Comparative Study of Two Packing Media for Anaerobic Filter Reactor for the Treatment of Cheese Whey

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Comparative Study of Two Packing Media for Anaerobic Filter Reactor for the Treatment of Cheese Whey

Major Project

Submitted in partial fulfillment of the requirements

For The Degree of

Master of Technology in Chemical Engineering

(Environmental Process Design)

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Declaration

This is to certify that

1. The thesis comprises my original work towards the degree of **Master of Technology in Chemical Engineering (Environmental Process Design)** at Nirma University and has not been submitted elsewhere for a degree.

2. Due acknowledgement has been made in the text to all other material used.

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Undertaking for Originality of the Work

I, Samir Vahora, 10MCHE13, give undertaking that the major project entitled "Comparative Study of Two Packing Media for Anaerobic Filter Reactor for Treatment of Cheese Whey" submitted by me, towards the partial fulfillment of the requirements for the degree of Master of Technology in Environment Process Design of Nirma University, Ahmedabad is the original work carried out by me and I give assurance that no attempt of plagiarism had been made.

I understand, that in the event of any similarity found subsequently with any published work or any dissertation work elsewhere, it will result in severe disciplinary action.

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Place:

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Certificate

This is to certify that the Major Project entitled "**Comparative Study Of Two Packing Media For Anaerobic Filter Reactor For The Treatment Of Cheese Whey**" submitted by **Mr. Samir Vahora (10MCHE13)**, towards the partial fulllment of the requirements for the degree of Master of Technology in Chemical Engineering of Nirma University of Science and Technology, Ahmedabad is the record of work carried out by his under my supervision and guidance. In my opinion, the submitted work has reached a level required for being accepted for examination. The results embodied in this major project, to the best of my knowledge, haven't been submitted to any other university or institution for award of any degree or diploma.

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Abstract

India has emerged as the largest milk producing country in the world with present level of annual milk production estimated as 121.8 million tonnes in 2010-11. We expect a production level of 155 million tonnes by the year 2016-17. The industry had been recording an annual growth of 4% during the period 1993-2005, which is almost 3 times the average growth rate of the dairy industry in the world.

The processing of milk not only yields various dairy and milk products but also generates some kind of waste or effluent. With the emergence of new techniques in the dairy industry, there lies a hidden responsibility for treatment of waste or effluent generated before its disposal.The strengthening of pollution control norms has forced the effluent treatment process to get more important for dairy industry. Now a day, the upgradation in the present techniques used for this treatment has gained importance. Anaerobic treatment process provides the advantage of energy production in form of biogas and less sludge production. In recent past, the process has earned more feasibility to cope up with the variability in effluent and rapid rate of its production after the development of several high rate reactors.

Amongst these several high rate reactors, anaerobic fixed reactors are the one which combines the advantage of rapid start up, ability to withstand shock loads, tolerance to high ammonia and VFA levels, ability to adapt intermittent feeding, simple construction and lower installation cost. Hence, it was selected to study its applicability and evaluate the performance for treatment of dairy effluent. Whey is considered to be the most unmanageable effluent due to its higher organic strength, exihibiting a BOD_5 values about 30,000 - 50,000 ppm and COD values about 60,000 - 80,000 ppm. Therefore, diluted cheese whey was selected to check the feasibility of anaerobic filter.

An important constituent of anaerobic filter is the packing media. Two pilot scale models are installed that were identical in every aspect except the packing media in them. The reactors were named A and B for Brickbats media and Polypropylene biorings media, respectively. After working out their volume calculation and porosity, they were started and commissioned and then operated at different HRTs. The performance was evaluated and a comparison was made between the reactors.

During the operation, the Organic Loading Rate(OLR) was increased in stepwise from 0.7 to 2.5 kgCOD/m^{3}d and the Hydraulic Retention Time (HRT) shortened to 5 days. The COD removal efficiency was more favorable in B (78%) respect to A(60%). The biomass concentration in the reactor was 4400 mg/l and 6500 mg/l in A and B respectively.

Under steady state conditions, the first-order, Stover-Kincannon and Grau-second-order kinetic models were used to represent the kinetics of organic matter removal in the anaerobic filter. The experimental data showed that the Grau kinetic models were the most suitable for predicting organic matter degradation.

ACKNOWLEDGEMENTS

Nomenclature

AD -   Anaerobic Digestion

BOD -   Biochemical Oxygen Demand

CDM -   Clean Development Mechanism

COD -   Chemical Oxygen Demand

CPCB -   Central Pollution Control Board

F/M -   Food to Microorganism ratio

GPR -   Gas Production Rate

HRT -   Hydraulic Retention time

OLR -   Organic Loading Rate

PP -   Polypropylene

SGP -   Specific Gas Production

SRT -   Solid Retention time

TS -   Total Solids

VFA -   Volatile Fatty Acids

VS -   Volatile Solids

VSS -   Volatile Suspended Solids

°C -   Degree Centigrade

mg / l -   milligram per liter

List of Figures

List of Tables

Contents

Chapter 1

INTRODUCTION

India has emerged as the largest milk producing country in the world with present level of annual milk production estimated as 121.8 million tonnes in 2010-11. We expect a production level of 155 million tonnes by the year 2016-17. The industry had been recording an annual growth of 4% during the period 1993-2005, which is almost 3 times the average growth rate of the dairy industry in the world. Milk processing in India is around 35%, of which the organized dairy industry account for 13% of the milk produced, while the rest of the milk is either consumed at farm level, or sold as fresh, non-pasteurized milk through unorganized channels. But the other side of this picture is not that much gloomy as it seems from one side [1][2].

Dairy industry, like most other agro-industries, generates strong wastewaters characterized by high biological oxygen demand (BOD) and chemical oxygen demand (COD) representing their high organic content. Dairy waste effluents are concentrated in nature, and the main contributors of organic load to these effluents are carbohydrates, proteins and fats originating from the milk. Since dairy waste streams contain high concentrations of organic matter, these effluents may cause serious problems, in terms of organic load on the local municipal sewage treatment systems. In addition to environmental problems that can result from discharge of dairy wastewaters, introduction of products such as milk solids into waste streams also represents a loss of valuable product for the dairy facilities.

The key parameters are BOD (with an average ranging from 0.8 to 2.5 grams per liter (g/l) of milk in the untreated effluent), chemical oxygen demand COD (normally about 1.5 times BOD level), total suspended solids (100 to 1,000 milligrams per liter (mg/l), total dissolved solids, phosphorus (10 to 100 mg/l), and nitrogen (about 6 percent of BOD level). Cream, butter, cheese, and whey production are major sources of BOD in wastewater. The strength of these organic compounds is measured in terms of BOD and COD. The waste load equivalents of specific milk constituents are: 1 kg of milk fat = 3

kg COD; 1 kg of lactose = 1.13 kg COD; and 1 kg protein = 1.36 kg COD [3].

In Indian scenario, the environmental pollution is pervasive, accelerating and inevitable, not only because of lack of responsiveness and alertness but due to the era of globalization where the quality of the product is the buzz word of any enterprise. So, tackling of effluent generated from the dairy processes is one of the most pertinent issues which we have to deal.

Effluent treatment is a responsibility for any industry and an inevitable process for it. With an increased attention over the environmental concerns, various pollution control acts and amendments have been developed and are enforced. Dairy industry in India also faces the poises of pollution control. Environmental Protection Act (EPA) 1986, Bureau of Indian Standards (BIS) 1986, air and water (Prevention and control of pollution; 1974 and 1981) are applicable for dairy industry. These standards make it a compulsion to cut down the strength of the effluent to the limits as stated in them. CPCB standards that applies to most of the dairy processing plants has laid the regulations for disposal of industrial effluent as applicable to dairy waste. The tolerance limits for other parameters is given in detail in Table 1.1.[1][2]

Table 1.1: CPCB Standard for Dairy Industry Effluent

Parameter	Standard
	Concentration in mg/l except pH
pH	6.5 - 8.5
BOD	100
Suspended Solids	150
Oil and Grease	10

Source:http://cpcb.nic.in/

Furthermore, Cheese production worldwide generates more than 145 million tonnes of liquid whey per year. Dairy wastewater comes from cheese producing industries; has a large COD value of about 50000-80000 mg/l. Cheese whey contains various organic

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[1]BOD may be made stringent upto 30 mg/l if the recipient fresh water body is a source for drinking water supply. BOD shall be upto 350 mg/l for the chilling plant effluent for applying on land provided the land is designed and operated as a secondary treatment system with suitable monitoring facilities. The drainage water from the land after secondary treatment has to satisfy a limit of 30 mg/l of BOD and 10 mg/l of nitrate expressed as N. The net addition to the groundwater quality should not be more than 3 mg/l of BOD and 3 mg/l of nitrate expressed as N. This limit for applying on land is allowed subject to the availability of adequate land for discharge under the control of industry, BOD value is relaxable upto 350 mg/l, provided the wastewater is discharged into a town sewer leading to secondary treatment of the sewage.

[2]Suspended solids limit is relaxable upto 450 mg/l, provided the wastewater is discharged into town sewer leading to secondary treatment of the sewage.

compounds as nutrients which are lactose (4.5-5% w/v), soluble proteins (0.6-0.8% w/v), lipids (0.4-0.5% w/v) and mineral salts (8-10% of dried extract). To make 1 kg of cheese, 9 kg of whey is generated. Because of its low concentration of milk constituents (6-7% dry matter); whey has commonly been considered a waste product [4]. Despite from the advantage of being a rich store of various important nutrients, there are problems in its disposal too.

A solution to this problem has now become an urgent need due to the increasing volumes of whey production, the centralization of production plants and strict legislative requirements regarding effluent quality. The rapid growth in the size of dairy operations has resulted in new laws and regulations governing the handling and disposal of effluent. Conventional treatment processes used for dairy industries wastewater are mainly aerobic processes, although anaerobic processes have also been employed increasingly in the last two decades.

Aerobic treatment is characterised by relatively high energy consumption and biomass production, leading to high operation costs and problems with the disposal of large amounts of sludge (incineration, seasonal variations in demand for it as fertilizer). Besides the relatively high COD/TN ratio of wastewater may require nutrient supplement. In comparison, for any wastewater treatment, anaerobic digestion reduces the COD of effluent; avoids use of costly aeration equipment and very little microbial biomass is produced. The biggest advantage is energy recovery in the form of methane. Up to 95% of the organic matter in waste stream can be converted into biogas.

It has been observed that among various anaerobic reactor configurations, in high rate anaerobic filter high COD removal efficiencies could be achieved even with extremely high COD contents, such as those present in the effluents generated during cheese making process. On the other hand, very dilute effluents can also be successfully treated.

The treatment capacity in any anaerobic treatment system is primarily determined by the concentration of active bacterial population retained within the anaerobic reactor. Due to the low growing nature of anaerobic bacteria, biomass has to be retained within the digester for a long period of time at a high concentration. Anaerobic filter is one of the anaerobic treatment systems which was initially designed to immobilize the biomass and achieve good system performances in terms of organic matter removal. However, a number of anaerobic filters have been installed commercially with little attention being paid to the nature of the packing. Often plastic media used in anaerobic filters have originally been designed for use in aerobic systems and therefore, have not been optimized for the special conditions required in anaerobic processes. This leads to long start-up time

and unstable operation and as well as low organic loading rates (OLR), resulting in large reactor volumes of high capital costs and requiring a large space allocation. The anaerobic filter can, therefore, often be unsatisfactory for industrial use. It is therefore, optimizing the support media for anaerobic biofilm systems would thus be of great benefit.

1.1 Scope of investigation

One of the most important aspects in the anaerobic filter design is the selection of efficient support material. It has been reported that the organic matter removal efficiency in fixed bed reactors is directly related to the characteristics of the support materials used for the immobilization of anaerobes. Factors affecting biofilm attachment are varied and numerous. It has been found out that there are strong correlations between size, shape, porosity and specific surface area of the packing material and the performance of anaerobic filters. The ideal packing material for the anaerobic filters has been described as one that maximizes both specific surface area and porosity.

A variety of natural materials such as smooth quartzite pebbles, shells, granite and other volcanic stones, zeolites, wooden blocks, brick ballast have been used for the attachment and growth of anaerobic biomass. Major drawbacks of these materials are that they have low porosity and they are bulky requiring strong supporting structure when to be used as packing media. In recent times, a few synthetic materials like polyvinyl-chloride sheets, needle-punched polyester, glassbeads, raschig rings, pall rings and rubber tyres have been tried as packing media. Essentially, these are media used for enhancing heat or mass transfer between two phases, where as for an effective packing material in an anaerobic reactor, the media should be able to support growth of good biofilm first which would in turn facilitate organic matter removal from the passing wastewater. These materials have high porosity and surface volume ratio and some of them are quite light in weight, too. Another advantage of synthetic media is its easy availability i.e. they are commercially available in the market in various sizes where as natural media (wood, stones, brickbats, pebbles etc.) of any one specific size needs to be prepared.

1.2 Objectives of the study

When a full scale anaerobic filter is designed, media related characteristics should be taken in to consideration in order to achieve optimum performance and economy of treatment. This study is taken up to compare the performance of natural and commercially available synthetic support material for the anaerobic filter reactor. Main objectives of the proposed work are:

- Select two packing media i.e. one natural and one synthetic and use them in pilot scale reactors

- Collect performance data and monitor the performance of two reactors

- Compare two packing media for their efficiency and cost

Chapter 2

REVIEW OF LITERATURE

2.1 Dairy effluent and its characteristics

Wastewaters from the dairy industry are usually generated in an intermittent way, so its flow rate and composition changes significantly. Moreover, since the dairy industry produces a variety of products the characteristics of these effluents also vary greatly, depending on the type of system and the methods of operation used. The use of acid and alkaline cleaners and sanitizers in dairy industry additionally influences wastewater characteristics and typically results in a highly variable pH [5]. The characteristics of the dairy wastewater and cheese whey are given in Table 2.1.

Table 2.1: Physical and Chemical Characteristics of the Dairy Wastewater

Components	Concentration(mg/lit)		
	Dairy	Whey	Whey permeate
pH	5.6 - 8	–	–
COD	1120 - 3360	75000	50000
BOD	320 -1750	40000	35000
Lactose	–	40000	40000
Propionate(mmol/lit)	–	5	4
K(mmol/lit)	–	38	36
Ca(mmol/lit)	–	7	2
Suspended Solids	28 -1900	–	–
Total Solids	–	50000	42000
Oil and Grease	68 - 240	–	–

2.2   Effluent treatment processes

Effluent treatment can employ a series of treatment and different options at various stages. The several methods which can be employed are classified below:

2.2.1   Primary treatment

It comprises of elementary physical treatment processes (such as screening, equalization, sedimentation, scum removal/oil removal/skimming) and chemical treatment processes (such as neutralization, flocculation, sedimentation, clarification).

2.2.2   Secondary treatment

The secondary treatment processes covers the majority of work done for reduction in strength of the effluent. The various processes that can be used as secondary treatment include biological treatment processes, chemical treatment processes, membrane methods and electrolytic methods.

Since the dairy effluent is practically biodegradable and have low suspended solids, only biological processes are economically viable and technically feasible for its treatment. The treatment removes major portion of the organic pollutant load from the effluent. The dairy effluent contains essential nutrients and comfortable water temperature leading to high rate of decomposition by microbes of different genera which may include bacteria, fungi, algae and protozoa. The biological treatment processes are categorized according to the growth phase and method of contacting the organic foods with microflora. They are also categorized according to the presence or absence of molecular oxygen upon which they are further classified into aerobic and anaerobic treatment methods.

