TREATMENT OF A RECYCLED PAPER MILL WASTE WATER USING AN UPFLOW ANAEROBIC SLUDGE BLANKET (UASB) REACTOR

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DECLARATION

This thesis is my own original work and has not been presented for the award of a degree in any other university.

Mustafa Ahmed Mohammed Elkanzi

This thesis has been submitted for examination with my knowledge as supervisor.

Nyanchaga.

Mr. E.N. Nyangeri

Dr. P.N. Odira

To my mother, Sittna Mohamed Abdelhamid

for making a lot of sacrifice that

"I can go to school",

and

to my brothers and sisters.

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LIST OF ABBREVIATIONS

A:	Surface area of the reactor
AAFEB:	Anaerobic expanded bed reactor
ABR:	Anaerobic Battled Reactor
AF:	Upflow Anaerobic Filter
AFF:	Down Flow Anaerobic Filter
AGLR:	Anaerobic Gas Lift Reactor
[AT]:	Total Concentration of free and saline acetic acid in solution
b:	Rate of cell death and decay
BOD_7:	Bilogical Oxygen Demand (7 days)
Bv:	Applicable space loading rate
C:	Waste water strength (mgCOD/l).
CMP:	Chemi-Mechanical Pulp
COD:	Chemical Oxygen Demand
CTMP:	Chemi-Thermo Mechanical Pulp
D:	Dilution Rate + 1/HRT
E.H.E.:	Environmental Health Engineering
FB:	Fluidized Bed reactor
f_e:	The fraction of electron donor used for energy
f_s:	The fraction of electron donor used for synthesis
f_{smax}:	Maximum fraction of electron donor used for synthesis
GSS:	Gas Solids Seperator
H:	Reactor height (m)
HRT:	Hydraulic Retention Time

K: Maximum observed specific rate of substrate removal (gCOD/gvss.d)

K_o: Observed specific rate of substrate removal (gCOD/gVss.d)

K_s: Half Saturation Constant (gCOD/L)

K_I: Inhibition Constant (gCOD/L)

L: length of the channel

MG: Machine Glazed Paper

NAD^+: Nicotinamide Adenine Dinoceleolide

NH_3-N: Free and Saline Ammonia

O.L.R.: Organic Loading Rate

PGW: Pressurized Ground Wood

P_o: phosphorous concentration in raw waste water

PM1: Paper machine number one

PM2: Paper machine Number two

Q: Hydraulic flow rate

Q_{CH4}: Volumetric flow rate of methane (Vol/Vol.d)

Q_{xc}: Critical Sludge residence time (Vol/Vol.d)

R: The effluent recycled to feed ratio

Rc: Half reaction for bacterial cell synthesis

Rd: Half reaction for electron donor

Re: Half reaction for electron acceptor

RMP: Refiner Mechanical Pulp

S_e: Soluble Substrate Concentration (gCOD/L) in digester effluent

SGW: Conventional Stone Ground Wood

S_o: Feed Soluble COD Concentration (gCOD/L)

SRT_{min}: Minimum Solids Residence Time (day)

Ta: Allowable hydraulic retention time

Tav: Average travelling time in a channel

T_c: Mean cell residence time

T_d: Hydraulic residence time

TMP: Thermo Mechanical Pulp

TSS: Total Suspended Solids

T_x: Solids residence time

UASB: Upflow Anaerobic Sludge Blanket

U_{max}: Maximum specific growth rate (L/day)

U_o: Observed specific growth (d^{-1})

U_o^*: Maximum U_o attainable (d^{-1})

Vc: Critical liquid upflow velocity

VFAs: Volatile Fatty Acids

Vr: Reactor volume

VSS: Volatile Suspended Solids

W: Biomass conversion factor into COD (gCOD/gVSS)

Wd: width of the channel

X: Biomass Concentration in the digester (gVss/L)

X_e: Solids concentration in the effluent (gVss/L)

Y: True growth yield

Z: Conversion factor of methane volume into COD(gCOD/L)

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ABSTRACT

Manufacturing of paper by recycling of waste paper is currently receiving attention all over the world especially in the developing countries as a consequence of the high cost associated with production of paper from wood and the global environmental campaign against deforestation. As paper manufacturing from waste paper involves many steps of process, it results in effluents whose characteristics vary considerably.

Application of Anaerobic treatment systems in the developing countries especially tropical countries (e.g. sub-saharan) can highly be feasible because the system could be operated successfully at ambient temperature and hence the cost for heating the system will be omitted. Moreover, the methane gas produced by such systems can contribute considerably to solving the problems associated with energy availability in these countries.

In this study, the characteristics of a recycled paper mill (Chandaria paper mill, Nairobi, Kenya) waste water was investigated and the feasibility of its treatment anaerobically was studied in a laboratory scale UASB rector.

The waste water was found to be highly biodegradable with a COD concentration ranging between 1900 and 2300 mg/l and a BOD

concentration ranging between 1100 and 1300 mg/l. The COD/BOD correlation being expressed by:-

$BOD_5 = 0.59\ COD + 2.24$

The total suspended solids concentration was in the range of 500-900 mg/l. The waste water was acidic (PH between 3 and 5) and deficient in basic inorganic nutrients (phosphorous 3-5 mg/l and NH_3-N 0.0). Approximately all the total kjeldahl nitrogen (TKN) exist in the waste water was associated with organic matter at a concentration of 11-26 mg/l. The sulphate content was between 87 and 164 mg/l. The final industrial effluent flow rate was ranging between 1700 and 2100 m^3/d and the waste water temperature level was at 22-28°C.

The treatability study showed that, it is feasible to treat this waste water in a UASB system seeded with sludge from a municipal anaerobic digester at ambient temperature (average 22°C) whereby the efficiency of the organic content removal in terms of soluble COD was 58-63% at an optimum organic loading rate between 12-15Kg COD/m^3/d. This corresponded to a hydraulic retention time (HRT) of 3 hours at an influent COD concentration of 2100 mg/l. The average total biogas production was equivalent to 0.2 litre/g COD removed.

