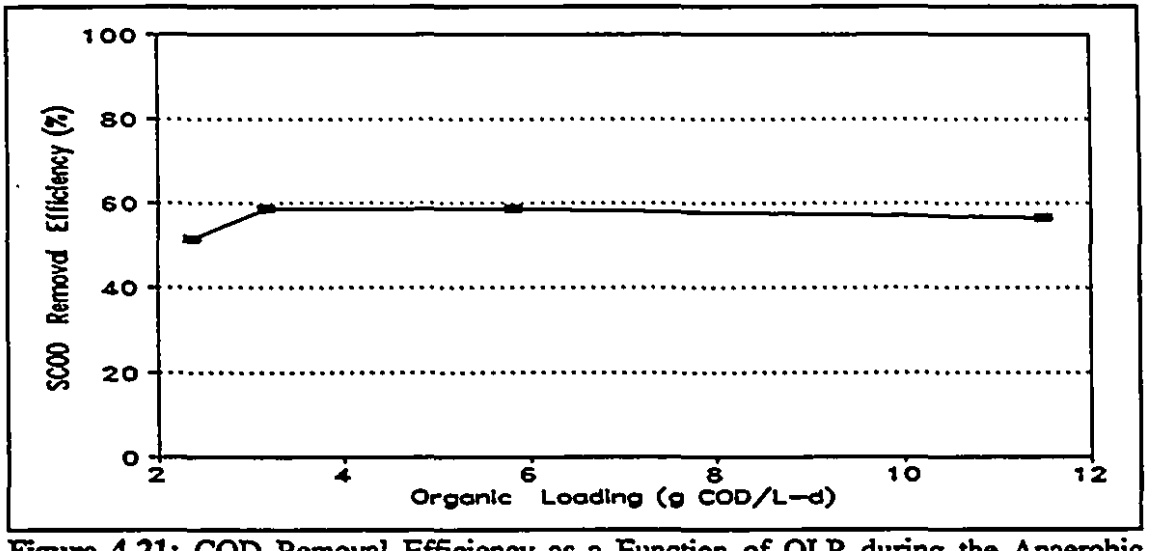

Figure 4.21: COD Removal Efficiency as a Function of OLR during the Anaerobic Continuous-Flow Study.

A possible explanation for the low COD removal efficiency could be a deficiency in the concentration of some trace metals necessary for methanogenic bacteria, as is sometimes

the case with industrial effluents (Speece, 1883). Research conducted by Lettinga *et al.* (1981) on the anaerobic treatment of wastes containing methanol and higher alcohols revealed that one or more trace metals are of major importance for the stability of the process. To test this hypothesis, from day 72 to 105, a mixture of trace metals was added to the influent. Although no improvement was observed and the removal efficiency did not exceed the previously reported values, the UBF reactor maintained almost the same performance even at the high organic loading rate of 11.45 g COD/L-d. It is likely that the addition of trace metals did help the microorganisms to sustain the high loads. However, from the data presented it is uncertain which of these elements was the most important to the process, or whether the absence of a specific element would have produced any observable effect at the high loading rates. As the costs of trace metals are minor, while the impact of their addition may be dramatic (Speece, 1983), it is recommended that one consider the addition of trace metals, and additional research must be conducted to identify the most important ones.

The lack of essential macro nutrients should not be the cause of the low removal efficiency. Throughout the study nitrogen and phosphorus were supplemented at an average of 340 mg N/L and 68 mg P/L. These additions were equivalent to approximately 20 mg N/g COD and 4 mg P/g COD in the feed. The concentration of these nutrients observed in the UBF effluent ranged from 63 to 152 mg N/L and from 21 to 50 mg P/L over the course of this study. Limiting concentrations of either nutrient were therefore not encountered.

Several other parameters might have contributed to the low removal efficiency, among which is the type of wastewater. Indeed one of the major problems encountered in anaerobic treatment is the fact that certain compounds cannot be degraded anaerobically and/or are toxic to methanogens. The presence of such compounds in the wastewater being treated might explain the low reported treatment efficiency. However, the chemical characterization and batch assay tests conducted at the beginning of this study revealed that the colonne effluent can be degraded successfully under anaerobic

conditions.

Moreover, this effluent did not cause any inhibitory effect to the methanogens. The extent of degradation as evaluated by the COD removal efficiency during the BMP bioassays varied between 45% and 55% when using a municipal digester sludge. In contrast, the plastifiant effluent proved to be toxic to methanogens and perhaps to non methanogens as well. Degradation of this effluent was concentration dependent and varied between 10.8% and 53.4%. Based on the fact that the influent to the UBF reactor was a mixture of equal volumes of the two effluents and considering the highest reported degradation percentages for the plastifiant and colonne effluents which were obtained separately (55.4 and 53.4, respectively), an average degradation of 54% would be expected. This value is slightly lower than the treatment efficiency (58%) obtained during the continuous-flow study and may be attributed to the better adaptation of the biomass in that study.

From these results it is uncertain whether adaptation of the biomass improved anaerobic degradation of the colonne or the plastifiant effluents. Though it was expected that the degradation of both effluents would improve, it is possible that degradation of plastifiant was limited by the presence of easily degradable substances in the colonne effluent or the unavailability of specific species of microorganisms capable of biodegrading the constituents of the plastifiant effluent.

Furthermore, the results of the batch assay tests indicated that the highest degradation of the plastifiant was achieved at a COD concentration of 1,800 $\pm$ 300 mg/L. Maximum assay concentrations suggested by Cornacchio *et al.* (1988) are 4,500 and 12,000 mg COD/L for the BMP and ATA tests, respectively. Hence, in the present case the 1,800 mg/L could be considered approximately 3 times more dilute for the BMP, 6 times more dilute for the ATA and 7 times when considering the original COD concentration of the plastifiant effluent.

Considering the above results with respect to degradation of the effluents, no correlation could be found between the wastewater dilution in the batch assay tests and that required for the continuous flow reactor. Nevertheless it is likely that the presence of persistent compounds might have limited the anaerobic treatment efficiency in both cases.

Accumulation of volatile fatty acids, high pH, low alkalinity and sludge washout are other possible factors which might have limited treatment efficiency. These will be discussed in the following sections.

Volatile Fatty Acid Production

High concentrations of volatile fatty acids (VFA) inhibit acetogenic and methanogenic bacteria thus leading to low treatment efficiencies. For the proper operation of an anaerobic reactor, the concentration of VFA should be maintained between 50 and 500 mg/L (Benefield and Randall, 1985). At higher concentrations, above 2,000 mg/L, VFA become toxic to anaerobic bacteria (McCarty, 1981). VFA were present in the effluent from the start of the experiment (Figure 4.22). A dramatic increase in the VFA concentration occurred when the OLR was increased from 2.37 to 3.16 g COD/L-d. The VFA concentration in the reactor reached 1,860 mg/L, 86% of which was due to acetate and 14% to propionate. Consequently, VFA were being produced at a much higher rate than they were consumed. However, after two days, the concentration of VFA was reduced to 860 mg/L, indicating an adaptation of the biomass to the new conditions and a restabilization of the system. Nevertheless, the concentration of acetate, which is the only VFA that can be used directly by methanogenic bacteria, was relatively high.

In order to avoid further buildup of VFA and disruption of methanogenic activity, 100 mL of sludge cultivated on a mixture of acetate and ethanol were added to the reactor. The high methanogenic activity of this added sludge was obvious. Within 24 hours, the VFA concentration dropped to zero and remained below 100 mg/L until the OLR was

increased to 5.82 g COD/L-d. This particular increase in VFA concentration was expected and was probably due to the higher loading rate. Bisogni (1994) reported that sudden increases in feed rate generally result in a volatile acid build-up after which the system will restabilize. In fact, within 9 days, or 3 HRTs, the methanogenic bacteria had become acclimatized to the new loading rate and low VFA concentrations were observed. At pseudo steady state (PSS) the VFA were at satisfactory levels with zero butyrate or propionate and acetate concentration generally below 240 mg/L.

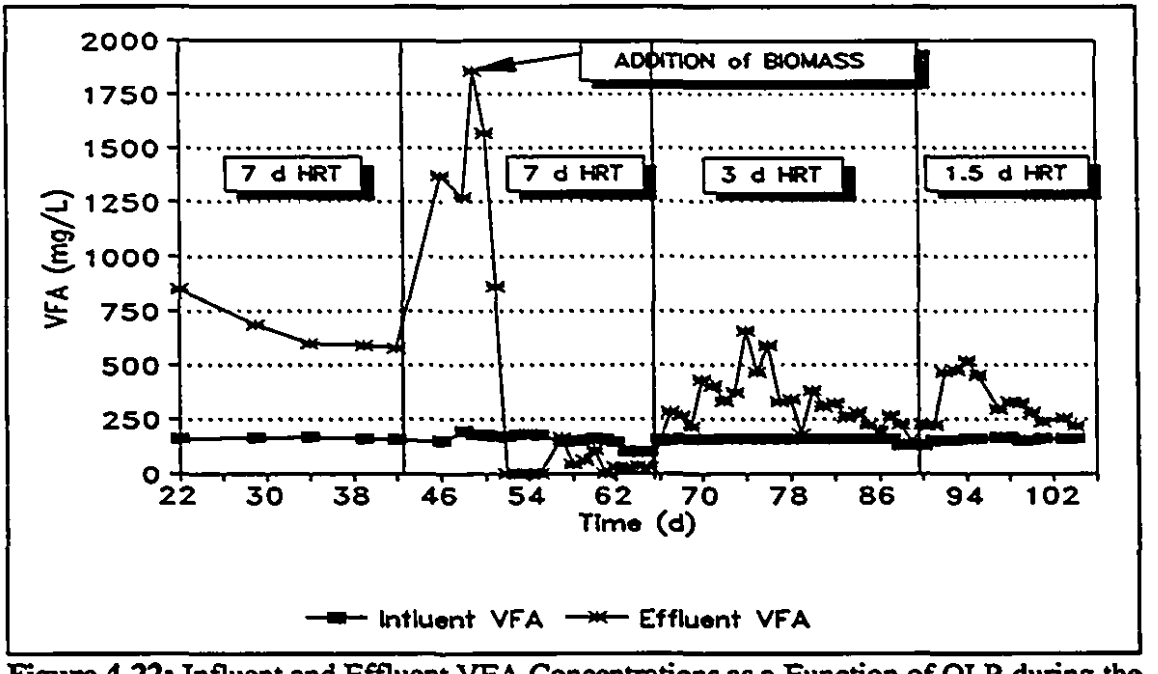

Figure 4.22: Influent and Effluent VFA Concentrations as a Function of OLR during the Anaerobic Continuous-Flow Study.