Several options are available for conventional aerobic treatments systems which include aerated lagoons, activated sludge processes, stabilization ponds, trickling filters, oxygen ditches, aerobic bio-filters and rotating biological contactors, etc.; amongst which use of activated sludge method is the most popular in dairy industry.

However, aerobic treatment is characterized by bad odour production, relatively high energy consumption and biomass production. It also leads to relatively high operation cost and problems with the disposal of large amount of sludge (incineration, seasonal variation in demand for it as a fertilizer) [6].

In contrast, anaerobic processes generate energy in the form of biogas, and produce sludge in an amount that is significantly lower than that resulting from aerobic systems. The utilization of methane gas as a renewable energy from the anaerobic digestion can be used to obtain certified emission reduction (CER) credit by clean development mechanism (CDM) under the Kyoto protocol [7]. The other benefits of anaerobic digestion system include:

1. A relatively clean liquid can be produced for flushing and irrigation.

2. Odour and flies are significantly reduced or eliminated.

3. Pathogens are substantially reduced in the liquid and solid products.

4. Greenhouse gas emissions are reduced and carbon credits can be earned through it [8].

5. Energy can be generated in form of biogas. Nearly 90 - 95% of dissolved material could be transferred to energy that can be utilized in other sections of the dairy plant and reduce the power grid size of the plant.

6. A rich fertilizer can be produced for sale to the crop producers leading to generation of income.

7. No aeration equipment is required. Therefore, associated capital and maintenance costs are low.

8. System loading is not limited by oxygen transfer.

9. Cellular material (sludge) is produced in smaller quantity and is more stable.

10. Some problematic chemicals difficult to degrade aerobically could be degraded anaerobically.

11. Sludge microbes are viable up to one year and can be re-activated.

12. Small space requirement.

2.3   History of anaerobic digestion

Historical evidence indicates that the anaerobic digestion (AD) process is one of the oldest technologies. Biogas was used for heating bath water in Assyria during the 10th century BC and in Persia during the 16th century. AD advanced with scientific research and, in the 17th century, Jan Baptista Van Helmont established that flammable gases evolved from decaying organic matter. Also, Count Alessandro Volta in 1776 showed that there

was a relationship between the amount of decaying organic matter and the amount of flammable gas produced. In 1808, Sir Humphry Davy demonstrated the production of methane production by the anaerobic digestion of cattle manure.

The industrialization of AD began in 1859 with the first digestion plant in Bombay, India. By 1895, AD had made inroads into England where biogas was recovered from a well-designed sewage treatment facility and fueled street lamps in Exeter. Further AD advances were due to the development of microbiology. Research led by Buswell and others in the 1930's identified anaerobic bacteria and the conditions that promote methane production.

As the understanding of AD process control and its benefits improved, more sophisticated equipment and operational techniques emerged. The result was the use of closed tanks and heating and mixing equipment to optimize AD. Regardless of improvement AD suffered from the development of aerobic treatment and low-cost coal and petroleum. While the developed world shunned AD except as a wastewater sludge digestion technique, developing countries such as India and China embraced this technology. Most of the AD systems were small digesters using combined human, animal and kitchen wastes. Many community digesters were installed to produce large volumes of biogas for village electrification.

China and India have now adopted a trend towards larger, more sophisticated farmbased systems with better process control to generate electricity. With time, AD systems are becoming more complex and not limited to agriculture or animal waste treatment. The technology is now being applied for municipal waste treatment as well as industrial waste. Taiwan flares most biogas from waste treatment and has cut down river pollution, caused by direct discharge from the animal production industry, by simply using standard AD systems that serve 5,000 farms [9].

2.4 Concept of anaerobic digestion process

Anaerobic digestion is the breakdown of organic material by a microbial population that lives in an oxygen free environment. Anaerobic literally means "without air". The end products of anaerobic digestion are natural gas (methane) for energy production, nutrient rich organic slurry, and other marketable inorganic products.

The biogas mostly consists of up to 65 - 75% methane (CH_4) and carbon dioxide (CO_2) 30 - 40% by volume with small quantities of hydrogen sulfide (H_2S) and hydrogen (H_2).

The biogas can be combusted in a cogeneration unit to produce green energy. The solids recovered in the form of sludge after digestion can be used as an organic supplement to the soil.

Anaerobic digestion is carried out in four stages by a group, or consortia of bacteria, working together to convert organic matter into gas and inorganic constituents. The first step of anaerobic digestion, termed as hydrolysis is the breakdown of particulate matter to soluble organic constituents. Hydrolysis or the liquefaction of insoluble materials is the rate-limiting step in anaerobic digestion of waste slurries. This step is carried out by a variety of bacteria through the release of extra-cellular enzymes. The soluble organic materials that are produced through hydrolysis consist of sugars, fatty acids, and amino acids. Those soluble constituents are converted to carbon dioxide and a variety of short chain organic acids by the acid forming bacteria in the second step termed as acidogenesis. This step is coupled with the third step acetogenesis that occurs through carbohydrate fermentation in which acetate is the main product with other metabolic processes. Other groups of bacteria reduce the hydrogen toxicity by scavenging hydrogen to produce ammonia, hydrogen sulfide, and methane in the step fourth, called as methanogenesis. In this step a group of methanogens converts acetic acid to methane gas. A wide variety of physical, chemical, and biological reactions take place.

The bacterial consortia catalyze these reactions. Consequently, the most important factor in converting waste to gas is the bacterial consortia. The acetic acid fermenting methane bacteria are also very important, since if they fail, 72% of the waste cannot be converted to methane gas [10]. The bacterial consortia are essentially the "bio-enzymes" that accomplish the desired treatment. A poorly developed or stressed bacterial consortium will not provide the desired conversion of waste to gas and other beneficial products. The processes involved are shown in the Figure. 2.1.

2.4.1 Hydrolysis

During hydrolysis, the first stage, bacteria transform the particulate organic substrate into liquefied monomers and polymers i.e. proteins, carbohydrates and fats are transformed to amino acids, monosaccharides and fatty acids respectively. Equation 1 shows an example of a hydrolysis reaction where organic waste is broken down into a simple sugar, in this case, glucose.

$$C_6H_{10}O_4 + 2H_2O \rightarrow C_6H_{12}O_6 + 2H_2 \tag{1}$$
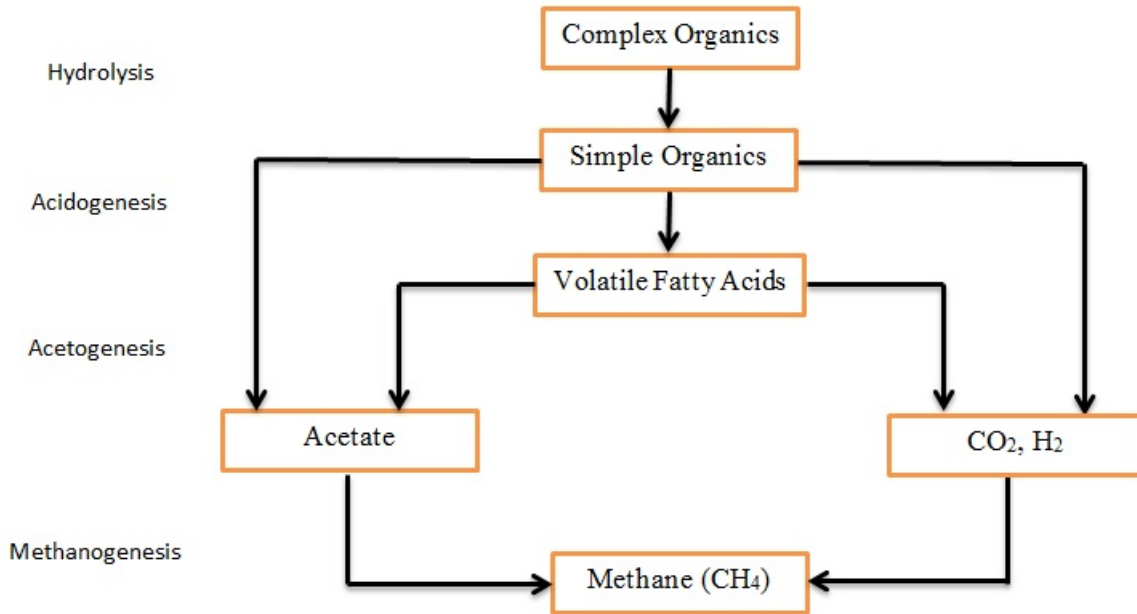
Figure 2.1: Stages of Anaerobic Digestion Process

2.4.2 Acidogenesis

In the second stage, acidogenic bacteria transform the products of the first reaction into short chain volatile acids, ketones, alcohols, hydrogen and carbon dioxide. The principal acidogenesis stage products are propionic acid (CH_3CH_2COOH), butyric acid ($CH_3CH_2CH_2COOH$), acetic acid (CH_3COOH), formic acid ($HCOOH$), lactic acid ($C_3H_6O_3$), ethanol (C_2H_5OH) and methanol (CH_3OH), among other. From these products, the hydrogen, carbon dioxide and acetic acid will skip the third stage, acetogenesis, and be utilized directly by the methanogenic bacteria in the final stage. Equations 2, 3 and 4 represent three typical acidogenesis reactions where glucose is converted to ethanol, propionate and acetic acid, respectively.

$$C_6H_{12}O_6 \leftrightarrow 2CH_3CH_2OH + 2CO_2 \qquad (2)$$

$$C_6H_{12}O_6 + 2H_2 \leftrightarrow 2CH_3CH_2COOH + 2H_2O \qquad (3)$$

$$C_6H_{12}O_6 \rightarrow 3CH_3COOH \qquad (4)$$
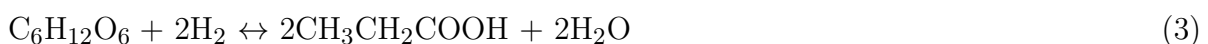
2.4.3 Acetogenesis

In the third stage, known as acetogenesis, the rest of the acidogenesis products, i.e. the propionic acid, butyric acid and alcohols are transformed by acetogenic bacteria into hy-

drogen, carbon dioxide and acetic acid. Hydrogen plays an important intermediary role in this process, as the reaction will only occur if the hydrogen partial pressure is low enough to thermodynamically allow the conversion of all the acids. Such lowering of the partial pressure is carried out by hydrogen scavenging bacteria, thus the hydrogen concentration of a digester is an indicator of its health. Equation 5 represents the conversion of propionate to acetate, only achievable at low hydrogen pressure. Glucose (Equation 6) and ethanol (Equation 7) among others are also converted to acetate during the third stage of anaerobic fermentation.

$$CH_3CH_2COO\text{-} + 3H_2O \leftrightarrow CH_3COO\text{-} + H^+ + HCO_3\text{-} + 3H_2 \tag{5}$$

$$C_6H_{12}O_6 + 2H_2O \leftrightarrow 2CH_3COOH + 2CO_2 + 4H_2 \tag{6}$$

$$CH_3CH_2OH + 2H_2O \leftrightarrow CH_3COO\text{-} + 2H_2 + H^+ \tag{7}$$
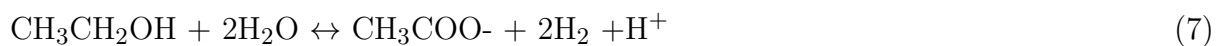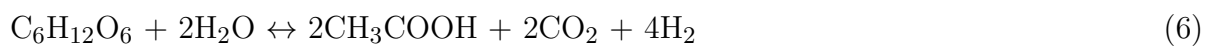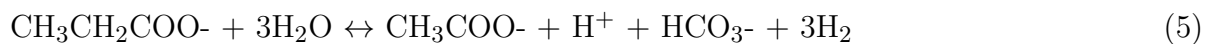
2.4.4 Methanogenesis

The fourth and final stage is called methanogenesis. During this stage, microorganisms convert the hydrogen and acetic acid formed by the acid formers to methane gas and carbon dioxide (Equations 8,9 and 10).The bacteria responsible for this conversion are called methanogens and are strict anaerobes. Waste stabilization is accomplished when methane gas and carbon dioxide are produced.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{8}$$

$$2C_2H_5OH + CO_2 \rightarrow CH_4 + 2CH_3COOH \tag{9}$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \tag{10}$$

2.5 Factors controlling the conversion of waste to biogas

2.5.1 Type of effluent

The biodegradability of effluent depends on its composition. For e.g. the vegetable market waste, oil mill effluent, paper mill effluent, dairy effluent and all others though are organic in nature, will have different biodegradability. Even the biodegradability of dairy effluent will differ if it is taken from different sections of the plant. Vidal et al.

(2000), studied the anaerobic biodegradability of two synthetic wastewaters. One rich in fat (COD ratio; Fats / Proteins / Carbohydrates: 1.7 / 0.57 / 1) and the other with a low fat content (COD ratio; Fats / Proteins / Carbohydrates: 0.05 / 0.54 / 1) in samples with total COD ranging from 0.4 to 20 g/l. They reported that anaerobic biodegradation of fat-rich wastes was slower than carbohydrate-rich wastes due to the slower hydrolytic step of fat degradation which prevented the accumulation of (VFAs) and favoured the overall process. The biodegradability of effluent can be estimated by biological kinetics studies in which the kinetic constants represent the treatability characteristics of the wastewater [11]. The biological treatment kinetics of dairy effluent indicates its excellent anaerobic treatment characteristics.

2.5.2 Concentration of effluent

The waste characteristics can be altered by simple dilution. Water reduces the concentration of certain constituents such as nitrogen and sulfur that produce products like ammonia and hydrogen sulfide that act as inhibitory to the anaerobic digestion process. High solids digestion creates high concentrations of end products that inhibit anaerobic decomposition. Therefore, some dilution can have positive effects. The literature indicates that greater reduction efficiencies occur at concentrations of approximately 6 - 7% total solids. Dilution also causes stratification within the digester [5].

2.5.3 Temperature

Anaerobic bacteria thrive within two ranges: the mesophilic range (from 25 – 40°C) and the thermophilic range (from 50 – 65°C). The optimum temperature for mesophilic digestion is 35°C and a digester must be maintained between 30°C and 35°C for most favorable functioning [12]. The psychrophilic conditions are rare and not feasible in tropical countries like India. The thermophilic zone performs better than mesophilic. It allows higher loading rates and achieves a higher rate of pathogen destruction as well as a higher degradation of the substrate but it is more sensitive to toxins and smaller changes in the environment. It is also less attractive from an energetic point of view since heat is required to be maintained for the process. On the contrary, bacteria operating in the mesophilic range are more robust and can tolerate greater changes in the environmental parameters, including temperature Ahn and Forster (2000), Yilmaz et al. (2008) and Kim et al. (2006), separately studied on two anaerobic filters, one mesophilic (35°C) and one thermophilic (55°C). Both were operated with a starch-based feed, paper mill wastewater and food based effluent respectively. The results showed a better performance of thermophillic reactors than mesophilic reactors at different organic loading rates and HRTs in terms of COD removal and biogas production [12][13][14]. Viraraghavan and

Varadarajan (1996), used anaerobic filters employing ballast rings as packing media and studied low temperature kinetics of the reactor. They reported a poor fit to the statistical model of the reactors performance at low temperatures (5°C and 10°C for septic-tank effluent and 12.5°C and 21°C for dairy wastewater) and low HRTs [15].

2.5.4 The presence of toxic materials

Toxic materials such as fungicides and antibacterial agents can have an adverse effect on anaerobic digestion. However, the anaerobic process can handle the small quantities of toxic materials without difficulty [5].