Measurement of different waste water parameters; COD, short chain fatty acids (propionic and acetic acids), sulphate, pH,

free and saline ammonia, organic nitrogen, and total suspended solids; along the rector length provided interesting information regarding the system behavior. The results conform with results obtained elsewhere.

CHAPTER ONE

INTRODUCTION

1.1 Trends Towards Recycling of Waste Paper:

Recycled paper industry is currently receiving attention all over the world. The interest of paper recycling varies from country to country. Amongst the common reasons quoted for this interest are: (UNEP, 1993)

1. To save virgin forest resources or to use these resources in different way like energy generation.
2. To reduce pressure on land which might be afforested to farm trees and remove the need for the intensive forestry which is demanding sites of great ecological importance e.g. countries like Brazil and Scotland.
3. To reduce energy consumption in the manufacture of paper and board products. The amount of energy saved ranges from 28% to 50%, depending on the type of paper being recycled.
4. Lower the contribution to the "green house effect" and acidification of environment via lowering the energy production (Regional Workshop symposium on waste recycling and reuse in developing countries.
5. To reduce the flow of waste to the environment and the associated disposal costs. Widespread and well organized recycling will ease the burden on overwhelmed landfill sites.

6. To reduce environmental (water, atmosphere) pollution by highly concentrated and toxic effluents from paper industries processing virgin wood fibres.

7. To reduce the cost of producing paper from virgin wood pulp.

1.2 Pollution from Recycled Paper Industry:

Experiences have shown that effluents generated by using waste paper is less problematic than those generated by using wood in paper production (UNEP, 1993). However, the current global interest and particularly in the developing countries, in recycled paper industry is expected to result in the production of abundant quantities of effluents having different characteristics from this industry. Moreover, the strength of these effluents can rather increase as the load (problem substances) imported with waste paper increases. This has been found, for example, in the COD concentration in some of the German Paper Mills (use waste paper) effluents, that have risen almost trebled on the average between 1979 and 1990 (Huter et.al., 1991).

1.3 Need for Development of Treatment Technology:

The continual extension in recycled paper industry puts a great strain in it's effluent treatment. There is need, therefore, to develop a technology that can adequately treat these effluents taking into account the technical and the economic aspects, existing treatment facilities, sustainability and applicability of the technology. A general solution for waste water treatment from recycled paper industry should not be expected because, the diverse character of production processes implies use of different raw materials and thus different waste water characteristic.

There are a multitude of treatment systems, each with different efficiencies, cost and sensitivity. Almost all waste water can be treated biologically. Fortunately, the effluents from recycled paper industry do not have inhibitory effects to micro-organisms, are rich in biodegradable organics and can successfully be treated in a biological system (Habets and Knelissen, 1985). The major biological treatment processes used for treatment of waste water can be Aerobic, Anaerobic, Anoxic and combined Aerobic/Anaerobic processes. Anaerobic process offers the most attractive solution for Treatment of effluents particularly with strong waste (Gray, 1989).

1.4 Treatment of Waste Water:

Biological anaerobic treatment offers the most attractive solution for treatment of effluents particularly strong waste due to the following reasons:

1. High efficiency for BOD & COD reduction
2. Production of energy as biogas
3. Production of biofertilizer
4. Small production of already stabilized biological

sludge

5. Lower capital investments
6. Lower operation and maintenance costs
7. Possibility of decentralized systems
8. There is a high resistance to shock loads and environmental stress situation.
9. The process is applicable at very small and very high scale as well as small area required.

It has, however, a major shortcomings for instance, the need for large hydraulic retention time (HRT) which often makes the process economically unfeasible.

The development of proper high rate treatment process, can be said to be definite breakthrough in the anaerobic treatment of waste water. The Upflow Anaerobic Sludge Blanket (UASB) is one of the high rate anaerobic systems most recently used in pulp and paper industry and in many other industries. The principle reason for this interest is that, in the UASB, the sludge generated is often in a well defined pellet form and exhibits good settling characteristics. Pellets formation, however, is not general and has been observed only with certain wastes. Therefore there is a considerable interest on whether or not the characteristics of wastes from recycled paper industry will support sludge pellet growth.

1.5 The Present Study:

The study "Treatment of a Paper Mill Waste Water using an up-flow Anaerobic Sludge Blanket (UASB) reactor" focused on the following objectives:

a) <u>Primary Objectives</u>

1. To investigate the characteristics strength of a recycled paper mill waste water.

2. To determine the conversion efficiencies of a recycled paper mill waste water in a laboratory scale UASB reactor at ambient temperature (average 22°c) by comparing the influent and effluent characteristics.

3. To ascertain the variation of the concentration of waste water parameters along the reactor length.

4. To ascertain the maximum loading rates without adverse change in effluent quality that can be applied and the corresponding hydraulic retention time (HRT).

b) <u>Secondary Objectives:</u>

1. To determine the total gas production

2. To observe the nature of the sludge

A recycled paper mill in Nairobi, Chandaria Paper Mill was selected as a case study. The mill production processes were initially investigated with the objective of providing practical knowledge about paper reprocessing and sources of waste. Detailed information about these processes which embodies; waste paper collection, classification, transportation and storage; stock preparation; approach flow system,; paper manufacturing; water use; white water purification and reuse; and waste water discharge, has been covered in details in chapter 4.

In the experimental investigation, the waste water streams generated from the mill were, firstly, identified, quantified and analyzed with objective of demarcating the pollutional load contributed by each stream as well as the final effluent which is directly discharged to the main city sewer. Then, waste water from the stream contributing the highest pollutional load was treated in a bench scale UASB reactor. The reactor was constructed from a standard size PVC pipe with a gas/liquid/solid separator arrangement at the top. The inside diameter of the reactor was 150 mm and the height was 1250 mm giving a total effective reactor volume of 23 liters. Seven sample ports were provided along the reactor height for concentration profiling. A perspex window was provided at the reactor side for observation of the formed sludge nature. The reactor was operated for a period of approximately 4 months at ambient temperature (average 22°c) at the Nairobi City Council Kariobangi Sewage Treatment Plant. The substrate was continuously fed into the reactor daily from a feed storage basin via a variable speed pump. The biogas produced was measured using the water seal method.