As soon as the OLR was increased further to 11.45 g COD/L-d, the VFA concentration increased up to a maximum of 520 mg/L, after which it again decreased gradually. Compared to the maximum concentrations reported during the previous OLRs (1,860 and 660 mg/L at 3.16 and 5.82 g COD/L-d, respectively), the new maximum value was much lower and demonstrated the improved adaptation of the biomass. Another reason for the low VFA concentration could be the positive effect of the addition of trace

metals. Over the next 9 days, or 6 HRTs, the VFA concentration continued to decrease steadily. By the end of the study, the acetate concentration was only 190 mg/L and the propionate 26 mg/L. These concentrations correspond to 241 mg/L COD and represent only 2% of the soluble effluent COD. Adaptation of the biomass was clearly occurring, and methanogenic bacteria were not in a growth limiting situation which would have been due to substrate inhibition (high VFA concentration) or lack of trace metals.

The above results illustrate the importance of methanogenic bacteria in anaerobic treatment and confirm the fact that methanogenisis is the rate-controlling step. These results also demonstrate that methanogenic bacteria can acclimatize, and that inhibition can be reversed.

pH and Alkalinity

Control of pH is essential for the successful operation of an anaerobic treatment process. Both the colonne and plastifiant effluents had very high pH values, outside the recommended range for anaerobic digestion. Consequently, it was necessary to adjust the pH of the influent to the UBF reactor. In an attempt to reduce the cost of acid required for neutralization, the UBF reactor was initiated with an influent pH of approximately 7.85. Though the pH values of the sludge and effluent were relatively high (around 8.5), the reactor performance was acceptable. It was speculated that by decreasing the pH of the influent, the effluent and sludge pH will decrease leading to a higher treatment efficiency. The influent pH was hence decreased gradually from 7.85 to 7.23. However, as shown in Table 4.13, neither the influent pH nor the OLR had an effect on the effluent pH which was always around 8.3 ± 0.3. It is essential to note that pH measured in the final reactor effluent was always around 0.5 pH units higher than that inside the reactor and was attributed to the loss of CO_2 from the aqueous phase.

After day 105, the influent pH was further reduced to 6.8, 6.0, and then 5.0. Similarly,

neither the effluent pH nor the treatment efficiency were affected. Stability of the influent was most probably due to high alkalinity and consequently high buffering capacity of the influent (Figure C.1 - Appendix C). In fact Nel and Britz (1986) defined the anaerobic digester pH as a measure of the alkalinity of the digester fluid contents. Moreover, Samson and Guiot (1990) reported that control of pH during anaerobic treatment is a function of VFA concentration, CO_2 fraction in the gaseous phase and alkalinity.

Table 4.13: Influent and Effluent pH as a Function of OLR.

Organic Loading Rate (g COD/L-d)	pH	
	Influent	Effluent
2.37	7.85	8.47
3.16	7.75	8.55
5.82	7.59	8.39
11.45	7.23	8.33
	6.69	8.35
	6.12	8.39
	5.12	8.35

Variations in the alkalinity of the reactor as a function of organic loading and influent alkalinity are illustrated in Figure 4.23. As in the case of pH, the alkalinity of the effluent was independent of the OLR and the influent alkalinity. In theory, when VFA are converted into methane, the pH is expected to increase considerably due to the removal of protons from the aqueous phase and the formation of CO_2. Throughout the course of the study, the effluent alkalinity varied between 4,600 and 5,700 mg/L as $CaCO_3$. This range indicates a very high buffering capacity and may explain the stability of the pH even when large amounts of VFA were produced. Although an alkalinity of about 2,500 mg/L is considered normal for an anaerobic reactor, values between 2,500

to 5,000 mg/L are desirable since they provide a good buffering capacity for large increases in volatile fatty acids (Stafford *et al.*, 1981).

The high alkalinity of the effluent was mainly due to the elevated sodium content in the influent Sodium concentrations in the influent to the UBF reactor ranged between 4.1 and 4.9 g/L. Though it is known that an anaerobic microbial population is able to adapt to high cation concentrations, the measured concentrations were relatively high and above the recommended optimum of 0.23 g/L (Nel and Britz, 1986).

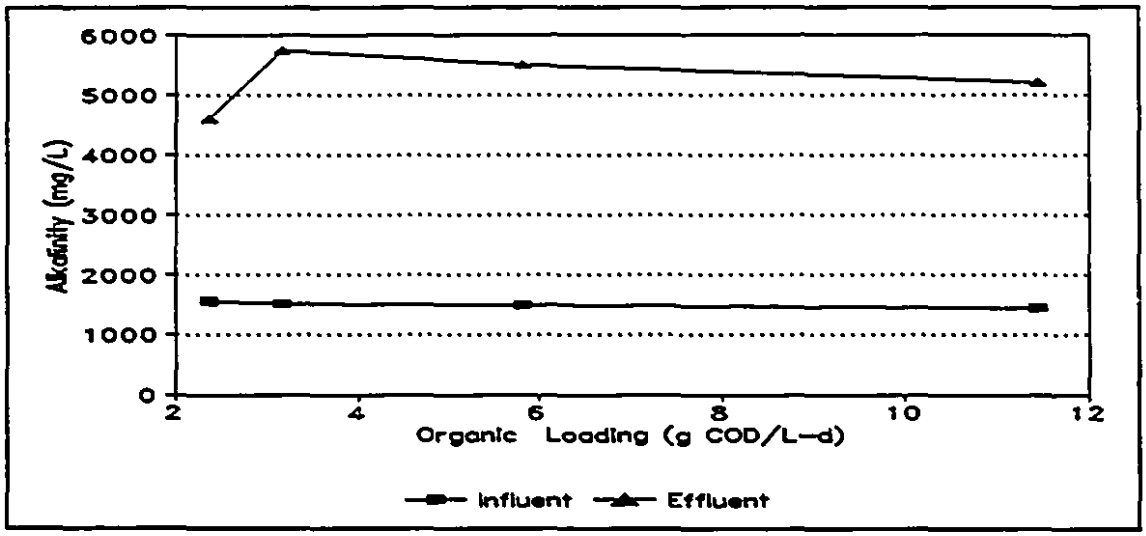

Figure 4.23: Influent and Effluent Alkalinity as a Function of OLR during the Anaerobic Continuous-Flow Study.

As mentioned earlier (Section 4.1.2), the plant uses sodium bicarbonate and sodium chloride to enhance the polymerization and oxidation-reduction of formaldehyde into non-toxic components. Since formaldehyde can be successfully degraded by anaerobic treatment (Frankin *et al.*, 1994) and since very high concentrations of sodium might have an inhibitory effect on anaerobic microorganisms (Boardman *et al.*, 1994), the plant should consider reducing the quantities of sodium added. Another advantage of the reduction of sodium is that lower amounts of acid would be required to bring the pH to the recommended ranges for anaerobic treatment. It is essential to note that prior to the

addition of sodium bicarbonate, the pH of the colonne effluent is around 7. Optimization of the quantities of sodium must take into consideration the maximum concentration of formaldehyde that can be degraded and the minimum alkalinity required for successful anaerobic treatment.

Methane Production and Yield

The economical value of the methane gas produced during anaerobic treatment is among the major advantages of this process. As shown in Figure 4.24, the methane production rate (MPR) increased exponentially with increasing OLR and no plateau was observed. At an organic loading of 11.45 g COD/L-d, the MPR was 2.2 L/L-d, indicating that the system was not overloaded and the methanogenic bacteria were not inhibited by the high loading rates applied.

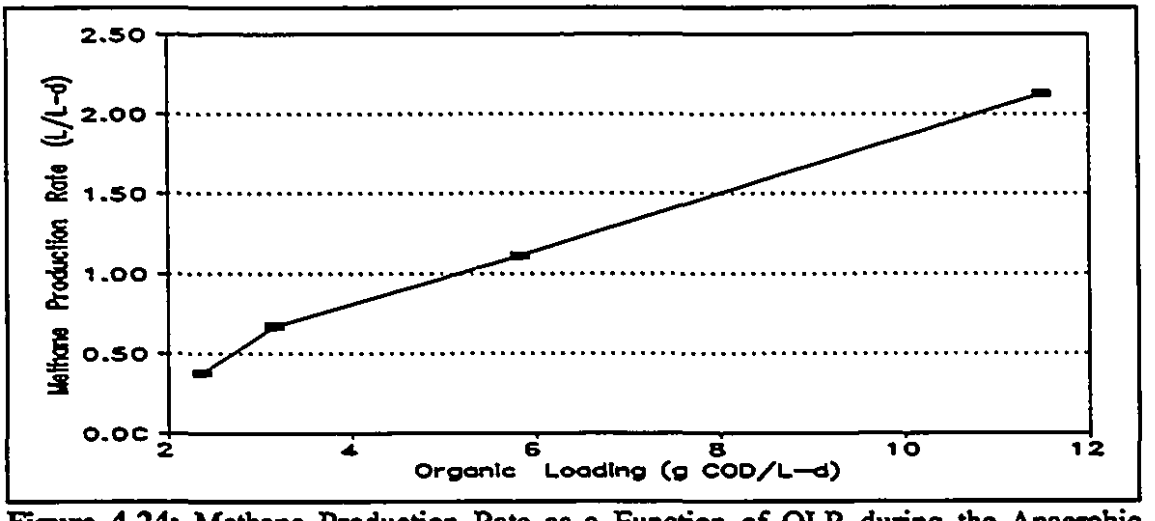

Figure 4.24: Methane Production Rate as a Function of OLR during the Anaerobic Continuous-Flow Study.

Variations in the composition of the biogas as a function of OLR are illustrated in Figure 4.25. The gas composition ranged between 74% and 79% methane, 9% and 13% CO_2,

and 1.8% and 12% N_2.

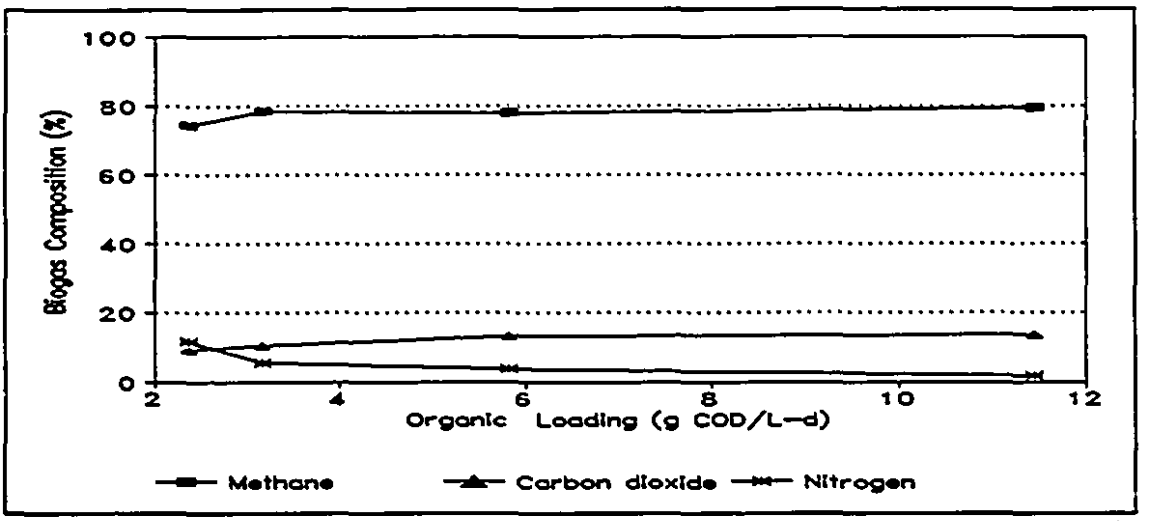

Figure 4.25: Biogas Composition as a Function of OLR during the Anaerobic Continuous-Flow Study.