2.5.5 The pH and alkalinity

The range of acceptable pH for the bacteria participating in digestion is from 5.5 to 8.5, though the closer to neutral, the greater the chance that the methanogenic bacteria will function. Most methanogens function in a pH range between 6.7 and 7.4, and optimally between 7.0 and 7.2. Methane producing bacteria require a neutral to slightly alkaline environment (pH 6.8 to 8.5) in order to produce methane [5]. Acid forming bacteria grow much faster than methane forming bacteria. If acid-producing bacteria grow too fast, they may produce more acid than the methane forming bacteria can consume and thus excess acid builds up in the system. The pH drops, and the system may become unbalanced, inhibiting the activity of methane forming bacteria. Ghaly A.E. (1996), investigated the performance of a two-stage, two-phase, unmixed anaerobic digester of 155 l working volume operating on acid cheese whey and dairy manure at various temperatures and hydraulic retention times. The effect of controlling the pH of the methanogenic stage of cheese whey digestion on the biogas production rate and pollution potential reduction was also investigated. He reported that increasing the temperature and/or decreasing the hydraulic retention time gives an increased rate of biogas production for both cheese whey (with and without pH control) and dairy manure [16].

2.5.6 Hydraulic retention time

The hydraulic retention time (HRT) is the average time that the wastewater or sludge is in the reactor. The conversion of volatile solids to gaseous products in an anaerobic reactor is controlled by the HRT. The HRT values affect the rate and extent of methane production of all the operational conditions within anaerobic reactor, for e.g. temperature, solids concentration, and volatile solids content of the feed sludge. It is calculated on the liquid volume basis. The hydraulic retention time is important since it establishes the quantity of time available for bacterial growth and subsequent conversion of the organic material

to gas [5]. The flow rate is the design factor for retention time. It should be designed such that the waste passes through the filter smoothly and uniformly without breaking the microbial flocs. It should be long enough to prevent the active biological cells being washed off [10]. Umana et al. (2008), studied over the effect of HRT in treatment of screened dairy manure in anaerobic fixed film reactor and found that methane yield is also a function of HRT. They also reported that the effluent alkalinity increases with an increase in HRT because of the organic matter decomposition in anaerobic conditions that ultimately increases the reactor's stability and pH [17].

2.5.7 Solid retention time

The solids retention time (SRT) is the average time that bacterial solids remain present in the reactor. It can also be defined as the mass of cells in the reactor to the mass of cells wasted per day. Since the generation time of methane-forming bacteria is relatively long as compared with that of aerobic bacteria and facultative anaerobic bacteria, typical SRTs for anaerobic reactors are more than 12 days. At retention time of less than 10 days significant washout of methane forming bacteria occurs. The SRT is not greatly affected by nature of the waste water or sludge under treatment, unless the wastewater or sludge is toxic to the bacteria. Longer SRTs can take care of organic and hydraulic shock loading, toxicity and fluctuations in pH and temperature [10]. It can be achieved either by increasing the volume of the reactor or by increasing the concentration of bacteria (solids).

2.5.8 The ratio of food to microorganisms

Organic matters in the wastewaters are natural food for the micro-organisms. So their increased concentration stimulates the microbial growth. At the same time their concentration should not be so high as to increase the burden on the biological mass. The ratio of the kg of waste supplied to the kg of bacteria available to consume the waste is the food to microorganism ratio (F/M). This ratio is the controlling factor in all biological treatment processes. Lower F/M ratio will result in a greater percentage of the waste being converted to gas. Usually for laboratory and pilot scale models organic loading rates used ranges between 0.4 to 27 kg COD/m^3 d. For full scale industrial application, it is between 4 to 16 kg COD/m^3 d. However, if the culture is well acclimatized in the reactor, it can take shock loading without resulting in the complete washout of the system.

2.5.9 Carbon and Nitrogen ratio

Nitrogen present in the feedstock has two benefits:

- It provides an essential element for synthesis of amino acids, proteins and nucleic acids; and

- It is converted to ammonia which, as a strong base, neutralizes the volatile acids produced by fermentative bacteria, and thus helps maintain neutral pH conditions essential for cell growth.

An overabundance of nitrogen in the substrate can lead to excessive ammonia formation, resulting in toxic effects. Bacteria need a suitable ratio of carbon to nitrogen for their metabolic processes. C:N (carbon to total nitrogen) ratios higher than 23:1 were found to be unsuitable for optimal digestion, and ratios lower than 10:1 were found to be inhibitory.

2.5.10   Organic loading rate

The rate of digester loading Neither the hydraulic retention time (HRT), nor the solids retention time (SRT) tells the full story of the impact that the influent waste concentration has on the anaerobic digester. One waste may be dilute and the other concentrated. The concentrated waste will produce more gas per gallon and affect the digester to a much greater extent than the diluted waste. A more appropriate measure of the waste on the digester's size and performance is the loading. The digester loading can be calculated if the HRT and influent waste concentration are known. Increasing the loading will reduce the digester size but will also reduce the percentage of substrate converted to gas.

2.6   Advancements in anaerobic reactors

In recent times, the emphasis has shifted to high rate bio-methanation systems which are based on the concept of sludge immobilization techniques (UASB, fixed films, etc) [18]. The main concept of the high rate anaerobic reactor is to retain the biomass especially the methanogenic bacteria in the reactor. The anaerobic fixed film reactor is that lets the biomass adhere and grow on the media. Therefore, the reactor can maintain more biomass that will increase the efficiency and the stability of system. The high efficiency in degrading organic materials in wastewater and producing biogas is due to the attached microorganism on the supporting material (biofilm) in the system. High rate anaerobic treatment is becoming more and more applied for the treatment of domestic sewage, especially in the developing countries, because of low constructional, operational and maintenance costs, small land requirements, low excess sludge production and biogas production. For tropical areas where the temperature ranges between 20°C and 35°C, the anaerobic process holds prospects for the treatment of waste. Eldmenn et al., worked

with dynamic, pulsating anaerobic filter and compared its performance with UASB. In a pulsating, dynamic anaerobic filter, the support for the anaerobic bacteria is moved gently up and down. Now a day, multifed system are also available. The effectiveness of a multi-fed upflow anaerobic filter process for the methane production from a rice winery effluent at ambient temperatures and reported that the multi-fed upflow anaerobic filter was proved to be more efficient than the single-fed reactor in terms of COD removal efficiency and stability against hydraulic loading shocks [19][20].

2.6.1 Hybrid reactors(Anaerobic Filter)

Hybrid reactors have become a trend for modern anaerobic digestion process. These hybrid reactors are in fact the combination of two different high rate reactors to work as one unit. Anaerobic filter reactor can also be operated with multiple phases using different combinations. Benis et al. (2009),worked on the multistage bioreactors, which fall into the category of hybrid reactors [21]. Cordoba et al. (1995), studied the performance of two reactors, one was anaerobic fixed film reactor and the other was hybrid reactor whose upper portion served as anaerobic fixed film reactor and the bottom portion as UASB reactor. He concluded that a combined system resulted in an increased efficiency of removal of organic matter [22].

Banu et al. (2007), operated on two-stage anaerobic treatment using hybrid upflow anaerobic sludge blanket reactor (HUASB) with polyurethane foam (PUF) and polyvinyl chloride (PVC) and concluded that two stage or two phase digestion is expected to constitute a better alternative for the complete treatment of dairy wastewater than single stage high-rate anaerobic reactors and two phase anaerobic reactors [23].

2.6.1.1 Advantages of anaerobic filter

The anaerobic fixed film reactor has the following advantages or the process capabilities [24]:

1. Rapid start-up with a minimum of operational problems.

2. Ability to withstand shock loadings without significant decrease in digestion efficiency.

3. Tolerance to high ammonia and VFA levels and to extremes of pH.

4. Ability to adapt to intermittent feeding and rapidity of restart after lengthy shut down periods.

5. Ability to accept high loading rates and to operate at short retention times of the order of several hours to several days.

6. High COD and VFA removal (70 - 95%).

7. High methane content (more than 70%) in the biogas produced.

8. Similar operational performance on wide range of support media.

9. Inexpensive to construct and maintain.

10. Anaerobic filters can be coupled up with other high rate reactors in multiple stage process, enabling the concept of hybrid reactors.

2.6.2 Role of packing media

One of the most important aspects in the anaerobic fixed film reactor design is the selection of efficient support material.The packing mediaplaced in a particular section only, mostly it is placed at the neck for upflow reactors and it is placed at the bottom for down flow reactors. It has been reported that the organic matter removal efficiency in these reactors is directly related to the characteristics of the support materials used for the immobilization of anaerobes. Factors affecting biofilm attachment are varied and numerous. It has been found that there are strong correlations between size, shape, porosity and specific surface area of the packing material and the performance of anaerobic fixed film reactors. The ideal packing material for the anaerobic filters has been described as the one that maximizes both specific surface area and porosity.

The choice of packing media depends both on characteristics of effluent or substrate and its own inherent characteristics such as specific surface area, porosity, surface roughness, pore size and orientation of the packing material. High specific surface area and porosity, large pore size and rough surface for packing material improve the performance of an anaerobic fixed film reactor. Oriented and porous packing media show better performances than random and non-porous packing material. The reactor with non-porous packing showed instability above an organic loading rate (OLR) of 4 kg COD/m^3 d, while the reactor with porous packing was still stable at OLRs up to 21 kg COD/m^3 d[5]. Now-a-days synthetic packing media are available with much higher surface/volume ratio in comparison with conventional rock media. Apart from porosity and surface area surface characteristics also affect the biomass retention characteristics. It has been observed that methanogens have difficulty in adhering to the surface like glass and polyvinyl chloride (PVC). On the other hand, activated carbon, ceramic and porcelain provide adequate roughness to promote microbial growth on the surface.

Performance of fixed film reactors with natural and synthetic media was tested at mesophilic and psychrophilic temperatures by D R Vartak et.al (1997). Eight digesters were maintained in an environmental chamber, with the temperature varied between 37°C and 10°C. Two digesters were packed with limestone gravel; two with pieces cut from non-woven polyester matting; two with a combination of limestone gravel and polyester pieces and two had no packing. Digester operation was initiated at a temperature of 37°C. After the digesters reached stable operation at the initial temperature, the temperature was lowered slowly to 10°C. The temperature was held at 10°C for 5 weeks after stabilizing. The polyester medium with its high porosity and surface to volume ratio had the best overall performance for methane productivity at both 37°C and 10°C [25].

A number of biofilm support media including foam cubes, bamboo rings, fire bricks, PVC rings and gravels were employed to immobilize biomass for reduction in biological oxygen demand (BOD) , COD and volatile suspended solid (VSS) of dairy wastewater in batch and repeated batch cultivation systems by J I Qazi et.al (2011). Performance data were collected at 1, 2, 4, 6 and 8 d HRT. It was observed that an increase in HRT caused corresponding increase in COD reduction up to 6 d HRT and then on COD reduction was almost constant. It was also apparent from these experiments that the efficiency of COD removal was associated with the nature and properties of support material involved in the attachment of biomass. It was categorized as: fire bricks>gravels >foam cubes>PVC rings>bamboo rings. The same trend was observed in both batch and repeated batch operation. In addition, it was also felt that the performance of support material might be attributed to chemical properties interlinked with its physical properties [26].

H. Patel (2000) studied the anaerobic digestion of waste water from a petrochemical plant, manufacturing Nylon-6 in continuously fed, up-flow fixed-film column reactors using different biomass support materials such as bone char, charcoal, bricks, plastic beads and polyurethane foam under varying hydraulic and organic loading rates. Experimental results showed bone char as the best support material with high biomass-retaining capacity because of its high specific surface area and pore specific volume. This system could treat waste water at hydraulic retention times (HRT) as low as 2.5 days with organic loading rates as high as 21.76 kg COD/m^3 d using acidic feed of pH 2.5 resulting in a 95% COD reduction with biogas production of 11.76 m^3/m^3 of reactor volume day. Total alkalinity of 1700 mg $CaCO_3$ /l and pH of 7.5 of the treated wastewater were observed at 2.5 days HRT, indicating that methanogenesis appear to be alkalizing step and wastewater with pH as low as 2.5 can be treated as such without neutralization with retention of methanogenic biomass on bone char [27].

Ugurlu and Forster (1992) studied two thermophilic anaerobic filters, one with porous media and the other with a non-porous media. The performance of the filters was monitored during and after the application of organic shock. The results show that, in general, the filter with the porous packing had greater stability. They also reported that the filters were less tolerant of organic shocks that were applied at a constant hydraulic retention time than to those in which the hydraulic retention time was also varied. Activated carbon, polyvinyl chloride supports, hard rock particles, and ceramic rings were the film supports which were tried. Reactor configuration and operation (upflow or downflow) also had a marked effect on performance of the reactor [28].

Bodkhe (2008) used a module of inclined tube settlers (ITS) that was incorporated in the reactor to control input of SS to the anaerobic filter to avoid media clogging [29]. Reticulated polyurethane foam (porous media) appeared to be an excellent colonization matrix for an anaerobic filter reactor as it provided a high specific surface area and a high porosity [30]. Zaher et al. (2008), Anderson (2002), Reyes et al. (1999) worked on fixed bed systems and used automobile tyre, straw, waste tyre rubber as packing material and reported satisfactory results [31][32][33].

S A Habeeb et. al (2011) while studying the performance of hybrid reactor using palm oil mill effluent observed an increase of COD removal after day 40th in reactor with palm oil shell as media while the same was lower for reactor with fine gravel as media. The removals were 82% and 78% respectively. Similar trend was observed for TSS and turbidity removal also [34].

Laboratory scale experiments were carried out by S. Ghaniyari-Benis et.al (2009) using a multistage anaerobic biofilm reactor of three compartments with a working volume of 54- L for treating synthetic medium-strength wastewater containing molasses as a carbon source. PVC Pall Rings with nominal size 25 mm, thickness 1 mm, surface area 206 m^2/m^3 and porosity 90% was used as packing media. It proved to be an efficient reactor configuration for the treatment of medium-strength synthetic wastewater. For an OLR of 9 kg COD/m^3 d, the molasses based wastewater was treated with 88.3% COD removal efficiency. This reactor also showed high resistance and good recovery when toxic shock was applied [21].

Han-Qing Yu et.al (2006) performed a lab-scale investigation to examine the effectiveness of a multi-fed upflow anaerobic filter for the methane production from a rice winery effluent at ambient temperatures. They used string shaped three-dimensional plastic fibrous media. The experiment was carried out in two identical 3-liter upflow filters, one single-fed reactor and the other multi-fed reactor. The results showed that the multi-fed

reactor, operated at the ambient temperatures of 19–27°C and influent COD varying from 8.34 to 25.76 g/l, could remove over 82% of COD even at an organic loading rate of 37.68 g COD/l d and a short hydraulic retention time of 8 h. This reactor produced biogas with a methane yield of 0.30–0.35 l CH_4/g $COD_{removed}$. The multi-fed upflow anaerobic filter was proved to be more efficient than the single-fed reactor in terms of COD removal efficiency and stability against hydraulic shock loading [20].

Attachment, strength and performance of a porous media in an upflow anaerobic filter treating dairy wastewater was studied by O. Ince et.al (2000). The media used was raschig rings of porous sintered glass. The reactor performed well in terms of COD removal efficiency, methane yield and methane percentage. The attached biomass consisted of a mixture of various auto-fluorescent methanogenic populations of rod, cocci and sarcina shaped and filamentous species. The filaments were at low numbers indicating a non-filamentous biofilm. Accumulation of biomass on the media was significant and was not susceptible to high shear stresses. There was approximately 50% reduction in the compressive strength of the sintered glass media after eight months of operation. Consequently, it could be concluded that any kind of material which loses its compressive or mechanical strength or swells over a short duration cannot be considered for use as support medium in any microbial film process [35].