The result on the mill waste water characteristic showed that, the mill final effluent was the stream contributing the highest pollutional load with a COD between 1900 and 2300 mg/l and a BOD between 1100 and 1300 mg/l. The COD/BOD_5 is expressed by:

$BOD_5 = 0.59COD + 2.24$

The effluent volume ranged between 1700 and 2100 m^3/d. PH and inorganic nutrients analysis showed that the waste water was acidic (PH between 3 and 5) and deficient in the basic inorganic nutrients (phosphorous between 3 and 5 mg/l and free ammonia was nil). The total suspended solids (TSS) concentration was in the range of 500-900 mg/l and the sulphate concentration was between 87 and 164 mg/l. the waste water temperature leveled at 22-28°C.

The results on the treatability study showed that, treatment of this waste water in a UASB system seeded with sludge from a municipal anaerobic digester at ambient temperature (average 22°C) is satisfactorily feasible whereby the efficiency of the organic content removal in terms of soluble COD was 58-63% at an optimum organic loading rate between 12-15kgCOD/m^3/d.
This corresponded to a hydraulic retention time of 3 hours at an influent COD of 2100 mg/l. The average total biogas production was equivalent to 0.2 liter/g COD removed.

Measurements of different waste water parameters; COD, short chain fatty acids (propionate and acetate), sulphate, PH, free and saline ammonia, organic nitrogen, and total suspended solids; along the reactor length provided interesting information regarding the system behavior. The results conform with those obtained elsewhere.

CHAPTER TWO

THE UASB PROCESS

2.1 Description of the UASB Process:

The UASB process is a high rate anaerobic waste water treatment process. It was developed in the Netherlands by Lettinga and his co-workers in 1980. It is now the most widely used anaerobic treatment process in Western Europe (Lettinga and Hulshoff, 1986). Table 2.1 shows the number and volume of full scale UASB reactor constructed before September 1990 for treatment of different type of waste waters. The process relies on the development of a highly settleable sludge within the reactor, and require no support media. It is characterized by a very high sludge retention time (SRT) and has the highest loading rate of any anaerobic process.

COD removal efficiencies as high as 90% are obtainable with waste strengths ranging from 1500-20000 mgCOD/l, and at detention times as low as 3-4 hrs. Under these conditions, organic loads of upto 40 kg COD/m^3/d are possible (Souza, 1986). Applications for the UASB in treatment of various industrial and domestic waste waters have been reported.

Table 2.1: Full Scale UASB Plants Constructed Before September 1990 (Lettinga and Hulshoff , 1986)

WASTE WATER	NUMBER OF UASBs	UASB VOL. M^3
Alcohol	20	52,000
Bakers, Yeast	5	9,900
Bakery	2	347
Brewery	30	60,000
Candy	2	350
Canneries	3	2,800
Chemical	2	2,600
Choclate	1	285
Citric acid	2	6,700
Coffee	2	1,300
Dairy and Cheese	6	2,300
Distillery	8	24,000
Domestic sewage	3	3,200
Fermentation	1	750
Fruit juice	3	4,600
Fructose	1	240
Landfill Leachat	6	2,695
Paper and Pulp	28	67,197
Pharmaceutical	2	400
Potato process	27	25,610
Rubber	1	650
Soft drinks	4	1,300
Sugar	19	23,000
Slaughter house	3	950
Vegetable	3	2,800
Yeast	4	8,550
Potato wheat	16	33,500
Total	205	339,000

Souza (1986) indicates that the UASB reactor consists basically of a tank at the bottom of which the digester is located and at the top of which a settler preceded by a gas separation system is located. The waste water to be treated is uniformly distributed at the bottom of the reactor and through a biological sludge layer which transforms the organic material into biogass and new cells. The gas produced is prevented from entering into the settler through the gas deflectors and only enters certain areas of the reactor. The portion of the sludge which reaches the settler is separated and returns to the bottom of the reactor. The effluent is uniformly withdrawn from the surface of the settler (Fig 2.1)

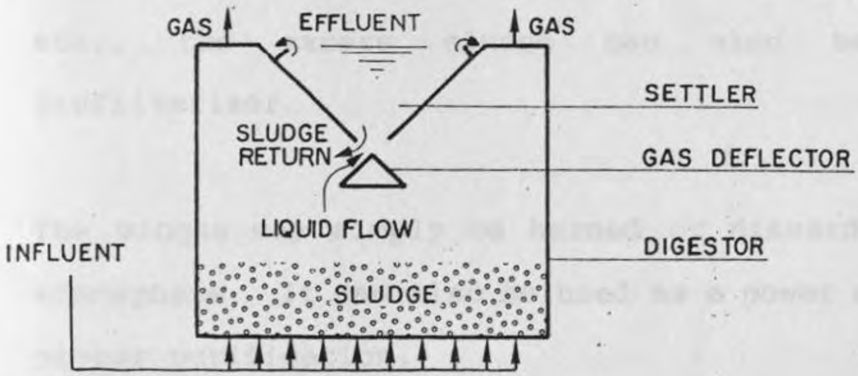


Fig 2.1: Schematic Diagram of a UASB reactor (Souza, 1986)

It is very important for the proper functioning of the UASB reactor that biological sludge be available in adequate quantities, and that it has or may acquire better settling characteristics and methanogenic activity. A high level of substrate-sludge contact, an efficient gas/solids separation, plus an adequate bacteria selection process greatly contribute to the development of the desired sludge.

The excess sludge, especially the granular type, can be used for the inoculation and start-up of other UASB units for eventual re-inoculation of the unit it self. Generally the excess sludge from a UASB reactor is relatively stable and has superior dewatering characteristics and can directly be injected into dewatering systems such as drying beds, vacuum filters, etc., the excess sludge can also be used as biofilterizer.

The biogas may simply be burned or discarded into the atmosphere. It can also be used as a power source after proper purification.