The high methane content was in accordance with the high pH of the reactor effluent. During the digestion process, a considerable amount of the carbon dioxide formed in the reactor and not used by methanogens reacted with the sodium hydroxide to produce sodium carbonate. Hence, most of the excess carbon dioxide was removed from the reactor and methane was set free, explaining the relatively high methane content.

An increase in the CO_2 content of the biogas was directly related to a decrease in pH. At the 5.82 and 11.45 g COD/L-d OLRs, the pH of the reactor decreased slightly, hence the CO_2 increased from 9% to 13%. This can be explained by the regulation mechanism of the carbonate/bicarbonate/CO_2 buffering system of the process (Brune *et al.*, 1982): at lower pH, CO_2 is less soluble and its partial pressure (gas phase) is higher.

The presence of nitrogen could be associated with the solubilisation of N_2 from the atmosphere in the cooled feed tank. As a result, N_2 was pumped with the influent into

the reactor. The nitrogen content in biogas has been described by Gorur *et al.* (1986) who concluded that the amount of N_2 in the reactor head space is a function of the feed temperature, the partial pressure between the atmosphere and reactor environment, the organic loading rate as well as the amount of CH_4 and CO_2 produced. In fact, as shown in Figure 4.25, percent nitrogen decreased with an increase in OLR and percent CH_4 and CO_2 produced.

Methane yield expressed in L CH_4/g COD-d was also computed to assess the performance of the reactor. McCarty (1964) reported that 0.35 L of methane can be produced from 1.0 g of COD consumed at standard temperature and pressure (STP). As shown in Figure 4.26, methane yield was lowest (0.27 L/g COD-d) at the lowest OLR (2.37 g COD/L-d), then increased to reach a value of 0.31 L/g COD-d at the organic loading of 3.16 g COD/L-d, after which it decreased to 0.29 L/g COD-d.

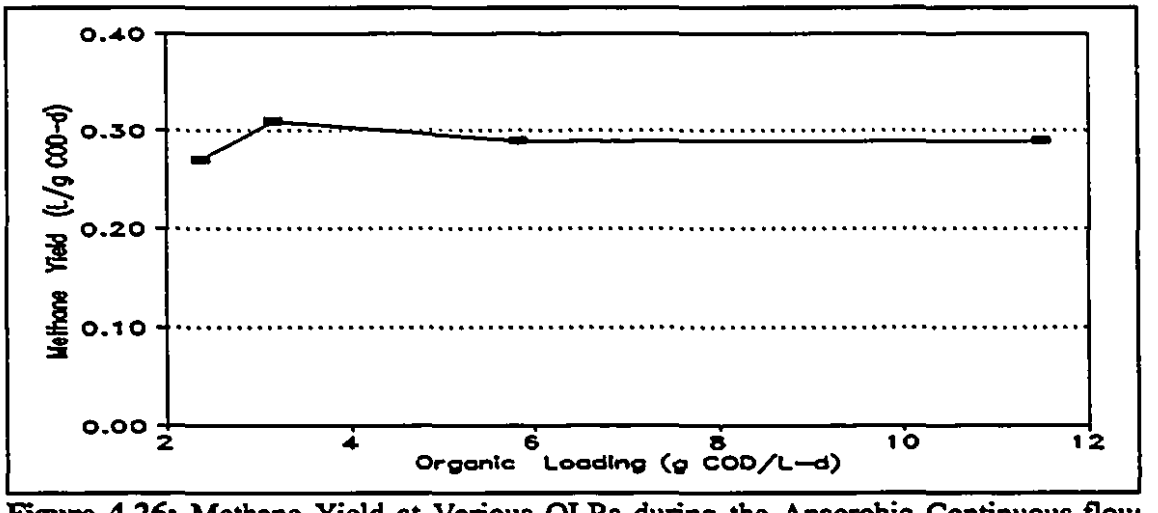

Figure 4.26: Methane Yield at Various OLRs during the Anaerobic Continuous-flow Study.

The relatively low methane yield can be related to several factors among which are the presence of toxicity, biomass growth, overloading of the system and CO_2 solubility. The low methane yield (0.27 L/g COD-d) reported at an OLR of 2.37 g COD/L-d can be

attributed to the limited methanogenic activity. Indeed, during this stage, the methanogenic bacteria were not well adapted to the wastewater constituents and the conversion of COD could not be carried out completely until the end (production of CH_4). This was further illustrated by the accumulation of VFA in the reactor.

During the second OLR tested (3.16 g COD/L-d), the reactor was seeded with a small amount of highly active methanogenic bacteria. The effectiveness of this process was clearly demonstrated by the negligible concentrations of VFA in the effluent. Consequently, the degradable compounds were completely converted to methane, leading to a high methane yield of 0.31 L/g COD-d. Moreover, the absence of toxicity to the added sludge and the adaptation of the original sludge must have lead to biomass growth. This was evident from the methane yield which was lower than the theoretical value of 0.35 L/g COD-d.

In the last two phases of the study (OLR of 5.82 and 11.45 g COD/L-d), the methane yield decreased to 0.29 L/g COD-d. During these periods, no toxicity or overloading of the system were noticed. The percent COD removal and the VFA concentration were almost similar to the values reported during the previous phase (OLR of 3.16 g COD/L-d). However, as a result of the slight reduction in the pH of the reactor, the CO_2 content of the biogas was slightly higher. A decrease in the solubility of CO_2 at lower pH and its subsequent loss via the biogas phase probably played an important role in the decrease in methane yield. Thus smaller amounts of CH_4 were formed from CO_2 under such conditions.

Biomass Washout

From the start of the experiment until day 21, considerable amounts of biomass were lost from the reactor. This was attributed to unadapted poorly settleable sludge and to the

lack of good granules in the municipal sludge. After this initial period, sludge concentration stabilized at 12 g VSS/L. However, during the transition periods following each increase in the OLR, a very high sludge washout was experienced. By the end of the experiment (day 105), the concentration of biomass in the reactor was 9.28 g VSS/L. Figure 4.27 illustrates the biomass washout rate based on the effluent volatile suspended solids and the difference between total and soluble effluent COD divided by the conversion factor of 1.42 g COD/g VSS (Guiot and van der Berg, 1985). Regardless of the technique used to evaluate biomass washout, the rate of sludge washout increased with increasing OLR and reached 0.11 to 0.13 g VSS/d at an organic loading of 11.45 g COD/L-d.

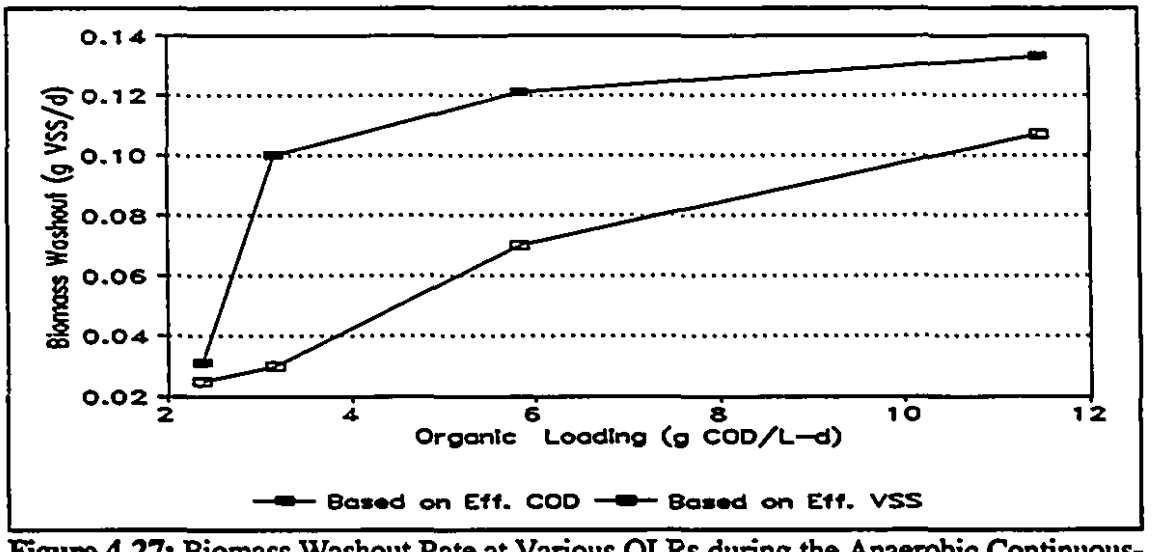

Figure 4.27: Biomass Washout Rate at Various OLRs during the Anaerobic Continuous-Flow Study.

Sludge washout may be explained by the circulation pattern of the gas produced. In fact during the treatment process, gas is produced continuously. Gas bubbles accumulate in the form of gas pockets, after which a sudden gas flow occurs. This flow carries away some cells, leading to biomass washout. Some washout of sludge fines may be healthy for the treatment system, since it is a means for eliminating some inactive solids.

However, excess washout rates can have a negative impact on the treatment efficiency and hence reduce the organic loading that can be successfully accommodated. Indeed, the loading capacity of a treatment system is essentially governed by the amount of active biomass retained in the reactor (Guiot, 1991).

As a consequence of the high biomass washout, the sludge load gradually increased and the sludge retention time decreased. The reactor received sludge loads over a relatively broad range (0.20 to 1.23 g COD/g VSS-d). At an OLR of 11.45 g COD/L-d, a specific load of 1.23 g COD/g VSS-d was reported, indicating that the system was highly loaded (Henze and Harremoes 1983). In fact, the 1.23 g COD/g VSS-d was much higher than the average values reported in the literature and may partly justify the low treatment efficiencies. Lettinga *et al.*, (1981) reported maximum sludge loads of 0.7 g COD/g VSS-d at OLR of 14 g COD/L-d. Furthermore, in most full-scale anaerobic digesters the specific load is maintained at approximately 0.5 g COD/g VSS-d.