Three types of carriers were studied in methanogenic biofilm reactors by Anthony Manoni Mshandete et.al (2007). The carrier materials were consisted of sisal fibre waste, pumice stone and porous glass beads and the bioprocess evaluated was the methanogenesis of sisal leaf waste leachate. Process performance was investigated by step-wise increasing the organic loading rate. The best results were obtained from the bioreactor packed with sisal fibre waste. It had the highest COD removal efficiencies in the range of 80-93% at OLRs in the range of 2.4-25 g COD/ l d. The biodegradation of the sisal fibre was measured at the end of the experimental period and it was observed that though this media performed well, around 50% of the sisal fibre waste was degraded during the experimental period of about 8 months [36].

Sumi S. and Lea Mathew studied the performance of an upflow anaerobic hybrid reactor (UAHR) for the treatment of synthetic wastewater at different organic loading rates and filter media volumes. The filter media used in the reactor was polyurethane foam (PUF) blocks of size 2.5cm x 2.4cm x 2.3cm. During a nine-month operation, organic loading rate was increased from 0.414 to 1.696 g COD/l d, with corresponding reduction in HRT from 48 hours to 12 hours. The filter media volume was increased from 20% to 40%. The optimum performance of reactor was attained at HRT of 18 hours for 35% filter media

volume. The reactor effectively removed 90.50% of COD, 93.27% of BOD and 87.14% of turbidity at optimum condition [37].

M. Wu et.al (2000) studied influence of media-packing ratio on performance of anaerobic hybrid reactors(AHR). Four laboratory upflow anaerobic hybrid reactors, each with a total unpacked volume of 7.85 l, with varying packing depths, were operated at organic loading rates from 1 to 24 g COD/l d. The media-packing ratios were 75%, 60%, 40% and 20% of the total reactor height in the AHRs. The results indicated that 20% media packing ratio was satisfactory even when high organic loading rate was expected. When operated at 1 and 2 g COD/l d, COD profiles along the reactor height from bottom to top showed a plug-flow regime. From 4 to 12 g COD/l d, the COD profiles were distorted in the reactors with 20%, 40% and 60% packing, while at 16 g COD/l d and above, COD profile indicated homogeneity in each reactor, suggesting a perfectly-mixed regime [38].

Two laboratory-scale anaerobic fixed bed reactors were evaluated for treating dairy manure in upflow mode and semicontinuous feeding by Oscar Umana et.al (2008). One reactor was packed with a combination of waste tyre rubber and zeolite (R1) while the other had only waste tyre rubber as microorganism immobilization support (R2). Higher COD, BOD_5, total and volatile solids removal efficiencies were always achieved in the reactor R1. No clogging was observed during the operation period. Methane yield was found to be a function of HRT and of type of support used, and was 12.5% and 40% higher in reactor R1 than in R2 for HRTs of 5.5 and 1.0 days, respectively [17].

G.Sunil kumar (2007) while investigating the treatment of distillery spent wash used anaerobic hybrid and USAB reactors for the treatment . The start-up and granulation study demonstrated that early start-up and granulation were achieved in case of hybrid reactor (45 days) as compared with UASB reactor (60days). The investigation of the effect of HRT on the performance of reactors indicated that at optimum HRT (5 days) and OLR 8.7 kg COD/m^3 d, the COD removal in hybrid and USAB reactor was found to be 79% and 74.5% respectively. The rate of sludge washout was reducing by 25% in hybrid reactor as compared with the USAB reactor. The study on the shock loading capacity of the reactors revealed that hybrid reactor is capable of resisting organic shock load up to two times as compared to the USAB reactor capable of resisting the shock loading up to 1.5 times of normal organic load [39].

Rajesh Babu (2006) studied treatment of sago wastewater using Hybrid Upflow Anaerobic Sludge Blanket (HUASB) reactor, at organic loading rates varying from 10.7 to 24.7 kg COD/m^3 d. Polyurethane foam (PUF) cubes were used as carrier material. After 130 days of start-up, the reactor produced appreciable decrease in COD of wastewater and

removed solids efficiently. The COD removal varied from 91-87%. While the removal of total solids was in the range of 61-57%, that of volatile solids varied from 70-67%. The ideal OLR for the reactor was 23.5 kg COD/m^3 d. The reactor could be operated at a considerably higher OLR of 23.5 kg COD/m^3 d, which is twice the loading rate suggested for the treatment in anaerobic filter [40].

R. Rajkumar (2011) performed an experiment on bench scale continuous upflow anaerobic filter (UAF) reactor for poultry slaughterhouse wastewater and the pleated PVC ring was selected as packing media. Because of its pleated surface, it can retain more biomass on surfaces rather than plain surfaces. The reactor took 147 days for complete start-up with removal efficiencies of total COD and soluble COD of 70 and 79% respectively. The maximum total COD removal efficiency of 78% was achieved at an organic loading rate of 10.05 kg/m^3 d and at an HRT of 12 h. The average methane content varied between 46 and 56% and methane yield at maximum removal efficiency was 0.24 m^3 CH$_4$/kg COD$_{removed}$ d. Sludge granules of 1-2 mm were observed in the interstices of packing media [41].

P. Chaiprasart (2003) monitored performances of three anaerobic hybrid reactors with various nylon fibre densities per packed bed volume (33, 22, and 11 kg/m^3 in R1, R2, and R3, respectively) as supporting media through their ability to remove organic compounds in cassava starch wastewater. The COD removal efficiency was more favourable in R1 (87%) and R2 (84%) than in R3 (70%). The total biomass in the reactors with greater nylon fibre densities was also higher and increased from 20.4 to 67.3 g VSS and to 57.5 g VSS in R1 and R2, respectively.

The amount and density of the media in an AHR considerably affected the wastewater treatment performance since the media played a direct role in retaining the biomass inside the system by either being a place for attachment or acting as a gas/solid separator. As opposed to 11 kg/m^3, the densities of nylon fibre of 33 and 22 kg/m^3 seemed to generate better system stability even though the specific treatment was slightly lower. Also, the COD removal efficiency of more than 80% was readily achieved in higher medium density reactors compared to merely 70% in the least density one in the experiment [42].

D. Ioannis (2006) reported his experience of operating upflow anaerobic filter reactors with ceramic saddles, plastic rings, and crushed stone packing for the treatment of raw municipal wastewater under a wide range of hydraulic and organic loadings and operating conditions. Column profile sampling, draining, and biomass evaluation studies were conducted to ascertain the functioning of the reactors and accumulation of biosolids. The

distribution of organics and solids with column height and length of operation was different in the three reactors. Crushed stone packing with lowest void ratio was characterized by a gradual increase in concentration, starting at the 20 cm position and progressing to higher elevations. No signs of clogging were observed in any of the three reactors, indicating that biomass accumulation did not constitute a problem for the long-term operation of an UAF treating raw municipal wastewater [43].

A. Ramakrishnan (2006) performed the treatment of synthetic coal wastewater at the mesophilic temperature of 27±5°C in anaerobic hybrid reactors. Synthetic wastewater with an average COD of 2240 mg/l, phenolic concentration of 752 mg/l and a mixture of volatile fatty acids was fed to three hybrid reactors. The filter media consisted of PVC rings. Hybrid UASB reactors could successfully degrade synthetic coal waste water with an influent phenolic concentration of 752 mg/l at an organic loading rate of 2.24 g COD/l d and an HRT of 24 h at mesophilic temperature (27±5°C). Particle size distribution in the sludge bed revealed that the granules of smaller diameter dominate in the upper portion of the sludge bed while those of larger diameter occupy the lower portion of the sludge bed [44].

G. Srinivasan (2009) studied the Diphasic Fixed Film Fixed Bed (DFFFB) Anaerobic digester for dairy wastewater. The experiment was run for different combinations of influent COD - 8000, 8996, 9956, 10976 and 11981 mg/l and flow rate of 0.006, 0.012, 0.024, 0.036 and 0.048 m^3/d. The overall reactor performance showed maximum removal of COD as 70.40% at a flow rate of 0.006 m^3/d for a OLR of 1.265 kg COD/m^3d .The maximum yield of bio-gas at 0.330 m^3 of gas/ kg COD removed was observed at an average influent COD of 11981 mg /l corresponding to an OLR of 14.812 g COD/l d [45].

T. Yilmaz (2008) performed an experiment on two anaerobic filters. One mesophilic (35°C) and one thermophilic (55°C) reactor were operated with paper mill wastewater at a series of organic loadings. Each filter was packed with raschig rings. The HRT ranged from 6 to 24 h with OLR 1.07–12.25 g COD/l d. At loading rates up to 8.4 g COD/l d, there was no difference in terms of the removal of soluble COD (SCOD) and gas production. At the higher organic loading rate, the SCOD removal performance of thermophilic digester was slightly better compared to mesophilic digester. Similar trend was also observed in terms of the daily methane production [46].

Table 2.2: Performance of Different Packing Media

Reactor	Feed	Packing Media	OLR (g COD/l d)	Biogas Yield (m^{3}CH$_4$/kg COD)	COD Removal (%)	Ref.
Hybrid	Distillary Spent Wash	PVC Pipe	8.7	52.37 lit/d	79	39
Hybrid	Sago Wastewater	Plastic cut rings	23.4	30.7 m^3/d	83	40
Hybrid	Cassava starch wastewater	Nylon Fiber	0.5-0.4	–	70-87	42
Hybrid	Domestic Sewage waste	Reticulated Polyurethane foam (RPF)	(influent COD) 518 ppm	–	55	30
Hybrid	Synthetic wastewater	Polyurethane foam (PUF)	0.4-1.7	–	90.5	37
Hybrid	synthetic coal wastewater	PVC rings	2.24	0.5	88±1	44
Anaerobic filter	Paper mill wastewater	Rashing rings 35°C 55°C	7.93 ± 1.40 8.41 ± 0.48	0.295 0.317	> 70%	46
Up flow anaerobic filter	Poultry slaughter house wastewater	Pleated PVC ring	14.3	0.24	78	41
Up flow anaerobic filter	Dairy Wastewater	Sintered glass rasching ring	21	0.32	80	35
Up flow fixed film anaerobic bio reactor	Low pH Petrochemical Wastewater	Bone char Charcoal Plastic beads Bricks Polyurethane foam	27.2 18.1 18.1 6.0 4.1	0.01 0.02 0.01 0.08 0.02	45 49 51 56 44	27
Anaerobic Fixed Film	Dairy Wastewater	Gravels	–	–	96	26

cont...

Reactor	Feed	Packing Media		OLR (g COD/l d)	Biogas Yield (m³CH₄/kg COD)	COD Removal (%)	Ref.
Fixed bed Ananerobic digester	Flush Dairy Manure	Automobile tires		–	–	40-60	31
Fixed bed Ananerobic digester	Screened Dairy Manure	Tyre Rubber + Zeolite Tyre Rubber		12	–	46.2 41	17
Packed Bed	Sisal leaf waste leachate	Sisal fiber waste		25	–	80-93	36
Packed Bed	Dairy Cattle Wastewater	Limestone Gravel Non-woven Polyester Combination	37°C 10°C 37°C 10°C 37°C 10°C	0.12	0.19 0.06 0.21 0.06 0.19 0.05	94 82 94 77 94 76	24
HUASB	Palm oil mill effluent	Palm shell Fine gravel Palm shell 37°C		1.85	—	78 76 82	34
Multistage anaerobic filter	Low strength wastewater	Waste tyre rubber		(COD less than 1000 ppm)	—	60	33
Multistage anaerobic reactor	Synthetic medium strength wastewater containg molasses	PVC pall rings		9	—	88.3	21
Multi-fed upflow anaerobic filter	Rice winery effluent	Plastic fibrous media		37.68	0.30 -0.35	82	20
DFFFB	Dairy wastewater	—		14.812	0.330	75	45

Chapter 3

MATERIALS AND METHODS

3.1 Experimental setup

Two anaerobic filters were constructed to run the experiments with different packing media simultaneously. The complete experimental set up is described below:

- **Collection tank:**

A PVC tank with a capacity of 500 liters was used as a collection tank. Raw cheese effluent was collected from the dairy industry and stored in the tank which was then used to feed to the mixing tank.

- **Mixing tank :**

Two PVC tanks of 1000 liters capacity for mixing of influent with water. First tank was provided with tap which drains the influent to later tank which was located below it. There was a provision of tap water for dilution of highly concentrated cheese whey. Mixing and recycling was performed by slurry pump.

- **Anaerobic reactors:**

The two anaerobic reactors were constructed with 1.06 m in diameter and 3.5 m in height. The reactors were constructed of brick masonry. An MS gas cap was fitted on the top and necessary piping for influent, effluent and sampling ports were connected using flexible and rigid PVC pipes and fittings. Biogas was collected from top of the reactor and and connected to wet type gas flow meter for biogas measurement. Two pumps were installed to feed the reactors individually and recycle the reactor content, if necessary. Dimensional sketche is given in Figure 3.1.

- **Gas flow meter:**

Individual wet type gas flow meters were connected to both the reactors for biogas measurement. The gas flow meter is shown in Figure 3.2.
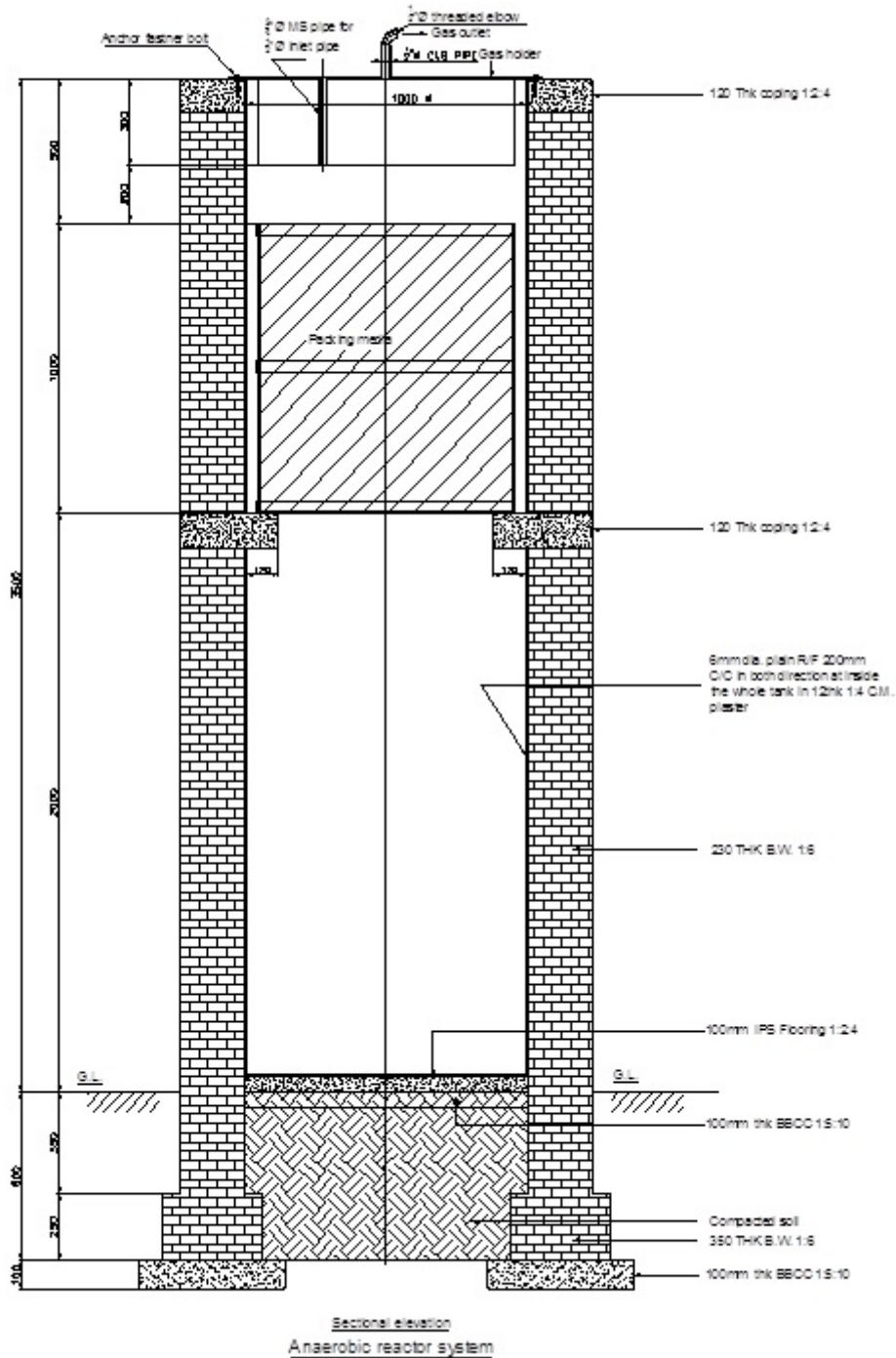

Figure 3.1: Dimensional diagram of Anaerobic Filter

Figure 3.2: Wet type Gas Flow Meter

Figure 3.3: Pilot Anaerobic Filters

3.2 Description of the pilot reactors

The various major aspects that were kept in mind while designing the reactor are discussed below:

3.2.1 Height to diameter ratio

The ratio between height and diameter should be decided judicially. In vertical fixed film reactors if the diameter is very large then there are the chances of short-circuiting in the path i.e. the effluent in the middle portion only will get into the effect, rest of it remains untreated. On the contrary, diameter should not be very less as it affects in poor stability of design and results into the lower volume of the reactor. The height upto outlet and diameter of the experimental reactor was kept 3.4 m and 1.06 m respectively so as to get a height : diameter ratio of 3.2 : 1 was taken, and hence, total volume of reactors are 3.0 m^3.

