METHANOGENIC ACTIVITY TEST FOR THE ACETYL EFFLUENT

A DISSERTATION

Submitted in partial fulfillment of the requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(With Specialization in Industrial Pollution Abatement)

By

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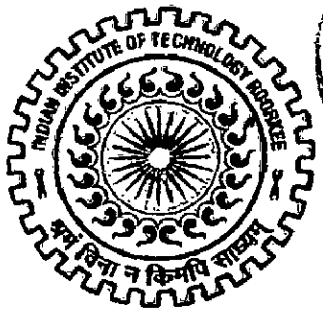

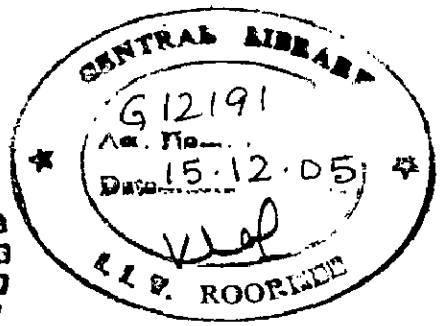

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CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitled **"METHANOGENIC ACTIVITY TEST FOR THE ACETYL EFFLUENT "** in the partial fulfillment of the requirements for the award of the degree of **Master of Technology** in **Chemical Engineering** with specialization in **Industrial Pollution Abatement,** submitted in the Department of Chemical Engineering, Indian Institute of Technology, Roorkee, Roorkee, is an authentic record of my own work carried out during the period from June 2004 to June 2005 under supervision of **Dr. I. M. Mishra,** Professor, Department of Chemical Engineering, Indian Institute of Technology, Roorkee, Roorkee and **Mr. Ashwani Kumar,** Sr. Manager (EHS) Jubilant Organosys Ltd., Gajraula.

The matter, embodied in this dissertation has not been submitted by me for the award of any other degree.

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This is to certify that the above statement made by the candidate is correct to the best of our knowledge and belief.

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ABSTRACT

Treatment of wastewater generating from alcohol recovery column-II of acetyl section of Jubilant Organosys Limited, Gajraula was a problem as it has very high concentration of lower carboxylic acids. The COD of effluent fluctuates between 18,000 mg/l and 32,000 mg/l while BOD varies from 9,500 mg/l to 15,000 mg/l. The total generation of wastewater was between 650 and 850 m^3/day. Bio-degradability of the acetic acid is poor but as the wastewater contained mixture of formic acid, acetic acid, etc, and ethyl acetate and aldehyde. The biodegradation of this wastewater was envisaged.

The methanogenic activity tests were conducted to test the treatability of this effluent in a UASB treatment system. The activity test employed in this study used to evaluate the microbial activity for the utilization of substrate in wastewater, which contains lower carboxylic acids as acetate. The active biomass (sludge) used in the experiment was also collected from JOL, Gajraula.

It was observed that the activity followed the methane production rate. The activity tests for finding kinetic coefficients were performed using the optimum value of COD/VSS ratio i.e.0.5. The yield coefficient as calculated from the experiment was equal to 0.04125 gVSS/gCOD. The efficiency of the wastewater treatment system as calculated was having a value of 77.31%. The volume (ml) of CH_4 produced per (mg) of COD reduction was found to be 0.35 ml/mg indicating the generation of methane from the wastewater taken for the experiment.

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NOMENCLATURE

SYMBOLS

A Surface available for hydrolysis (m^2)

B ***Volume of methane produced under normal condition of temperature and pressure per gram of substrate added.***

B_0 Volume of methane produced under normal condition of temperature and pressure per gram of substrate added at infinite retention time

E Specific efficiency

K Dimensionless less kinetics parameter

K_{sbk} Surface based hydrolysis constant (kg/m^2 day)

k_{max} Max substrate removal rate constant per unit time

k_s Half velocity constant, mass per unit volume

M Mass of substrate (kg)

P Saturation water vapour pressure, mm Hg at T°C

r Substrate utilization rate (gCOD/gVSS.day)

S Substrate concentration in the effluent

S_0 Feed COD concentration

T Temperature in deg C.

t Time (days)

X Concentration of Biomass (gVSS/l)

Y Yield Coefficient (gVSS/gCOD)

Z COD/VSS Ratio

μ_{max} Max. specific growth rate constant, per unit time

ABBREVIATIONS

ABR	:	Anaerobic Blanket reactor
BOD	:	Biochemical Oxygen Demand
BOD_3	:	Biochemical Oxygen Demand for 3 day at 27 °C
COD	:	Chemical Oxygen Demand

COD_i	:	Initial Reactor COD
COD_f	:	Final Reactor COD
CPCB	:	Central Pollution Control Board
EDTA	:	Ethylene Di-Amine Tetra Acetic acid
GLS	:	Gas Liquids-Solids
HRT	:	Hydraulic Retention Time
HUSB	:	Hydraulic Upflow Sludge Blanket
JOL	:	Jubilant Organosys Limited.
LCFA	:	Long Chain Fatty Acids
MLD	:	Mega Liter per Day
MUR	:	Methanogenic Upflow Reactor
OLR	:	Organic Loading Rate
OMSW	:	Olive Mill Solid Waste
SEM	:	Scanning Electron Micrograph
SRT	:	Solids Retention Time
SVI	:	Sludge Volume Index
TDS	:	Total Dissolved Solids
TS	:	Total Solids
TSS	:	Total Suspended Solids
UASB	:	Upflow Anaerobic Sludge Blanket
VFA	:	Volatile Fatty Acids
VSS	:	Volatile Suspended Solids

Chapter 1
INTRODUCTION

1.1 GENERAL

Rapid urbanization and industrialization in the developing countries pose severe problems in collection, treatment and disposal of effluents. This situation leads to public health problem. Decreasing assimilative capacity of water bodies, need for water conservation and with the increasing global demand of cleaner environment and its enduring benefits to the humanity, sustainable development, protection and improvement of our ecology lot of treatment technologies were developed for the treatment of waste generated by different industries. Research and development endeavor in recent years is directed towards wastewater treatment technologies, which are compatible with the environmental and economic conditions. Development, selection, and application of appropriate technology for wastewater treatment are therefore major component of such preventive action.

One such promising treatment technique for wastewaters is the Upflow Anaerobic Sludge Blanket (UASB) system, a high-rate anaerobic treatment method. Anaerobic treatment of wastewater gained wide attention among the researchers and sanitary engineers chiefly because of their economical edge over the conventional aerobic methods. Zero oxygen requirement which cuts down the aeration costs and energy requirements; very low excess sludge production which reduces the costs of sludge handling, stabilization and disposal; production of biogas with good energy content which can be used as a fuel, are the major advantages of this system.

1.2 INDUSTRIAL DESCRIPTION

Jubilant Organosys Limited, Gajraula is strategically located at Bhartiagram, Gajraula (100 km from Delhi on Delhi-Lucknow Highway, NH-24). The company has an extensive product range of chemicals. The chemicals include vinyl acetate monomer, acetic anhydride, acetic acid, acetaldehyde, pyridine, picoline, di-methyl formaldehyde, poly vinyl alcohol, poly vinyl acetate (used for the production of

adhesives) and many others. Beside, it also manufactures industrial alcohol. Distillery spent wash (waste water from distillery) is treated by anaerobic process followed by aerobic process. Biogas generated through the anaerobic process is used as non-conventional energy source.

In acetaldehyde plant, soft water from distillation column containing 93.54 % alcohol and 6.46 % water is taken to alcohol recovery column-II for alcohol recovery. Wastewater generating from the bottom of column with average flow rate, 720 m^3/day is taken for experiment.

1.3 BIOLOGICAL TREATMENT OF WASTE WATER

Biological treatment of wastewater basically reduces the pollutant concentration through microbial coagulation and removal of non-settle-able organics colloidal solids. Organic matter is biologically stabilized so that no further oxygen demand is exerted by it. Anaerobic and aerobic biological treatment systems are conventionally adopted for the treatment of wastewater. The rate of stabilization of organic matter is high in case of aerobic process as compared to that in anaerobic process. Modification of these two basic processes has resulted in the development of various types of applied biological treatment systems. These modified treatment systems for the domestic and industrial effluents, are summarized in Table 1.1.

Table 1.1 Major biological treatment processes used for wastewater treatment

(Metcalf & Eddy, 2003)

Type	Common Name	Use
AEROBIC PROCESS: The process in which Biodegradation of waste in presence of oxygen and converts to CO_2 and H_2O.		
Suspended Growth	Activated sludge process Step aeration Aerobic Digestion Aerated Lagoons BOD removal Extended Aeration Oxidation Ditch	BOD removal & Stabilization
Attached Growth	Trickling Filters Rotating Biological Contractor Packed Bed Reactors Roughing Filters	BOD removal Nitrification
Combined Processes	Trickling Filters, Activated Sludge	BOD removal
ANOXIC PROCESS: The process by which nitrate-nitrogen is converted biologically to nitrogen gas in the absence of oxygen. The process is also known as anoxic denitrification.		
Suspended Growth	Suspended growth denitrification	Denitrification
Attached growth	Fixed film denitrification	
ANAEROBIC PROCESS: The process in which Biodegradation of waste takes place in absence of oxygen to form Biogas which contains about 60 % CH_4 and hence can be used as energy supplement.		
Suspended Growth	Anaerobic digestion Two stage Anaerobic Contact process	Stabilization BOD removal
Attached Growth	Anaerobic filter Anaerobic Lagoons (ponds)	BOD removal and stabilization.
Combined	Facultative ponds	BOD removal

Processes	Tertiary ponds Anaerobic facultative Lagoons Aerobic Lagoons	

1.4 COMPARISON OF TREATMENT PROCESSES

Anaerobic treatment processes are being applied to the treatment of wastewater generated by food industry, distillery etc. Anaerobic treatment is the biological stabilization of organic substrate under anaerobic condition. It involves the decomposition of organic and inorganic matter in absence of molecular oxygen. Anaerobic digestion is one of the most widely used biological reactor system for the stabilization of sludge.

Aerobic treatment processes such as activated sludge process, trickling filters, oxidation ponds and aerated lagoons, with more or less intensive mixing devices, have been successfully installed for domestic wastewater as well as industrial waste water treatment. Anaerobic digestion may be followed by aerobic treatment process and hence for some cases this combined treatment process can be seen.

That the anaerobic treatment is an inefficient process is a fallacy, as the experience with sludge digestion suggests. Most of the organic material being treated is not readily susceptible to biological degradation and only about 50% reduction in solids is possible. There are some disadvantages of the anaerobic treatment when it is compared to aerobic treatment.

One of the disadvantages is the slow growth rate of anaerobic organisms, which can result in system failure if a high loss of microorganisms (biological solids) in the effluent occurs. However, it is the slow growth rate and low yield of the anaerobic organisms that results in the production of lower amounts of biological sludge compared to aerobic processes.

Second disadvantage is that the anaerobic process has been considered unsuitable for the treatment of low concentrated wastewaters (COD < 1000 mg/liter) because of the low utilization rate of the substrate at low concentrations.

Thirdly, a relatively high operating temperature has been required for efficient performance of anaerobic digestion. This requires an external heat source, especially in non-tropical regions of the world.

Table 1.2 Merits of anaerobic treatment processes

- Very low cost treatment technology compared to aerobic conventional systems For example, a comparison of energy balance for Aerobic and Anaerobic process for the treatment of a wastewater having following characteristics: flow rate 100 m^3/day, wastewater strength 10 kg/m^3 and temperature 20°C shows that net energy produced by anaerobic digestion as methane produced is 10.4 X 10^6 kJ/d and that for aerobic digestion energy requirement is 1.9X10^6. (Metcalf & Eddy 2003)
- Requires little or no external supplied energy. In fact energy is produced in the form of biogas.
- The technology is flexible and could be applied at any scale.
- The space loading rates applied to the systems are much higher compared to conventional treatment technologies. Organic loading rates of 3.2 to 32 kg COD/m^3.d can be applied in anaerobic processes against the 0.5 to 3.2 kg COD/m^3.d in aerobic processes.
- The higher space loading rates allow smaller reactor volumes and less land requirements.
- The volume of sludge produced under anaerobic conditions (≈ 15%) is significantly lower compared to sludge production under aerobic conditions (≈ 67%) and hence lower sludge handling and disposal costs.
- Fewer nutrients required. Many industrial wastewaters lack adequate nutrients to support aerobic growth. The cost of nutrient addition is much less for anaerobic processes because less biomass is produced.

The anaerobic reactor performance is usually evaluated in terms of process efficiency and stability through estimation of organic matter removal, VFA levels, quality and composition of biogas produced, etc. Methanogenic Activity Test on anaerobic sludge (biomass) has been gaining importance. Initially, these tests were mainly used to

select an adaptable sludge as inoculums but now these tests can also be used for many other purposes, such as to:

1. evaluate the performance of reactor
2. establish the degree of degradability and adaptability
3. estimate maximum applicable loading rate to a certain sludge
4. evaluate batch kinetic parameters.

The acetyl effluent from the alcohol recovery section (column II) as detailed in Chapter 2, Section 2.2 has very high concentration of lower carboxylic acids, viz. formic acid, acetic acid, etc, and ethyl acetate and aldehyde. The COD of effluent fluctuates between 18,000 mg/l and 32,000 mg/l while BOD varies from 9,500 mg/l to 15,000 mg/l. The total generation of wastewater is between 650 and 850 m^3/day. Treatment of this wastewater is a problem, due to poor bio-degradability of the acetic acid. Therefore, it was envisaged to conduct experiments to test the treatability of this effluent in a UASB treatment system.

1.5 OBJECTIVE OF PRESENT STUDY

Based on the requirements of the plant and the availability of an UASB reactor, the following objectives were set

- Treatment of acetyl effluent using anaerobic digestion by performing methanogenic activity test.
- Determination of the optimum COD/VSS ratio in the batch reactor for used in the continuous system.
- Study of reaction kinetics by calculating different parameters at optimum COD/ VSS ratio.
- The efficiency of the waste treatment process.

Chapter 2

ACETYL SECTION AND WASTE WATER CHARACTERISTICS

The present study concentrates on the treatability of the wastewater from the acetaldehyde plant of the JOL, Gajraula. (There are two acetaldehyde plants having two reactors in each plant. The total installed capacity of the plant is 230 MT/day, while the current average production is 220 MT/day).

The acetaldehyde is produced by catalytic vapor phase oxidation of ethanol. Silver mesh is used as the catalyst with air as an oxidizing medium. The reaction takes place at a temperature of 500 – 600 °C and a pressure of 0.25 – 0.4 barg.

The chemical reaction involved in the process is

$$C_2H_5OH + \frac{1}{2} O_2 \rightarrow CH_3CHO + H_2O \qquad \Delta H = -38.3 \text{ MJ/mole} \qquad (2.1)$$

2.1 PROCESS DESCRIPTION OF THE ACETALDEHYDE PLANT

The brief description of the process for the production of acetaldehyde is given below: Fig 2.1 illustrates the process flow diagram of the acetyl section. Alcohol from the alcohol tank is sent to the carburetor where it is mixed with the air and is heated to a temperature of 60 – 70 °C. The quantity of alcohol used in the process is 1.5 Ton/ Ton of aldehyde produced. From carburetor the air and alcohol mixture goes to the super heater where any droplet of alcohol is vaporized and then is fed to the reactor. The reaction is exothermic and the reaction temperature is maintained by bottom product of the distillation column. The reacting mixture from the reactor is sent to the condenser where the stream is partially condensed. The condensed stream contains mainly acetaldehyde and alcohol and is sent to the distillation column along with the absorption column bottom.

The top product from distillation column is pure acetaldehyde it is condensed and a part of it is refluxed and a part is taken as product. The uncondensed stream from the condenser, which contains mainly, uncondensed gases like oxygen and nitrogen, is sent to the absorption column for alcohol and acetaldehyde recovery and the lean

gases are vented through the top. The process also has an alcohol recovery column where alcohol is recovered from various streams and its top is fed to the carburetor and bottom, which is mainly water, is drained out.

The process can be divided into five different stages, namely

1. Carburation stage
2. Reaction stage
3. Absorption stage
4. Alcohol recovery stage
5. Distillation stage

The process flow diagram of the plant is shown in Fig 2.1.

2.1.1 CARBURATION STAGE

Carburetor is a cylindrical shaped equipment. It has long tubes with many small holes in them. Alcohol from the top of the recovery column is fed to the shell side of the carburetor. Also, the fresh alcohol is supplied to it similarly. The level of alcohol in the carburetor is maintained at 50% (approx). Air is fed to the tubes inside the equipment, which get mixed with the alcohol while coming out from the holes. It vaporizes alcohol and the resultant mixture is finally taken to the superheater. The temperature of the mixture is maintained at about 60 – 70 °C by passing steam inside the carburetor. The total content of alcohol in the outlet stream must be maintained to about 87 – 90 % of pure air amount.

In the superheater, the temperature of the mixture is raised to 110 °C so that all alcohol content gets into the vapor form.