2.2 Microbiology of Anaerobic Treatment:

Several techniques and methods have been developed and adapted by researchers such as (Hungate, 1969; Bryant, 1972, Miller and Willon, 1974; and Edward and McBride, 1975) to allow the isolation and studies of anaerobic bacteria. The resulting conclusion is that "the anaerobic ecosystem is the result of complex interactions among micro-organisms of several different species", the different steps involved in these microbial interactions have been described by Byrant (1976), Zeikus (1980), and McInerney and Bryant (1981a) to facilitate the explanation of the microbiology and biochemistry of the process. Fig 2.2 shows a diagram of metabolic steps involved in anaerobic digestion and the interactions between the micro-organisms. In the first stage, complex organic compounds are hydrolysed, resulting in simpler compounds, through enzymes produced by fermentative bacteria. In the second stage, acidogenesis occurs with the formation of hydrogen, carbon dioxide, acetate and higher organic acids than acetate due to the activity of fermentative bacteria. During the third stage acetogenesis occurs and the organic acids produced are converted to hydrogen and acetate by acetogenic bacteria. In addition, apart of the available hydrogen and carbon dioxide is converted into acetate by the homoacetogenic bacteria. During the fourth and last stage, a group of methanogenic bacteria both reduce the carbon dioxide and decarboxylate the acetate to form methane (CH_4).

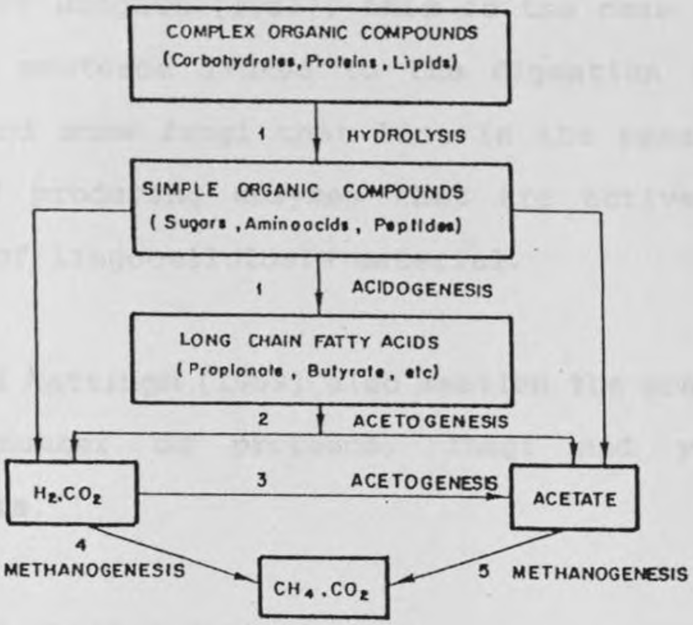


Fig 2.2: Metabolic steps and microbial groups involved in anaerobic digestion (Souza, 1986). 1) Fermentative bacteria; 2) H_2-producing acetogenic bacteria; 3) H_2-consuming acetogenic or homoacetogenic bacteria; 4) CO_2-reducing methanogenic bacteria; 5) Acetogenic methanogenic bacteria.

It is convenient to think of these stages as different trophic levels, and although all the four stages are normally occurring simultaneously within a digester, the microorganisms involved at each state are metabolically dependent on each other for survival.

Although bacteria are responsible for anaerobic digestion, some other microorganisms may have an important role in the initial stage of fermentation.

According to Hungate (1982), this is the case with the flagellate protozoa linked to the digestion tract of termites and some fungi that line in the rument, both capable of producing enzymes that are active in the breakdown of lingocellulosis material.

Toerien and Hattingh (1969) also mention the presence of a small number of protozoa, fungi and yeast in biodigesters.

2.2.1 Fermentative Bacteria:

The fermentative bacteria are responsible in the first two stages of anaerobic digestion, hydrolysis and acidogenesis. It produces enzymes which are liberated in the medium to hydrolyse organic compound such as cellulose, hemicellulose, pectin, starch and others into smaller molecular material which is transported to the interior of the cells and fermented into a variety of products such as ethanol, butyrate, acetate, propionate etc.

In addition to Acid forming bacteria there are also physiological groups present which include those producing protedytic, lipolytic, ureolytic or cellulytic enzymes (Toerien and Hattingh, 1969). Mono and disaccharides, long chain fatty acids, glycerol, amino acids and short chain peptides provide the main carbon source for growth, with saturated fatty acids, carbon dioxide and ammonia being the main end products. Acetic, propionic, butyric and lactic acids are the most frequently produced products during acidogenesis. Toerien (1970) found that these acids were produced by 87, 67, 10 and 70% respectively of the 92 acid-forming bacterial isolates he examined.

The final products of the metabolism of these bacteria depend on both the initial substrate and the environmental conditions. With regard to the later, emphasis is given to the regulating presence of Hydrogen. At low partial pressure of Hydrogen in digester the formation of organic compounds such as acetate, carbon dioxide and Hydrogen is thermodynamically favored. If the partial pressure of Hydrogen is maintained at a high level, only the formation to products such as propionate and some other organic acids, lactate and ethanol occurs (Zehnder, 1978).

According to Thauer <u>et. al.</u>, 1977) the partial pressure of hydrogen plays a central role in controlling the proportions of the various products produced by fermentative bacteria because the electrons released by oxidation during fermentation are accepted by the co-enzymes Nicotinamide Adenine Dinoceleolide (NAD^+), thereby reducing it to NADH (reduced Nicotinamide Adenine Dinoceleolide). The Oxidation of NADH back to NAD^+ with production of hydrogen is essentially for fermentation to continue since there are only small quantities of NAD^+ present in the cell. However the oxidation of NADH is endothermic.

$NADH + H^+ \longleftrightarrow H_2 + NAD^+ \qquad G^\circ = 18$ kJ

unless the partial pressure of hydrogen is maintained at low level (Wolin, 1982) as it is in the presence of efficiently metabolizing hydrogen-utilizing methanogenic bacteria. When hydrogen partial pressure increases, which may occur with organic hydraulic overload of the reactor, there is an increased tendency for propionate, and sometimes butyrate, valerate and cobroate to be produced rather than acetate, hydrogen and carbon dioxide. This is indicative of imbalance between the various stages of digestion.