3.2.2 Provision for inlet and outlet

The reactors were designed as upflow anaerobic fixed film reactors and the inlet and outlet provisions were made accordingly. The inlet port was positioned at the bottom of the reactor to enable plug flow inside the reactor and outlet was positioned at the side of top. The inlet ports were made of diameter of 0.5 inch and outlet ports were made of diameter of 1 inch. The PVC pipes are used for the inlet and outlet.

3.2.3 Provision for gas collection

The reactors designed were fixed dome type and the biogas generated in the process was collected in the void space left at the top of the reactor. This void volume is approximately 100 l. A gas valve was fitted in gas pipeline for sampling and to enable gas flow through a transparent tube into wet type gas flow meter that measure the volume of gas production.

3.2.4 Allotment of volume for packing media

The ratio of volume of packing media to the reactor volume bears a significant importance in designing the reactor. A very large amount of packing media may result into the poor flow rate and clogging of the reactor at high organic load. Therefore, the volume of packing media inside the reactor should be suitably selected as per the requirements and

nature of the effluent. 20% packing media ratio was selected for the design. Hence, a packing media height of 1 m was allocated for the media above the laser in MS cage.

3.2.5 Positioning of packing media

The packing media was placed at the height of 2 m so as to facilitate some UASB like mechanism at the bottom portion of the reactor.

3.2.6 Packing media

Two different packing media were used in this experiment viz. brickbats and polypropylene bioring for assessing the variation in performance of reactors arising due to packing media as shown in Figure 3.4. The basic requirement that is to be fulfilled by the packing media is that it should provide good surface for attachment of film, large surface area to volume ratio. If rough media surface in case of brickbats is useful for promoting rapid biofilm growth and reduce sloughing. Due to high surface volume ratio of Biorings should provide more surface for biofilm attachment. Some critical characteristics of these two media are summarized in Table 3.1.

Figure 3.4: Brickbats and Bioring Packing Media

Table 3.1: Characteristics of Two Packing Media

Parameter	Reactor A	Reactor B
Type of media	Brickbats	PP Bioring
Effective volume, liters	2725	2945
Size of media, mm	30 - 40	25 x25
Weight of media, kg	535	60
Surface volume ratio, m^2/m^3	—	210
Void space, %	55	89
Cost, Rs/m^3	3900	12600

3.2.7 Volume calculations

The calculations of volume of reactors across various heights were worked out properly. This included the calculations of effective volume of the reactor, volume occupied by packing media inside the reactor, volume between sampling ports, and etc. These calculations were accomplished by completely filling the reactor with water and then evacuating it and measuring the volume of water dispensed between the two positions. After measurement of volume of reactor, packing media was inserted in both the reactors. After filling the packing media, the volume of reactor between the inlet and the outlet was again recorded; these difference in both points are the volume of packing media.

3.2.8 Calculation of Void space of reactors

Void space of packing media (r) is defined as the void space of the media per unit volume of reactor. Void space calculation was done for both the packing media. The formula used for estimation of void space is given formula below [47]:

$$r = \frac{V1 - V}{V} * 100 \tag{3.1}$$

where,

r is the voidage of the packing media (%),

V_1 is the empty bed reactor volume (l),

V is the total volume of packing media (l)

3.2.9   Provision for sample collection

The reactors were to be studied for monitoring COD removal profile. Three sample ports were provided at different positions in the reactors. These ports were operated through valves for the sample collection. These ports were designed for frequent operation whenever required for the analysis of effluent inside the sample at different locations, which provide an information of the state of reactor. Later, these ports were regularly used in HRTs taken for performance evaluation, and taking samples to study the COD removal profile at various heights of the reactors.

3.3   Parameters used for assessing the performance of a reactor

3.3.1   Hydraulic Retention Time

Describes the ratio of the reactor volume to the flow rate of the feed. It hence expresses the average time a fluid element spends in the digester (strictly true for ideal reactors).

$$HRT = \frac{V}{Q} \tag{3.2}$$

where,

HRT = hydraulic retention time (d)

V = reactor volume (m^3)

Q = flow rate (m^3/day)

3.3.2 Organic Loading Rate

Describes the substrate quantity introduced into the reactor volume in a given time, whereby the substrate can be defined as TS, VS, COD or BOD.

$$L = \frac{Q*S}{V} \tag{3.3}$$

Where,

L = Organic Loading Rate (kg / m^3 d)

Q = substrate flow rate (m^3/d)

S = substrate concentration in the inflow (kg/m^3)

V = reactor volume (m^3)

3.3.3 Substrate removal effectiveness

Also called substrate conversion, this parameter can be expressed in several ways and the substrate measured in terms of TS, VS or COD. Generally, the simplest and most used equation is:

$$E = \frac{(QS - QS_e)}{(QS)} * 100 \tag{3.4}$$

Where,

E = TS, VS or COD removed, as percentage (%)

Q = inlet and outlet flow rate (m^3/d)

S = TS, VS or COD concentration in the inlet flow rate (kg/m^3)

S$_e$ = TS, VS or COD concentration in the effluent flow rate (kg/m^3)

3.3.4   The pH of the treated effluent

The pH, defined as potential of hydrogen ions [H+] is a primary gauge of digester health, which changes in response to biological conversions during different processes of anaerobic digestion. A stable pH indicates system equilibrium and digester stability. A falling pH point towards acid accumulation and instability [5]. The pH value and temperature of sample was determined by EUTECH PCSTestr 35.

3.3.5   Biogas recovery

Biogas recovery or yield is defined as amount of biogas produced per unit of COD removal. Anaerobic digestion achieves good degradation yield of organic matter (over 78%) and produces biogas, which can be converted to energy up to 0.2– 0.4 m^3 CH_4 / kg COD removal. An accepted or normal range of biogas production is 0.4-0.6 m^3 /kg COD removal at 35°C.The quality of biogas is measured in terms of its methane content.The biogas produced varies in composition depending upon the type of waste, operating temperature of reactor and type of the reactor. Typically dairy waste is likely to produce biogas of 55-60% methane [10]. Gas produced from both reactors will be collected in inverted glass bottles over water and its compositions will be analyzed by Orsat apparatus and Perkin Elmer Clarus 500 gas chromatograph equipped with thermal conductivity detector (TCD) and Porapak Q (2 m, 80/100 mesh, PCi make) column.The temprature setting used as follows: injection at 125ºC, Oven at 40ºC and Detector at 100ºC. Nitrogen served as a carrier gas at a flow rate 30ml/min.

3.3.6   Gas Production Rate

Describes the ratio between the produced biogas and reactor volume in a given time.

$$GPR = \frac{Q_{biogas}}{V} \qquad\qquad (3.5)$$

Where,

GPR = (m^3 gas/m^3 reactor d)

Q_{biogas} = biogas flow rate (m^3/d)

V = reactor volume (m^3)

3.3.7 Specific Gas Production

Indicates the biogas produced by a unit of mass of substrate, in terms of the total volatile solids (VS) or chemical oxygen demand (COD) in the feed, as m^3 biogas/kg substrate fed. This index is strictly linked both to the biodegradability of the fed substrate and to the process attitude. The SGP value is often used to compare the performances of different anaerobic processes [48].

$$SGP = \frac{Q_{biogas}}{QS} \qquad (3.6)$$

Where,

SPG = specific gas production (m^3 biogas/kg feed)

Q$_{biogas}$ = biogas flow rate (m^3/d)

Q = inlet flow rate (m^3/d)

S = substrate concentration (COD) in the influent (kg substrate/ m^3)

3.4 Kinetic Modeling

Mathematical modelling is an important tool for both design and operation of biological systems. It helps in evaluating the reactor performance at different operating data before transferring the concept to a full scale system. Kinetic studies can be used in predicting treatment efficiencies of a full-scale system operating under similar operating conditions. For the purpose, it is important to select an appropriate mathematical relationship between process variables and determine kinetic coefficients precisely.A number of models like first order Monod type, Grau second order multicomponent, Stover-Kincannon, Chen and Hashimoto, Contois, Young and McCarty etc. have been introduced for anaerobic processes. Among them, Grau model is one of the widely used models [49][50].

3.4.1 First order model

The rate of change in substrate concentration in a complete mixed system, considering first-order degradation kinetic and substrate concentration (S) dependence can be

expressed as:

$$\frac{dS}{dt} = \frac{Q}{V}S_0 - \frac{Q}{V}S - k_1 S \tag{3.7}$$

Where,

(dS/dt) = substrate removal rate

k_1 = first order rate degradation kinetic constant (d^{-1})

Q = flow rate (l/d)

V = reactor volume (l)

S_0 = initial substrate concentration (mg/l) and;

S = substrate concentration at any time t (mg/l)   Under steady state conditions, the rate of change in substrate concentration $(-dS/dt)$ is negligible, then Equation (3.7) reduces to:

$$\frac{S_0 - S}{t} = k_1 S \tag{3.8}$$

The value of the first-order kinetic constant can be obtained by plotting $(S_0-S)/t$ versus S, according to Equation (3.8). The value of k_1 is obtained from the slope of the straight line.

3.4.2   Stover-Kincannon model

In this model, the consumption of substrate is expressed as a function of the OLR, due to the monomolecular kinetics of biofilm reactors, such as rotating biological reactors, trickling filters and UAFs. Because of the difficulties in measuring the active surface area, which supports the biofilm, the reactor's effective volume is used for the Stover-Kincannon model. This model is defined as:

$$\frac{dS}{dt} = \frac{U_m * (Q * S_0/V)}{k_B + (Q * S_0/V)} \tag{3.9}$$

Where,

(dS/dt) is substrate removal rate

k_B is the saturation constant (g / l d)

U_m is the maximum substrate removal rate (mg/ l d)

Q is the flow rate (l/d)

V is the reactor volume (l)

S_0 is the initial substrate concentration (mg/l) and;

S is the substrate concentration at any time t (mg/l)   here the substrate consumption rate dS/dt is expressed as:

$$\frac{dS}{dt} = \frac{Q}{V}(S_0 - S)$$
(3.10)

Equation (3.10) is obtained from the arrangement and linearizing of Equation (3.9).

$$\frac{V}{Q*(S_0 - S)} = \frac{k_B}{U_m}\frac{V}{Q*S_0} + \frac{1}{U_m}$$
(3.11)

3.4.3   Grau second order kinetic model

The Grau second order kinetic model for substrate utilization was applied to the data collected under the study and coefficient of correlation was found out to assess the applicability of the model to the reactors and operating conditions used during the present study.   The general equation for substrate utilization in the model is,

$$-\frac{dS}{dt} = k_s * X * (\frac{S}{S_0})^2$$
(3.12)

Where,

- (dS/dt) is substrate removal rate

k_s is the substrate removal rate kinetic constant (d^{-1})

X is the concentration of microorganisms (mg/l)

S_0 is the initial substrate concentration (mg/l) and;

S is the substrate concentration (mg/l) at any time t

The immobilized biomass (X) on the support was determined as VSS and was quantified in duplicate at the end of the experiments. This was done by separation of the biofilm from the media of a determined volume, through successive washing with deionized water in a sonicator. The VSS gravimetric quantification was made according to standard methods given in Appendix A [51]. If this equation is integrated within the boundary conditions i.e. S between S_0 and S and time t between 0 and t ,

$$\int -\frac{dS}{(S/S_0)^2} = \int k_s * X * dt \qquad (3.13)$$

$$(S_0/S)(S_0 - S) = k_s * X * t \qquad (3.14)$$

Linearizing the above equation, it becomes

$$\frac{(S_0 * t)}{(S_0 - S)} = t + \frac{S_0}{k_s * X} \qquad (3.15)$$

Considering second term on the right side as a constant,

$$\frac{(S_0 * t)}{(S_0 - S)} = t * n + m \qquad (3.16)$$

This equation represents a straight line. A plot of $(S_0 * t)/(S_0-S)$ versus t would give a straight line with slope as n and y axis intercept as m.

Chapter 4

RESULTS AND DISCUSSION

4.1   Startup of reactors

Initially both the reactors and piping were tested for leakages. The reactors were then charged with culture to develop methanogenic biomass in the reactor. Filtered cattledung slurry was used for culture development. The feeding was done using pump at a flow rate of 200 l/h. The flow rate was adjusted to provide smooth and steady feeding. The reactors were fed for experimental work at this flow rate. The reactors were filled completely up to outlet and then observed for few days for any gas production. The biogas produced was measured daily.

Combustible gas started producing within 15 days' time. Once the culture was ready, both the reactors were commissioned with diluted cheese whey from a dairy effluent plant at 15 d hydraulic retention time. Cheese whey was obtained from local dairy,Anand. It had a pH of 3.3; COD, 56 g /l, total solids, 1.3 g/l, and a total nitrogen, 1.06 g/l.The dilution of cheese whey by mixing with other wastewater is a method for reducing the instability and low efficiency problems caused by its high organic content, especially for high-rate anaerobic systems, such as Upflow Anaerobic Sludge Blanket (UASB) reactors or up flow anaerobic filters [52][53].

4.2   Acclimatization of reactors

When the gas production reached a steady state, a small quantity of effluent to be treated was started feeding . After that the reactor was acclimatized for the running HRT. Again after reaching the stability, the reactors were shifted to the next HRT.