ACH PLANT

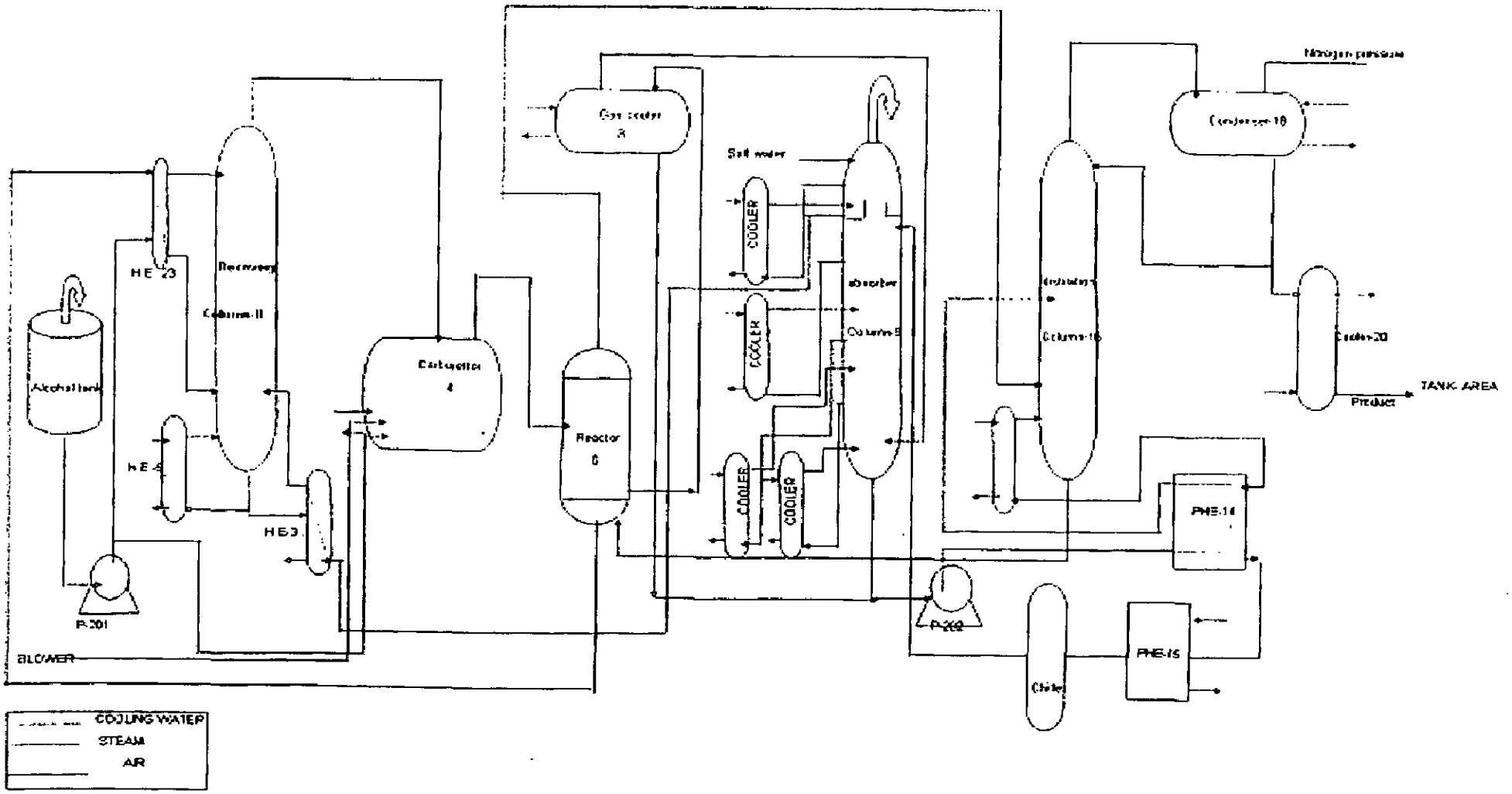

Fig 2.1 Process Flow Diagram of the Acetyl Section

2.1.2 REACTION STAGE

The reactors used in the plant are of shell and tube type in which the superheated mixture of air and alcohol is passed through the shell side or reaction side of the equipment. The silver catalyst is also present in the shell side. The cooling medium, which is the bottom product of distillation column, is passed through the tube side of the equipment.

The temperature and pressure inside the reactor is maintained at 500 – 600 °C and 0.25 – 0.4 bar (gauge) respectively. In the shell side alcohol is converted to acetaldehyde and water vapors. A 40% conversion is obtained and the remaining reactants along with the product mixture are taken to the condenser. Now the condensed stream that mainly contains acetaldehyde, alcohol and water is taken to the distillation column through a heat exchanger (which heats it), while the uncondensed gases are taken to the absorption column.

A part of cooling stream gets vaporized and taken out from the top of the reactor and fed to distillation column. Simultaneously, the liquid stream inside the tubes is sent to the recovery column.

2.1.3 ABSORPTION STAGE

The absorption column is used to get acetaldehyde and alcohol vapors from the uncondensed gases from the reactor. These uncondensed gases are fed to the bottom of the absorption column and the bottom product of distillation column absorbs the acetaldehyde from it. The bottom product, which contains about 14% acetaldehyde, is send to the distillation column Alcohol is absorbed at the top by soft water and the gases are vent out. 4 inter stage coolers are installed with absorption column to maintain the temperature of column within value of 45^0C.

The alcohol and water mixture is sent to the alcohol recovery column containing about 16% alcohol.

2.1.4 DISTILLATION STAGE

In the distillation column the pure acetaldehyde is obtained from the top. The main feed to the column is the condensed material after the reactor and condenser. It contains about 14% acetaldehyde, 48% alcohol and 38% water.

The temperature at the top is 88 ^{0}C. 99.99% pure acetaldehyde is obtained as the top product. The bottom is at a temperature of 115-125 ^{0}C. The bottom product which contains mainly water and alcohol is divided in three streams. namely one stream is reboiled and sent back to the column. second stream goes to the tube side of the reactor as the cooling medium and the third stream is sent to the absorption column for the absorption of acetaldehyde through coolers and chillers.

The whole column is operated under a pressure of 2.5 barg.

2.1.5 RECOVERY STAGE

The recovery column is bubble cap column. In this column alcohol is recovered from the bottom stream of the tube-side of reactor and scrubbed liquid coming from absorption column. Heat is recovered from the stream leaving the reactor through heat exchanger. The heat exchanger preheats alcohol pumped from alcohol tank, which is further fed to the top of the recovery column.

The top product, which contains almost pure alcohol, is sent to the carburetor. The bottom product, which is mainly water, is divided into two streams. One is reboiled and fed to the column and the other is used to heat the scrubbed liquid coming from the absorption column and is drained.

There are four units of acetyl section-each having alcohol recovery column. Bottom product (wastewater) is collected in a pit and then it is pumped. The dimension of the alcohol recovery column is shown in Table 2.1. The block diagram of the recovery stage is shown in Fig 2.2

Table 2.1: Dimension of the alcohol recovery column-II

Diameter (mm)	1400	1400	1700	1800
No. of Trays	50	50	50	50
Tray Spacing (mm)	200	200	200	300

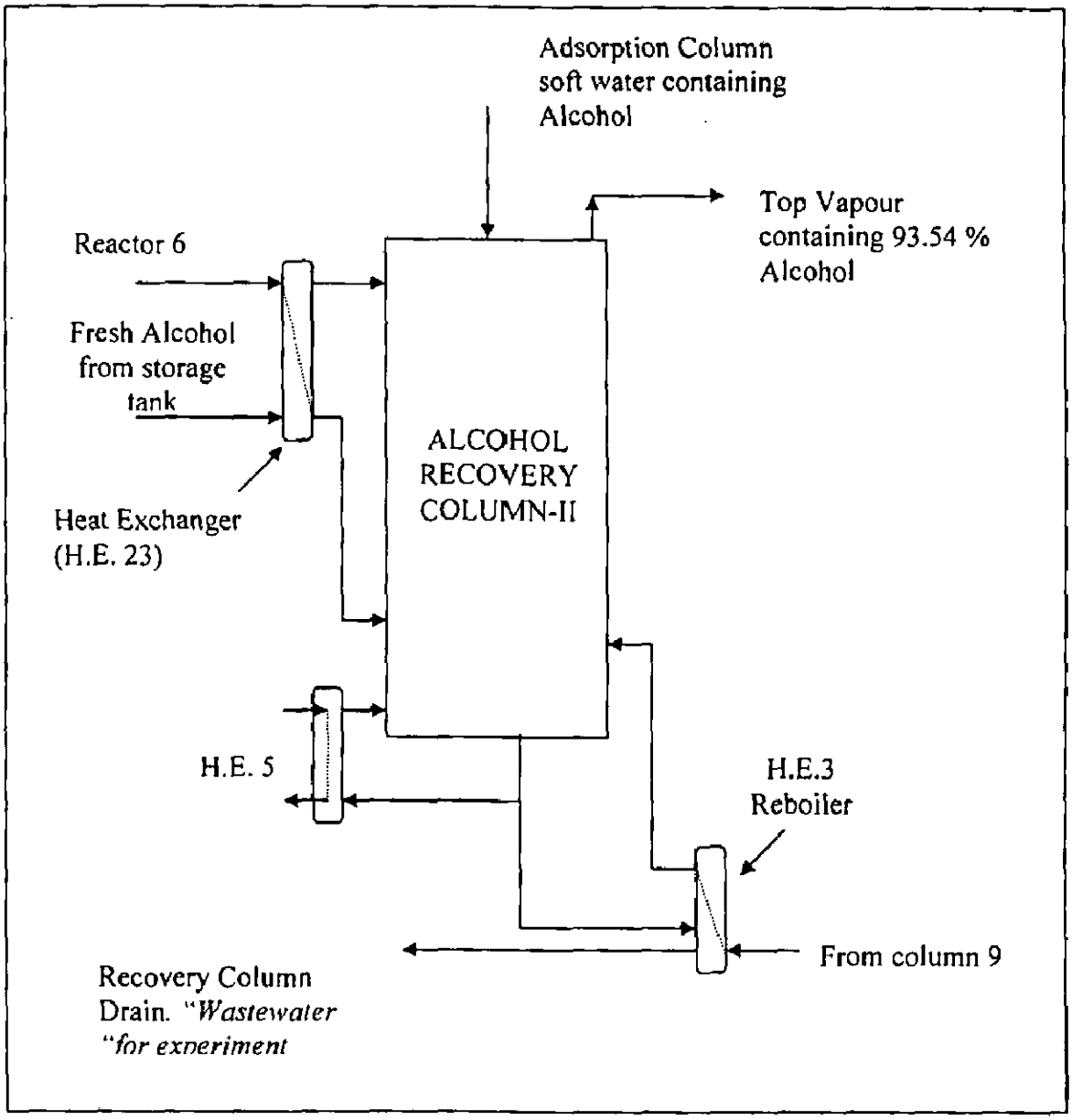

Fig 2.2 Block Diagram of Alcohol Recovery Column-II

(Detailed process flow diagram is shown in Fig 2.1)

2.2 WASTE WATER CHARACTERIZATION

Wastewater (the effluent from the acetyl section) is generated from the alcohol recovery column-II. This wastewater contains 8-10% acetic acid, 1% aldehyde, 1-2% formic acid, and 3-4% ethyl acetate.

Grab samples of wastewater were collected every two hour for seven days. These samples were analyzed for COD, BOD, TSS, TDS and the flow rate of water was determined by a weir system. The characteristics of the composite samples (after mixing all the 24 h samples) were determined. These characteristics are shown in Table 2.2.

Table 2.2: Characteristics of Acetyl Section wastewater on seven days (Composite Samples)

Day	COD (mg/l)	BOD (mg/l)	Ratio BOD/COD	Flow rate (m^3/day)	TSS (mg/l)	TDS (mg/l)
1	24840	11893	0.48	740	156	610
2	25760	12564	0.49	759	136	650
3	27600	12564	0.46	707	180	630
4	20080	9877	0.49	684	232	620
5	31124	14519	0.47	835	132	890
6	18072	10013	0.55	727	208	700
7	26780	11549	0.43	752	148	675

Table 2.3: Characteristics of the composite mixture of organic wastewater on a day

S.No.	Parameter	Value
1	PH	2.45
2	Temperature (°C)	60
3	VFA (mg/l)	37020
4	COD (mg/l)	25066
5	BOD (mg/l)	11926
6	BOD/ COD ratio	0.475
7	TSS (mg/l)	168
8	TDS (mg/l)	687
9	Colour	Colourless

Chapter 3

LITERATURE REVIEW

Adequate water supply and sanitary disposal of wastes are fundamental to a reasonable quality of life. Poor sanitation and lack of access to safe water contribute to many health issues and deaths. The explosion of industrialization and urban growth worldwide is polluting groundwater and degrading the quality of surface waters by overloading them with more wastewater-borne organic material than can be assimilated naturally. The key issues that constrain wastewater treatment in most developing countries are difficulties in managing the relatively few facilities that exist, followed closely in importance by the high cost of building conventional treatment facilities.

India, which had sufficiently rich water resources with a vast network of rivers and alluvial plains holding a plenty of groundwater is rapidly becoming a water starving nation. Increase in population and urbanisation are stressing the water resources to an irreversible extent both by consumption and contamination. The urban India has become a massive and perhaps a frightening reality as far as waste management is concerned. According to a Central Pollution Control Board (CPCB) Sewage Newsletter (2005), in India for the year 2003, out of 22,900 MLD of domestic wastewater generated, only about 5,900 MLD (26%) is treated before letting out, the rest i.e., 17,100 MLD is disposed of untreated. It is estimated that the total cost for establishing treatment system for the entire domestic wastewater would be around Rs. 7,560 crores. Operation & maintenance cost would be in addition to this cost. The disadvantages of conventional treatment methods that are most prominent in developing countries include high power consumption, vulnerability to power outages, high maintenance requirements and the need for close supervision by skilled operators.

The future scenario of India's wastewater management has serious challenges as it has been estimated by Central Pollution Control Board of India that by 2051 it would be required to treat 132000 MLD of wastewater generated by a population of 1093 million (CPCB Sewage newsletter, 2005). This emphasizes the urgent need for alternative

technologies, which are energy efficient, economical and simpler to operate and maintain along with good treatment efficiencies.

3.1 ANAEROBIC TREATMENT TECHNOLOGY

Although the aerobic processes have well developed so far than the anaerobic processes, they demand for high capital costs and more number of skilled manpower for operation and maintenance. This is primarily because of their requirement of external source of oxygen demanding the installation and operation of aerators. Adding to this are the costs for handling, treatment and disposal of the excess sludge produced at the end of aerobic treatment. Anaerobic digestion by its inherent process nature does not require any external oxidant and produce several times lesser excess sludge with the production of biogas with good methane content. The approximate carbon flow during aerobic degradation and anaerobic degradation is shown in Table 3.1.

Table 3.1 Carbon flow during (A) aerobic degradation in an activated sludge system under (a) saturating and (b) limiting substrate supply and during (B) anaerobic degradation. Gallert and Winter (2004).

(A) Aerobic degradation:
(a) Saturating substrate supply = high-load conditions
1 unit substrate carbon ⟶ 0.5 units CO_2 carbon + 0.5 units cell carbon
(b) Limiting substrate supply = low-load conditions
1 unit substrate carbon ⟶ 0.7 units CO_2 carbon + 0.3 units cell carbon
(B) Anaerobic degradation:
1 unit substrate carbon ⟶ 0.95 units (CO_2 + CH_4) carbon + 0.05 units cell carbon

In spite of all these merits the anaerobic processes rather got a delayed start in full scale applications due to various apprehensions like high bacterial sensitivity to some environmental conditions (mainly pH, temperature, and toxic compounds), long starting processes, and the production of malodorous compounds. But at present most of these perceived disadvantages have vanished almost completely. Except for some industrial wastewaters chemical addition for pH maintenance in the optimum range is not needed for others including domestic wastewater (Seghezzo et al., 1998). Anaerobic bacteria have been found to adapt quite easily to psychrophillic conditions and high rate anaerobic treatment has been achieved (Kato et al., 1997; Singh and Viraraghavan, 2003; Lew et al., 2003) with some experiences with sewage also (Wang 1994; van der Last and Lettinga, 1992).

An adequate construction and a proper operation and maintenance will eliminate completely the malodors from anaerobic reactors. The presence of dissolved oxygen which was believed to inhibit the methanogens and acetogens was found to be less detrimental than presumed especially because of the granular sludge where the methanogens inside the aggregates are well protected (Kato et al., 1997). With most of these perceived threats vanishing anaerobic treatment methods are all set to dominate the wastewater treatment technologies in the near future especially in developing countries for all types of wastewaters under various environmental conditions (Letting et al., 1997).

3.1.1 High-rate anaerobic treatment

Anaerobic reactors may be classified as suspended growth when the bacteria are suspended in the bulk liquid or attached film when the bacteria are attached as dense films to solid media within the reactor. Both types of reactors may be further categorized according to the efficiency of digestion as low and high rate. The septic tank is the oldest and most familiar low rate anaerobic reactor. Others include the Imhoff tank, the anaerobic filter, anaerobic ponds and biogas-producing digesters that are typically used in farm waste management to dispose of manures and crop residues and to provide a fuel for on-farm use and composted sludge as a soil conditioner (Journey and Mcnivan, 1996). However due to the presumed drawbacks as mentioned earlier the anaerobic treatment

methods were not seen suitable for large-scale treatment. But the things changed in the past two decades with the advent of the high-rate systems.

3.1.2 Various high-rate reactors

High-rate systems are reactor systems in which high retention of the viable biomass is possible under high loading conditions providing a good contact between the incoming wastewater and the retained sludge. For achieving this concept of high retention of biomass and good contact time it becomes very much obvious that decoupling of the hydraulic and solids retention times is essential (HRT<<SRT). Otherwise the reactor volume will have to be too large to achieve the desired retention. This decoupling was possible because of the dense granules in which the main groups of anaerobic bacteria live in syntrophic associations closely enough minimizing the distance for mass transfer. The dense granules have good settling properties and are more easily retained in a suspended growth reactor at higher flow velocities than less dense associations of bacteria. Higher flow velocities imply shorter average hydraulic retention time and correspondingly smaller reactor volume (Hulshoff Pol et al., 2004, Journey and Mcnivan, 1996, Mahmoud, 2003).

Different configurations of high-rate anaerobic reactors have come up (Metcalf and Eddy, 2003) which are capable of treating a wide range of wastewaters at different conditions. Upflow anaerobic sludge blanket (UASB) concept has become very popular and is most promising though there is a place left for new configurations (Lettinga et al., 1997). The high rate attached film reactor type has not so far been demonstrated for municipal wastewater treatment in a typical developing country setting. The main reason seems to be the relatively more demanding operational requirements than the UASB, including sophisticated feed inlet distribution, high rates of effluent recycle and the requirement for a primary treatment step upstream of the reactor (Journey and Mcnivan, 1996). The Expanded Granular sludge bed (EGSB) system is also a promising concept in which very high upflow velocities are employed and are found to be successful for treating low strength wastewaters (Kato et al., 1997,Wang, 1994) at low temperatures due to

elimination of dead zones and better sludge-wastewater contact (Seghezzo et al., 1998; Seghezzo, 1997)

3.2 THE UASB REACTOR SYSTEM

The popularity and efficiency of the UASB system lies in its capability to retain solids effectively without any media. The formation of anaerobic granular sludge can be considered as the major reason of the successful introduction of the UASB reactor concept. This granulation process allows loading rates in UASB reactors far beyond the common loading rates applied so far in conventional activated sludge processes. The resulting reduction in reactor size and required area for the treatment leads to lower investment costs in addition to the reduced operating costs due to the absence of aeration. The superior settling characteristics and high specific methanogenic activity of the granules are the major reasons for the high loading rates (Hulshoff Pol., et al., 2004).