Specific Removal Rate

The specific removal rate (SRR) expressed in g COD_{rem}/g VSS-d increased with increasing OLR and reached a value of 0.69 g COD/g VSS-d at an organic loading of 11.45 g COD/L-d (Figure 4.28). This indicates that the specific activity was limited by the substrate concentration and not by the biomass. Even at the highest applied OLR the SRR curve did not approach a plateau. These results show that at lower loading rates the system did not function at its full capacity and/or biomass activity increased during the gradual acclimatization.

Ideally, the organic loading rate should have been increased beyond 11.45 g COD/L-d to assess the maximum specific activity of the biomass. It should be noted that the highest obtained SRR (0.69 g COD/g VSS-d) was relatively low as compared to typical

values reported in the literature. Henze and Harremoes (1983) estimated the SRR for an anaerobic mixed culture to be approximately 1 g COD/g VSS-d. Moreover for the UBF reactor, Guiot (1991) reported 1.04 and 0.91 g COD/g VSS-d for the higher and lower performance boundaries. In the absence of additional data on the SRR at higher OLR, it may be difficult to draw exact conclusions regarding the maximum SRR.

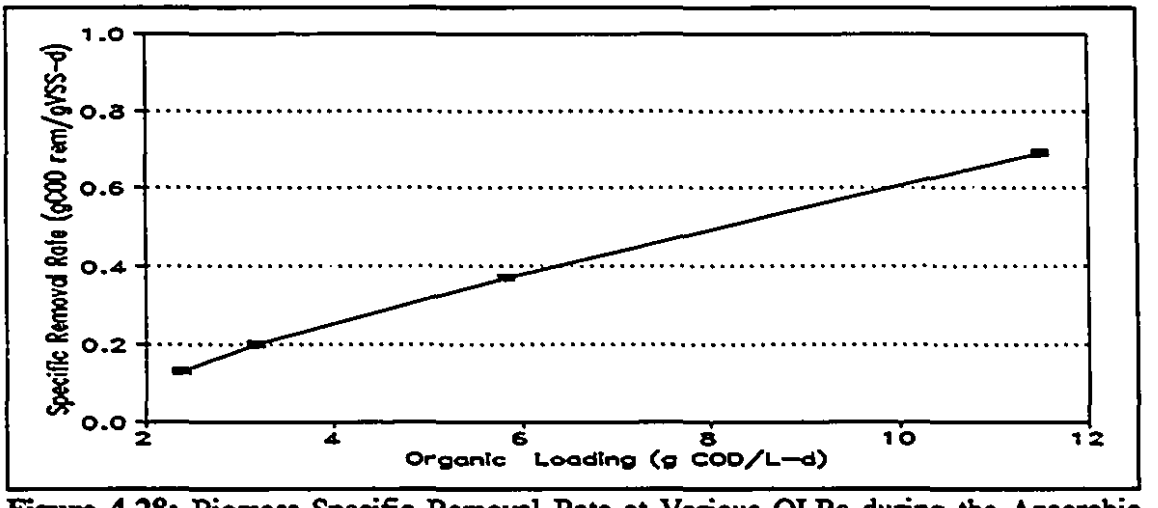

Figure 4.28: Biomass Specific Removal Rate at Various OLRs during the Anaerobic Continuous-Flow Study.

Application of Anaerobic Digestion for Treatment of the Selected Effluents

Overall, the performance of the UBF reactor was satisfactory and consistent with the results of batch assay tests. Adaptation of the sludge to the constituents of the wastewater was evidenced by the relatively low concentration of VFA and the high percentage of methane in the biogas. Even at the highest applied OLR, the reactor was not overloaded and the treatment efficiency was almost similar to the values reported at lower OLRs. It appears that under favourable conditions, an adapted microbial population is capable of fermenting the selected effluents at low HRT. However, the high residual COD (around 7,000 mg/L) clearly indicates that the treated effluent cannot

be discharged into receiving water bodies.

The results of both the batch assay tests and those of the continuous flow reactor point to a significant impact of the type of sludge with respect to degradation of the selected effluents. Although in the continuous flow reactor, COD removal efficiency was higher than all values obtained during the BMP tests conducted with the municipal digester sludge, the treatment efficiency of the effluents did not exceed 58%. In contrast, for batch assay tests conducted with the mixed biomass, COD removal efficiencies up to 61.5% and 67.2% were reported for the colonne and plastifiant effluents, respectively. Hence, it is believed that anaerobic species capable of degrading certain persistent compounds were not present in the municipal digester sludge and could not develop.

At present there is insufficient insight with respect to the effect of anaerobic sludge on the degradation of these effluents and continuation of the research is therefore required. Once a suitable anaerobic sludge for treatment of the effluents has been identified, the anaerobic digestion process will undoubtedly represent a cost-effective treatment method. Moreover in view of the rapid acclimatization of the sludge to the constituents of the wastewater, it is probable that under favourable environmental conditions the process could be operated at very high OLR.

From the present results, it is evident that anaerobic treatment alone will not produce an acceptable effluent. In order to ensure that a suitable final effluent is obtained, aerobic polishing of the anaerobically treated effluent should be considered.

Application of a two step process (i.e. sequential anaerobic-aerobic treatment) appears to be attractive, although it might not be advantageous in terms of equipment and maintenance requirements. On the other hand, a single step aerobic system could offer a simpler and more efficient alternative. To assess the aerobic treatability of the effluents, a continuous-flow aerobic reactor was used and the results are presented in the

following section.

4.3.2 Aerobic Treatment

Aerobic treatability of the selected effluents was evaluated by means of a continuous flow activated sludge reactor. The aerobic reactor was operated at 7 d HRT and 30 d sludge retention time (SRT) until steady state was achieved with respect to effluent soluble COD and mixed liquor suspended solids (MLSS) values. The performance of the aerobic reactor at steady state is summarized in Table 4.14.

Table 4.14: Performance of the Activated Sludge Reactor at Steady State.

Parameter	Average Value
Days of operation	30
Influent soluble COD (mg/L)	16,150
Effluent soluble COD (mg/L)	2,370
% removal	85.3
Influent pH	7.6
Effluent pH	9.1
Influent alkalinity (mg/L as $CaCO_3$)	1,500
Effluent alkalinity (mg/L as $CaCO_3$)	5,600
MLSS (mg/L)	6,180
MLVSS (mg/L)	4,480
Organic loading (mg COD/L-d)	1,550
F:M on a COD basis (d^{-1})	0.52

Treatment efficiency

Figure 4.29 illustrates influent and effluent soluble COD concentrations during operation of the aerobic activated sludge reactor. From the start up of the reactor, the COD removal efficiency was relatively high. Effluent SCOD was approximately 2,400 mg/L or 15% of influent SCOD.

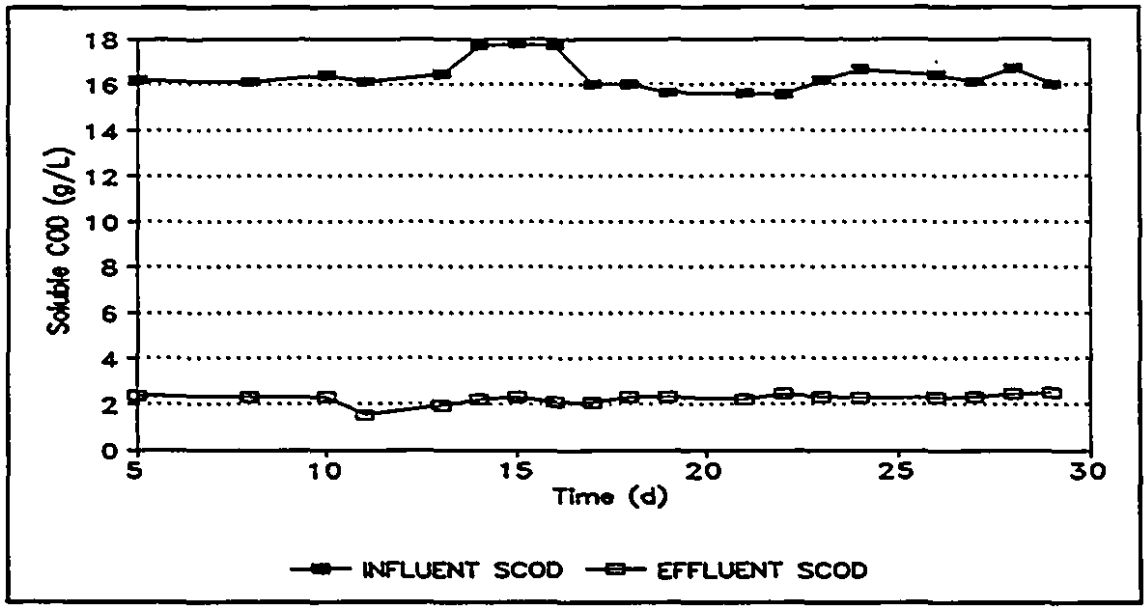

Figure 4.29: Influent and Effluent Soluble COD Concentrations during the Aerobic Continuous-Flow Experiment.

Comparing the percentage of COD removed by the anaerobic UBF reactor (around 58%) with that obtained with by the aerobic activated sludge reactor, it is evident that the selected effluents were neither toxic nor inhibitory to aerobic microorganisms. It appears that the two waste streams can be efficiently treated by the aerobic process. However, since the influent BOD_5 concentration was only 60% that of the COD concentration, it is probable that the high COD removal efficiency was partly due to volatilization by air stripping. This is discussed below.

Volatilization of Contaminants

To assess the effect of volatilization on the COD removal efficiency, two identical reactors similar to the aerobic continuous flow reactor were set-up. Both reactors were filled with the influent without addition of any biomass. The rates of influent feeding and gas bubbling were similar to those applied to the aerobic activated sludge reactor. The main difference between the two reactors was with respect to the type of gas used. In order to evaluate the effect of stripping under aerobic and anaerobic conditions (i.e. conditions which promote the growth of aerobic and anaerobic bacteria), one reactor used air, while nitrogen gas was the source of gas for the second reactor.

Figure 4.30 illustrates COD concentrations of the effluents from the two reactors as a function of time. During the first 12 hours of operation, the behaviour of the two reactors was almost identical. The reduction in COD was only 4.7 and 4.8% in the air and nitrogen bubbled reactors, respectively. However, after 72 hours of operation SCOD removals were 30% and 10% for the air and nitrogen aerated reactors, respectively. These results indicate that volatilization of some contaminants was occurring.