4.3 Operation of reactors

Both the reactors were operated at different HRTs (15 and10 days). During the study, HRT was gradually lowered and the response of reactors was analyzed for evaluating the effect of HRT on various parameters of the reactors. The reactors were operated at higher HRT periods (15 and 10 days) in the initial stages of experiment. The operation at these HRTs was an intermediate, and was done to check the response of reactors, slowly acclimatize the culture for higher loading rates and bringing the reactors to lower HRTs without disturbing the reactors.

The HRTs were shifted after the reactors had achieved stability at their current HRT. The stability was sought by consistency in gas production and stable pH. The data were collected for the pH, ambient temperature, COD removal and quantity and quality of biogas production. Biogas generated was measured daily using gas flow meter. A influent for reactors was prepared first and then it was divided in two parts for feeding both the reactors. This measure was adopted to rule out the chances of variation in the feed. The quantity of feed for each reactor was decided on the basis of the HRT.

4.3.1 HRT of 15 days

The operation was started at lower organic loading rate and higher hydraulic retention time after acclimatization of the reactors. The reactors were started at an HRT of 15 days. An effluent having cheese whey diluted with water was fed in the startup HRT. During this period, reactor A (Brickbats) was fed with 182 l and reactor B (Bioring) with 196 l. The biogas produced was 0.37 m^3/kg $COD_{removed}$ for reactor A and 0.38 m^3/kg $COD_{removed}$ for reactor B. The methane content were 69.5 and 69.8% respectively.

4.3.2 HRT of 10 days

After stabilization of reactors with 15 days, the HRT was shifted to 10 days. During this period, reactor A was fed with 275 l and reactor B with 295 l of effluent. The biogas produced was 0.38 m^3/kg $COD_{removed}$ for reactor A and 0.50 m^3/kg $COD_{removed}$ for reactor B. In the biogas the methane content are 62.61 and 64.27% respectively.

4.3.3 HRT of 8 days

The volume of effluent from dairy industry fed to the reactors was changed to 340 l for reactor A and 370 l for reactor B for this HRT. The organic loading rate increased upto an average value of 1.18 kg/m^3d in both reactors.

4.3.4 HRT of 5 days

The final HRT achieved during the study was 5 days. The reactors were operated for 20 days at this HRT. The volume of effluent fed to the reactors was changed to 545 l for reactor A and 590 l for reactor B. The organic loading rate increased upto 2.57 kg/m^{3}d in both reactors.

The average data of all HRT for reactor A and reactor B are shown in table 4.1 (a) and (b).

The biodegradation efficiency is characterized by COD reduction. Here, the reactor A gave better COD reduction at 5 days HRT. When the HRT was reduced gradually (loading rate increased), the gas production increased in both the reactors. For both the media types, culture development was equally fast. At higher retention times, both the reactors performed more or less at similar efficiency.

Table 4.1: Performance of Reactor

(a) Performance of Reactor A

| Sr. No. | Retention Time (d) | Effluent (l/d) | pH | | COD (mg/l) | | COD Removal (%) | OLR (kg/m³ d) | BIOGAS | | |
			In	Out	In	Out			Avg. per day (l)	m³/kg COD_feed	m³/kg COD_removal
1	15	182	3.88	6.38	10809	1741	83.89	0.72	615	0.31	0.37
2	10	275	3.77	5.72	10161	4408	56.62	1.02	774	0.28	0.49
3	8	340	3.93	5.93	9400	2605	72.28	1.18	1418	0.44	0.61
4	5	545	3.35	6.70	12833	5100	60.26	2.57	3054	0.44	0.72

(b) Performance of Reactor B

| Sr. No. | Retention Time (d) | Effluent (l/d) | pH | | COD (mg/l) | | COD Removal (%) | OLR (kg/m³ d) | BIOGAS | | |
			In	Out	In	Out			Avg. per day (l)	m³/kg COD_feed	m³/kg COD_removal
1	15	196	3.88	6.41	11010	1828	83.39	0.73	681	0.32	0.38
2	10	295	3.77	5.78	10062	3967	60.57	1.01	891	0.30	0.50
3	8	370	3.93	5.37	9400	2816	70.04	1.18	1473	0.42	0.60
4	5	590	3.35	6.55	12833	2833	77.92	2.57	4614	0.61	0.78

4.3.5 Effect of ambient temperature on COD removal

The ambient temperature plays an important role in the COD removal especially in tropical countries where mesophilic bacteria are predominant. It catalyzes the reactions. It also bears an importance in reference to the growth and activity of microorganisms. Therefore, dependency of COD removal over the ambient temperature was studied during the experimental trails. However, during the 10 days HRT maximum and minimum ambient temperature were 24°C and 6°C respectively, therefore there was sudden decrease in COD removal efficiency. The effect of temperature could be clearly when there are large variations in ambient temperature, for e.g. seasonal variations. The temprature effect is more in Brickbats compare to Bioring packing media. During startup the COD removal of brickbats and bioring are 71.55 and 75.22% respectively. But after change in temprature the COD removal also decrease upto 56.62 and 60.57% respectively.

4.3.6 Effect of Shock loadings

The effects of shock loadings were observed for both the reactors while shifting the HRT, temperature fluctuation and change in OLR. When the HRT is shifted from higher to lower, the reactor pH decreased initially and recovered to normal conditions after five to six days of operation. Since, this pH shift was in the range of optimum pH range for methanogens, no decrease in COD removal and biogas production was observed. On the contrary, a hike in COD removal and biogas production was observed which was due to the increased organic loading rate that furnished more amount of substrate for microflora and ultimately increased their activity, providing more gas production and COD removal. When shock loadings were implemented by introducing lower HRT, there was a decrease in COD removal in combination with lower methane content in the biogas. It may be due to the lack of conversion of volatile acids to methane. However, reactor B got stabilized earlier to reactor A in majority of cases.

4.3.7 Quality of biogas

The quality of biogas was estimated to find out the methane content present in the gas as methane content is responsible for its calorific value. Pure methane(100%) has a calorific value of 1000 BTU/ft^3 (approx. 37,262 kJ/m^3) [10]. Normally, biogas contains methane ranging from 55 to 75% v/v. During the study, the methane content in the biogas produced ranged from 60% to 75%. It ranged from 60 - 72% in reactor A and 60 - 75% in reactor B. Reactor A obtained average methane content (v/v) of 69.5%, 62.61%, 72% and 71% during the HRTs of 15 d, 10 d, 8 d and 5 d, respectively with an overall average value of 68.78 %. Similarly, reactor B obtained average methane content (v/v) of 69.8%, 64.27%, 75% and 69% during the HRTs of 15 d, 10 d, 8 d and 5 d, respectively

with an overall average value of 69.52%. The average specific methane yield for reactor A was 0.31 m^3/kg COD for the HRT of 5 d. Similarly, reactor B obtained average specific methane yield of 0.42 m^3/kg COD. Bodkhe (2008) reported a specific biogas yield of 0.35 l CH_4/ gCOD removal with 70% of CH_4 content obtained using anaerobic filter reactor for treatment of municipal wastewater. The results obtained for the experimental reactor used in the study is similar to the our research finding.

4.4 Kinetic Study

The data on performance of the reactors with different packing media at different retention time enlisted in Table 4.1. These data were used in various kinetic mathematical models.

The determination of kinetic parameters was carried out using kinetic models in their linear form; Equations 3.11, 3.15 and 3.18. The model giving highest value of the linear correlation cofficient (R^2) helped us in identifying the most suitable kinetic model.

First-order model

A graphic representation of experimental data was made according to linearized form of first-order model, The first-order degradation constant values (k_1) were obtained from the slopes of the straight lines , with linear correlation values (R^2) of 0.78 and 0.72 for the respective reactor as shown in Figure 4.1.

Stover-Kincannon model

Figure 4.2 is the graphic representation of the Stover-Kincannon model in its linearized form, Equation (3.15), for the data series at different HRT. Least squares linear regresion was used to determine the intersection value $1/U_{max}$ and the slope K_B/U_{max}. Values for coefficients (R^2) were 0.85 in both reactors.

Gaur model

A plot of (S_0* t)/(S_0-S) versus t would give a straight line with slope as n and y axis intercept as m. When this model was applied to the data generated in the present experiments, the plots were as given in Fig.4.3. From the graph the m values were 3.13 and 4.89 and n value 3.98 and 3.53 respectively for reactor A and reactor B.

Then the substrate removal rate constant (k_s) was determined by $m = S_0/(k_s * X)$. The straight line equation befitting each set of data and the coefficient of correlation (R^2) are respectively.

Table 4.2: Kinetic Parameter

(a) Reactor A

Sr.No.	t	S_0	S	$(S_0-S)/t$	$V/Q(S_0-S)$	$V/Q\,S_0$	$(S_0*t)/(S_0-S)$	X
	d	mg/l	mg/l	mg/l d	mg/l d	mg/l d	d	mg/l
1	5	12833	5100	1546.	0.65	0.39	8.30	
2	8	9400	2605	849	1.18	0.85	11.07	4400
3	10	10161	4408	575	1.74	0.98	17.66	
4	15	10809	1241	604	1.65	1.39	17.88	

(b) Reactor B

Sr.No.	t	S_0	S	$(S_0-S)/t$	$V/Q(S_0-S)$	V/QS_0	$(S_0*t)/(S_0-S)$	X
	d	mg/l	mg/l	mg/l d	g/l d	g/l d	d	mg/l
1	5	12833	2833	2000	0.50	0.39	6.42	
2	8	9400	2816	822	1.22	0.85	11.42	6500
3	10	10062	3967	609	1.64	0.99	16.51	
4	15	11010	1828	612	1.63	1.36	17.99	

(c) Comparison of Kinetic Parameter

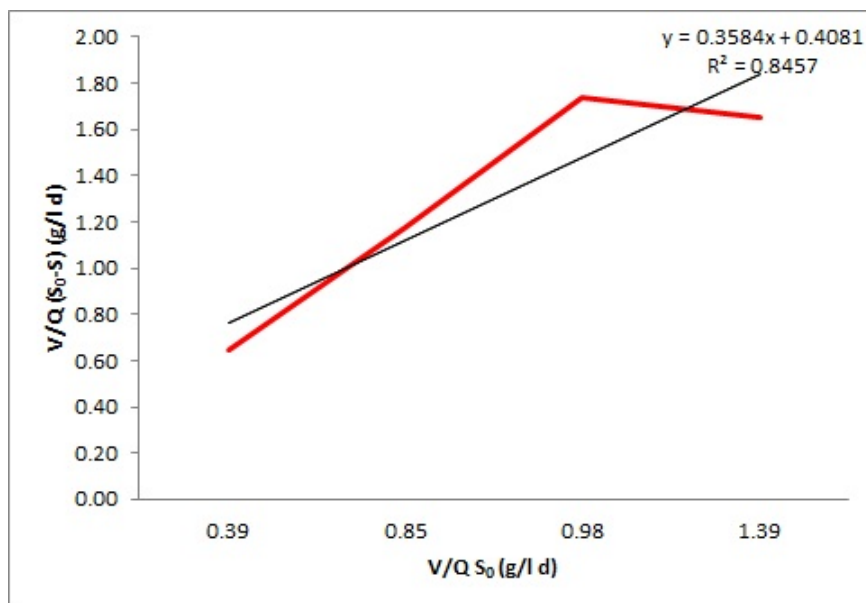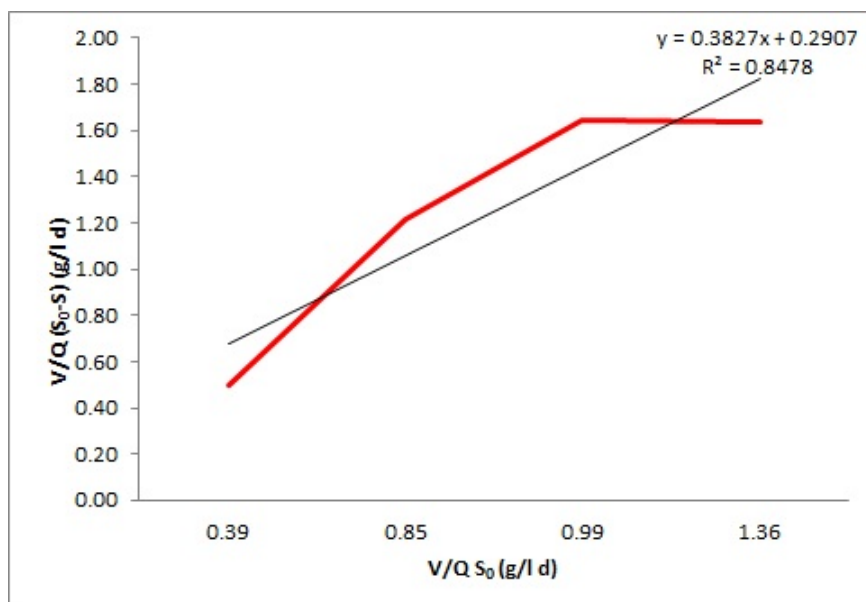| Reactor	First order		S-K Model			Gaur Model			
	k_1	R^2	k_B	U_m	R^2	k_s	m	n	R^2
	d^{-1}		g/l d	g/l d		d^{-1}	d^{-1}		
Reactor A	310	0.78	0.89	2.45	0.85	0.72	3.13	3.98	0.95
Reactor B	437	0.72	1.32	3.44	0.85	0.32	4.89	3.52	0.90
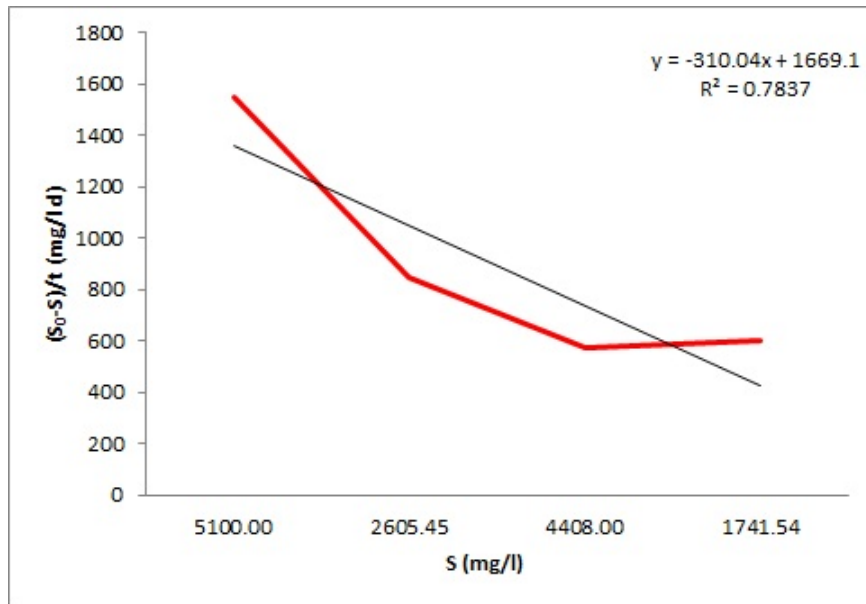
(a) Reactor A
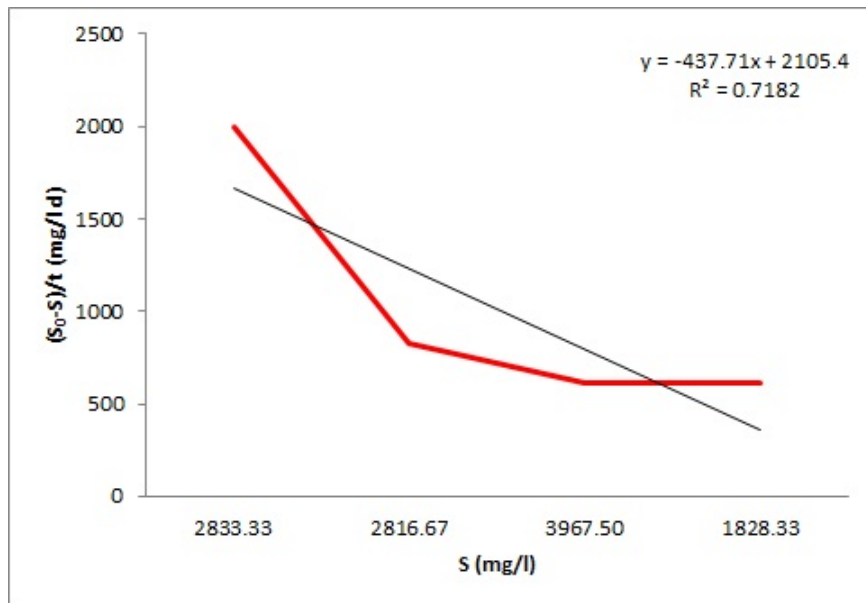
(b) Reactor B