3.2.1 The UASB concept

In the UASB concept, treatment is carried out in an upflow reactor with a feed inlet distribution system at the bottom of the reactor and gas-liquid-solids (GLS) separator at the top. The wastewater is evenly distributed over the reactor bottom and flows upward through a bed of anaerobic sludge. During passage through the sludge bed, suspended solids are entrapped and biodegradable material is consequently digested. Dissolved organics are removed from the solution by the anaerobic bacteria and converted into biogas while a small fraction of organics is utilized in production of new bacterial biomass. The biogas provides a gentle mixing in the sludge bed therefore no mechanical mixing is required. In the upper part of the reactor the produced biogas is collected in the GLS separator from where it is withdrawn. The water-sludge mixture enters a settling compartment where the sludge can settle and flow back into the digestion compartment. After settling the treated water is collected in gutters and discharged. A salient feature of the UASB concept is that anaerobic flocculent or granular type of sludge inherently has or will attain good settling properties provided the process is operated in the proper way

during the reactor start-up (Draaijer et al., 1992). Fig. 2.1 shows a schematic cross-sectional view of a UASB reactor.

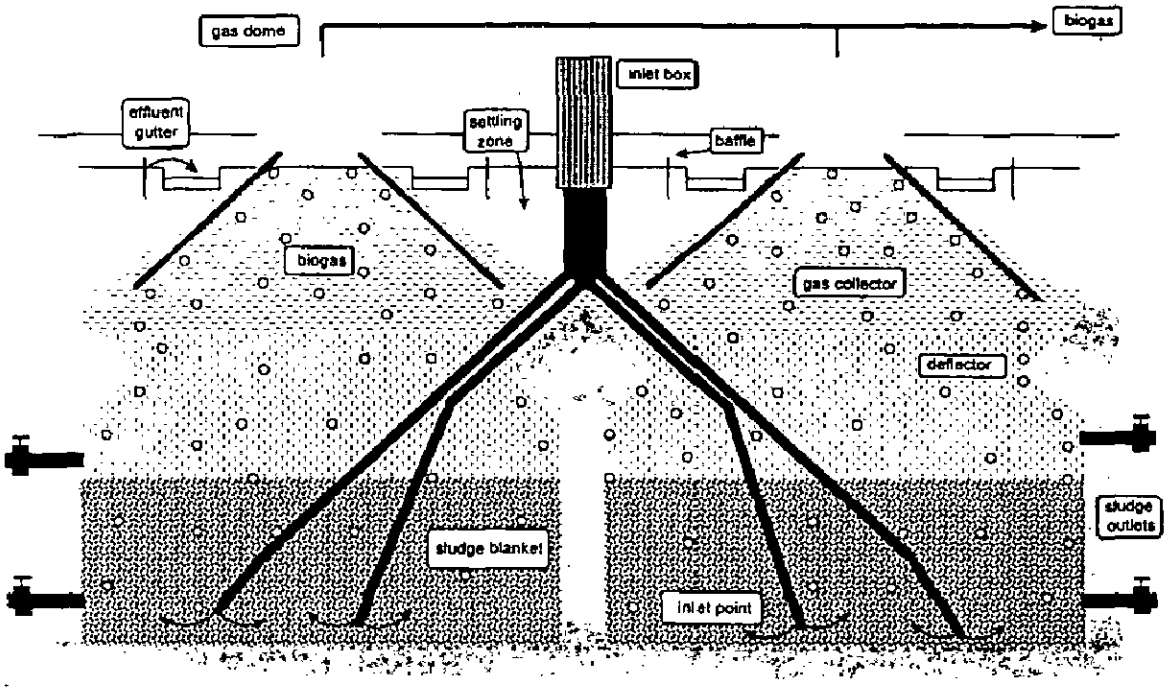

Figure 2.1 Schematic cross-sectional view of a UASB reactor

(Journey and McNivan, 1996.)

3.2.2 Design considerations

The functioning of UASB systems depends on both physical parameters and biological processes, which determine the final removal efficiency and conversion of organic compounds. The mechanisms are complex and depend on various interrelated operational parameters. The influent characteristics, reactor operational conditions and the sludge bed characteristics are the major influencing parameters as reviewed by Mahmoud et al., (2003).

The UASB reactor is designed around two main criteria: hydraulic retention time (HRT), the average amount of time that the liquid part of the wastewater stays in the reactor, and solids retention time (SRT), the average residence time of the solids in the reactor. For a wastewater with high concentrations of suspended solids, sedimentation of the solids is the main concern. The design criteria are largely dictated by the maximum upflow

velocity that the solid particles can withstand before being washed out of the reactor, generally between 0.5 and 1.0 m/hour for municipal effluents (Campos and Anderson, 1992; Mahmoud et al., 2003). The solids retention time should be long enough to allow the growth of enough anaerobic bacteria to digest the bulk of the organic material in the wastewater. The optimal SRT will determine at what HRT the UASB can be operated, and the HRT will dictate the volume of the reactor.

The critical elements of the UASB reactor design are the inlet distribution system for uniform distribution of the wastewater without any dead spaces, the Gas-liquid-solid (GLS) separator and effluent withdrawal design for restricting the sludge washout (Metcalf and Eddy, 2003; Lettinga and Hulshoff Pol, 1991; Draaijer et al., 1992). The sludge blanket concentration and height are an important aspect of UASB reactor design. It regulates the solid concentration reaching the GLS separator. By efficient GLS design and an adequate sludge waste strategy the SS and organic matter removal can be improved (Cavalcatni, 2003). The maximum organic load, which a reactor can assimilate, depends on proportioning of the reactor height into the bed and the blanket (Narnoli and Mehrotra, 1997). The sludge bed height was also found to influence short-circuiting flow. Chowdhary and Mehrotra (2004) showed short-circuiting increasing from 7 to 25% approximately on changing the bed height from ≈0.77 to ≈0.1m.

Anaerobic treatment is merely efficient for removing biodegradable organic matter, generally not for phosphate, ammonia and certainly not for sulphide. Therefore generally, depending upon the restriction set for effluent discharge, some adequate post treatment has to be applied for removing these compounds and remaining organic pollutants including also dispersed solids (Lettinga and Hulshoff Pol., 1991; Draaijer et al., 1992; Vieira and Garcia, 1992). A typical anaerobic enhanced primary effluent has substantial residual oxygen demand, mostly from the reduced form of nitrogen, ammonia. The readily oxidizable residual oxygen demand may be dealt with in an additional aerobic treatment step or conversion to plant biomass in an integrated treatment and production system. Pond technologies do not require any energy supply and can polish an anaerobic enhanced primary treated effluent and, with appropriate retention time, can remove pathogens to an acceptable level before discharge into a receiving stream or before reuse for irrigation or groundwater recharge (Journey and Mcnivan, 1996).

3.3 EFFICIENT SOLIDS RETENTION IN UASB REACTORS

Particulates or the suspended solids in wastewater can be degraded anaerobically only if they are efficiently retained physically by adsorption, settling or entrapment in the sludge bed. The particles present in wastewater are often separated as the suspended and colloidal part based on the particle size respectively larger than 4.4 μm and between 0.45 μm and less than 4.4 μm, although the size range for colloidal particles is not in agreement with the definition as used in colloidal chemistry (Elmitwali et al., 2001, Zeeman and Lettinga, 1999).

Wang et al., 1995 found that the removal of colloidal COD in anaerobic conditions being lower than under aerobic conditions. Zeeman and Lettinga (1999), report that colloidal COD represents 60 to 80% of the effluent COD_T of an anaerobic reactor. Elmitwali et al., (2001) studied the biodegradability of different fractions of domestic sewage found high methanogenesis of the colloidal fraction in domestic sewage (86±3 %) at 30^0C showing that the low removal of COD_{col} in continuous anaerobic reactors is due to low physical removal than biodegradability. Further he also observed that the hydrolysis of suspended particles results in more inert COD_S than the colloidal particles. These results and the present removal efficiencies of the full scale plants- which is normally around 75% for solids removal shows that further enhancement of solids retention is possible chiefly by improved phase separator design.

Cavalcatni, 2003 conducted experiments to show the improvement in solids retention when a modified phase separator is used instead of the conventional separator – the triangular prism with open base. He used parallel plates of depth 0.35m at spacing 0.07m set at an angle of 45^0 above the conventional phase separator in an UASB reactor to act as a high-rate settler and compared with the operation of an UASB with the conventional phase separator only at HRTs of 12 to 1.5 h. The reactor with the parallel plates was found to double the treatment efficiencies.

The modified design allowed high sludge ages even at low retention times which can allow higher efficiencies at lower reactor volumes. He also emphasized an adequate planned sludge wastage frequency so that the solids in the effluent can be controlled. It

was found that once the sludge holding capacity of the reactor is reached the net sludge production goes in the effluent.

3.4 ANAEROBIC DEGRADATION OF PARTICULATES

The organic polymers present in the domestic sewage are chiefly carbohydrates, lipids and proteins and sometimes composed of lignin (Zeeman et al., 1997; Miron et al., 2000). The anaerobic degradation of the organic polymers involves a series of steps. Organic polymers are firstly hydrolyzed into smaller subunits that can be assimilated by bacteria. This process is catalyzed by extra cellular enzymes from acidogenic bacteria, e.g., lipids are broken down to long chain fatty acids (LCFA) by lipases; proteins to amino acids by proteases and peptidases; cellulose to polysaccharides by cellulases and polysaccharides to sugar monomers. The monomers or smaller molecules from hydrolysis are converted by acidogenic bacteria into short or branched-chain fatty acids, alcohols, lactic acids, CO_2, H_2 and NH_3. The fatty acids, including LCFAs from lipid hydrolysis and other products of acidogenisis are further converted into acetate, CO_2 and H_2. Finally CH_4 is formed via two types of reaction: hydrogenotrohic ($4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$) and acetotrophic ($CH_3COOH \rightarrow CH_4 + CO_2$). The reactions in the series are carried out by different groups of bacteria some of which coexists in syntrophic relations, i.e., the product of one species assimilated by another group of bacteria. For interspecies hydrogen transfer between the obligate H_2 producing acetogens and the H_2 consuming methanogens is crucial for the degradation of short and long chain fatty acids.

3.5 ASPECTS OF ANAEROBIC HYDROLYSIS

The hydrolysis of the particulate matter is the overall rate-limiting step in the anaerobic degradation. The rate of hydrolysis of the organic polymers is sensitive to various factors like pH, temperature, detention time, substrate type and concentration, available biomass, particle size of the substrate and even the type and amount of hydrolysis intermediates (Eastman and Ferguson, 1981; Noike et al., 1985; Mahmoud et al., 2004).

3.5.1 Effect of pH on hydrolysis

The optimum pH for the hydrolysis of particulates, carbohydrates and lipids is near neutral. Eastman and Ferguson (1981) found that the hydrolysis rates of both nitrogenous and carbonaceous COD increase with the increase of pH from 5.1 to 6.67 during the digestion of primary sewage sludge at 35^0C. Diniopoulou et al. (1987) studied anaerobic acidogenisis of a meat extract based complex wastewater and recommended pH 7 as the optimum for maximum acidification at 35 ± 1^0C.

Gallert and Winter (2004) observed that the hydrolysis of carbohydrates proceed faster at slightly acidic condition (pH < 7). The optimal hydrolysis of proteins, however, required a neutral pH or weakly alkaline condition (pH~ 7.5-8). Palenzuela-Rollon (1999) monitored the effect of pH on the hydrolysis of proteins and lipids in fish processing wastewater. They found that the hydrolysis of proteins occured at all pH values (4 <pH<8) with the rate of hydrolysis higher at pH $\geq$ 6. Lipid hydrolysis required the presence of methanogens or hydrogen scavengers and hence occurred at pH $\geq$ 6.

3.5.2 Effect of temperature on hydrolysis

As the growth rate of microorganisms is generally higher at thermophilic conditions than at mesophilic and psychrophilic conditions, the hydrolysis rate falls with the fall of temperature (Lettinga et al., 2001). Wang et al. (1995) showed increasing rate of hydrolysis of domestic wastewater with increase in temperature during anaerobic digestion. He estimated the first-order hydrolysis rate constants as $0.007d^{-1}$, $0.024d^{-1}$ and $0.105d^{-1}$ at temperatures 10 ^{0}C, 20 ^{0}C and 30 ^{0}C, respectively. The slow hydrolysis rates at low temperatures may lead to the accumulation of solids. Zeeman and Lettinga (1999) reported decreasing hydrolysis of retained solids from 40 % to 5 % for a temperature fall of 25 ^{0}C to 15 ^{0}C at the same solid retention time (SRT) of 15 days.

2.5.3 Effect of seeding

Wang et al. (1995) carried out batch experiments to compare the hydrolysis of fresh raw sewage and the effluent of a Hydraulic Up-flow Sludge Blanket (HUSB) reactor, which he considered as a seeded sewage. He found the hydrolysis rate of HUSB treated sewage much higher than that of fresh raw sewage. He attributed the higher hydrolysis of seeded sewage to the higher concentration of hydrolyzing bacteria or a higher concentration of methanogenic bacteria reducing the concentration of intermediates. Apparently, accumulation of hydrolysis products has an inhibitory effect on hydrolysis. In a continuous reactor operated at low HRT this accumulation of the intermediates and hence their inhibition should be averted.

Banister and Pretorius (1998) studied the effect of age and size of seed inoculum on the rate of VFA production. He found that increasing the seed population of facultative microorganisms, capable of acid fermentation by addition of partially fermented sewage to fresh primary sludge significantly boosts the VFA yields, which would allow reduction in retention time. A 3-day-old seed gave more than double the VFA yields of unseeded sludge. However, he did not find any significant improvement in increasing the size of the seed from 10 % to 20 %. He observed lower VFA yield in another batch with same solid concentration and same seeding. He attributes this to the higher temperatures that prevailed during the later batch probably enhancing methanogenic activity and subsequent removal of VFAs.

Hutnan et al. (1999) compared the hydrolytic activity of sludge from different compartments of an ABR and an UASB. He found the hydrolytic activity in the first compartment of ABR much higher (36.8 kg/kg/d) than that of UASB sludge (3.5 kg/kg/d). The hydrolysis of solids could be enhanced if the wastewater is seeded with sludge from the first compartment of an ABR.

The adoption of an appropriate seeding with good hydrolytic activity would boost the hydrolysis rate.

3.5.4 Oxygen concentration

The hydrolysis rate was also found to get affected by the oxygen concentration present in the system. Wang et al. (1995) compared the hydrolysis rates at aerobic, anaerobic and micro-aerophilic conditions for raw domestic wastewater in simulated batch experiments. They found that the values of first-order hydrolysis rate constants increase in the order of anaerobic, microaerophilic and aerobic conditions. At 30 ^{0}C the estimated rate constants for aerobic, micro-aerophilic and anaerobic conditions were 0.612 d^{-1}, 0.216 d^{-1} and 0.105 d^{-1}, respectively.

3.5.5 Hydraulic retention time

HRT is a key parameter for the performance of a hydrolysis-acidification reactor, since it determines the solids solubilisation efficiency and the degree of acidification of the influent (Dinopoulou et al., 1988). The maximum process efficiency is usually obtained by operating the acidogenic step at short HRT, thus preventing the development of the methanogens (Eastman and Ferguson, 1981).

The vital role of HRT in the hydrolytic reactors is due to the fact that they affect the retention of the suspended solids, as higher up-flow velocities at low HRTs would wash away the solids as shown by Goncalves et al. (1994) and Ligero et al. (2001). These authors suggest optimal upflow velocities of around 0.9 m/h. Further, lower upflow velocities of about 0.6 m/h have been found to allow biogas formation. The HRT is also significant in the way that it decides hydrolysis of the dissolved polymers (Zeeman and Sanders, 2001).

3.5.6 Solids retention time

The solids retention time in hydrolytic reactors should be sufficient to achieve maximum hydrolysis without methanogenic conditions. Miron et al. (2000) studied the effect of SRT on the digestion of primary sludge (settled solids of domestic sewage) at a

temperature of 25 ^{0}C. Till SRT of 8 days, the acidogenic conditions prevailed with negligible biogas production.

Approximately 20% and 60% hydrolysis of the biopolymers was observed under acidogenic and methanogenic conditions. The carbohydrates and proteins are found to undergo substantial hydrolysis in the absence of methanogenesis but the lipid required longer SRTs and methanogenic conditions for sufficient hydrolysis (Mahmoud et al., 2004; Palenzuela-Rollon, 1999).

In general, it can be said that in the pre-hydrolysis reactors sufficient carbohydrate and protein hydrolysis can be achieved while lipid hydrolysis would not be substantial due to the non-methanogenic conditions. But, on the other hand, efficient retention of the lipids in the first-step would enhance methanogenesis in the second-step as explained by Palenzuela –Rollon (1999).

3.5.7 Effect of Mixing On Hydrolysis

Guerrero et al. (1999) studied the effect of mixing at 400 rpm on the hydrolysis rates of wastewaters from a fishmeal-processing factory by conducting batch assays at a temperature of 37 ^{0}C. It was observed that in the presence of stirring the solubilisation process proceed faster, around 0.08 g VSS/d during the first 25 days, whereas, afterwards no significant solubilisation was detected. In contrast, the solubilisation rate in the absence of stirring remained constant during the whole operation, around 0.04 g VSS/d. The VSS removal achieved at the end of the two assays amounted to 57 and 55% respectively. The effect of stirring on the hydrolysis was not significant however stirring increases the rate of hydrolysis.

Banister and Pretorius (1998) conducted anaerobic batch studies on primary sludges under mixed and unmixed conditions The VFA yields increased from 0.04 to 0.07 in 0.09 to 0.15 mg VFA-COD/mg COD in the mixed and unmixed reactors, respectively. Though there is no clear explanation for this negative effect of mixing on fermentation, the authors opined that the reduction of fermentation may be due to following:

i. mixing may allow for more contact with the inhibitory substances,

ii. keeping the solids in suspension may also disturb the microenvironment where fermentation is taking place within the reactor,

iii. mixing may allow for oxygen entrapment inhibiting fermentation or allowing some of the VFA to be metabolized,

iv. slow diffusion flow regimes enhance hydrolysis of carbohydrates and proteins and thus demanding longer times for the enzymes to diffuse and penetrate the macromolecular structure of the substrate.