The higher percentage COD removal obtained in the aerated reactor, as compared to the nitrogen fed reactor, was mainly due to the growth of aerobic microorganisms. Indeed, a considerable growth of aerobic bacteria was noted and observed microscopically in the air fed reactor, whereas negligible amounts of bacteria were detected in the nitrogen fed reactor. Also chemical oxidation, due to the presence of oxygen, might have contributed to the SCOD removal observed in the aerated reactor. As it is known that volatilization of contaminants takes place within a few hours, it may be concluded that volatilization of the influent's constituents occurred during the first day and did not exceed 5%. The observed COD reduction beyond the first day of operation was attributed to biomass growth.

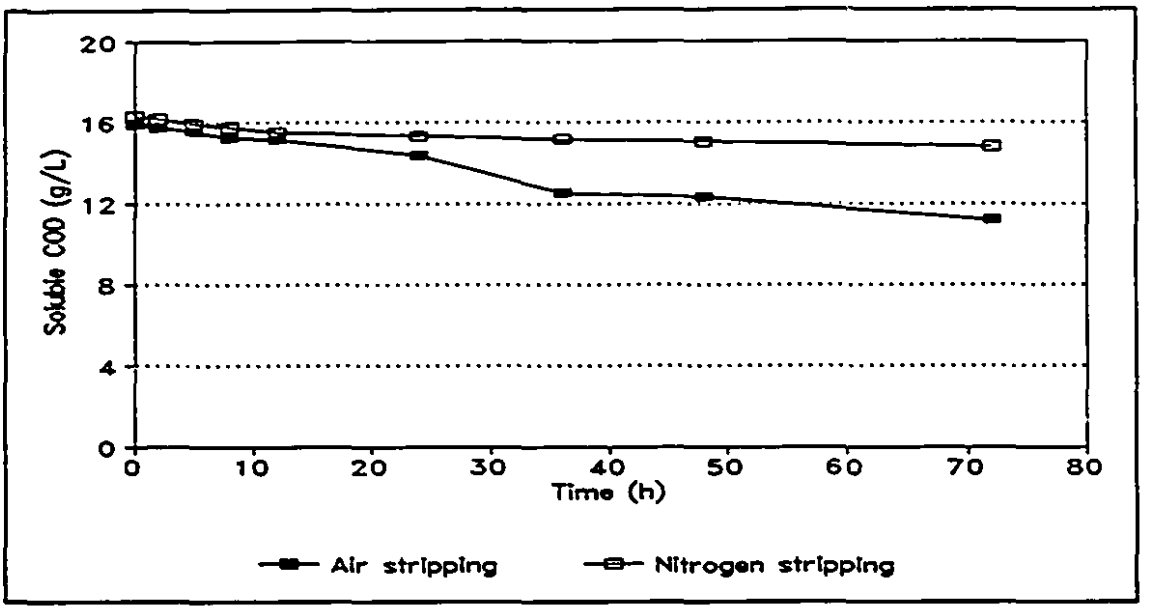

Figure 4.30: Effect of Stripping on SCOD Concentration.

It is worth noting that the fraction of contaminants that is stripped during biological treatment can vary depending on several factors. Compound-specific factors include Henry's Law Constant, the compound's biodegradation rate and initial concentration of the compound and other substrates (Eckenfelder and Grau, 1992). Design and operating parameters can also influence the rate of stripping. For instance, less stripping was reported from treatment systems operating at high SRT and diffused air oxygenation (Kincannon and Fazel, 1986; Eckenfelder and Grau, 1992).

The overall performance of the activated sludge reactor is summarized in Figure 4.31. Considering the high percentage of overall degradation and the low fraction due to air stripping, it is evident that the two selected effluents have high potential for aerobic treatment. However, a substantial amount of contaminants still remains in the aerobically treated effluent. It is probable that optimization of the design and operating conditions would increase the percentage biodegradation.

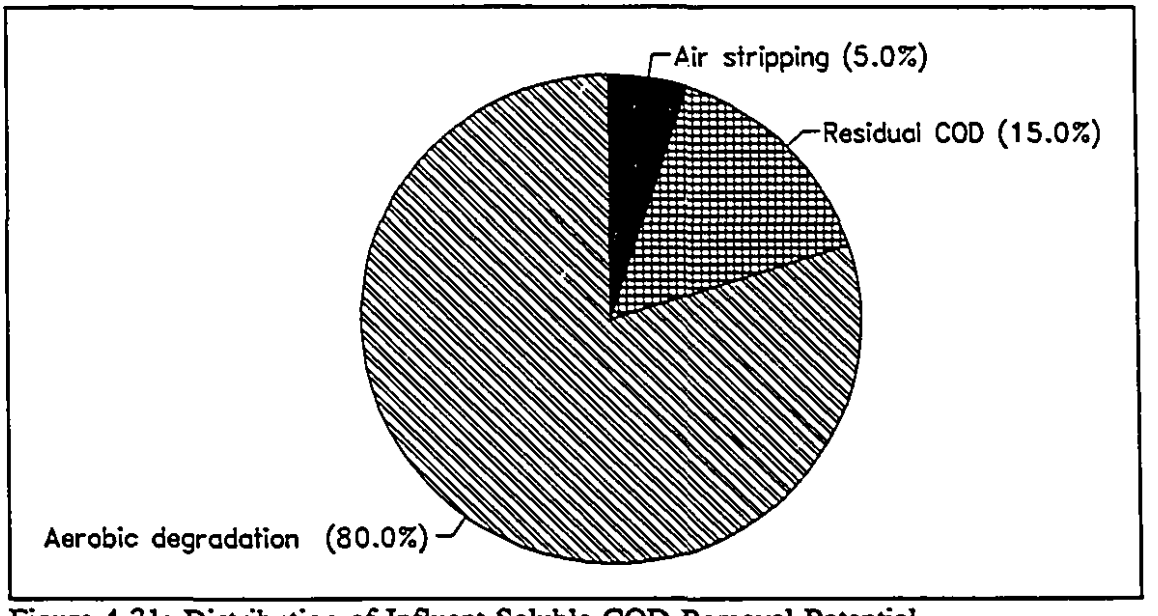

Figure 4.31: Distribution of Influent Soluble COD Removal Potential.

Design and Operating Conditions

Several parameters such as lack of macro nutrients, pH of the influent, dissolved oxygen (DO) concentration in the reactor, organic loading rate, F:M ratio and sludge age are of great importance and can affect the extent of aerobic treatability.

The availability of essential macro nutrients, pH of the influent as well as concentration of DO in the reactor were controlled and maintained within the optimum recommended range for aerobic treatment.

As mentioned in Section 4.2, nitrogen and phosphorus were added at an average of 820 mg N/L and 160 mg P/L of influent. The concentrations of these nutrients in the aerobically treated effluent ranged from 100 to 200 mg N/L and 80 to 120 mg P/L, indicating that the aerobic microorganisms were not nutrient limited. On the contrary,

the added amounts were far above the minimum requirements.

The optimum pH range for aerobic treatment generally lies between 6.5 and 9.0 (Reynolds, 1982). However it was found that bacteria tend to proliferate best under alkaline conditions while algae and fungi grow best under acidic conditions (Benefield and Randall, 1985). The pH of influent to the aerobic reactor was adjusted to approximately 7.6 using hydrochloric acid. Average pH of the mixed liquor and aerobically treated effluents were around 8.4 and 9.0, respectively. The pH values were within the recommended range leaning more towards the alkaline side, hence favouring the presence of bacterial microorganisms.

The DO in an aerobic treatment unit should always be above the requirements of the microorganisms for maintenance and synthesis of new cells. A minimum DO of 2 mg/L is usually recommended to support carbon removal and nitrification (Benefield and Randall, 1985). The concentration of DO in the reactor varied between 5.0 and 6.5 mg/L, thus it was more than sufficient for aerobic biological reactions. The reason for the high DO content is because aeration was also used as a means of mixing.

Considering the above results with respect to availability of macro nutrients, influent and effluent pH as well as presence of sufficient DO, it is unlikely that any modifications regarding these parameters would improve the quality of the treated effluent.

The F:M ratio is a major parameter that can greatly affect the performance of aerobic treatment systems. For chemical effluents, the F:M ratio can vary between 0.1 and 0.8/d on a COD basis (Eckenfelder and Grau, 1992). At very low F:M concentration, insufficient biodegradable substances are available to sustain continued growth, and endogenous metabolism occurs. On the other hand, at very high F:M ratios bacteria reproduce at maximum growth rate and microbes cannot form a readily settleable floc. As mentioned in Section 3.4.2 (Materials and Methods), the reactor was inoculated with

a sludge of 5,240 mg/L MLVSS and was operated at 7 d HRT. The resulting F:M ratio was around 0.44 /d on a COD basis.

From the start of the experiment, considerable amounts of SS and VSS were present in the effluent (Figure 4.32). During the first week of operation a dramatic increase in SS and VSS concentrations in the effluent was observed. This was attributed to adaptation of the sludge to the wastewater constituents as well as new environmental conditions. Although after this initial period the loss of solids from the reactor decreased, still a considerable amount was present in the effluent. As a consequence, the MLVSS decreased and the F:M ratio increased . At steady state, the MLSS and MLVSS were approximately 6,180 and 4,480 mg/L, respectively, and the F:M ratio was 0.52/d on a COD basis.

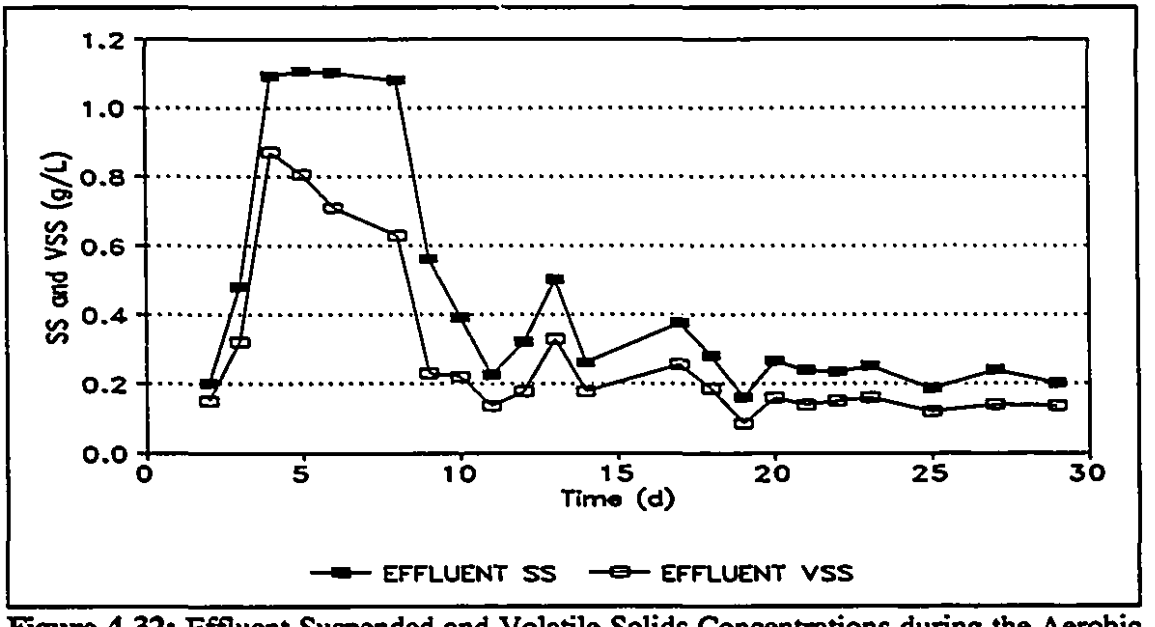

Figure 4.32: Effluent Suspended and Volatile Solids Concentrations during the Aerobic Continuous-Flow Experiment.