Figure 4.1: Graphic representation of the First order Kinetic Model

(a) Reactor A

(b) Reactor B

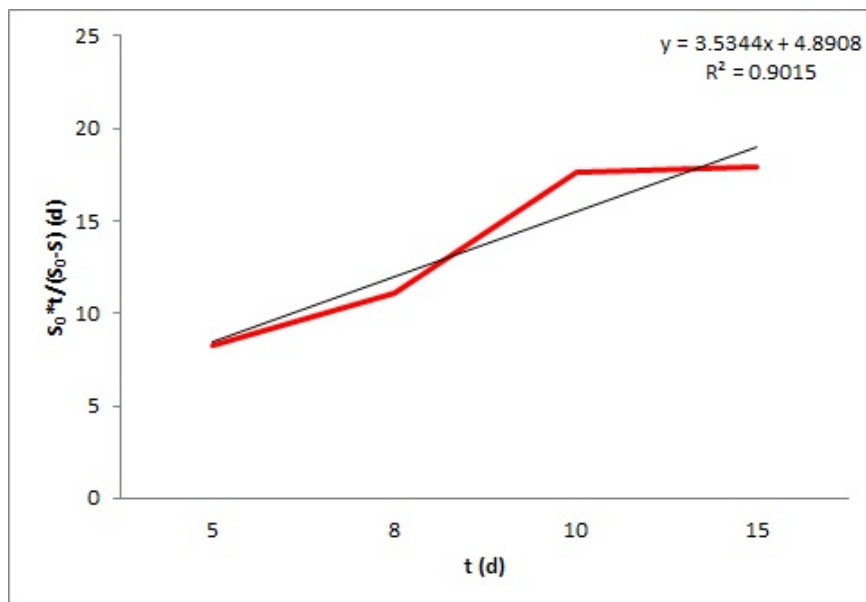Figure 4.2: Graphic representation of the Stover-Kincannon Kinetic Model
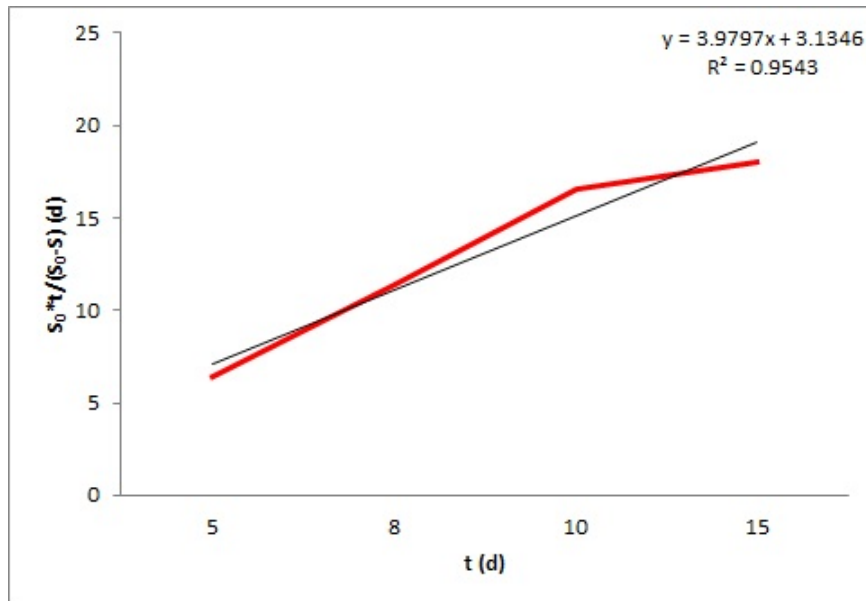
(a) Reactor A

(b) Reactor B

Figure 4.3: Graphic representation of the Grau Model

As could be seen, the coefficient of correlation is very high in Grau model. Suggesting that the model fits very well to the data collected in the present experiment. Hence, Grau model could be used to predict the performance of the reactors at other HRTs also.

Chapter 5

CONCLUSIONS

A critical analysis of literature reveals that anaerobic fixed film reactors have displayed better performance than any other type of anaerobic reactors. They not only work as anaerobic biological treatment for organic matter in the wastewaters but also trap passage of active biomass out of the reactor. Packing media when used even in smaller quantity as in case of hybrid reactors, could prevent sludge wash-out by 25% higher compared to UASB, which means that the physical filtering action provided by the packing media bed is more effective than the three-phase separator in UASB. A wide range of materials – natural and synthetic, porous and non-porous, heavy and light - have been used as packing material and it has been observed that these packing materials help in reducing hydraulic retention time and ultimately cost of the treatment.

Porous materials have been found better compared to non-porous ones as surface characteristics also play important role in microfilm development. Synthetic media of different kinds offered added advantages in terms of lower bulk densities and easy availability as these are commercially available.

Among two different types of packing media tried under the project, performance-wise synthetic (Bioring) found better than the Natural media (Brickbats). However, the synthetic media costliest of all and hence needed higher capital investment. But same time the natural media is heavy in weight and low voidage therefore the volume of reactor increse and high strength structure required for natural packing media. Also the coefficient of correlation is very high in Gaur model in both reactors. Hence, Gaur model could be used to predict the performance of the reactors at other HRTs also.

Overall, it was felt that synthetic media could be used in the large installation because of the advantages attached to it - avalibilty of bulk quantity, low weight, high surface

area, high voidage suitable for long term operation without clogging or short-circuiting and reasonably good performance.

Mostly, UASB mechanism types of reactors are used in dairy industry. The results obtained in the study support the adoption of anaerobic fixed film reactors for the treatment of dairy effluent at commercial scale. The design used in the study can offer the advantages of hybrid reactors in which both UASB and anaerobic fixed film reactors can be used in combination to get the better efficiency.

Chapter 6

FUTURE SCOPE OF STUDY

Anaerobic fixed film reactors have great potential and versatility to be used in combination with other reactors. The potential can be utilized in studying over other combinations. The reactors used in the study were pilot scale and their applicability can be checked on some larger scale. During the study the reactors performed was well at HRTs of 15, 10, 8 and 5 days; and the performance is expected to be satisfactory at further lower HRTs of 3 days, 2 days, etc. with some pH control. Similar configuration can be tested at lower HRTs. The reactors can be tried with certain modifications and other synthetic packing media like raschig rings, polyurethane foam, etc. or the same media could be tested for different configurations and shapes. The performance can be checked at different positions of packing media with different packing media ratios.

Bibliography

[1] http://mofpi.nic.in/ContentPage.aspx?CategoryId=145

[2] www.nddb.coop/nationaldairyplan

[3] http://www.ifc.org/ifcext/sustainability.nsf/Content/EHSGuidelines

[4] S.M.I.Gonzalez, "The biotechnological utilization of cheese whey: a review" Bioresource Technology, 57, 1996, pp.1 - 11

[5] B. Demirel, Yenigun O. and Turgut T. Onay, "Anaerobic treatment of dairy wastewaters: a review", Process Biochemistry 40, 2005, pp.2583 - 2595

[6] O. Francisco, Garrido J. M., Arroja B. and Mendez R., "Anaerobic filter reactor performance for the treatment of complex dairy wastewater at industrial scale", Water Research 37(17), 2003, pp.4099 - 4108

[7] P.E.Poh and Chong M.F., "Development of anaerobic digestion methods for palm oil mill effluent (POME) treatment", Bioresource Technology, 100, 2009, pp.1 - 9

[8] W. Biing-Teo, Show K.Y., Lee D.J. and Lai J.Y., "Carbon balance of anaerobic granulation process: Carbon credit", Bioresource Technology, 2008, Article in Press

[9] Anaerobic Digestion of biodegradable organics in municipal solid wastes www.seas.columbia.edu/earth/vermathesis.pdf

[10] G. Michael H. "The microbiology of anaerobic digesters", Published by John Wiley & Sons, 2003

[11] G. Vidal, Carvalho A., Mendez R. and Lema J.M., "Influence of the content in fats and proteins on the anaerobic biodegradability of dairy wastewaters", Bioresource Technology, 74(3), 2000, pp.231 – 239

[12] J. H. Ahn., and Forster C.F., "A comparison of mesophilic and thermophilic anaerobic upflow filters", Bioresource Technology, 73(3), 2000, pp.201- 205

[13] Y. Turan., Yuceer A. and Basibuyuk M., "A comparison of the performance of mesophilic and thermophilic anaerobic filters treating papermill wastewater", Bioresource Technology, 99(1), 2008, pp.156 – 163

[14] K. Jung Kon, Oh B. R., Chun Y. N., and Kim S. W., "Effects of temperature and hydraulic retention time on anaerobic digestion of food waste", Journal of Bioscience and Bioengineering, 102(4), 2006, pp.328 – 332

[15] T. Viraraghavan and Varadarajan R., "Low-temperature kinetics of anaerobic-filter wastewater treatment", Bioresource Technology, 57(2),1996, pp.165 - 171

[16] A.E.Ghaly, "A comparative study of anaerobic digestion of acid cheese whey and dairy manure in a two-stage reactor", Bioresource Technology, 58(1), 1996, pp.61 - 72

[17] O. Umana , Svetlana Nikolaeva , Enrique Sanchez , Rafael Borja, Francisco Raposo, "Treatment Of Screened Dairy Manure By Upflow Anaerobic Fixed Bed Reactors Packed With Waste Tyre Rubber And A Combination Of Waste Tyre Rubber And Zeolite: Effect Of The Hydraulic Retention Time", Bioresource Technology, 99, 2008, pp.7412–7417

[18] K. Arun, Rajeshwari K. V., Balakrishnan M., Lata K. and Kishore V. V. N. "Anaerobic digestion technologies for energy recovery from industrial wastewater - A study in Indian context", TERI Information Monitor on Environmental Science, 3(2), pp.67 – 75

[19] W. Edelmann, Baier U. and Engeli H. "Performance of a dynamic, pulsating anaerobic filter while treating industrial wastewaters including a comparison with UASB reactors", Available online at www.arbi.ch

[20] Y. Han-Qing, Zhao Q.B and Tang Y., "Anaerobic treatment of winery wastewater using laboratory-scale multi- and single-fed filters at ambient temperatures", Process Biochemistry. 41, 2006, pp.2477 – 2481

[21] S. Ghaniyari-Benis, Borja R., Monemian S. Ali and Goodarzi V., "Anaerobic treatment of synthetic medium-strength wastewater using a multistage biofilm reactor", Bioresource Technology, 100,2009, pp.1740 – 1745

[22] C. Pedro R., Francese A. P., and Sireriz F., "Improved performance of a hybrid design over an anaerobic filter for the treatment of dairy industry wastewater at laboratory scale", Journal of Fermentation and Bioengineering, 79(3), 1995, pp.270 - 212

[23] J. R. Banu, Kaliappan S. and Yeom I. T., "Two-stage anaerobic treatment of dairy wastewater using HUASB with PUF and PVC carrier. Biotechnology and Bioprocess Engineering, 12, 2007, pp.257 – 264

[24] Anonymous. "Development of high rate anaerobic filter reactor for methane recovery from industrial organic effluents", A report submitted to Gujarat Energy Development Agency by Sardar Patel Renewable Energy Research Institute, 1992, V.V. Nagar, Gujarat, INDIA

[25] D. R. Vartak, C. R. Engler, M. J. McFarland & S. C. Ricke, "Attached-Film Media Performance In Psychrophilic Anaerobic Treatment Of Dairy Cattle Wastewater", Bioresource Technology, 62, 1997, pp.79-84

[26] Q. Javed Iqbal, Muhammad Nadeem, Shagufta S. Baig, Shahjahan Baig and Quratulain Syed , "Anaerobic Fixed Film Biotreatment of Dairy Wastewater", Middle-East Journal of Scientific Research, 8(3), 2011, pp.590-593

[27] H. Patel and Datta Madamwar, "Biomethanation of low pH petrochemical wastewater using upflow fixed film anaerobic bioreactors", World Journal of Microbiology and Biotechnology, 16, 2000 pp.69-75

[28] A. Ugurlu and Forster C. F., "The impact of shock loadings on the performance of thermophilic anaerobic filters with porous and non-porous packings" , Bioresource Technology, 39(1), 1992, pp.23 - 30

[29] B. Sandeep, "Development of an improved anaerobic filter for municipal wastewater treatment", Bioresource Technology, 99, 2008, pp.222 - 226

[30] E. Tarek.A., Sklyar V., Zeeman G. and Lettinga G., "Low temperature pre-treatment of domestic hybrid or an anaerobic filter reactor", Bioresource Technology, 82, 2002, pp.233 - 239

[31] U. Zaher, Frear C., Pandey P. and Chen S., "Evaluation of a new fixed-bed digester design utilizing large media for flush dairy manure treatment", Bioresource Technology, 99, 2008, pp.8619 - 8625

[32] J. Andersson and Bjornsson L., "Evaluation of straw as a biofilm carrier in the methanogenic stage of two-stage anaerobic digestion of crop residues", Bioresource Technology, 85, 2002, pp.51 - 56

[33] O. Reyes, Sanchez E., Rovirosa N., Borjac R., Cruz M., Colmenarejod M. F., Escobedo R., Ruiz M., Rodroguez X. and Correa O., "Low-strength wastewater treatment by a multistage anaerobic filter packed with waste tyre rubber" Bioresource Technology, 70, 1999, pp.55 - 60

[34] S. A. Habeeb, AB. Aziz Abdul Latiff, Zawawi Daud, Zulkifli Ahmad, "A Biodegradation And Treatment Of Palm Oil Mill Effluent (POME) Using A Hybrid Up-Flow Anaerobic Sludge Bed (HUASB) Reactor", International Journal Of Energy And Environment, 2(4), 2011, pp.653-660

[35] O. Ince, B. Kasapgil Ince and T. Donnelly, "Attachment, Strength And Performance Of A Porous Media In An Upflow Anaerobic Filter Treating Dairy Wastewater", Water Science and Technology,41(4-5), 2000, pp.261–270

[36] M. Anthony Manoni, Lovisa Björnsson, Amelia Kajumulo Kivaisi, Mugassa Steven Thomas Rubindamayugi, Bo Mattiasson, "Performance Of Biofilm Carriers In Anaerobic Digestion Of Sisal Leaf Waste Leachate", Electronic Journal of Biotechnology, 11(1), 2008, pp.1-9

[37] S. Sumi, Lea Mathew, "Influence Of Media Packing Depth And HRT On Performance Of Anaerobic Hybrid Reactors", Proceedings of 10th National Conference on Technological Trends (NCTT09) held at College of Engineering Trivandrum, 2009, pp.6-7

[38] M. Wu, F. Wilson, J.H. Tay, "Influence Of Media-Packing Ratio On Performance Of Anaerobic Hybrid Reactors", Bioresource Technology, 71, 2000, pp.151-157

[39] G.Sunil Kumar, Gupta S.K., and Singh Gurdeep, " Anaerobic Hybrid Reacor – A Promising Technology for theTreatment of Distillery Spent Wash" , Journal of Indian School of Mines, 11(1), 2007, pp.25-38.