Since carbohydrates and proteins are the primary sources of organic substrate in domestic raw sludge, it would appear that the absence of mixing or slow/intermittent mixing regimes supported hydrolysis and higher VFA production yields in primary sludge.

These batch studies show that mixing might not enhance hydrolysis significantly or may inhibit hydrolysis. But in the hydrolytic reactors it is vital to ensure that no accumulation of hydrolysis and acidification products occur to prevent biogas formation. So a slow intermittent mixing would be essential. The intermittent slow mixing, either mechanical (Goncalves et al., 1994) or hydraulic by sludge recirculation (Ligero et al., 2001; Barajas et al., 1998) has been found advantageous.

3.5.8 Particle size and surface to volume ratio

The surface of substrate available for the enzymatic attack is an essential factor in hydrolysis of substrates. The branching and helical structure of starch is found to facilitate hydrolysis of starch and hence faster than cellulose. However starch also forms grains sometimes may be up to 1mm diameter, thousand times bigger than bacteria, and hence an unfavorable surface to volume ratio. Celluloses when lignin encrusted has fewer surfaces for enzymatic attack and hence show poorer hydrolysis than celluloses in crystalline forms. The low surface availability thus retards hydrolysis even when the enzymes catalyzing the hydrolysis are present in sufficient amounts (Gallert and Winter, 2004). Accounting for the particle sizes in a wastewater is rather difficult which restricts the application of the surface based hydrolysis kinetics to complex wastewaters. The anaerobic hydrolysis kinetics is discussed below.

3.5.9 Anaerobic hydrolysis kinetics of particulates

Many authors describe the hydrolysis with first order kinetics based on biodegradable substrate at constant pH and temperature (Eastman and Ferguson, 1981; Mahmoud et al., 2004, Wang et al., 1995):

$$\frac{dX}{dt} = -k_h.X \tag{3.1}$$

with:

X = concentration of bio-degradable substrate (kg/m^3),

t = time (days),

k_h = first order hydrolysis constant (1/day).

The first order relation is however an empirical relation. Eastman and Ferguson (1981) explain that the first order kinetics reflects the cumulative effect of all the microscopic individual processes during the anaerobic digestion. Large particles with a low surface to volume ratio would be hydrolyzed more slowly and, hence, even when the reactor conditions and substrate type are kept constant, different k_h values can be found due to changes in the particle size distribution of the substrate (Hills and Nakano, 1984; Chyi and Dague, 1994- as referred by Zeeman and Sander, 2001).

To gain more insight into the hydrolysis process some authors have tried to develop and/or verify a deterministic model for the anaerobic hydrolysis (Vavilin et al., 1996). In this model, it is assumed that the substrate particles are completely covered with bacteria that secrete an excess of hydrolytic exo-enzymes during digestion. The hydrolysis rate is therefore, constant per unit area available and the hydrolysis constant, k_{sbk}, is not affected by the particle size of the substrate. The model is referred to as the Surface Based Kinetic (SBK) model (Zeeman and Sanders, 2001).

$$\frac{dM}{dt} = -k_{sbk}.A \tag{3.2}$$

with:

M= mass of substrate (kg),

t = time (days)

K_{sbk} = surface based hydrolysis constant (kg/m^2 day),

A = surface available for hydrolysis (m^2).

Sanders et al. (2000) presented a mathematical description of the surface related hydrolysis kinetics for spherical particles in a batch digestion and a verification of this model with particulate starch as a substrate. CH_4 production and particle size distribution (PSD) were determined in time during batch digestion of two starch fractions with different PSD and fitted with the model.

The theoretical PSD, calculated based on CH_4 production, showed good similarity with the experimental PSD, proving that the SBK model is capable to describe the anaerobic hydrolysis of particulate substrates and that the amount of substrate surface available for hydrolysis is the essential factor determining the hydrolysis rate. Hydrolysis of particulate polymers can be described by surface based kinetics, but for use in practice the determination of the available surface is so complicated that the empirical first order relation is advised.

Borja and Rincón (2003) had demonstrated anaerobic digestibility of two-phase olive mill solid waste (OMSW) with a wide range of organic loading rates (OLR), hydraulic retention times (HRT) and feed chemical oxygen demand (COD) concentrations (S_0). Methane production is directly correlated with COD reduction. A reduction of 1 g COD is equivalent to the production of 0.35 liter of methane at STP. Knowing the COD loading to the reactor and the volume of methane produced, the remaining COD in the digester can be calculated. If B denotes the volume (in litres) of methane produced under normal conditions of pressure and temperature per gram of substrate (COD) added to the digester, and B_0 is the volume of methane produced under normal conditions of pressure and temperature per gram of substrate added at infinite retention time or for complete utilization of substrate, the biodegradable COD in the reactor will be directly proportional to $(B_0 - B)$, and B_0 will be directly proportional to the biodegradable COD loading.

Values for the kinetic parameters μ_{max} and K can be obtained from the intercept and the slope of the adjusted lines. Thus, according to equation

$$\Theta = \frac{1}{\mu_{max}} + \frac{K}{\mu_{max}} \frac{B}{(B_0 - B)} \qquad (3.3)$$

Thus, by first calculating the value of B_0, the graph of Θ versus $B/(B_0-B)$ produces a straight line with an intercept of $1/\mu$max and with a slope of K/μ_{max}.

μ_{max} = 1/intercept, and K = slope/intercept. Values for the two kinetic parameters (μ_{max} and K) with their confidence limits at 95%.

3.5.10 Specific Efficiency

Lawrence et al (1970) suggested the application of process kinetics to design of anaerobic processes. The efficiency of waste treatment process was given by

$$E = \frac{100(S_0 - S_1)}{S_0} \qquad (3.4)$$

3.6 METHANOGENIC ACTIVITY TEST

Isa et al (1993) established a simple procedure of activity test. Methanogenic activity test refers to the rate at which methanogens utilize their substrates to produce CH_4 and CO_2. The importance of the test is in its widespread uses, which include;

- Reactor performance study
- Stimulation and inhibition studies
- Biodegradability and adaptability
- Determinations of kinetic coefficient like yield-coefficient, substrate utilization rate and half velocity constant.

and had given a simple procedure for the determination of methanogenic activity of the sludge. It can be used with proper methodology for conducting studies of anaerobic process including treat-ability of different wastes and the determination of kinetic coefficients.

In an activity test, substrate and microbial sludge should be in such proportions that the former remains unlimited. Using Monod's equation, substrate utilization rate is obtained as,

$$dS / dt = -k_{max} S^*X / (k_s + S) \qquad (3.5)$$

Where,

S = substrate concentration mass per unit volume

t = time

k_{max} = max substrate removal rate constant per unit time

$= \mu_{max}/Y$

μ_{max} = max, specific growth rate constant, per unit time

Y = yield coefficient

$= - dX/dS$

k_s = half velocity constant, mass per unit volume

X = micro-organism concentration, mass per unit volume

For $S>>k_s$, $(k_s + S)$ is approximately equal to S, there by making right hand side of above expression a constant for a given value of X. This implies that any increase in substrate concentration beyond this point will not change the substrate utilization rate. Estimation of this rate yields the Activity of sludge sample.

Jawed and Tare (1999) presented the application of simple methanogenic activity test procedure to monitor reactor biomass in terms of relative population level of methanogenic species by using two different test substrates. The observed value of activity (g CH_4-COD/g VSS-d) of sludge correlates well with the reactor performance and clearly demonstrate change in relative pollution levels of methanogenic species with changing operational conditions.

Nopharatana et al. (1997) have demonstrated the use of an activity test to evaluate stages of a sequencing anaerobic digestion process. Ideally, the activity of microbial groups can be measured to identify the slowest steps in the degradation process. Two sequencing experiments were studied. The activity assays, indicated that the microbial concentrations in the OLD reactor in that experiment were low. It was confirmed that using leach-ate from the fresh-waste reactor to inoculate another waste bed when its cellulose activity peaked (i.e. a few days after sequencing was terminated), could further shorten start-up periods in the new waste bed.

Chapter 4

EXPERIMENTAL PROCEDURE

4.1 EXPERIMENTAL SET UP

4.4.1 Apparatus

The methanogenic activity test of wastewater was carried out at lab scale in a 500 ml serum bottle with all necessary arrangements such as leak proof rubber tube, 22 gauge and 3.5 cm long needles, milliliter syringes. These bottles were kept in a thermostat chamber at 35°C. The schematic diagram of the experimental setup is shown in Fig 4.1 and the lab scale setup is shown in Fig 4.2. The methane produced in the experiment was collected by the downward water displacement system in a 500 ml bottle containing NaOH (aqueous) solution (5 M). NaOH solution is used as it absorbs CO_2 and allows CH_4 to pass through it. The methane produced is the displaced volume of water in the bottle.

4.1.2 Preparation of Nutrient solutions

The nutrient solution (macro and micro) used in the reactor (for the activity test) was prepared by using different chemicals as given in Table 4.1. These chemicals were of laboratory reagent grade supplied by M/s s.d.Fine Chemicals Limited, Mumbai. The composition of solutions was ascertained from the previously reported values (Isa et al 1993, Kus and Wiesmann 1994, Borja et al 2003). These solutions are added as 1.0 ml/l of the reaction mixture.

Table 4.1 Lists of Chemicals for the Preparation of Nutrients

Micro Nutrients		Macro Nutrients	
Chemical	**Quantity (mg/l)**	**Chemical**	**Quantity (g/l)**
$FeCl_3 \cdot 4H_2O$	2000	NH_4Cl	170
$CoCl_2 \cdot 6H_2O$	2000	KH_2PO_4	38
$MnCl_2 \cdot 4H_2O$	500	$CaCl_2 \cdot 2H_2O$	8
$CuCl_2 \cdot 2H_2O$	30	$MgSO_4 \cdot 4H_2O$	9
$ZnCl_2$	50		
H_3BO_3	50		
$NiCl_2 \cdot 6H_2O$	50		
EDTA	1000		
Yeast Extract added as 200 mg/l of reaction mixture.			

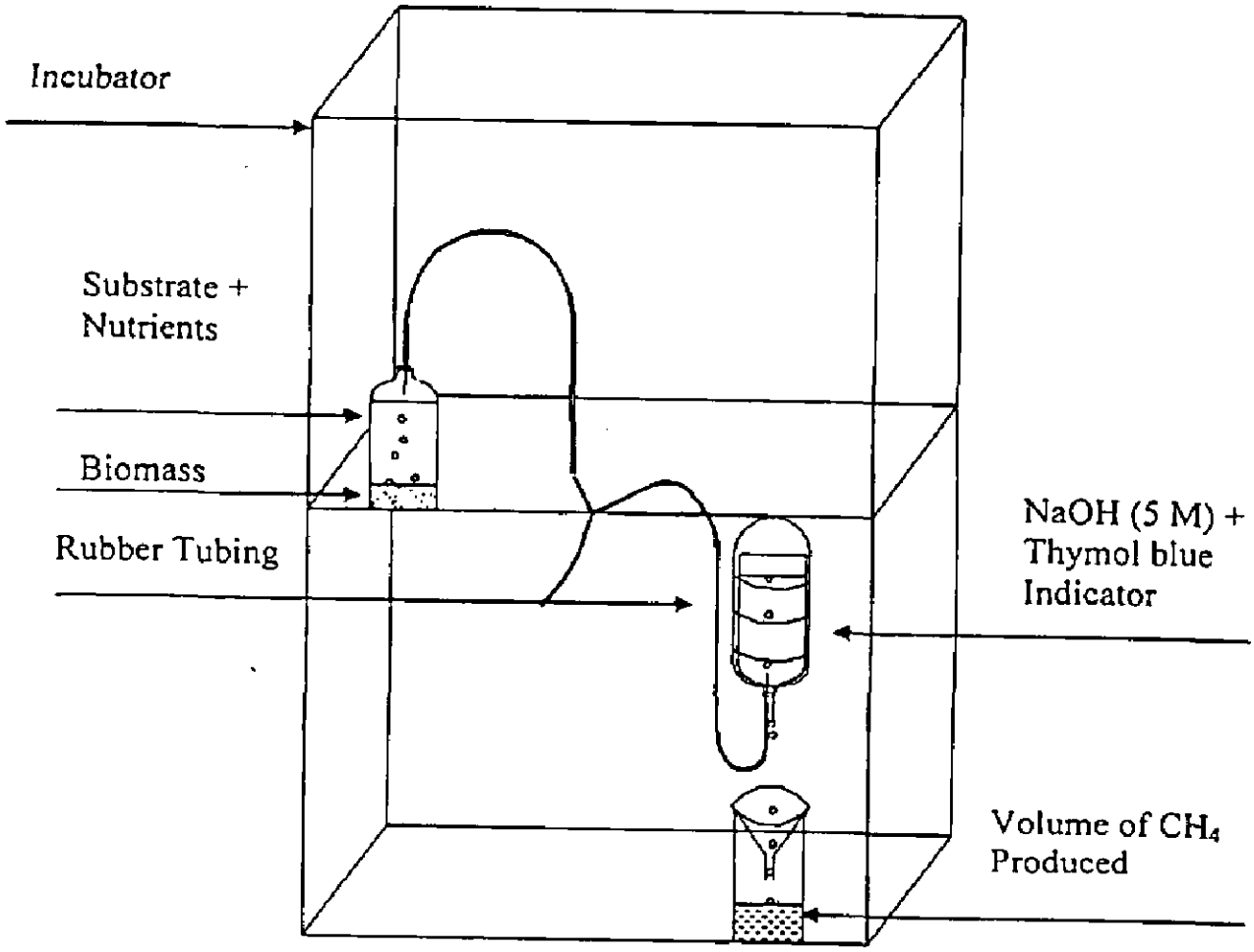

Fig 4.1 Experimental Setup of Methanogenic Activity Test

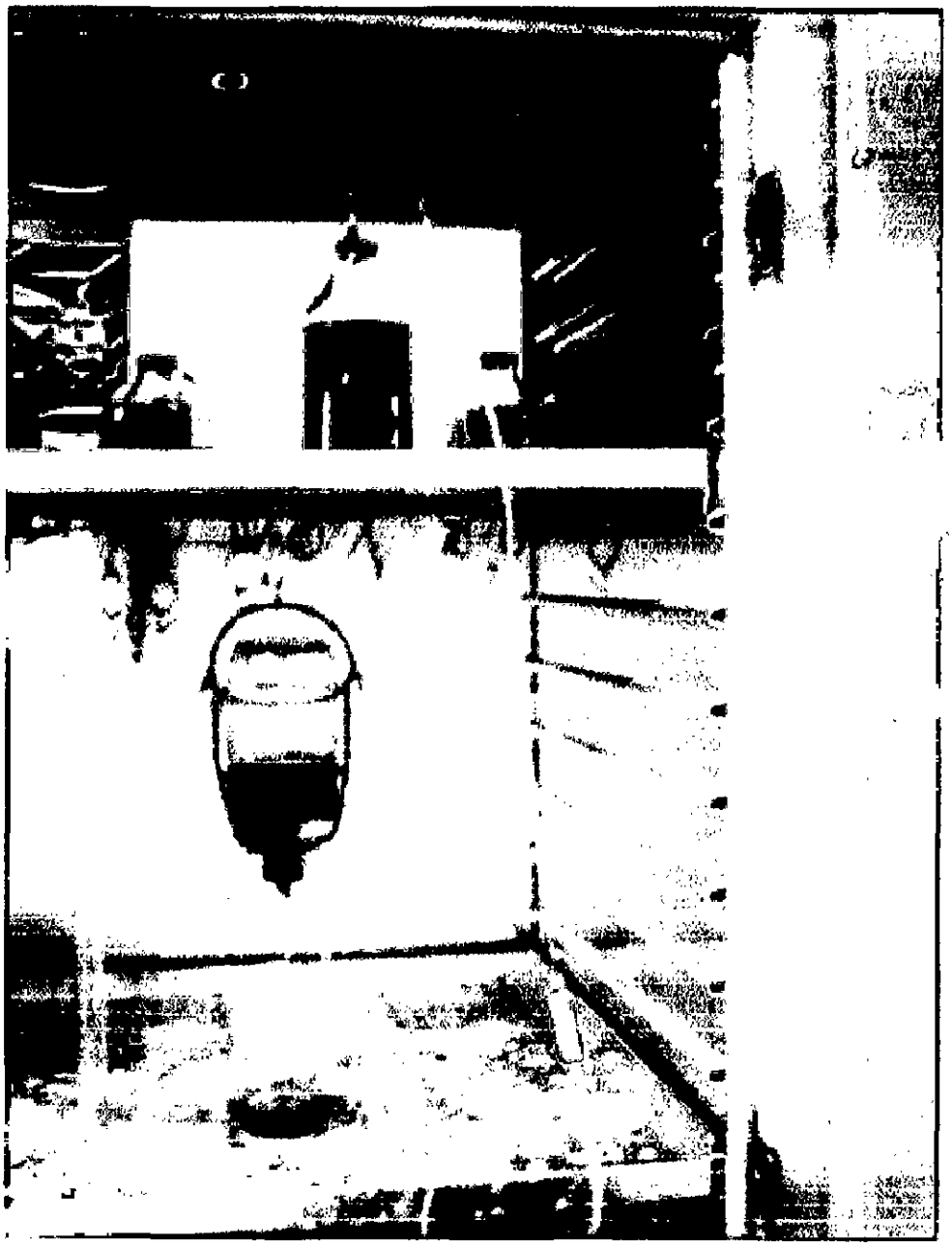

Fig 4.2 Actual Setup of Methanogenic Activity Test in Biochemical Lab IIT Roorkee

4.2 ACTIVATED BIOMASS

The activated biomass used as the inoculum in the reactor for the experiments was taken from an operating Methanogenic Upflow Reactor (MUR) for the treatment of Distillery wastewater (spent wash) of M/s Jubilant Organosys Limited, Gajraula. This reactor (MUR-IV) has a volume of 8400 m^3, with 30m diameter and 12.5 m height.

The volatile suspended solid (VSS) was determined by collecting samples from different sample points located at different height of the reactor. The individual VSS load at different heights was added to find the value of the COD/VSS ratio of the reactor. The value of VSS obtained at different sample points is tabulated in Table 4.2.

The characteristics of the distillery spent was fed to the MUR are given below;

COD of Distillery Spent wash	=	109687.13	mg/l
Effluent Feed rate to MUR	=	520	m^3/day
Total COD Load	=	57037.3	kg/day
COD/VSS Ratio "Z"	=	0.511	

Table 4.2 Calculation of VSS at different sample points located at different heights of MUR-IV.