The MLSS and MLVSS concentrations were within average values reported in the

literature for activated sludge (Verstraete and van Vaerengergh, 1986). However, the F:M ratio was relatively high and might have limited treatment performance. Indeed, comparing the treatability of the same chemical effluent at various F:M ratios, Eckenfelder and Grau (1992) reported that when all design and operating parameters were identical, the best quality effluent was achieved at a F:M ratio of 0.19/d.

The applied organic loading rate (1,550 mg/L-d) and the selected SRT (30 d) are also important parameters which might have affected the reactor performance. A wide range of values has been reported for the treatment of chemical effluents depending on the origin and composition of the waste stream (Eckenfelder and Grau, 1992). In these experiments only one OLR and one SRT were used, hence it was not possible to assess whether these parameters had an impact on the treatment efficiency. However, the results do suggest that a lower F:M should be applied. Since mixed liquor concentration in the reactor was within the recommended range for activated sludge, it is probable that a lower OLR should be applied to achieve a low F:M ratio and consequently a better quality effluent. At present insufficient data are available with respect to the effect of OLR, SRT and F:M on the quality of the aerobically treated effluent, and continuation of the research is recommended.

Applicability of an Aerobic Process for Treating the Selected Effluents

The performance of the aerobic activated sludge reactor was satisfactory and much better than that of the anaerobic UBF reactor. Effluent COD was about 66% less than that obtained by anaerobic treatment. However, even with aerobic treatment, the residual COD (around 2,400 mg/L) was relatively high. Optimization of the design and operating parameters (namely HRT, SRT, F:M, and SRT) would lead to a much better quality effluent.

Considering the present results and those reported during anaerobic digestion (Section 4.3.1), it is evident that a one-step process is risky and cannot guarantee a suitable quality effluent. The application of a two-step process appears to be more suitable for treatment of the selected effluents. However, even then it is uncertain whether an acceptable effluent can be achieved. Indeed, it is possible that the residual COD of the aerobically treated effluent was due to compounds which are simply not biologically degradable. To assess the suitability of a two-step process with respect to the treatability of the selected effluents, a sequential anaerobic-aerobic continuous flow experiment was carried out.

4.3.3 Sequential Anaerobic- Aerobic Treatment

The sequential anaerobic-aerobic process pre-treated the mixture of colonne and plastifiant effluents in an anaerobic reactor, then polished the anaerobic effluent in an aerobic reactor. The anaerobic reactor was operated at 1.5 d HRT, while the aerobic polishing reactor operated at 4 d HRT. The results presented in this section cover the aerobic reactor only. All data collected from the anaerobic reactor have been presented and discussed in Section 4.3.1.

At the beginning of the sequential anaerobic-aerobic experiment, the MLSS and MLVSS concentrations in the aerobic reactor were 6,180 and 4,480 mg/L, respectively. Average SCOD concentration of the anaerobically treated effluent was approximately 7,200 mg/L. It was thought that by operating the aerobic reactor at 4 d HRT, both the F:M ratio (0.41/d) and OLR (1.2 g COD/L-d) would be lower than those considered in the previous aerobic continuous-flow experiment, hence a better quality effluent might be obtained. On the other hand, at 4 d HRT the actual size of a treatment plant would be much smaller than the one required for 7 d HRT. The aerobic polishing reactor was operated until a steady state condition was achieved with respect to effluent SCOD. The principal

results at steady state are given in Table 4.15.

Table 4.15: Performance of the Aerobic Polishing Reactor at Steady State.

Parameter	Average Value
Days of operation	27
Influent soluble COD (mg/L)	7,290
Effluent soluble COD (mg/L)	1,875
% Removal	74.3
Influent pH	8.27
Effluent pH	9.16
Influent alkalinity (mg/L as $CaCO_3$)	5,350
Effluent alkalinity (mg/L as $CaCO_3$)	5,550
MLSS (mg/L)	5,500
MLVSS (mg/L)	4,100
Organic loading (mg COD/L-d)	1,240
F:M on a COD basis (d^{-1})	0.45

Treatment Efficiency

Influent and effluent soluble COD concentrations are illustrated in Figure 4.33. Within 16 days or 4 HRT, steady state was achieved and the effluent SCOD was only 1,875

mg/L. As expected, effluent COD was lower than the average value (2,370 mg/L) achieved during the previous continuous-flow aerobic study and may be attributed to the lower applied OLR and F:M ratio. Although loss of solids in the aerobically treated effluent slightly reduced the mixed liquor solids concentration, the F:M was still lower than that reported during the previous study.

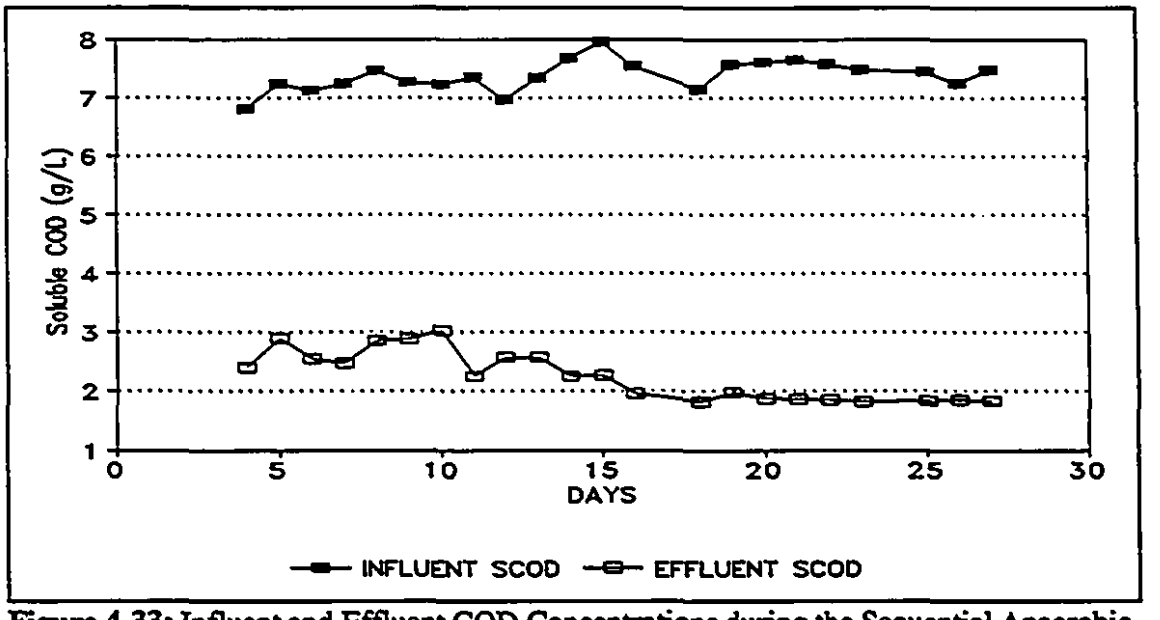

Figure 4.33: Influent and Effluent COD Concentrations during the Sequential Anaerobic-Aerobic Study.

Comparing the results listed in Tables 4.14 and 4.15, it can be noted that a 20% and 13.5% reduction in the OLR and F:M lead to a 21% decline in effluent COD concentration. However, it is not certain whether the changed OLR or the changed F:M had a greater effect on the effluent quality. Though it is expected that reducing both parameters would make improvements, it is probable that the biomass was limited by the availability of easily biodegradable substrates. Indeed, the influent to the aerobic reactor was pre-treated in the anaerobic reactor where most easily degradable substrates were removed. In view of the lack of data regarding typical F:M ratios to be considered for

anaerobically pre-treated chemical effluents and considering the importance of other design parameters (namely HRT, SRT, OLR, MLSS and MLVSS) and their interactions in predicting the quality of the aerobically treated effluent (Zaloum, 1989), it is suggested that further studies should be conducted in order to develop appropriate parameters for aerobic polishing of the effluents.

It is worth noting that environmental conditions such as pH and the presence/availability of essential macro nutrients and DO content did not seem to have affected treatment performance. In the present experiment anaerobically pre-treated effluent was fed to the aerobic reactor without any pH adjustment or nutrient supplementation. Still, the pH of the aerobic polishing reactor remained in the alkaline region within the recommended range and no nutrient deficiencies were detected.

Application of the Sequential Anaerobic-Aerobic Process for Treating the Selected Effluents

The overall performance of the sequential anaerobic-aerobic process is presented in Figure 4.34. COD discharged from the anaerobic reactor was around 7,300 mg/L and the final effluent discharged from the aerobic reactor had a COD of approximately 1,875 mg/L. The residual COD of the treated effluent was lower than the values obtained during a one-step anaerobic and/or aerobic process.

Compared to the one-step anaerobic or aerobic processes, it appears that a sequential anaerobic-aerobic process is a better alternative for treating the selected effluents. Considering the above results, it seems that an optimization of the operating parameters of the aerobic reactor can improve the final effluent quality. Moreover, the results of the anaerobic batch experiments in Section 4.2 point to a strong effect of the type of sludge with respect to degradation of the waste streams. A joint or simultaneous

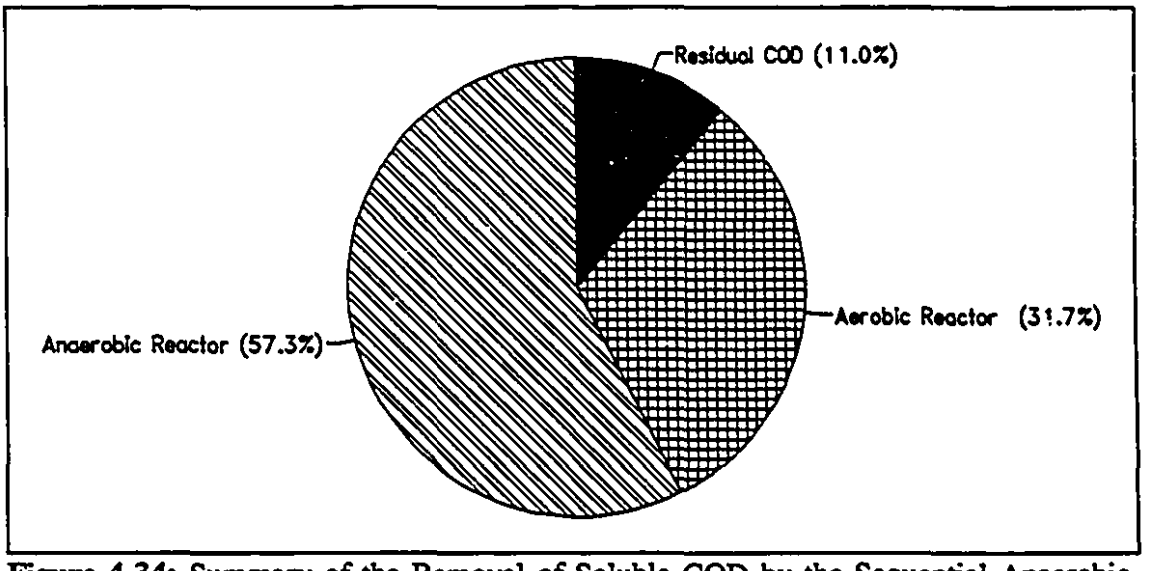

Figure 4.34: Summary of the Removal of Soluble COD by the Sequential Anaerobic-Aerobic Process.

optimization of both processes would be necessary to achieve the best quality effluent at lowest cost.