[40] J.Rajesh Babu, Sudalyandi K., Dieter Beck, "Treatment of Sago Wastewater Using Hybrid Anaerobic Reactor", Water Quality Research Journal Canada, 41(1), 2006, pp. 56-62.

[41] R.Rajkumar,T.Meenambal,, J.Rajesh babu,I.T.Yeom, " Treatment of Poultry Slaughterhouse wastewater in Upflow ananerobic Filter under Low

Upflow Velocity", International Journal Environment Science Technology, 8(1), 2011, pp.149-158.

[42] P. Chaiprasert, Worakrit Suvajittanont, Benjaphon Suraraksa, Morakot Tanticharoen, Sakarindr Bhumiratana, "Nylon fibers as supporting media in anaerobic hybrid reactors: it's effects on system's performance and microbial distribution", Water Research, 37(19), 2003, pp.4605-4612.

[43] D. Ioannis, Manariotis1 and Sotirios G. Grigoropoulos, Anaerobic Filter Treatment of Municipal Wastewater: Biosolids Behavior, Journal of Environmental Engineering, 132(1), January 1, 2006.

[44] A.Ramakrishnan, S.K. Gupta, "Anaerobic biogranulation in a hybrid reactor treating phenolic waste", Journal of Hazardous Materials, B137, 2006, pp.1488–1495.

[45] G. Srinivasan, R. Subramaniam and V. Nehru kumar, "A Study on Dairy Wastewater Using Fixed-Film Fixed Bed Anaerobic Diphasic Digester", American-Eurasian Journal of Scientific Research, 4(2), 2009, pp.89-92.

[46] T. Yilmaz, Ahmet Yuceer, Mesut Basibuyuk, "A comparison of the performance of mesophilic and thermophilic anaerobic filters treating papermill wastewater", Bioresource Technology, 99, 200, pp.156–163.

[47] A. R. Tembhurkar and V. A. Mhaisalkar, "Study of Hydrodynamic Behavior of a Laboratory Scale Upflow Anaerobic Fixed Film Fixed Bed Reactor", Journal of Enviro. Science & Engg., 48(2), 2006, pp.75 - 80

[48] F. Heeb, "Decentralised anaerobic digestion of market waste", Swiss Federal Institute of Aquatic science and Technology, Switzerland, 2009.

[49] E. Padilla-Gasca and Alberto Lopez Lopez, "Kinetics of Organic Matter Degradation in an Upflow Anaerobic Filter Using Slaughterhouse Wastewater", Journal of Bioremediation and Biodegradation, 1(106), 2010, pp.1-6

[50] V. Diamantis and A. Aivasidis, "Kinetic Analysis and Simulation of UASB Anaerobic Treatment of a Synthetic Fruit Wastewater", Global NEST Journal, 12(2), 2010, pp 175-180

[51] Standard Methods for the Examination of Water and Wastewater, Method 209C, 16th Edition, 1985,p. 96.

[52] F. Y. Chang, and C.Y. Lin, "Biohydrogen production using an up-flow anaerobic sludge blanket reactor", International Journal Hydrogen Energy, 29, 2004, pp. 33-39.

[53] H. Gannoun, E. Khelifi, H. Bouallagui, Y. Touhami, " Ecological clarification of cheese whey prior to anaerobic digestion in upflow anaerobic filter", Bioresource Technology, 99, 2008, pp.6105–6111

Appendix A

Appendix A

CHEMICAL OXYGEN DEMAND

Theory:

Chemical Oxygen Demand is the oxygen require for the chemical oxidation of organic matter by strong chemical oxidant ($K_2Cr_2O_7$) under acidic condition. The degree of oxidation depends upon the type of substance, pH value, temperature, reaction time and the concentration of oxidizing agent. The main disadvantage of this test is that oxygen is also consumed by oxidation of inorganic substance such as nitrites, chlorides,sulphides, reduced metal ions. Also some of the organic materials like amino acids, ketones, or saturated carboxylic acids, benzene, pyridine etc are not oxidized by dichromate. Consequently this test is a poor measure of strength of organic wastes unless all these factors are considered. One of the chief limitations of COD test is its inability to differentiate between biologically inert organic matter. In addition it does not provide any evidence of the rate at which biologically active material would be stabilized under condition that exist in nature.

The major advantages of COD test is the short time required for evaluation. The determination can be made in about three hours rather than 5 days require for measurement of BOD.

Practical Relevance of Experiment and Application of Data:

COD test can often be interpreted in terms of BOD values after sufficient experience has been accumulated to establish reliable correlation factors. The COD test is used extensively in the analysis of industrial waste water. The test is widely used in the

operation of treatment facilities because of the speed with which the results can be obtain.

Application of COD Data in Environmental Engineering Practices:

1. The COD test is used extensively in the analysis of industrial wastes.

2. It is particularly useful in design to determine and control the losses in sewer system.

3. This test is widely used in place of BOD test in operation of treatment facilities because of the speed with which the results can be obtained.

4. It is useful to asses the strength of the wastes which contain toxins and biologically resistant organic substances.

5. The ratio of BOD to COD is useful to asses the amenability of the waste for biological treatment.

6. BOD/COD >0.8 indicates highly biodegradable waste and BOD / COD <0.3 indicates biologically inert waste.

Principle:

The organic matter present in the sample gets oxidized completely by $K_2Cr_2O_7$ in the presence of H_2SO_4 to produce CO_2 and H_2O. The excess $K_2Cr_2O_7$ remaining after the reaction is titrated with Standard Sodium Thiosulphate as titrant and Starch as indicator. The colour change is from blue to light green. The dichromate consumed gives the oxygen required for the oxidation of the organic matter.

Reagents:

1. Potassium Dicromate – 2.5gm Potassium dichromate + 500 ml 85% Orthophosphoric acid + 500ml Conc. Sulphuric acid

2. Mercuric Sulfate – 50 g $HgSO_4$ + 250 ml Water + 50 ml Conc. H_2SO_4 + 200 ml Water

3. Potassium Iodide – 55 g KI in 200 ml Water

4. Sodium Thiosulphate – 6.205 gm $Na_2S_2O_3$ $5H_2O$ + 1 lit Water

5. Starch Indicator – 2 g Starch in 100ml Water

Procedure:

- Take 1ml sample + 9 ml water - mix well in a test tube.

- Take 5 ml sample from above in a conical flask.

- Add 1 ml of mercuric sulphate solution.

- Add 20 ml potassium dichromate solution.

- If sample turns green, it means that higher dilution is required. Dilute 1 ml sample in 19 ml water and repeat from step 2 onwards.

- Heat the sample for 10 min on a steam bath after the temperature of the sample reached at 92°C.

- Cool the sample to room temperature.

- Add 150 ml distilled water.

- Again let it cool to room temperature.

- Add 10 ml potassium iodide solution.

- Add 1-1.2 ml starch solution. The sample will turn blue.

- Titrate the sample with 0.025 N sodium thiosulphate.

- End point will be from blue to light green.

- Note down the burette reading (B).

- Follow the same procedure for blank but instead of sample take 5 ml distilled water.

- Note down the burette reading for blank as (A).

Calculation:

$$COD(ppm) = \frac{(A-B)*N*D}{S} * 8000$$

Where,

A= ml of sodium thiosulfate used for Blank

B= ml of sodium thiosulfate used for Sample

N= normality of sodium thiosulfate = 0.025

D=dilution factor (1ml sample + 9ml DW =10 l sample + 19ml DW = 20 and so on)

S=Sample taken(5 ml)

Total Suspended Solids(TSS) and Volatile Suspended Solids(VSS)

Definitions:

Total Suspended Solids is defined as those solids which are retained by a glass fiber filter and dried to constant weight at 103-105^{0}C.

Apparatus:

1. Glass microfiber filters discs, Whatman filter paper no. 44

2. Disposable aluminum dishes

3. Suction flask, 1000 mL

4. Oven for operation at 103-105°C

5. Muffle furnace for operation at 550 ± 50°C

6. Desiccator

7. Analytical balance,

Procedure for Total Suspended Solids

- Preparation of the glass fiber filter disk: Insert the filter disk onto the base and clamp on funnel. While vacuum is applied, wash the disk with three successive 20 mL volumes of deionized water. Remove all traces of water by continuing to apply vacuum after water has passed through. Remove funnel from base and place filter in the aluminum dish and ignite in the muffle furnace at 550°C $\pm$ 50°C for 30 minutes. Rewash the filter with an additional three successive 20 mL volumes of deionized water, and dry in an oven at 103-105^{0}C for one hour. When needed, remove dish from the oven, desiccate, and weigh(A).

- Select a sample volume (S) that will yield no more than 200 mg of total suspended solids.

- Place the filter on the base and clamp on funnel and apply vacuum. Wet the filter with a small volume of deionized water to seal the filter against the base.

- Shake the sample vigorously and quantitatively transfer the sample to the filter. Remove all traces of water by continuing to apply vacuum after sample has passed through.

- Rinse the funnel onto the filter with small volume of deionized water. Remove all traces of water by continuing to apply vacuum after water has passed through

- Carefully remove the and filter from the base. Dry at least one hour at 103-105°C.

- Cool in a desiccator and weigh(B).

- Retain the sample in the dish for subsequent ignition at 550°C if volatile suspended solids is desired.

Calculation of Total Suspended Solids:

$$TSS(mg/l) = \frac{(B-A)}{S} * 1000$$

Where,

A = weight of filter and dish + residue in mg

B = weight of filter and dish in mg

S = volume of sample filtered in ml

Procedure for Volatile Suspended Solids

- After determining the final weight in the total suspended solids analysis, place the filter and dish in the muffle furnace and ignite at 550°C for 30 minutes.

- Allow to partially air cool, desiccate and weigh(C).

Calculation of Volatile Suspended Solids:

$$VSS(mg/l) = \frac{(B-C)}{S} * 1000$$

Where:

B = weight of residue + filter and crucible in mg from Total Suspended Solids test
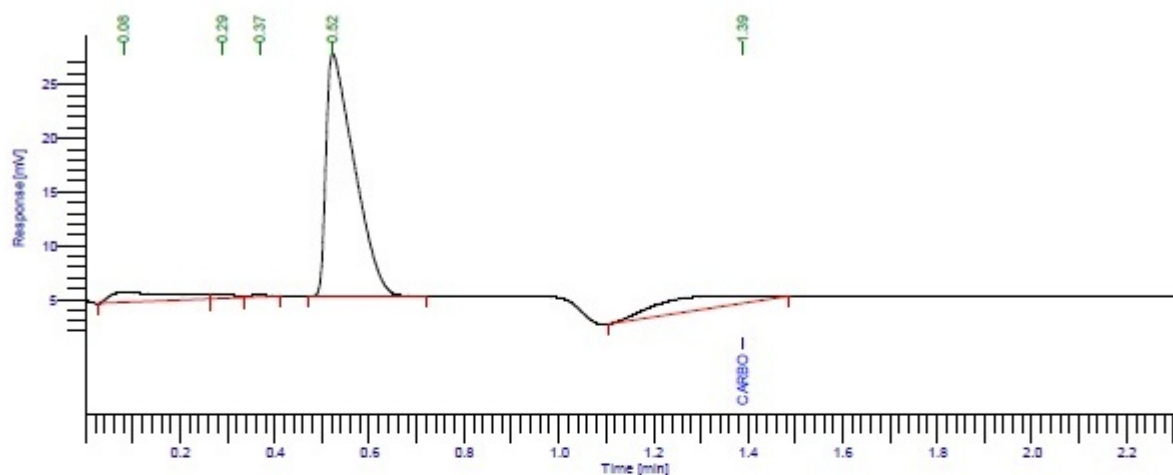
C = weight of residue + filter and crucible in mg after ignition

S = volume of sample filtered in ml

Appendix B

Appendix B

Result File : d:\clarus-500 gc\data\samir\datb010.rst
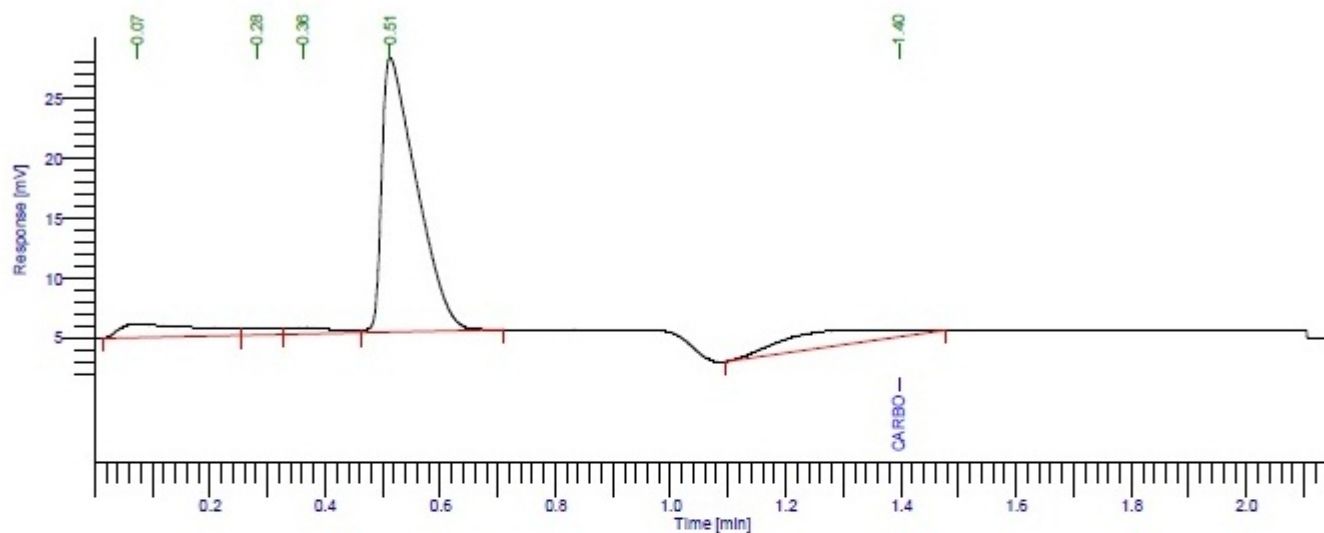Sequence File : D:\Clarus-500 GC\Sequence\TCD.seq

DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	TF
1		0.081	8540.56	943.99	7.05	-------
2		0.290	1215.82	321.93	1.00	-------
3		0.368	580.59	182.34	0.48	-------
4		0.522	93629.53	22616.13	77.28	-------
5	Carbon Dioxide	1.389	17194.12	673.75	14.19	-------
			121160.63	24738.15	100.00	0.0000

Figure B.1: Reactor A Gas Chromatograph

Result File : d:\clarus-500 gc\data\samir\datb008.rst
Sequence File : D:\Clarus-500 GC\Sequence\TCD.seq

DEFAULT REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	TF
1		0.073	11356.60	1129.63	8.70	----------
2		0.282	2393.49	604.57	1.83	----------
3		0.361	3261.30	544.35	2.50	----------
4		0.513	96108.64	22932.73	73.60	----------
5	Carbon Dioxide	1.395	17469.53	576.41	13.38	----------
			130589.56	25787.70	100.00	0.0000

Figure B.2: Reactor B Gas Chromatograph