Sample points.	VSS (mg/l)	VSS (kg)
0.75 m	15315	7719
1.5 m	15890	8009
3 m	15255	15377
6 m	11865	23920
9 m	14670	29575
Total		111619

Activated biomass sludge from the sample point located at 3m from the bottom of the reactor has been taken for the experiment. The characteristics of this sludge sample are tabulated in Table 4.3.

Table 4.3 Characteristics of the Activated Biomass Sludge used in the Activity Test for Experiment.

S.No.	Parameter	Value
1	TSS (mg/l)	33224
2	VSS (mg/l)	15255
3	TDS (mg/l)	28998
4	TS (mg/l)	62222
5	VFA (mg/l)	4054
6	Settling for 30 min (ml/l)	260
7	SVI (l/gm)	7.83
8	% Moisture Content	83.7
9	% Dry Sludge	16.3
10	Colour	Brown
11	pH	6.2
12	Temperature (°C)	38

4.3 PROCEDURE

The methanogenic activity test was conducted to assess the performance of the treatment method by observing CH_4 gas production. A known quantity of acetyl effluent was added along with sludge and nutrients in 500 ml serum bottle. The quantity of acetyl effluent and the sludge in reactor is calculated on the basis of COD/VSS ratio of the operating MUR-IV. Make up water was then added up to the 500 ml mark. The flask was properly capped and connected to water displacement system containing 5 M NaOH solution and thymol blue indicator. The reaction mixture was swirled and mixed manually. The first reading of the gas production was taken after 16 h of the commencement of the experiment. This reading was referred to as the zero reading. After that subsequent readings were noted in 4-h time interval.

In the first phase of the experiment, for finding out the optimum value of "Z" the COD/ VSS ratio for the reactor, the gas production was observed for 60 h after zero reading.

Four sets of different wastewater concentration and having 0.75 Z, Z, 1.25 Z and 1.5 Z; values were taken for the optimization of Z.

In the second phase of the experiment for calculating the kinetic coefficient, the gas production was observed for 36 h after zero reading and then the feed was changed by decanting the supernatant of the reaction bottle. A solution containing the same amount of acetyl effluent and nutrients as obtained by considering the optimum value of "Z" (COD/VSS ratio) was kept ready and poured immediately in the reaction bottle after decantation of its supernatant. The volume was again made-up to 500 ml by adding distilled water and the bottle was capped and connected to the liquid displacement system for recording gas production. This constitutes second feeding. Likewise, the procedure was repeated for the third feeding. After the third feeding the methane production was observed, till the gas production was ceased.

4.4 ANALYTICAL METHODS

The determination of various parameters such as, COD, BOD_3, TSS, SVI and TDS was made in accordance with the Standard Methods (APHA 1989). COD was measured by open reflux method using dichromate. pH was observed by using a digital pH meter.

The Fatty acids containing 10 or fewer carbon atoms are classified as water-soluble and those containing more than 10 carbon atoms are classified as water insoluble. The volatile fatty acids have the first six lower molecules by weight and the acid classified as soluble are only those that can be distilled at atmospheric pressure. It is assumed that only 70% of the volatile acids will be found in the distillate.

The sample of the wastewater was centrifuged or settled. 50 ml of supernatant liquor was taken in a distillation flask. 50 ml of water was added, and then 5 ml of concentrated H_2SO_4 was slowly mixed, so that the acids do not remain at the bottom of the flask. 75 ml of the distillate was collected in a conical flask and was titrated with 1 N NaOH solution using phenolphthalein indicator. Total volatile fatty acid is calculated by using the following formula

$$\text{VFA (mg/l)} = \frac{\text{ml of NaOH X N of NaOH X 60 X 1000}}{\text{ml of sample x 0.70}}$$

Scanning electron microscopy (SEM) of active biomass sample was also taken by using LEO Electron Micrograph at the Institute Instrumentation Centre, IIT, Roorkee.

Chapter 5

RESULTS AND DISCUSSION

5.1 EFFECT OF COD/VSS RATIO ON CH_4 GAS PRODUCTION

Table 5.1 gives the detail of the 4 sets of the experiments conducted with different values of COD/VSS ratio, viz. 0.75 Z, Z, 1.25 Z, and 1.5 Z. Z value is taken as 0.5 as shown in section 4.2, for the MUR having value 0.511. to have these values of Z, 100 ml biomass, and 1.525 g of VSS was taken for the four sets of experiment by varying volume of wastewater in the reactor.

COD of organic wastewater (mg/l) = 25066

COD of Biomass (mg/l) = 40560

Volume of reactor (ml) = 500

Volume of micronutrients (ml) = 0.5

Volume of macronutrients (ml) = 0.5

Final VSS in the reactor (mg/l) = 15260.6

Table 5.1 Experimental Detail for finding optimum COD/VSS ratio

S.No.	Parameter	Set 1	Set 2	Set 3	Set4
1	COD/VSS ratio	0.75 Z	Z	1.25 Z	1.5 Z
2	Volume of wastewater (ml)	22.5	30	37.5	45
3	Distilled Water (ml)	377.5	370	362.5	355
5	Initial reactor COD_i (mg/l)	7170	7547	8330	9310
6	Final reactor COD_f (mg/l)	5816	5781	5411	3527
7	CH_4 produced (ml)	216	299	330	475.5
8	COD reduced (mg)	677	883	1068	2010
9	CH_4 (ml) produced/ mg of COD reduced	0.319	0.3386	0.3089	0.2366

The observation tables for the methane produced for the sets of experiments were summarized in Appendix 1. The cumulative CH_4 produced versus time were plotted. In Figs 5.1 through Fig 5.4. These figures show the experimentally observed values of methane produced at 4 h time intervals for three days. The experimental data have been fitted by least square technique as given in MS Excel. The slope of straight line giving the best fit of the experimental data gives the value of the ml CH_4 produced per unit time. These slopes as obtained for the 4 values of the COD/VSS ratio are given in Table 5.2.

Table 5.2: R^2 values and slopes of linear fits of the cumulative CH_4 production versus Time data.

S.No.	"Z" COD/VSS Ratio	Slope	R^2
1	0.75 Z	4.084	0.9829
2	Z	5.2438	0.9891
3	1.25 Z	5.7857	0.9888
4	1.5 Z	7.1954	0.9457

The value of the methanogenic activity of the effluent is calculated by using the slope of the cumulative CH_4 produced versus time graph as suggested by Isa et al. (1993). The value of the activity as (ml CH_4 produced / g VSS. day) and as COD equivalent CH_4 produced (g CH_4-COD/gVSS.day) has been calculated. Appendix-2 shows the calculation of the activity. Table 5.3 shows the values of the activity as obtained for different values of COD/VSS ratio.

From Fig 5.5 the optimum value of COD/VSS ratio was obtained. This figure shows the trend of ml CH_4 produced/mg of COD reduced. The optimum value of the COD/VSS ratio was found to be equal to "Z" i.e.~0.5.