The data collected during the characterization stage indicate that the flow of pastifiant and colonne effluents is approximately 400 m^3/d. Based on the HRTs achieved in the continuous-flow studies, the approximate size of the treatment unit (excluding the settler) would be 600, 2,800 and 2,200 m^3 for the anaerobic, aerobic and sequential anaerobic-aerobic processes, respectively. Hence, it is recommended to use anaerobic digestion if a cost-effective pre-treatment is to be obtained, while for an economical complete treatment a sequential anaerobic-aerobic process is recommended.

Finally it is worth noting that selection of the two effluents from this particular plant was based on the assumption that by treating the two most concentrated waste streams, which constitute approximately 40% of the final effluent, and then mixing them with the other

streams will generate a final effluent with an acceptable quality. In view of the great fluctuations experienced at the plant and considering the optimization program undertaken by the plant, a mass balance to determine the final quality effluent could not be developed.

5. CONCLUSIONS AND RECOMMENDATIONS

Effluent Characterization

Chemical characterization of the various waste streams generated at the Monsanto plant, Lasalle, revealed that two highly concentrated effluents ("colonne" and "plastifiant") are amenable to biological treatment. These two streams constitute approximately 40% of the polluted flow and most of the COD discharged by this plant. Although compounds toxic to anaerobic microorganisms were identified in both effluents, the biodegradation potential of these effluents (BOD around 58% of COD) was relatively high, suggesting that both streams are good candidates for anaerobic treatment.

Batch Assay tests

Batch assay tests, including biochemical methane potential (BMP) and anaerobic toxicity assays (ATA) confirmed the anaerobic degradation potential of both effluents but also the presence of toxicity to anaerobic microorganisms.

The BMP assays revealed a moderate degree of anaerobic treatment with soluble COD removals of 45% to 61% and 11% to 67% for the colonne and plastifiant effluents,

respectively. Contrary to the findings of Battersby and Wilson (1989) which were obtained with organic compounds, the biodegradation potential of both effluents was found to vary depending on the type of sludge. A mixture of several biomasses from different sources was shown to be superior for the anaerobic degradation of these effluents. Although this mixture was not originally adapted to the constituents of the wastewater, the availability of a wider variety of microbes is believed to have helped the mineralisation of some persistent/complex compounds.

The results of the ATA tests were consistent with those reported for the BMP. Storage of sludge was found to decrease the biomass activity and increase lag periods. However, neither the potential degradation nor the extent of toxicity were affected. Lag periods of 10 to 80 days were noted with both effluents and were attributed to biomass activity, applied specific load (ratio of substrate to inoculum), and adaptation of sludge to the effluents' constituents.

During ATA tests, the colonne effluent exhibited no toxicity at any tested concentrations, indicating that this effluent is not inhibitory to methanogenic bacteria and can be treated anaerobically. In the case of the plastifiant effluent, an inhibition of anaerobic microorganisms was found to be directly proportional to the increase in concentration. The highest non-toxic concentration was between 1 500 and 2 100 mg/L. Hence it was concluded that anaerobic treatment of the plastifiant would be suitable provided it is diluted or mixed with other biodegradable effluents.

Results of the batch assay tests also indicate that these tests, which were originally developed for organic compounds, are appropriate for determining the presence or absence of anaerobic toxicity and the extent of degradability of wastewaters. In the case of complex wastewaters, it seems essential to evaluate the biodegradation of the effluents with sludges from different sources. The sludge which would show the highest degradation potential would then be used for conducting ATA tests. The purpose of

these ATA assays would be to confirm the results of the BMP tests, to detect any possible toxicity effects and to identify the approximate length of time required for adaptation. Allowing for long incubation periods is also necessary to ensure accurate results. Decreased rate or total cessation of gas production are not necessarily signs of irreversible toxicity. The eventual acclimation of an anaerobic microbial population to the toxicant, as indicated by a return to normal gas production can be achieved and one example of this was reported by Chou *et al.* (1978).

Continuous-Flow Studies

Continuous-flow studies revealed a reasonable treatability of the selected effluents by either anaerobic, aerobic or sequential anaerobic-aerobic techniques. The performance of the various processes was found to be a function of several parameters such as sludge type, concentration of biomass in the reactor and specific load or F:M ratio. A one-step anaerobic or aerobic process was shown to be applicable if the treated effluents are discharged to a municipal treatment plant, while for direct discharge into receiving water bodies, a two-step sequential anaerobic-aerobic process should be implemented.

The performance of the anaerobic reactor was consistent with the results of the BMP and ATA experiments. The average COD removal efficiency was 58% and very close to the values reported during the BMP tests. Lag periods observed at the beginning of the ATA tests were confirmed by a dramatic increase in the VFA content of the reactor during the first month of operation. However a rapid adaptation of the sludge to the wastewater constituents was noted. The anaerobic reactor was capable of handling a wide range of organic loading rates (2.37 to 11.45 g COD/L-d) without being overloaded. A constant COD removal efficiency and a linear increase in gas production were reported, indicating that the effluents can be treated anaerobically even at higher organic loading rates. A significant impact of the type of sludge with respect to the extent of treatment efficiency

was noted. The presence of anaerobic species capable of degrading some persistent compounds would improve the treatability of the waste streams. Hence, it is concluded that anaerobic digestion can offer a stable and cost-effective pre-treatment for the selected effluents.

The aerobic activated sludge reactor yielded an 80% COD degradation and a negligible amount of air stripping at an OLR of 1.55 g COD/L-d. Higher treatment efficiencies could be achieved by lowering the OLR and increasing the HRT. This process would necessitate a large size treatment plant and may not be feasible or possible to implement. Hence, the aerobic process should be used to pre-treat the waste streams prior to their discharge to a municipal treatment plant or to post-treat the anaerobically treated effluents.

The sequential anaerobic-aerobic process was found to be the most efficient and suitable for treating the selected effluents. Pre-treatment of the waste streams in the anaerobic reactor resulted in a considerable decline of the organic load to the aerobic reactor. Although an overall treatment efficiency of 89% was reported, it is believed that a higher percentage removal can be achieved. The selection of an appropriate anaerobic sludge and optimization of the operating parameters to the aerobic reactor should lead to a better final effluent and a more economical treatment system.

Recommendations for Future Research

Significant discrepancies were noted in the literature with respect to the concentration of diluted COD in the assay tests in relation to the original wastewater strength. Differences regarding the ideal source of sludge to be used as inoculum as well as the type and amount of substrate to be added to the ATA tests were also noted. Hence, to maximize the benefits of the batch tests and to use the assessed data for designing an

anaerobic treatment plant, the BMP and ATA techniques should be optimized and standardized.

Considerable fluctuations in the strength of the waste streams were experienced during the characterization stage. Although the industry is engaged in an optimization project to limit such fluctuations, it is believed that some variations in the concentrations of the effluents will always be encountered. Hence, a close monitoring program should be undertaken to assess the size of an equalization basin to be provided ahead of the treatment unit.

The effect of different anaerobic sludges on degradation of the selected effluents should be further investigated. This could be achieved by running BMP tests with biomasses from different sources.

A refined analysis of the optimum design and operating parameters of the anaerobic, aerobic, and sequential anaerobic-aerobic reactor should be undertaken. Also a mass balance to predict the final effluent quality should be developed.

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APPENDIX A

Constituents of the Biochemical Methane Potential (BMP) and Anaerobic Toxicity Assay (ATA) Tests

Table A.1: Constituents of the BMP Tests.

Test Concentrations (mg/L)	WW (mL)	DW (mL)	DM (mL)	SS (mL)	BB (mL)	In (mL)
Colonne Effluent:						
13,800	6	24	10	0.5	2	8
6,900	3	27	10	0.5	2	8
4,600	2	28	10	0.5	2	8
1,600	0.7	29.3	10	0.5	2	8
Plastifiant Effluent:						
4,600	17	13	10	0.5	2	8
1,600	6	24	10	0.5	2	8
800	3	27	10	0.5	2	8

Table A.2: Constituents of the ATA Tests.

Test Concentrations (mg/L)	WW (mL)	DW (mL)	DM (mL)	SS (mL)	BB (mL)	In (mL)	VFA (mL)
Colonne Effluent:							
12,500	5.4	14.6	10	0.5	2	8	10
4,200	1.8	18.2	10	0.5	2	8	10
2,100	0.9	19.1	10	0.5	2	8	10
Plastifiant Effluent:							
12,500	18	2	10	0.5	2	8	10
4,200	6	14	10	0.5	2	8	10
2,100	3	17	10	0.5	2	8	10

WW: wastewater
DW: dilution water
DM: defined medium
SS: sulfured solution
BB: bicarbonate buffer
In: Inoculum
VFA: volatile fatty acid

APPENDIX B

Chromatograms of the GC/MS Analysis for the Colonne and Plastifiant Effluents.

Figure B.1: Chromatogram of the Colonne Effluent.