2.2.2 Acetogenic Bacteria:

This group of bacteria is essential for anaerobic degradation because it catabolizes propionate and other organic acids larger than acetate, alcohols and certain aromatic compounds (i.e. benzoate) into acetate, carbon dioxide and hydrogen. It is capable of survival only at very low hydrogen concentration in their environment. They can therefore, only survive if their Hydrogen products of metabolism is continuously removed from the medium. (Novaes, 1986). Studies carried out with these bacteria emphasized the important role of Hydrogen.

These studies have shown narrow association between the Hydrogen-consuming bacteria, thereby, regulating the Hydrogen level in their environment. A classic work in this regard by Bryant <u>et. al.</u> (1967) about the synthrophic association of an acetogenic organisms called "organisms S" with a methanogenic Hydrogen-consuming bacterium in which the production of acetate and water from ethanol through "organisms S" occurred if the level of hydrogen was kept low by the methanogenic bacterium. Some papers, recently, have shown several association between acetogentic bacteria and other bacteria in anaerobic environment. Boone and Bryant (1980), have shown the interaction of acetogenic bacterium that degrades proinate to acetate, carbon dioxide and hydrogen (called syntropnobactor Wolinii) with hydrogen-consuming bacterium which is sulphate reducing organisms (Desulfovibrio Species). McInerney and Bryant (1981b) showed that lactate was completely degraded to methane and carbon dioxide by syntrophic associations of the sulphate reducing bacteria (Desulfovibrio species and Methanosarcina barkeri) in the absence of electron acceptors such as sulphate.

2.2.3 Homoacetogenic Bacteria:

This group has only recently been emphasized as an important step in anaerobic digestion due to the importance of its final product, acetate. The bacteria involved in this step are characterized as chemolitotropic, hydrogen and carbon dioxide users (Novaes, 1986).

Zeikus (1981) has attempted to describe the homoacetogenic bacterial metabolism. Homoacetogenic bacteria have high thermodynamic efficiencies in their metabolism due to no formation of hydrogen and carbon dioxide during growth on multi-carbon compounds.

2.2.4 Methanogenic Bacteria:

This group is responsible for the final stage of anaerobic digestion where they convert the products of acetogenic stage into gases, mainly carbon dioxide and methane. Methane formation from acetic acid is a single step process carried out by one group of methanogenic bacteria.

Acetic acid ----> methane + carbon dioxide

Methane fermentation of propionic acid is two step process carried out by one group of methanogenic bacteria, with acetic acid as intermediate step.

Step 1 = $CH_3CH_2COOH + 0.5H_2O \text{ ----> } CH_3COOH + 0.25CO_2 + 0.75CH_4$

Step 2 = $CH_3COOH \text{ ----> } CH_4 + CO_2$

Overall = $CH_3CH_2COOH + 0.5H_2O \text{ ----> } 1.25CO_2 + 1.75CH_4$

Complete stabilization of the substrate occurs as the end products are only gases (Gray, 1989).

The methanogenic bacteria are obligate anaerobes, able to utilize only certain determined substrates. The nutritional requirements are quite simple, bacterial growth occurs in media that have ammonia and sulphide or cystein as sources of nitrogen and sulpher respectively. They use organic substrate or specific carbon sources such as acetate, hydrogen, carbon dioxide and formate. Some strains are autotrophic, using only carbon dioxide or carbon monoxide as carbon sources (Huser <u>et. al.</u>, 1982).

Two temperature ranges have been described 35 to 40°c for mesophilic bacteria and 55 to 65°c for thermophilic bacteria and the ideal PH for growth and methane production is between 6.8 and 7.2, but may vary among the known species (Souza, 1986).

The process of hydrogen consuming methane fermentation is appreciably more advantageous on energetic grounds than acetate decarboxylation but only 27-30% of the methane produced is produced via this process, while 70% is generated from acetate because of the limited substrate supply in natural situations. The acetate utilizing methane bacteria only produce methane when a supply of acetate is available and this can only be achieved by symbiosis with acetogenic organisms (Gray, 1989).

2.2.5 Sulphate Reducing Bacteria:

Sulphate reducing bacteria have an important role to apply in anaerobic digestion because they act as either an acetogenic bacteria, favoring methogenesis, or as bacteria that compete for nutrients with methanogenic bacteria, and thus inhibit methanogenesis depending on the sulphate concentrations in the media. Sulphur compounds act as terminal electron acceptor for sulphate reducing bacteria (Karhadkar et. al., 1987). Competition is probably because sulphate reducing bacteria have higher affinity for hydrogen than methanogenic bacteria (Krinstjanson and Schonheit, 1983).

Sulphate reducing bacteria only utilizes a restricted range of carbon compounds, such as lactate and matate, and rely on the metabolic products of other anaerobic bacteria that utilize more complex organic compounds. Studies about the influence of sulphate in anaerobic reactors are of importance for waste treatment at high concentration of sulphate. The inhibition of methanogenesis due to high concentration of sulphate apart from being due to competition for hydrogen with sulphate reducing bacteria, is also due to the production of sulphides which are toxic to the methanogenic. Free hydrogen sulfide at 50 mg/l decreased methanogenic activity by 10-50% (Karhadkar et. al., 1987).

2.3 Stoichiometric Approach to Energy and Synthesis:

Energy and synthesis are coupled reactions which cannot be separated. The maximum rate of energy expenditure occurs during maximum rate of synthesis. In other words, the maximum rate of removal of organic matter per unit of micro-organisms occurs during maximum growth of microorganism culture (Mara, 1974).

It is essential in the design of biological treatment systems to be able to calculate the necessary inputs into the system such as oxygen and nutrients as well as the outputs such as carbon dioxide, sludge and methane. This stoichiometric approach to energy production and cell synthesis has been developed by McCarty (1971). Table 2.2 of half reactions allows the organic substrate that has been utilized by the bacteria to be divided into two portions; first, that which has been oxidized to produce energy, and secondly that which is used for synthesis of new cellular material. The energy and synthesis reactions add together to become the overall reaction or total metabolism (Christensin and McCarty, 1975).