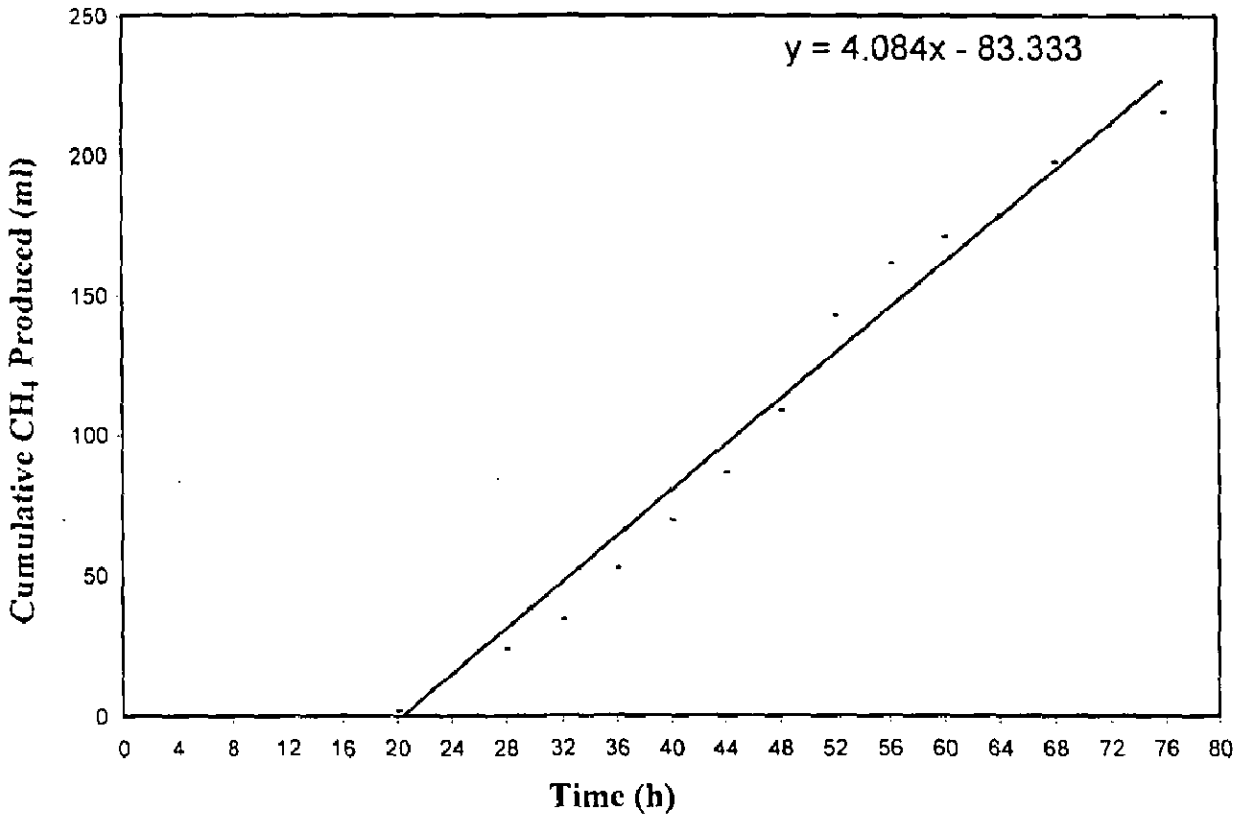

Fig 5.1 Cumulative CH_4 Production versus Time for 0.75 Z

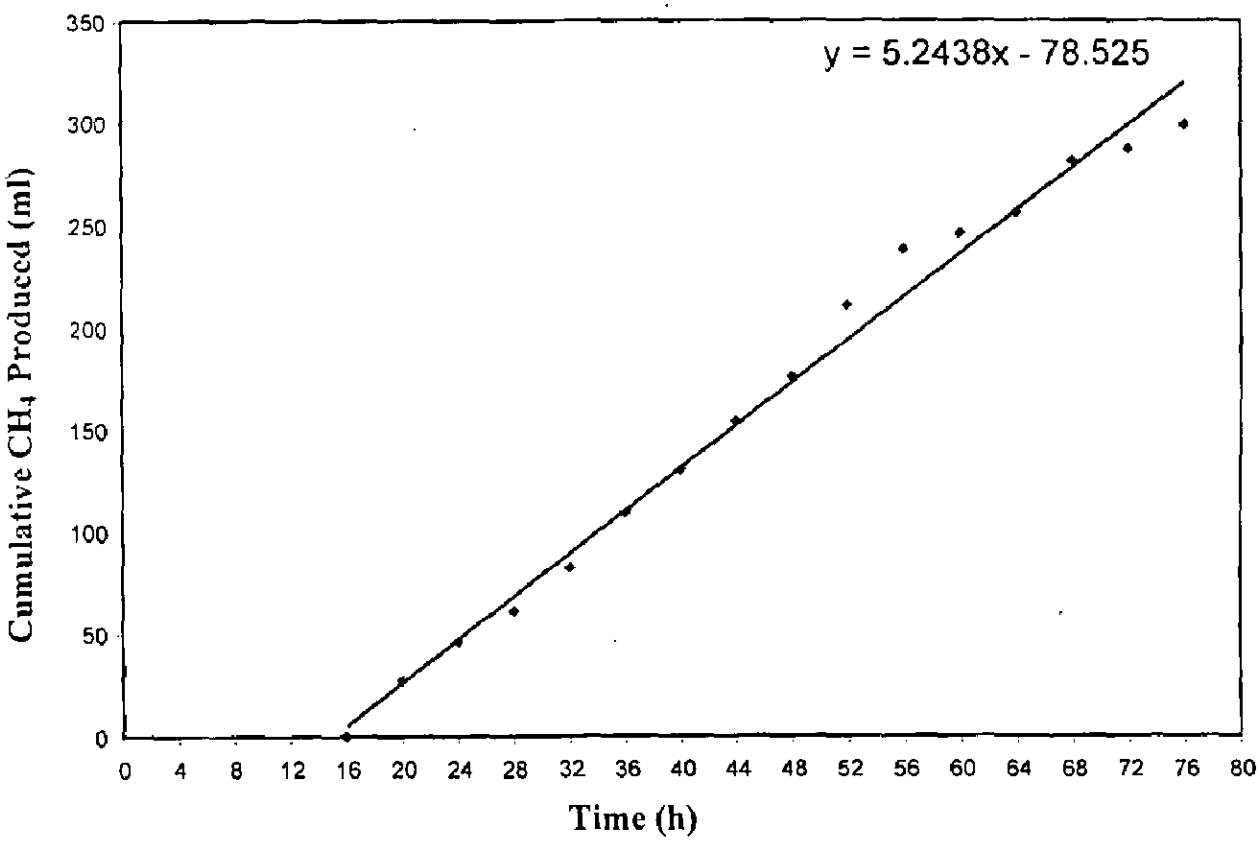

Fig 5.2 Cumulative CH_4 Production versus Time for Z

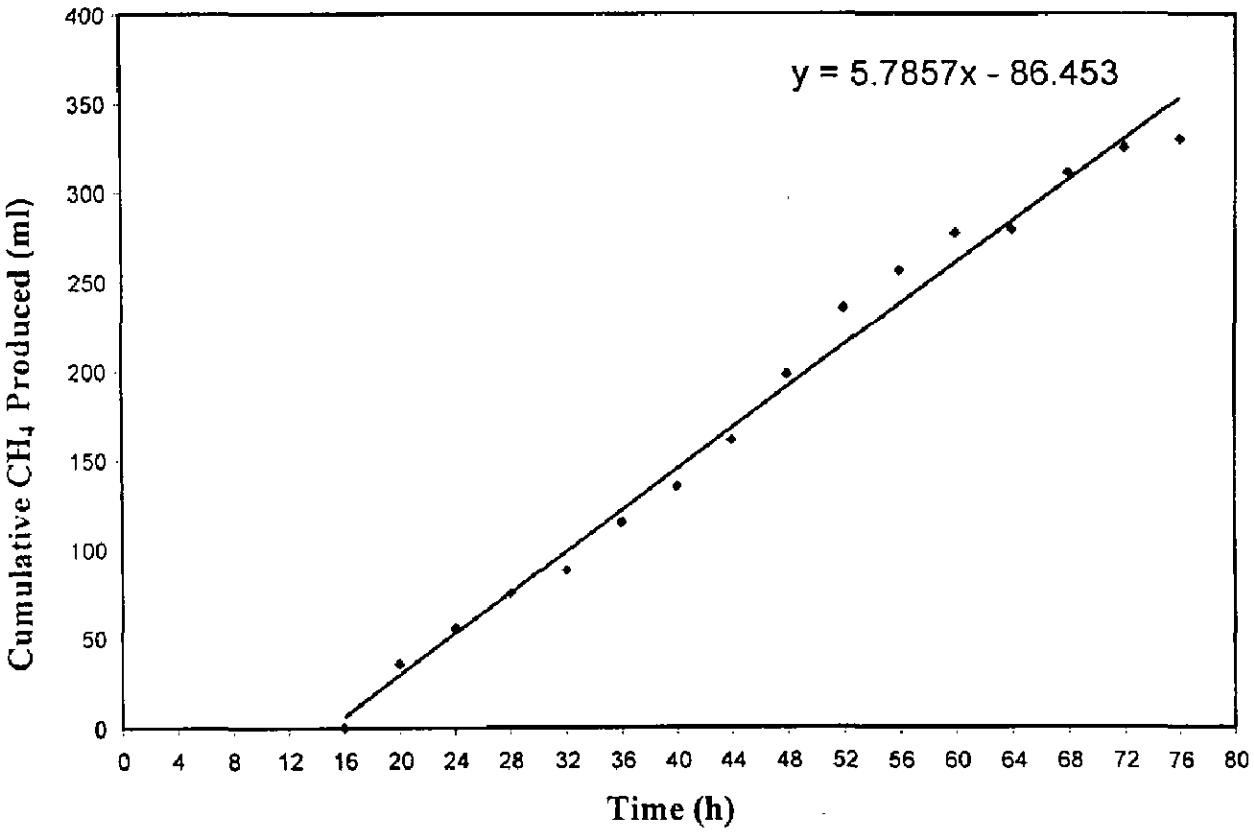

Fig 5.3 Cumulative CH_4 Production versus Time for 1.25 Z

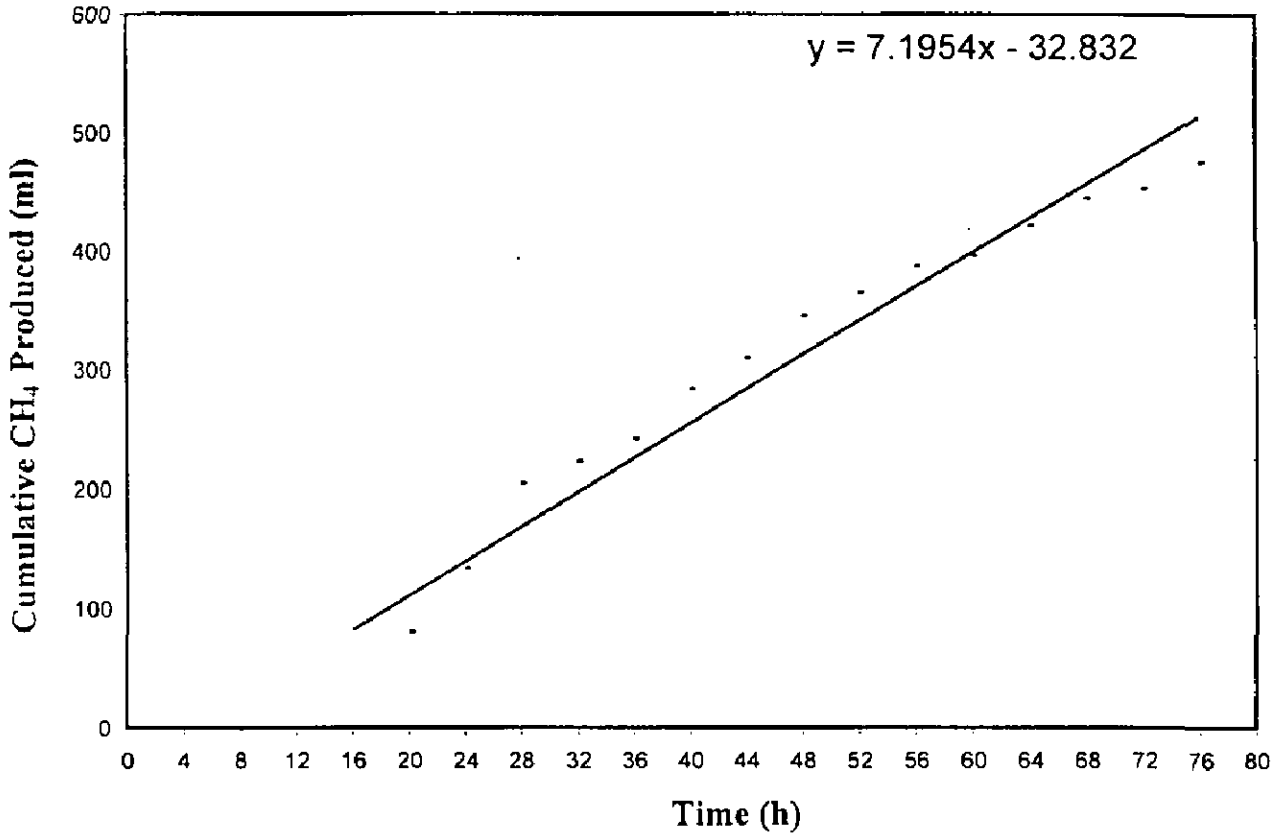

Fig 5.4 Cumulative CH_4 Production versus Time for 1.5 Z

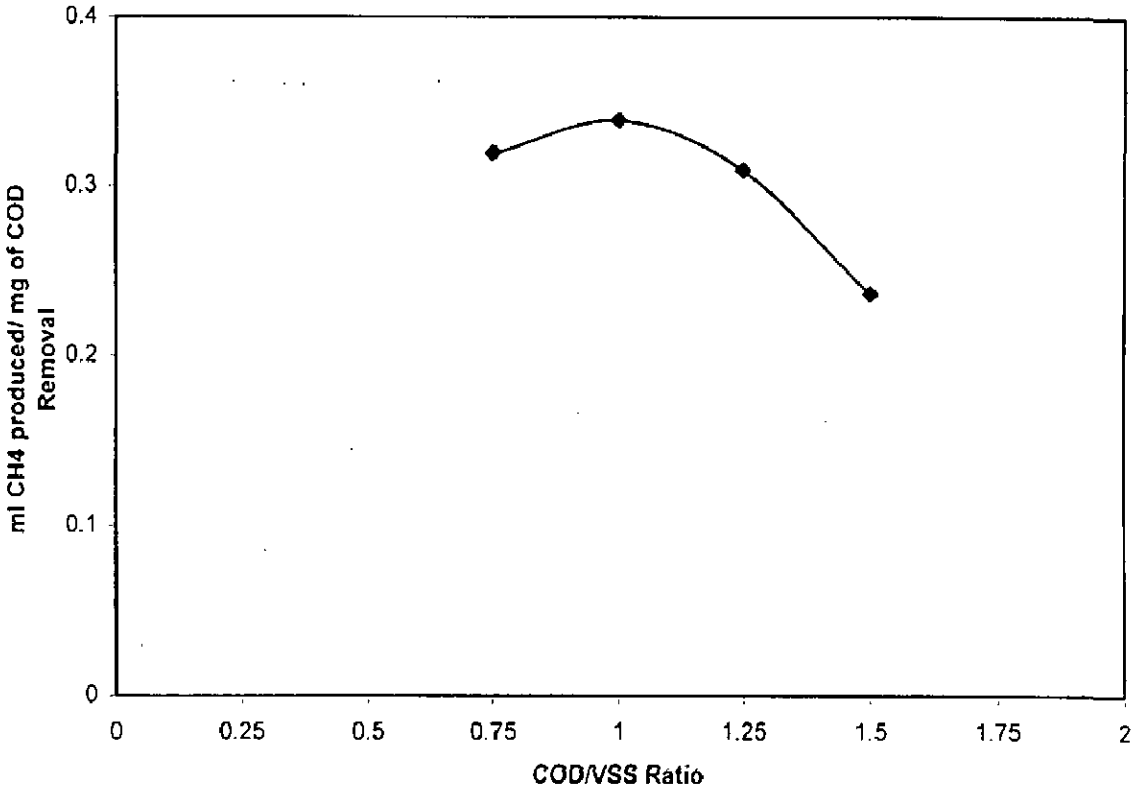

Fig 5.5: Ratio of ml CH_4 Produced/ kg COD Reduced versus "Z"

Table 5.3: Values of the methanogenic Activity for different values of COD/VSS ratio

S.No.	COD/VSS Ratio	Activity ml CH_4/g VSS/day	Activity g CH_4-COD/g VSS/day
1	0.75 Z	64.23	0.028
2	Z	82.47	0.036
3	1.25 Z	90.99	0.04
4	1.5 Z	113.16	0.05

(Ref. Appendix 2 for calculation)

The values of the activity found have been tabulated in Table 5.3. This table shows the value of activity for different COD/VSS ratio as ml CH_4/gVSS/day and as g CH_4-COD/g VSS/day. Fig 5.6 is the plot of Activity of different COD/VSS ratio. It is clear from this figure that the increase in the ratio of COD/VSS increases the activity and then it decreases after an optimum value. It is found that the optimum value of COD/VSS ratio is 0.5. As further increase in COD/VSS ratio increases the activity as shown in the Fig 5.6 but the amount of ml CH_4 produced /mg COD reduced is decreased. Hence the optimum COD/VSS ratio is taken equal to 0.5.

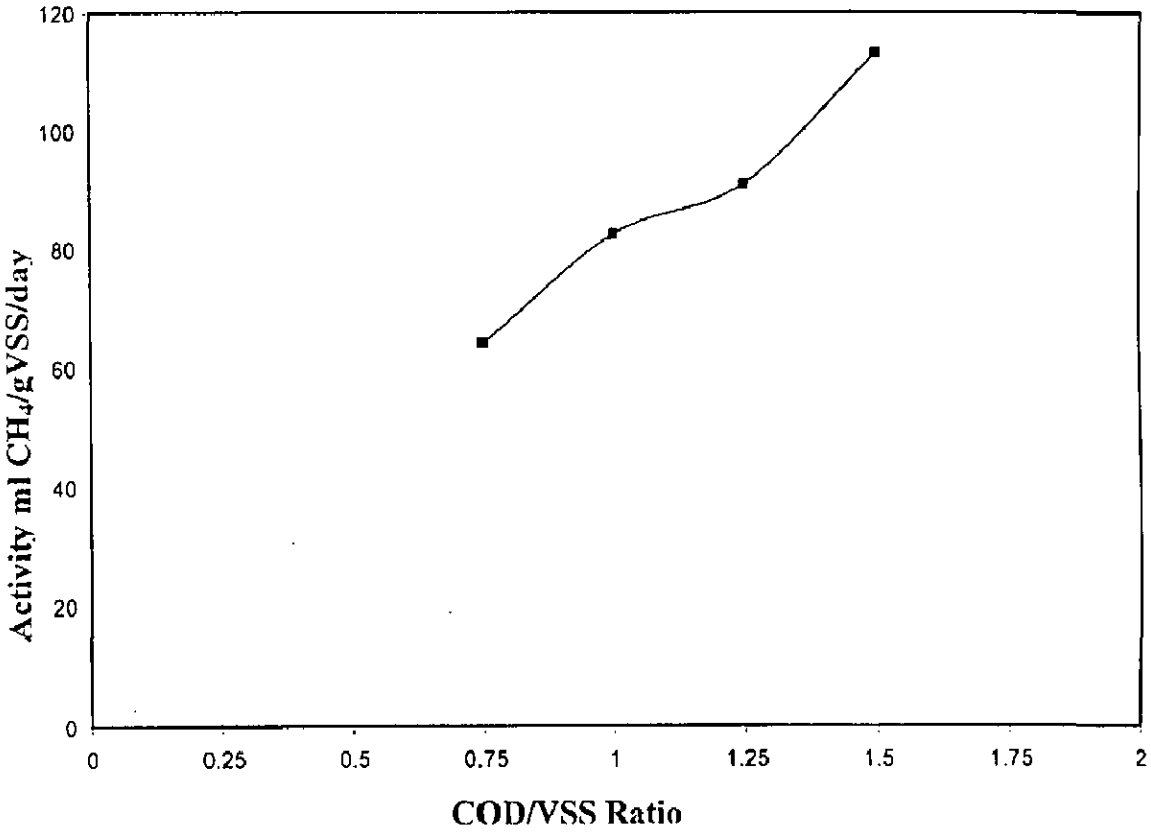

Fig 5.6 Activity versus COD/VSS "Z" Ratio

5.2 CALCULATION OF KINETICS COEFFICIENT

For calculating the yield coefficient the activity test at optimum COD/VSS ratio equal to 0.5 was performed. To determine the yield coefficient, the activity of sludge is determined with the help of the cumulative CH_4 production versus time graph and the difference in VSS content of the reaction mixture after second and third feeds. The difference in VSS between second and third feeds represents the synthesis of biomass. The substrate consumed during the synthesis of biomass is taken as the COD equivalent of total CH_4 produced after third feed. Yield coefficient is calculated as the ratio of synthesis of biomass to the total substrate consumed (Isa et al. 1993).

Figs 5.7 through Fig 5.9 show the graph using cumulative CH_4 versus time for different Feeds. Table 5.4 summarizes the results of all the experiments.

Table 5.4: R^2 values and slopes of linear fits of the cumulative CH_4 production Versus Time data.

S.No.	Feed No.	Slope	R^2
1	Feed 1	2.5644	0.9943
2	Feed 2	2.8916	0.9917
3	Feed 3	3.7457	0.9894

Table 5.5: Values of Activity for different Feeds

S.No.	Feed No.	Activity ml CH_4/g VSS/day	Activity g CH_4-COD/g VSS/day
1	Feed 1	40.32	0.018
2	Feed 2	45.48	0.02
3	Feed 3	58.91	0.026