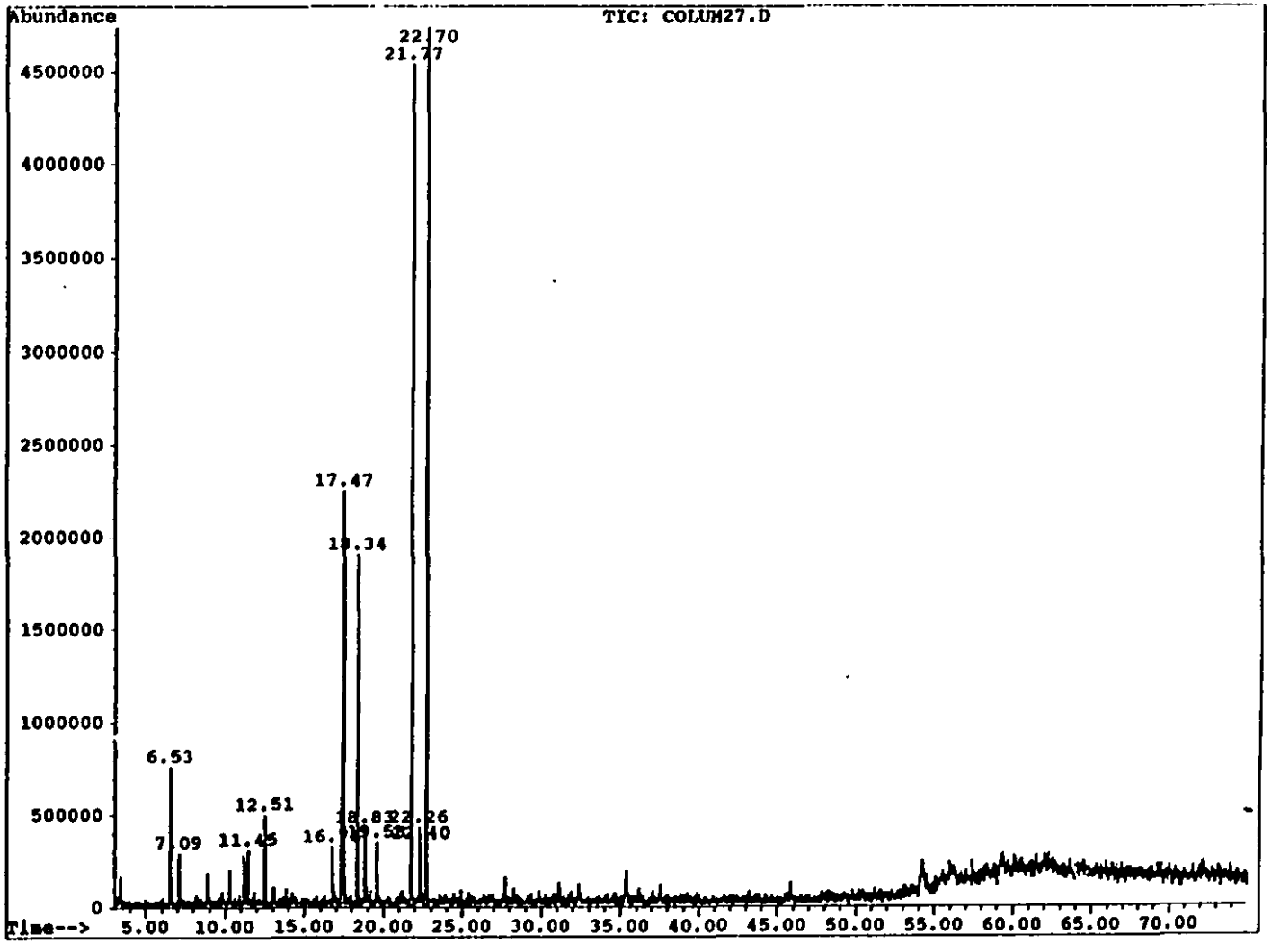
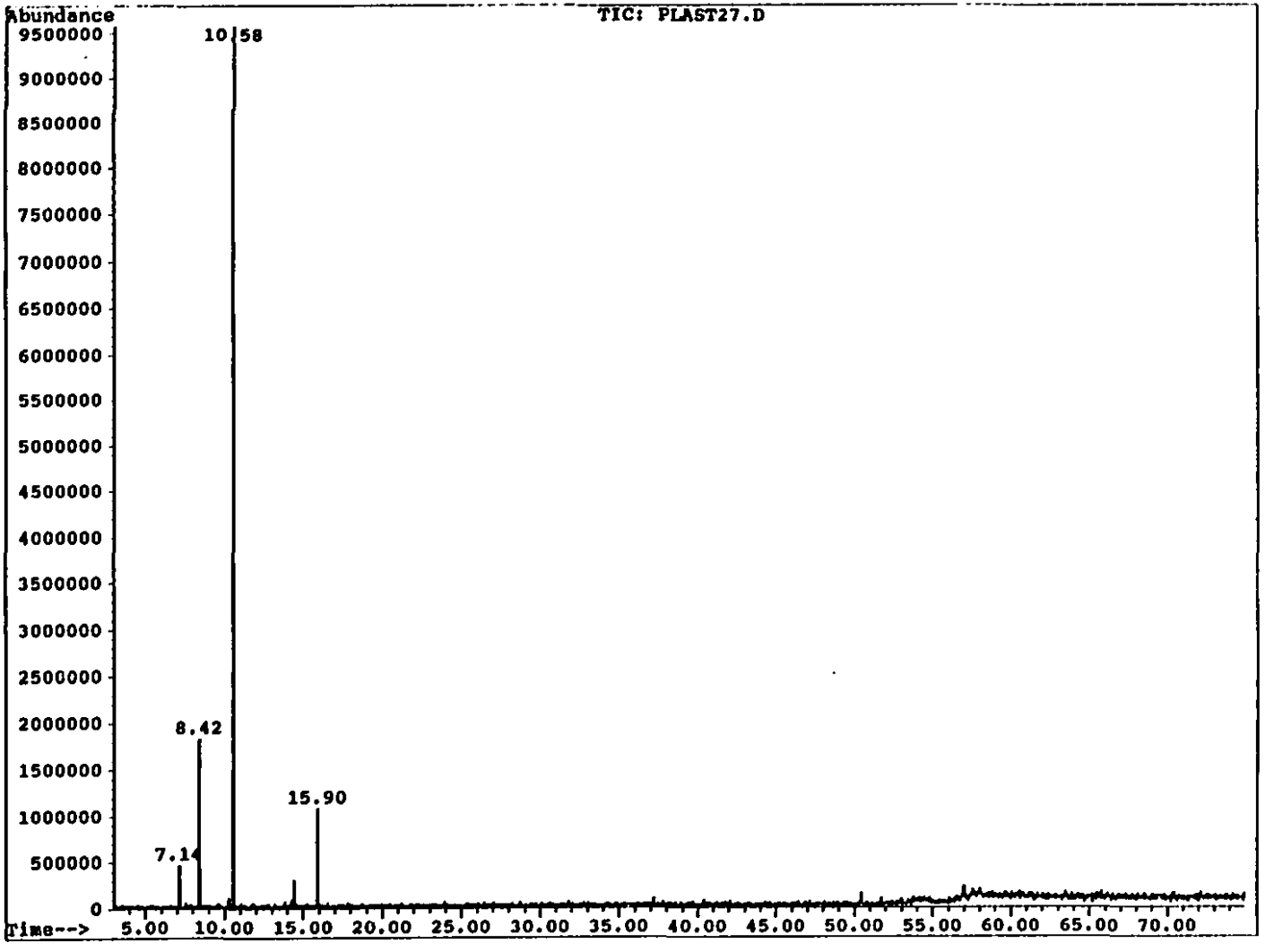


Figure B.2: Chromatogram of the Plastifiant Effluent.



APPENDIX C

Graphical Illustration of the Buffering Capacity of the Influent to the Continuous-Flow Reactors

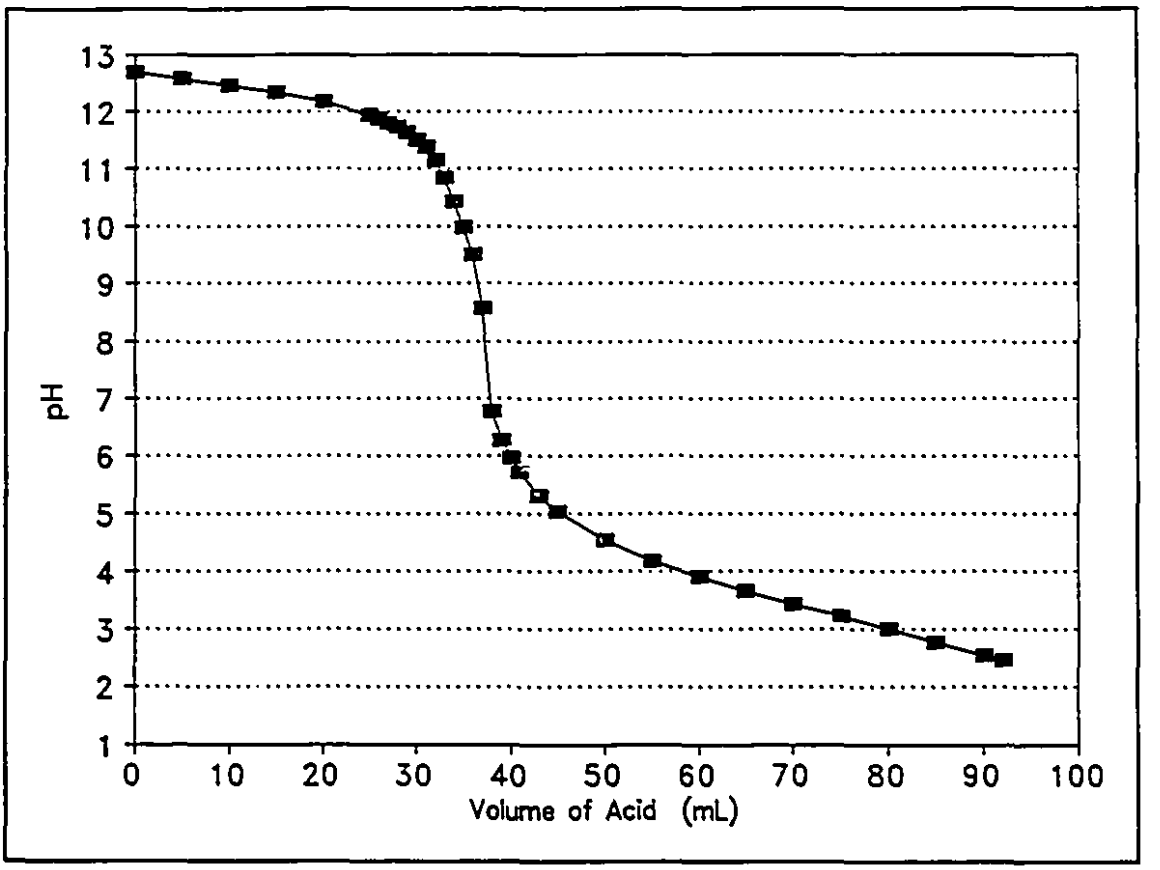


Figure C.1: Influent Alkalinity Titration Curve Using 0.1 N HCl as Titrant.