Using table 2.2 it is possible to calculate the energy yield for the metabolism of all commonly encountered substrate under aerobic, anoxic or anaerobic conditions. For example, if we assume the composition of domestic sewage to be $C_{10}H_{19}O_3N$, the energy yields for different electron acceptors can easily be calculated by using equation 7 for electron donor and equation 3 for aerobic conditions, equation 4 for anoxic conditions or equation 6 for anaerobic conditions (Table 2.2).

Thus, the energy yield from the metabolism of domestic sewage under aerobic conditions is calculated by writing the half reactions:

Donor: $1/50C_{10}O_3H_{19}N + 9/50H_2O$

$$= 9/50CO_2 + 1/50NH_4^+ + 1/50HCO_3^- + H^+ + e^-$$

$$G^o = +7.6 Kcal/e^-$$

Acceptor: $1/4O_2 + H^+ + e^- = 1/2H_2O$

$$G^o = -18.675\ Kcal/e^-$$

Adding the half reactions and multiplying by 50 yields:

$$C_{10}H_{19}O_3N + 18H_2O + 12.5O_2 = 9CO_2 + HN_4^+ + HCO_3^-$$

The energy yield by the reaction is:

$$G^o = G^o \text{ of products } - G^o \text{ of reactions}$$

As each mole of waste water utilized results in the transfer of 50 electrons (Table 2.2), The energy resulting from the aerobic metabolism of waste water is:

$$G^o = \frac{\text{50 electrons}}{\text{mole of wastewater}} * [-18.675Kcal/e^- - 7.6Kcal/e^-]$$

$$= -1313.75Kcal \text{ per mole waste water.}$$

TABLE 2.2 Oxidation half reactions

(Christensen and McCarty 1975)

Equation no.	Half-reaction*		$\Delta G^{\circ}(W)^*$ kcal per electron equivalent
	Reactions for bacterial cell synthesis (R_c)		
	Ammonia as nitrogen source:		
1	$1/5CO_2 + 1/20HCO_3^- +$ $1/20NH_4^+ + H^+ + e^-$	$= 1/20C_5H_7O_2N + 9/20H_2O$	
	Nitrate as nitrogen source:		
2	$1/28NO_3^- + 5/28CO_2 +$ $29/28H^+ + e^-$	$= 1/28C_5H_7O_2N + 11/28H_2O$	
	Reactions for electron acceptors (R_a)		
	Oxygen:		
3	$1/4O_2 + H^+ + e^-$	$= 1/2H_2O$	−18.675
	Nitrate:		
4	$1/5NO_3^- + 6/5H^+ + e^-$	$= 1/10N_2 + 3/5H_2O$	−17.128
	Sulphate:		
5	$1/8SO_4^{2-} + 19/16H^+ + e^-$	$= 1/16H_2S + 1/16HS^- + 1/2H_2O$	5.085
	Carbon dioxide (methane fermentation):		
6	$1/8CO_2 + H^+ + e^-$	$= 1/8CH_4 + 1/4H_2O$	5.763
	Reactions for electron donors (R_d)		
	Organic donors (heterotrophic reactions)		
	Domestic wastewater:		
7	$9/50CO_2 + 1/50NH_4^+ +$ $1/50HCO_3^- + H^+ + e^-$	$= 1/50C_{10}H_{19}O_3N + 9/25H_2O$	7.6
	Protein (amino acids, proteins, nitrogenous organics):		
8	$8/33CO_2 + 2/33NH_4^+ +$ $31/33H^+ + e^-$	$= 1/66C_{16}H_{24}C_5N_4 + 27/66H_2O$	7.7
	Carbohydrates (cellulose, starch, sugars):		
9	$1/4CO_2 + H^+ + e^-$	$= 1/4CH_2O + 1/4H_2O$	10.0
	Grease (fats and oils):		
10	$4/23CO_2 + H^+ + e^-$	$= 1/46C_8H_{16}O + 15/46H_2O$	6.6
	Acetate:		
11	$1/8CO_2 + 1/8HCO_3^- + H^+ + e^-$	$= 1/8CH_3COO^- + 3/8H_2O$	6.609
	Propionate:		
12	$1/7CO_2 + 1/14HCO_3^- + H^+ + e^-$	$= 1/14CH_3CH_2COO^- + 5/14H_2O$	6.664
	Benzoate:		
13	$1/5CO_2 + 1/30HCO_3^- + H^+ + e^-$	$= 1/30C_6H_5COO^- + 13/20H_2O$	6.892
	Ethanol:		
14	$1/6CO_2 + H^+ + e^-$	$= 1/12CH_3CH_2OH + 1/4H_2O$	7.592
	Lactate:		
15	$1/6CO_2 + 1/12HCO_3^- + H^+ + e^-$	$= 1/12CH_3CHOHCOO^- +$ $1/3H_2O$	7.873
	Pyruvate:		
16	$1/5CO_2 + 1/10HCO_3^- + H^+ + e^-$	$= 1/10CH_3COCCO^- + 2/5H_2O$	8.545
	Methanol:		
17	$1/6CO_2 + H^+ + e^-$	$= 1/6CH_3OH + 1/6H_2O$	8.965
	Inorganic donors (autotrophic reactions)		
18	$Fe^{3+} + e^-$	$= Fe^{2+}$	−17.780
19	$1/2NO_3^- + H^+ + e^-$	$= 1/2NO_2^- + 1/2H_2O$	−9.430
20	$1/8NO_3^- + 5/4H^+ + e^-$	$= 1/8NH_4^+ + 3/8H_2O$	−8.245
21	$1/6NO_2^- + 4/3H^+ + e^-$	$= 1/6NH_4^+ + 1/3H_2O$	−7.852
22	$1/6SO_4^{2-} + 4/3H^+ + e^-$	$= 1/6S + 2/3H_2O$	4.657
23	$1/8SO_4^{2-} + 11/16H^+ + e^-$	$= 1/16H_2S + 1/16HS^- + 1/2H_2O$	5.085
24	$1/4SO_4^{2-} + 5/4H^+ + e^-$	$= 1/8S_2O_3^{2-} + 5/8H_2O$	5.091
25	$H^+ + e^-$	$= 1/2H_2$	9.670
26	$1/2SO_4^{2-} + H^+ + e^-$	$= 1/2SO_3^{2-} + 1/2H_2O$	10.595

* Reactants and products at unit activity except $(H^+) = 10^{-7}$.