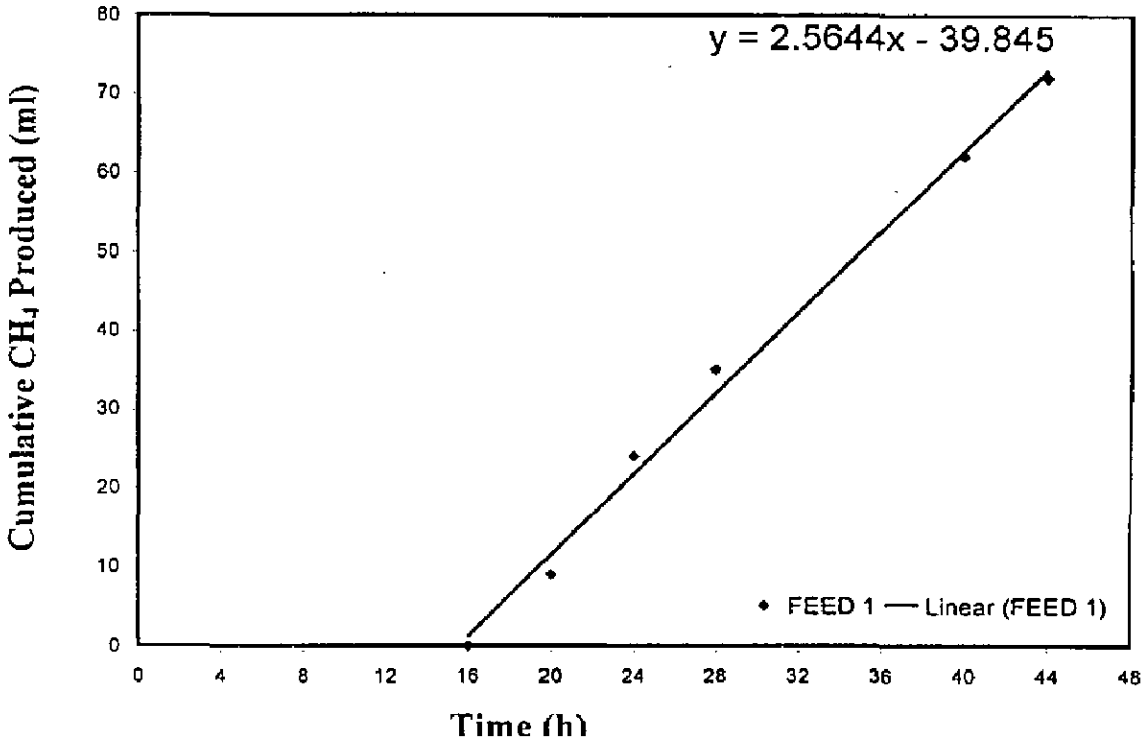

Fig 5.7 Cumulative CH_4 production versus Time for Feed 1

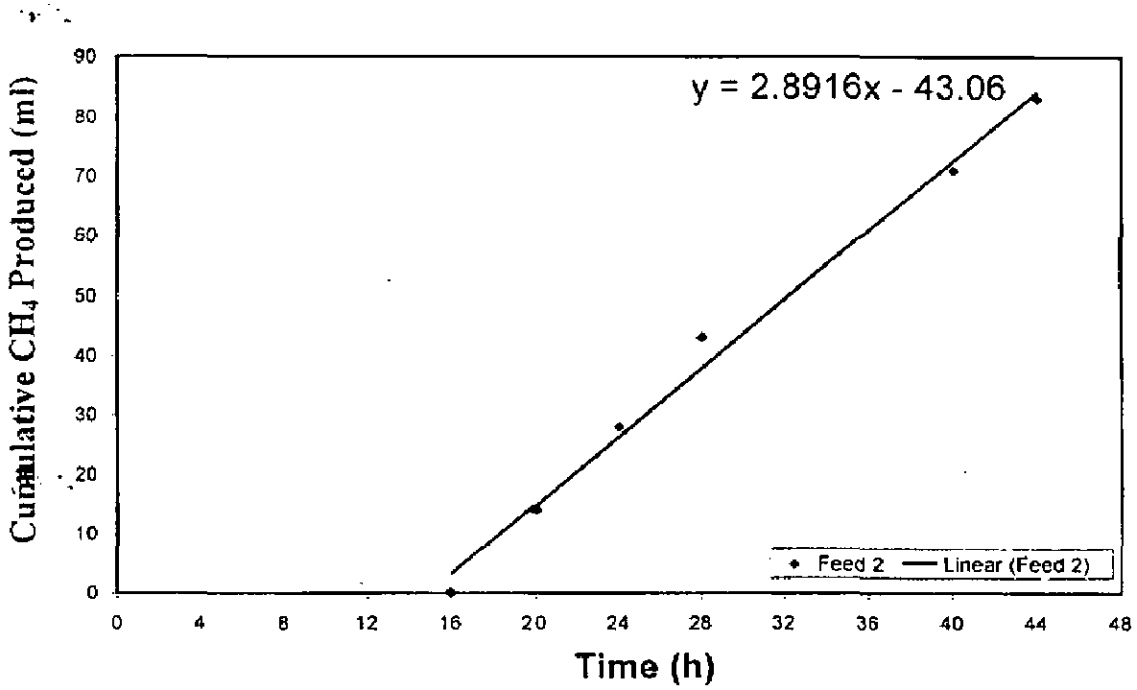

Fig 5.8 Cumulative CH_4 production versus Time for Feed 2

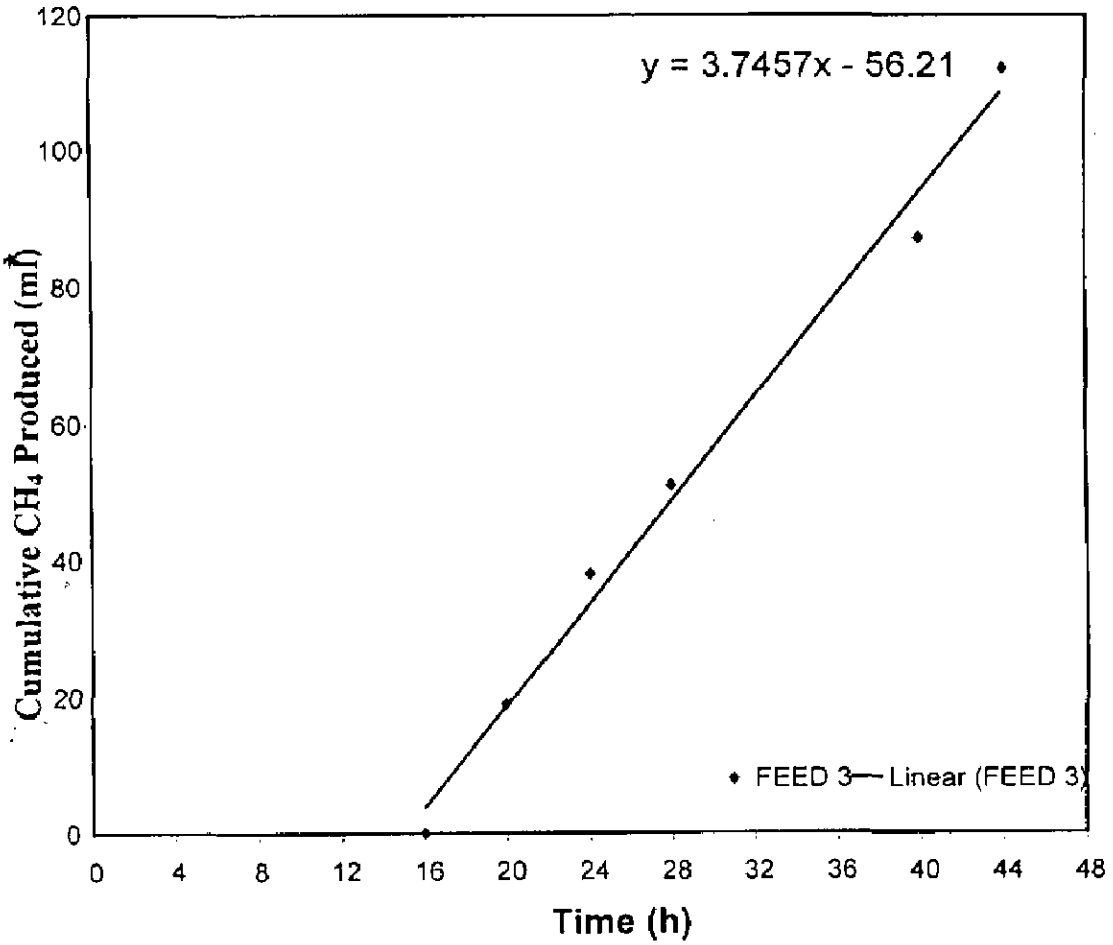

Fig 5.9 Cumulative CH_4 production versus Time for Feed 3

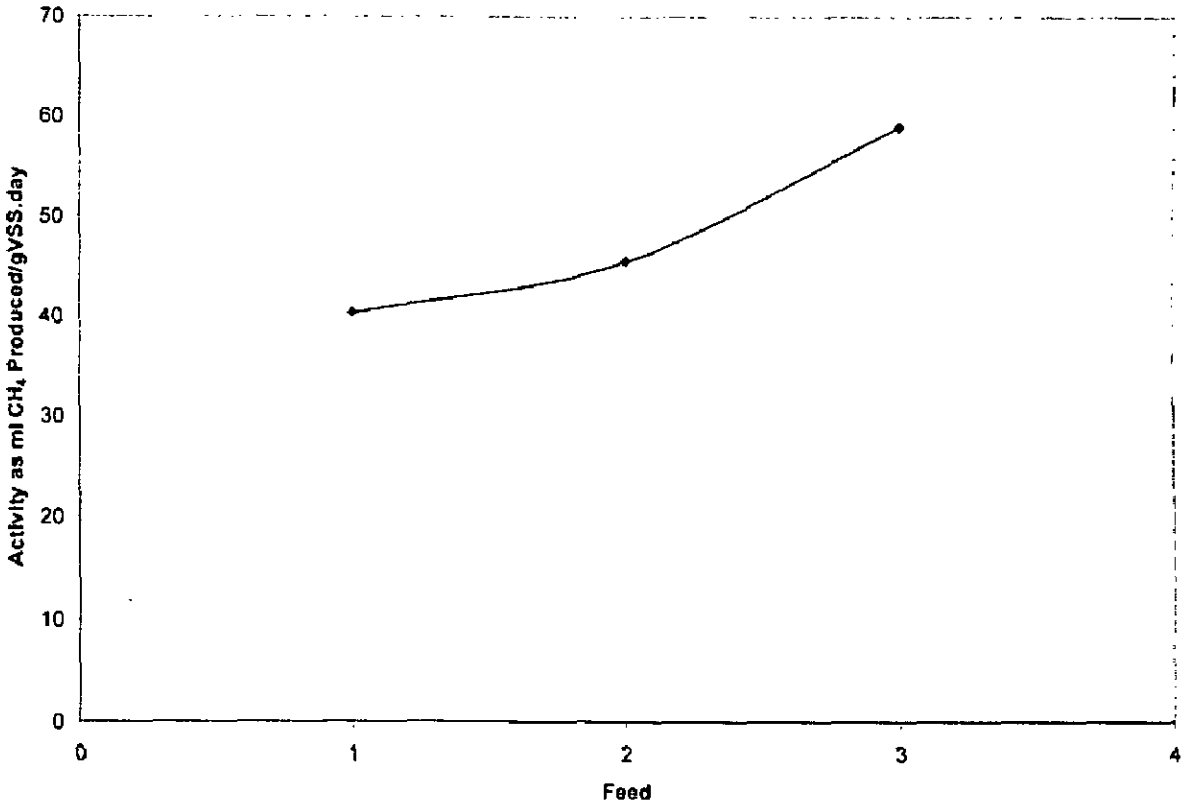

Fig 5.10 Activity as ml CH_4 produced/gVSS.day versus Feed

Figs 5.7 through Fig 5.9 shows the cumulative CH_4 produced versus time. It was found that the slope of the best-fit curve increases as the feed was changed. As first feed corresponds to the activity of biomass while maximum CH_4 production rate is achieved after second and third feed is shown in Fig 5.10.

5.2.1 Substrate Utilization Rate and Yield Coefficient

The calculation of Yield Coefficient is shown in Appendix-3. The value obtained is 0.04125 gVSS/gCOD. The value of yield coefficient for acetate containing substrate as given in the literature is between 0.01 and 0.054 gVSS/gCOD. Our value of yield coefficient fills in the range. Substrate values as COD equivalent of methane produced after third feed till the methane production ceases are given in Table 5.6. Substrate utilization at different times was found by subtracting this value from the initial substrate concentration (S_0), which is the sum of the substrate consumed in the yield of biomass and the COD equivalent of the total CH_4 produced (Isa et al. 1993).

Table 5.6 Values for Substrate Consumed

S.No.	CH_4 Produced (ml)	COD equivalent of CH_4 produced "S"(g COD)	S_0-S (g COD)
1	125	0.055	0.161
2	143	0.063	0.153
3	161	0.071	0.145
4	178	0.078	0.138
5	180	0.079	0.137
6	182	0.08	0.136
7	182	0.08	0.136

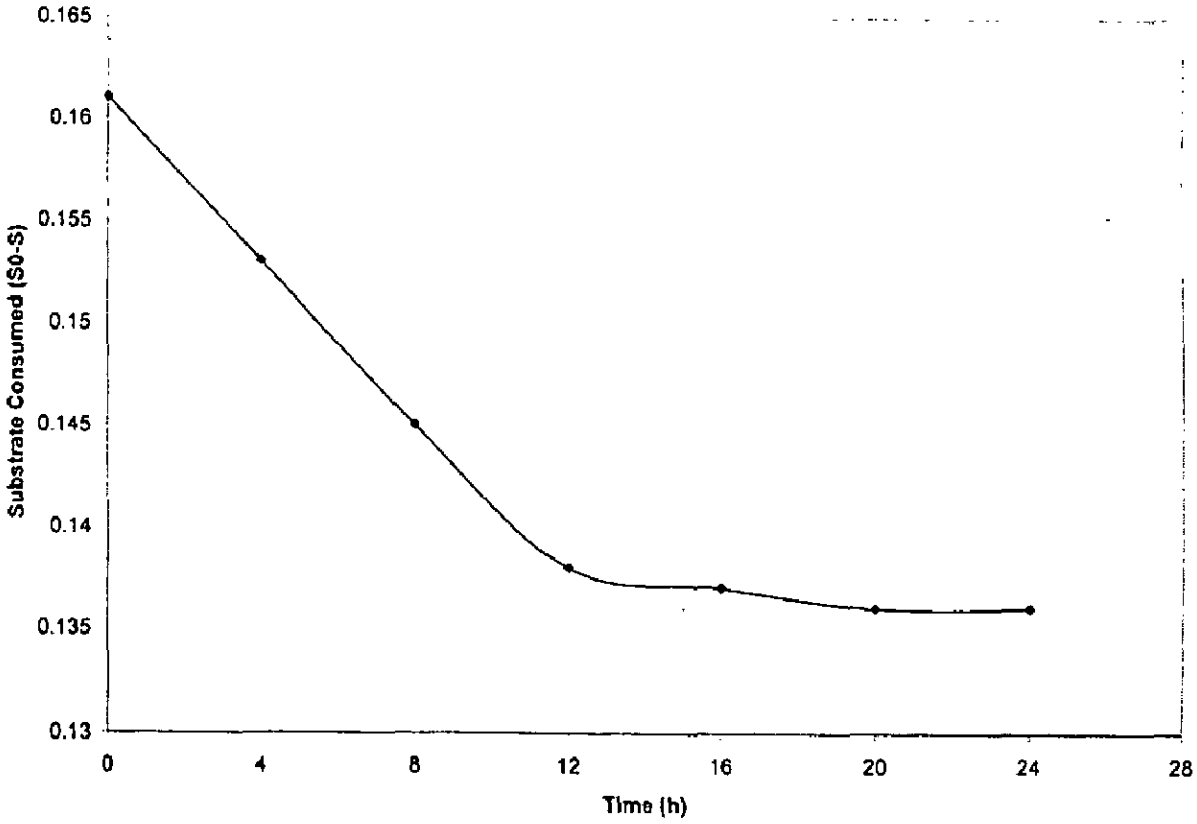

Fig 5.11 Substrate Utilization Curve

The substrate utilization curve was plotted using substrate consumed as the ordinate and the time as the abscissa. Fig 5.11 shows the substrate utilization curve. From this figure, the substrate utilization rate i.e. ($\Delta S/\Delta t$) was calculated by finding the maximum slope of the curve. The calculations are shown in Appendix-3.

The value of the maximum substrate utilization rate was found to be 0.314 g COD/gVSS.day. Fig 5.11 shows that substrate utilization decreases initially and then after some time it becomes nearly constant. This may be because of the non-biodegradable part of the substrate.

The efficiency of the wastewater treatment was found to be 77.31 %.

5.3 RESULTS OF SCANNING ELECTRON MICROGRAPH

The SEM (Scanning Electron Micrograph) of active biomass taken for experiment was performed. Figures 5.12 through 5.20 show the SEM photographs with different magnification. It was concluded from figures that biomass is active having good oxidizing properties as observed by white patches in the figure.

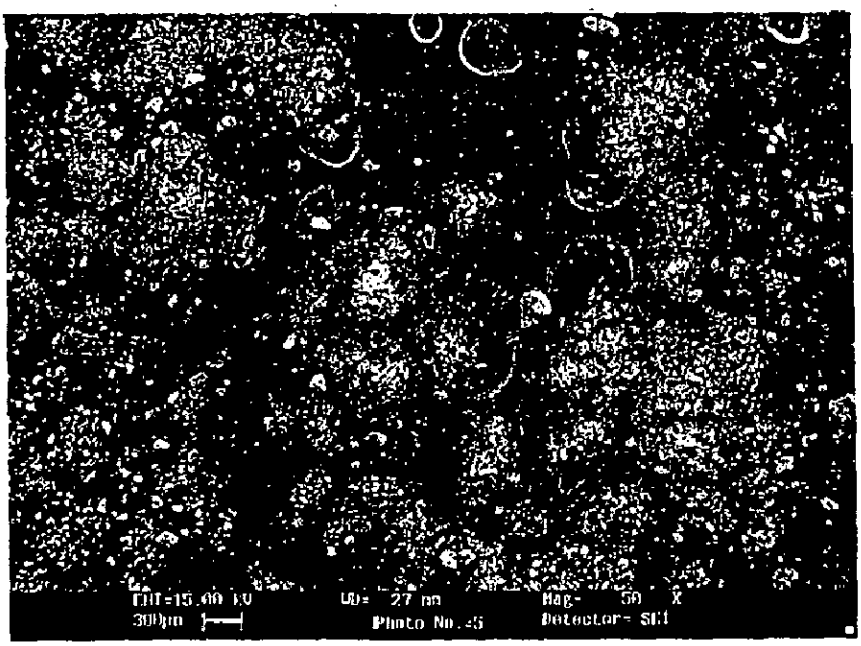

Fig 5.12 SEM of a Sludge Sample of MUR-4 with magnification 50X 300µm.

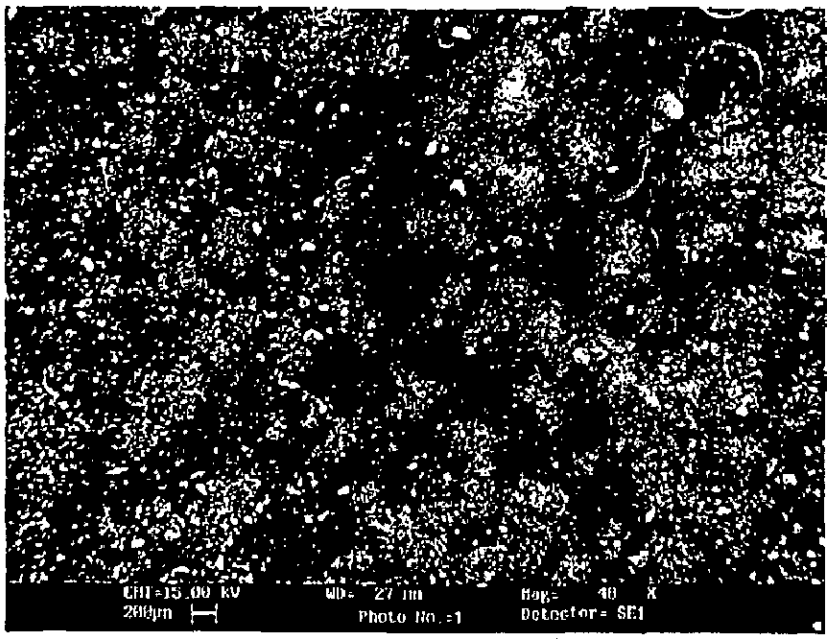

Fig 5.13 SEM Micrograph of a Sludge Sample of MUR-4 with magnification 48X, 200µm.

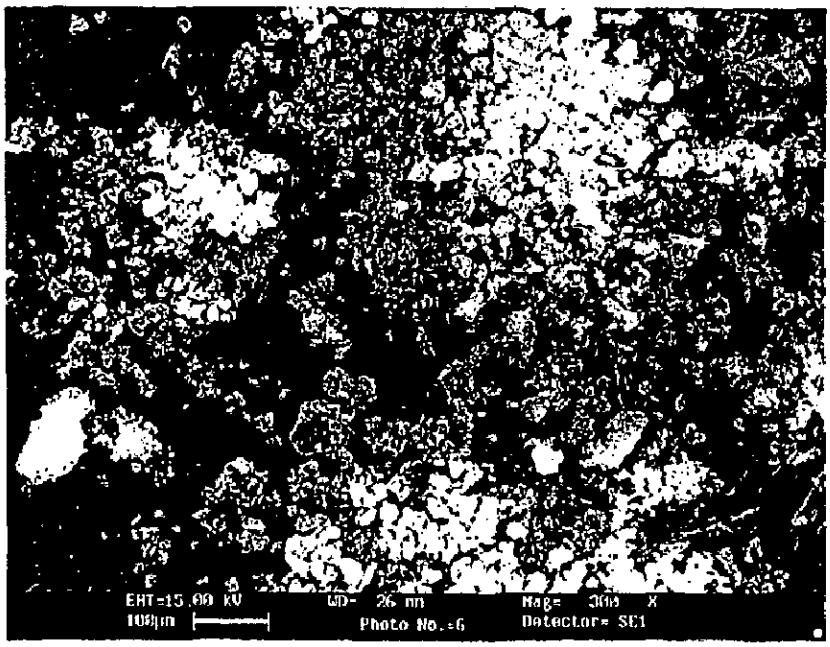

Fig 5.14 SEM Micrograph of a Sludge Sample of MUR-4 with magnification 500X, 100µm.

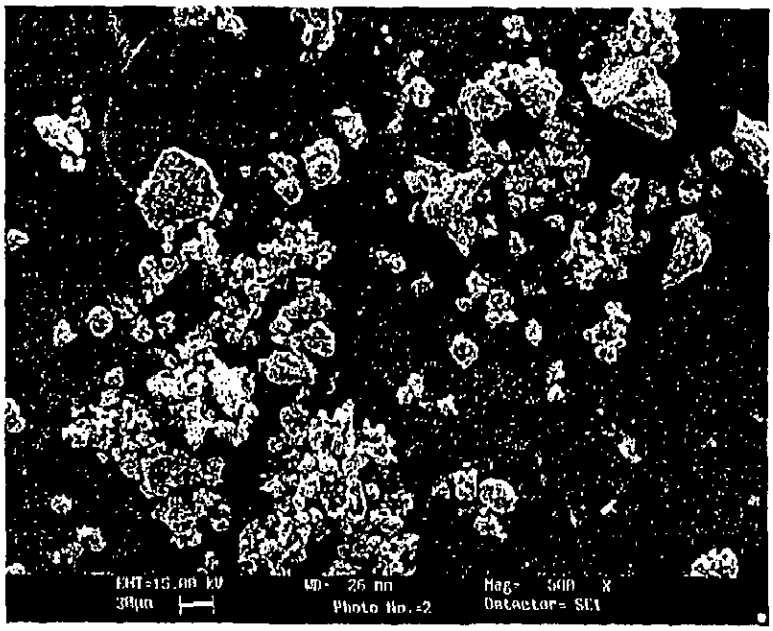

Fig 5.15 SEM Micrograph of a Sludge Sample of MUR-4 with magnification 500X, 30µm

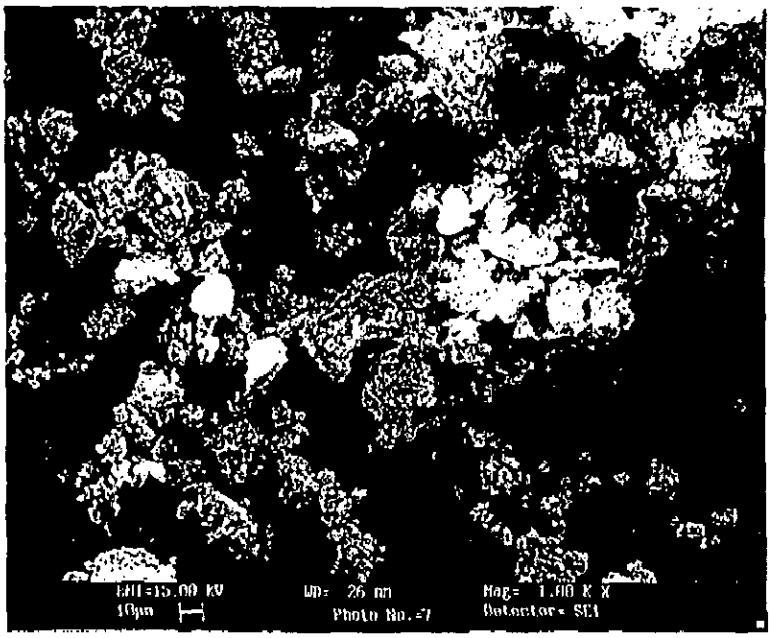

Fig 5.16 SEM Micrograph of a Sludge Sample of MUR-4 with magnification 1000X, 10µm

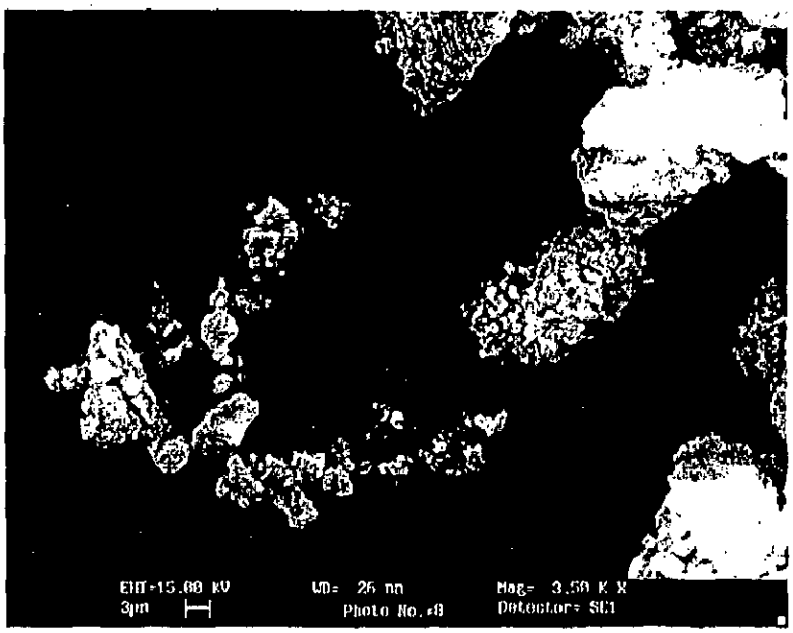

Fig 5.17 SEM Micrograph of a Sludge Sample of MUR-4 with magnification 3.50 KX, 3µm

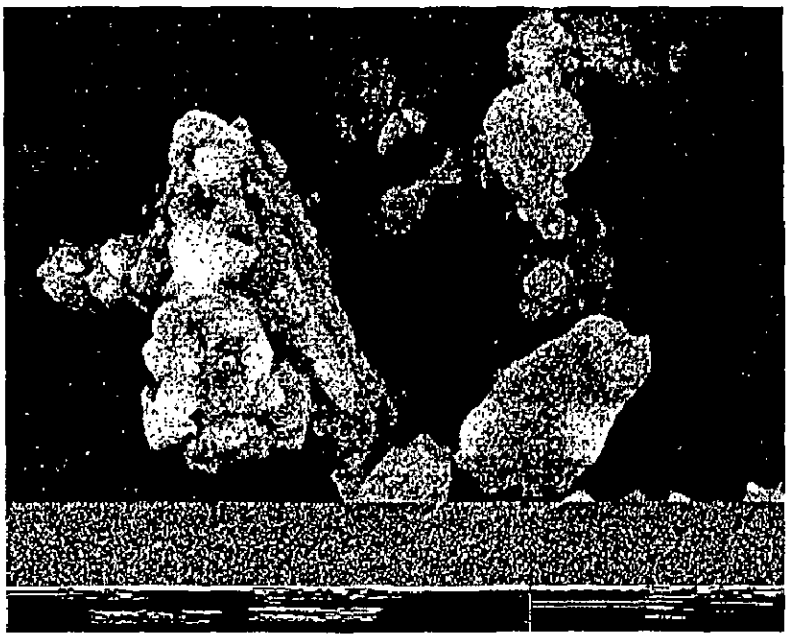

Fig 5.18 SEM Micrograph of a Sludge Sample of MUR-4 with magnification 10.00 KX, 1µm.

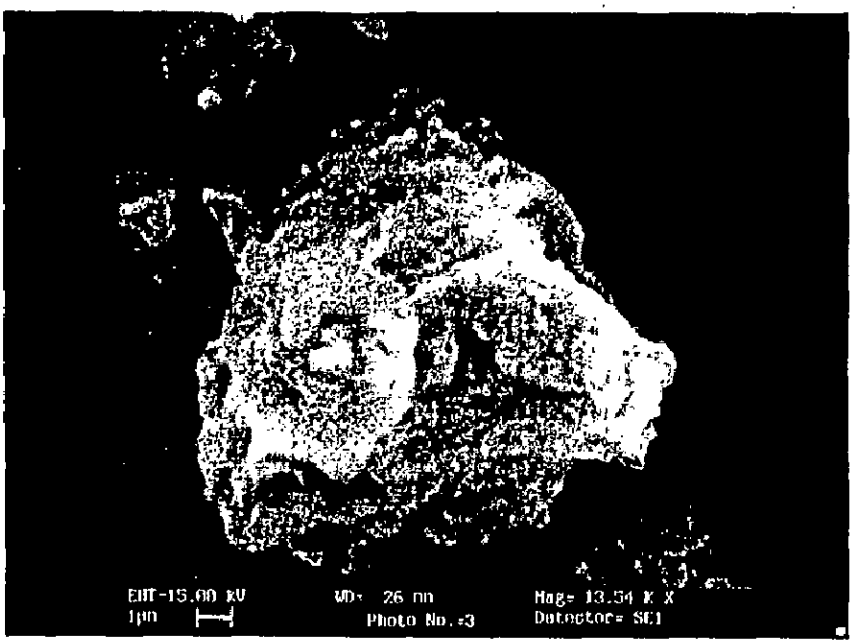

Fig 5.19 SEM Micrograph of a Sludge Sample of MUR-4 with magnification 13.54 KX, 1μm.

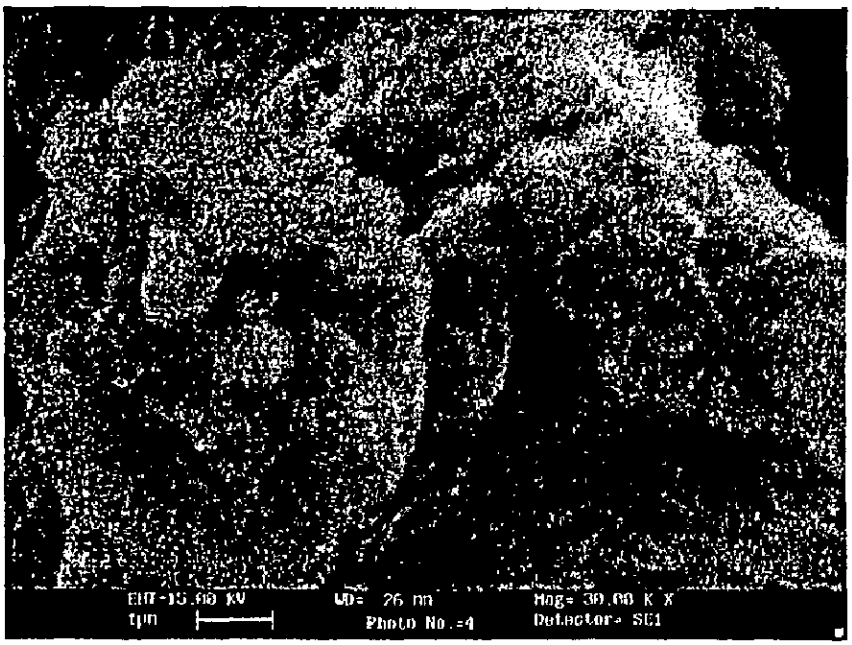

Fig 5.20 SEM Micrograph of a Sludge Sample of MUR-4 with magnification 30.00 KX, 1μm.

Chapter 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

In the present work, a methanogenic activity test was performed to observing the digestion of wastewater generated from the acetyl section of Jubilant Organosys Limited (JOL), Gajraula, by anaerobic process.

The active biomass of the operating methanogenic upflow reactor (MUR-IV) treating distillery spent wash, JOL, Gajraula, was taken for the methanogenic activity test. The operating MUR is having a COD/VSS ratio of 0.511. Using this ratio as base, the methanogenic activity test were performed by assuming "Z" COD/VSS ratio equals to 0.5. Four sets of experiments were performed by keeping the same amount of VSS and by changing the COD load. The sets of experiments were performed for 0.75 Z, Z, 1.25Z, and 1.5Z. The optimum value is reported as Z ~ 0.5.

- The yield coefficient, and the substrate utilization rate as calculated from the experiments are in the range as reported in the literature.
- Efficiency of wastewater treatment was calculated and it was found that the efficiency is 77.31 %.
- The volume of CH_4 produced/mg of COD reduced is found to be 0.35 ml/mg. This indicates that the anaerobic treatment of wastewater used in experiment coming from alcohol recovery column-II may be feasible.

6.2 SCOPE OF FUTURE WORK

Using the kinetics of methanogenesis, an anaerobic digester can be designed. Optimum COD/VSS ratio may be used to find the recirculation rate of the sludge in the continuous reactor.

The treatment procedures for the sludge and the effluent generating from the anaerobic treatment of acetyl wastewater are also recommended as anaerobic treatment is followed by aerobic treatment process.

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APPENDIX I

EXPERIMENTAL DATAS

Table 1.1: CH_4 Produced in Test for 0.75 Z, Set 1

DAY	8:00 AM	12 NOON	4:00 PM	8: 00 PM	12:00 AM	4:00 AM
0		FEED 1	0	0	0	3
1	20	32	45	59	72	89
2	114	152	171	180	188	206
3	210	212	TEST TERMINATED			

Table 1.2: CH_4 Produced in Test for 0.75 Z, Set 2

DAY	8:00 AM	12 NOON	4:00 PM	8: 00 PM	12:00 AM	4:00 AM
0		FEED 1	0	0	0	1
1	10	16	24	46	67	84
2	104	134	152	162	170	190
3	212	220	TEST TERMINATED			

Table 1.3: CH_4 Produced in Test for Z, Set 1

DAY	8:00 AM	12 NOON	4:00 PM	8: 00 PM	12:00 AM	4:00 AM
0		FEED 1	0	10	22	30
1	50	64	85	112	134	158
2	177	210	239	246	256	280
3	286	292	TEST TERMINATED			

Table 1.4: CH_4 Produced in Test for Z, Set 2

DAY	8:00 AM	12 NOON	4:00 PM	8: 00 PM	12:00 AM	4:00 AM
0		FEED 1	0	10	18	24
1	42	58	79	106	127	151
2	175	212	237	246	256	282
3	288	306	TEST TERMINATED			

Table 1.5: CH_4 Produced in Test for 1.25z, Set 1

DAY	8:00 AM	12 NOON	4:00 PM	8: 00 PM	12:00 AM	4:00 AM
0		FEED 1	0	10	22	33
1	54	76	89	116	135	160
2	198	234	256	274	268	308
3	330	335	TEST TERMINATED			

Table 1.6: CH_4 Produced in Test for 1.25z, Set 2

DAY	8:00 AM	12 NOON	4:00 PM	8: 00 PM	12:00 AM	4:00 AM
0		FEED 1	0	12	26	38
1	57	74	87	115	136	162
2	198	234	257	280	290	314
3	320	325	TEST TERMINATED			

Table 1.7: CH_4 Produced in Test for 1.5z, Set 1

DAY	8:00 AM	12 NOON	4:00 PM	8: 00 PM	12:00 AM	4:00 AM
0		FEED 1	0	21	52	82
1	134	212	229	248	280	312
2	350	360	377	390	412	440
3	449	487	TEST TERMINATED			

Table1.8: CH_4 Produced in Test for 1.5z, Set 2

DAY	8:00 AM	12 NOON	4:00 PM	8: 00 PM	12:00 AM	4:00 AM
0		FEED 1	0	15	46	79
1	134	198	218	237	288	308
2	341	371	398	403	432	450
3	458	464	TEST TERMINATED			

Table 1.9 : Observation Table of Activity Test for finding Yield Coefficient

DAY	8:00 AM	12 NOON	4:00 PM	8:00 PM
0			**FEED 1**	
1	0	9	24	35
2	62	72	**FEED 2**	
3	0	14	28	43
4	71	83	**FEED 3**	
5	0	19	38	51
6	87	112	**TEST TERMINATE**	125
7	143	161	178	180
8	182	182		

APPENDIX II

CALCULATION OF ACTIVITY

The Methanogenic activity is calculated as (Isa et al 1993)

$$\text{Activity (ml } CH_4 \text{ /g VSS/ day)} = \frac{\text{[Slope (ml } CH_4\text{/hr) X 24 (hr/day)]}}{\text{Final VSS (g)}}$$

Methane can also be converted to its COD equivalent based on stoichiometric oxidation of CH_4 to CO_2 and H_2O. (Isa et al 1993)

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

The COD equivalent of methane can be calculated as

$$\text{1.0 ml } CH_4 \text{ at T °C} = \frac{273}{273+T} X \frac{760-p}{760} X \frac{1}{350} \text{ X 1g COD} \qquad (2.1)$$

Where, T = temperature in deg C.

P = saturation water vapour pressure, mm Hg at T°C.

350 = stoichiometric volume of CH_4 in ml equivalent to 1g COD at STP

2.1 CALCULATION OF COD EQUIVALENT

Experiment Temperature = 35 ^{0}C

= 308 K

Saturation Water Vapour pressure at 100 °C = 760 mm Hg

For Calculation of Saturation Water Vapour pressure at T °C using Ideal Gas Law,

P*V = n*R*T (2.2)

For constant volume,

$$\frac{p1}{T1} = \frac{p2}{T2} \qquad (2.3)$$

Putting values in equation 1.3,

$$\frac{760}{373} = \frac{p2}{308}$$

p2 = (760*308)/373

= 627.5

So, Saturation Water Vapour pressure at 35 °C = 627.5 mm Hg

Now, putting values in equation 1.1 for calculating COD equivalent of CH_4 produced,

1 ml of CH_4 at 35° C = 273/(273+35) X (760-627.5)/760 X (1/350)

= **4.415×10^{-04} g COD**

2.2 CALCULATION OF ACTIVITY

2.2.1 For 0.75 Z (Fig 5.1)

Slope of curve	=	4.084
Activity	=	(4.084*24)/ 1.526
	=	64.23 ml CH_4/g VSS/day
COD equivalent CH_4 produced	=	64.23 * 4.415 X 10^{-04} g COD
	=	0.028 g CH_4-COD/gVSS/day

2.2.2 For Z (Fig 5.2)

Slope of curve	=	5.2438
Activity	=	(5.2438*24)/ 1.526
	=	82.47 ml CH_4/g VSS/day
COD equivalent CH_4 produced	=	82.47 * 4.415 X 10^{-04} g COD
	=	0.036 g CH_4-COD/gVSS/day

2.2.3 For 1.25 Z (Fig 5.3)

Slope of curve	=	5.7857
Activity	=	(5.7857*24)/ 1.526

	=	90.99 ml CH_4/g VSS/day
COD equivalent CH_4 produced	=	90.99 * 4.415 X 10^{-04} g COD
	=	0.04 g CH_4-COD/gVSS/day

2.2.4 For 1.5 Z (Fig 5.4)

Slope of curve	=	7.1954
Activity	=	(7.1954*24)/ 1.526
	=	113.16 ml CH_4/g VSS/day
COD equivalent CH_4 produced	=	113.16 * 4.415 X 10^{-04} g COD
	=	0.05 g CH_4-COD/gVSS/day

2.2.5 For Feed 1 (Fig 5.7)

Slope of curve	=	2.564
Activity	=	(2.564*24)/ 1.526
	=	40.32 ml CH_4/g VSS/day
COD equivalent CH_4 produced	=	40.32 * 4.415 X 10^{-04} g COD
	=	0.018 g CH_4-COD/gVSS/day

2.2.6 For Feed 2 (Fig 5.8)

Slope of curve	=	2.8916
Activity	=	(2.8916*24)/ 1.526
	=	45.48 ml CH_4/g VSS/day
COD equivalent CH_4 produced	=	45.48 * 4.415 X 10^{-04} g COD
	=	0.02 g CH_4-COD/gVSS/day

2.2.7 For Feed 3 (Fig 5.9)

Slope of curve	=	3.7457
Activity	=	(3.7457*24)/ 1.526
	=	58.91 ml CH_4/g VSS/day
COD equivalent CH_4 produced	=	58.91 * 4.415 X 10^{-04} g COD
	=	0.026 g CH_4-COD/gVSS/day

APPENDIX III

CALCULATION OF KNETICS COEFFICIENT

3.1 YIELD COEFFICIENT

Assuming activity to be same for second and third feeds,

Initial VSS of Feed	=	15.255	g/l
VSS after second feed	=	15.2573	g/l
VSS after third feed	=	15.2606	g/l
Difference in VSS	=	$3.3X10^{-3}$	g/l

Difference in VSS between second and third feeds represent synthesis of biomass. The substrate consumed during the synthesis of biomass is taken as COD equivalent of total methane produced after the third feed. (Isa et al 1993)

CH_4 produced after third feed till CH_4 production ceases	=	182 ml
COD equivalent CH_4 produced	=	$182 \times 4.415 \times 10^{-4}$
	=	0.08 g COD
Yield Coefficient	=	Difference in VSS/COD equivalent
		$3.3 \times 10^{-3} / 0.08$
		0.04125 gVSS/gCOD

3.2 CALCULATION OF SUBSTRATE UTILIZATION RATE AND HALF VELOCITY CONSTANT

Initial Substrate Concentration	=	Substrate Consumed in Yield of Biomass	+ COD Equivalent of total CH_4 produced
Yield of Biomass	=	15.2606-15.255	
	=	$5.6X10^{-3}$	
Substrate Consumed	=	0.136 g COD	

COD equivalent of CH_4 produced = 0.08 g COD

S_0 Initial Substrate Concentration = 0.136 + 0.08

= 0.216 g COD

Maximum Substrate Utilization Rate = Maximum Slope of Substrate utilization Curve/ VSS in the reaction bottle.

Maximum slope of substrate utilization curve = -0.002 g COD/h

Maximum substrate utilization rate = (0.002 * 24)/1.526

= **0.0314 gCOD /gVSS.day**

3.3 CALCULATION OF WASTEWATER TREATMENT EFFICIENCY

Value of CH_4 produced at the end of third feed = 112 ml

COD equivalent of CH_4 produced = $112*4.415 \text{ X } 10^{-4}$

= 0.049

Efficiency is given by = (0.216-0.049)/0.216

= 0.7731

= **77.31 %**