In a similar way, the energy yield from waste water under anoxic conditions using nitrate as electron acceptor or anaerobic conditions using carbon dioxide as electron acceptor can be calculated.

Synthesis is the biochemical process of substrate utilization to form new protoplasm for growth and reproduction. The primary product of metabolism is energy and the major use of energy is for synthesis, and as energy release and synthesis are coupled then the maximum rate synthesis occurs simultaneously with maximum rate of energy yield or metabolism (Gray, 1989). As part of the substrate goes into energy formation and the remainder goes to cell synthesis, all the reacting material can be expressed as:

$f_s + f_e = 1$

Where:

f_e = the fraction of electron donor used for energy

f_s = the fraction of electron donor used for synthesis

The electron donors (substrate) gives up electrons that are transported via complicated biochemical pathways to the ultimate or terminal electron acceptor (oxygen, nitrate, carbon, sulphate or organic compounds (Gray, McCarty (1975) calculates the amount of substrate metabolized by bacterial to form energy and new cells using a balanced half equation. The overall reaction is constructed from three half reactions, one for synthesis of bacterial cells, which are assumed to be $C_5H_7O_2N$ (Rc) (Table 2.2), one for the electron acceptor (Re) and one for the electron donor (Rd), which combine to give the relationship where R is the overall reaction.

$$R = f_sRc + f_eRe - Rd$$

The ratio f_e to f_s depends on the age of the cell culture as well as the substrate electron donor. An increase in the age of the cell in the system will reduce the net amount of substrate material converted to new cell mass (Gray, 1989). The age of cells is commonly referred to as sludge age or mean cell residence time (T_c) and is defined as the average time in days an organism remains within the treatment system. Maximum values of f_s are given in table (2.3) for various substrates.

It is convenient to estimate the fraction f_s by using the relationship (Gray 1989):

$$f_s = f_{smax}\ [1 - 0.8bT_c/(1 + bT_c)]$$

where: b = rate of cell death and decay which is assumed to be 0.03

T_c = mean cell residence time.

Table 2.3: Maximum Cell Yield ($f_{s\,max}$) for various electron donors and electron acceptors (Gray, 1989).

ELECTRON DONOR	ELECTRON ACCEPT.	$(f_s)_{max}$
Carbohydrate	O_2	0.72
Carbohydrate	NO_3	0.60
Carbohydrate	SO_4	0.30
Protein	O_2	0.64
Protein	CO_2	0.08
Fatty acid	O_2	0.59
Fatty acid	CO_2	0.05
Fatty acid	SO_4	0.06
Glucose	O_2	0.79
Lactose	O_2	0.74
Sucrose	O_2	0.75
Glycine	O_2	0.52
Alanine	O_2	0.52
Propionate	O_2	0.58
Acetate	O_2	0.58
Methanol	NO_3	0.36
Methanol	CO_2	0.15
Propionate	CO_2	0.07
Acetate	CO_2	0.06
Glucose	CO_2	0.27
Sewage sludge	CO_2	0.11
S	O_2	0.22
S_2	O_2	0.11
S_2O_3	NO_3	0.20
NH_4	O_2	0.10
H_2	O_2	0.04
Fe	O_2	0.07

Table 2.3 gives a (f_{smax}) value of 0.11 for sewage sludge and as the digester has a mean cell residence time of 20 days, f_s is calculated as:

$f_s = 0.11\ [1 - 0.8(0.03)(20)/(1 + (0.03)(20))] = 0.077$

As $f_s = 1 - f_e$, $f_e = 0.923$

Therefore, the revised reactions using the relationship

$R = f_sRc + f_eRe - Rd$ are:

$Rcf_s = 0.0154CO_2 + 0.0039HCO_3^- + 0.0039NH_4^+ + 0.007H^+ + 0.007_e^- \text{----->} 0.0039C_5H_7O_2N + 0.035H_2O$

$Ref_e = 0.115CO_2 + 0.923H^+ + 0.923e^- \text{---->} 0.115CH_4 + 0.231H_2O$

$Rd = 0.02C_{10}H_{19}O_3N + 0.36H_2O \text{---->} 0.18CO_2 + 0.02NH_4^+ + 0.02HCO_3^- + H^+ + e^-$

When added and normalized by dividing by 0.02, the overall reaction is:

$R = C_{10}H_{19}O_3N + 4.7H_2O \text{---->} 0.195C_5H_7O_2N + 5.75CH_4 + 2.48CO_2 + 0.81NH_4^+ + 0.81HCO_3^-$

Therefore, for each mole of sewage sludge 0.195 moles of new cells are produced and 5.75 moles of methane is released.

The value of f_{smax} for any specific waste water, if not given in table 2.3 can be calculated from basic constituents. For instance, Domestic sewage consists approximately of 50% protein 40% carbohydrate and 10% fats (Gray, 1989). Thus, by referring to table 2.3

f_{smax} (sewage) = % Protein x f_{smax} (protein) + % carbohydrates x f_{smax} (Carbohydrates) + % fats x f_{smax} (fats) = 0.5 x 0.64 + 0.4 x 0.72 + 0.1 x 0.59 = 0.67 (Gray, 1989)

In anaerobic decomposition, the low energy yield per unit of substrate due to lack of electron acceptors is a limiting factor, which results in the incomplete breakdown of the substrate. Metabolism and synthesis cease when the supply of biologically available energy is exhausted. With aerobic metabolism, the biologically available carbon is the limiting factor, with no shortage of electron acceptors because of the abundance oxygen (Gray, 1989).

Incomplete metabolism, a small amount of biological growth, and the production of high energy products, such as acetic acid and methane, characterizes the anaerobic reaction. In contrast, the complete metabolism and synthesis of substrate, ending up with a large amounts of biological growth is characteristic of aerobic metabolism (Gray 1989).

2.4 Bacterial Aggregation and Granulation:

All modern high rate anaerobic treatment systems are based on some kind of sludge immobilization principle. Different immobilization principles applied in modern high rate anaerobic treatment systems are: (Souza, 1986).

1 - Bacteria Sludge Attachment
  a) to stationary packing materials (attached film). Examples, Up-flow anaerobic filter (AF) and Down-flow anaerobic filter (AFF).
  b) to particulate carrier material (attached film). Examples, Fluidized bed reactors (FB) Anaerobic expanded bed reactors (AAFEB) ,Floating bed systems, and Anaerobic Gas Lift reactor (AGLR).

2 - Bacterial Sludge Aggregation (floc formation) Examples, Up-flow sludge blanked reactor (UASB), Up-Flow Anaerobic filter (AF), and Anaerobic baffled reactor (ABF).

The UASB system selects for well settling sludges, thus allowing for an efficient separation between solids retention time and hydraulic retention time, while maintaining good conversion efficiencies. Its main difference with other advanced anaerobic treatment systems (Van Den Berg 1984) is the absence of an added substratum to which the active biomass is supposed to adhere. The development of well settling biomass is thus a prerequisite for successful operation of UASB system.

The most striking example of well settling sludge are the so called granular sludges. Their availability makes a rapid start up of new reactors possible, and UASB systems seeded with granular sludge have been successfully applied to polish a wide variety of waste under mesophilic as well as psychrophilic and thermophilic conditions. Other various types of well methanogenic sludges could also be grown in UASB reactors such as; spaghetti-like type (referred to as pellets); spikey granules; methanosacrina-dominated granules (Dolfing, 1986). This variety reflects the principle that different sludges develop in reactors which treat different waste streams or operate under different conditions. It should, however, be noted that the composition of the waste stream is not the only factor , which determines the type of sludge that will develop. The source of the seed sludge also plays a role (Dolfing, 1986). Although granular sludge may be aesthetically the most desirable type, there are indications that the pellet type is at least as efficient as the granular type (Dolfing, 1986).

2.4.1. Physical and Chemical Characteristics of Granules:

The chemical composition of granular methanogenic sludges is comparable to the chemical composition of bacteria in general. The Protein and Carbohydrate values (about 50% and 21% of the total dry weight, respectively, are comparable to those by weight for "a typical bacterium" (Dolfing, 1986). Granules from reactors treating industrial waste waters have generally higher ash content (19-46%) than those of synthetic wastes (Wu, 1991) due to presence of inert suspended solids in the feed.

The specific gravity of UASB granules generally ranged between 1.00-1.8 (Van der Meer, 1979; Dolfing; et. al., 1985; Wu et. al., 1985; Hulshoff, 1989). The density of granules depends on several factors including starting inoculum material, feed composition and operational conditions (i.e. PH, COD loading rate, VFA concentration) in the reactor. (Hickey et. al., 1991).

The size of granules can vary from 0.1 to 8mm in diameter. The granule size distribution depends on the microbial population, feed composition and gas flux rate in the reactor. High biogas flux rates result in a more even size distribution and a smaller mean sized granule. This is assumed to be due to the higher shear exerted by the higher gas flux rates that limit the stable granule size (Hickey et. al., 1991).

Dolfing (1986) noted that good settling properties of the granular sludge are mainly due to aggregation of the micro organisms.

Metabolic activity of sludge is a measure of the biomass connected with various metabolic groups of bacteria in granules. It is normally estimated by comparing the methane production of he granules as a response to the addition of specific substrates and methane production rates of pure cultures. Alternatively, it could be expressed in terms of specific substrate conversion rates (Specific COD). Generally speaking, granular sludges have higher volumetric activities than the other types of sludges, since they are the most dense in structure and contain more biomas on volumetric basis (Hickey et. al., 1991). The metabolic activities of granular sludges vary accordingly as a function of the feed composition, growth condition, microbial composition of granules and the substrate used for activity test. Granules from full-scale UASB reactors treating complex waste waters usually posses activities between 0.5 to 1.0 kg COD/VSS.day (Hickey et. al., 1991)

Thiele et. al. (1990) reported that at mesophilic conditions, the activities of granules developed on VFAs mixtures in UASB reactor can be as high as 7-8 kg COD/kg VSS.day).

On the other hand, for investigation of biodegradability or toxicity of waste water, application of specific substrate conversion rate rather than COD removal rates is recommended (Wu et. al., 1989). Feed composition has strong effect on the microbial populations that are developed within granules and, therefore, on specific substrate conversion rate. For instance, granules developed on starch industrial wastes exhibits much higher glucose conversion than VFA degradation rates (Dubouguier et. al., 1988a), while granules developed on brewery waste water, which contain ethanol and propionate as major COD sources, had high specific ethanol and propionate conversion rates but a relatively poor glucose conversation rate. Hickey et. al. (1991) found that, from a laboratory study using UASB for treatment of brewery waste water, granules developed on waste water containing sulfate had higher propionate and acetate conversion rates than granules developed when sulfate was removed from the substrate.

2.4.2 Bacterial Aggregation:

Sam Soon et. al., (1987) attempted to identify the conditions necessary to form sludge pellets in the UASB system. From observations of concentration profiles along the line of flow in laboratory scale UASB reactor treating apple Juicing Waste and glucose they identified three zones of behavior.

i) A lower active zone (high hydrogen partial pressure): In this zone volatile fatty acids (Acetic and propionic acids) concentration rise to maximum - the bed level of which the peaks occur defines the upper limit of this zone; free and saline ammonia (NH_3-N) reduces to a minimum and soluble organic nitrogen concentration increases to a maximum; pellets growth is restricted to this zone, the yield being approximately 0.36 mg VSS/mgCOD/ utilized; the pellets have a COD/VSS ratio of 1.23± 0.6 mg COD/mgVSS; the soluble COD recedes to about half its influent value. The continuous increase in propionic acid concentration indicates that the rate of generation and the rate of utilization of hydrogen is such that a high H_2 partial pressure is maintained.

ii) An upper active zone (low hydrogen partial pressure): In this zone the soluble COD concentration reduces to a minimum; the propionic and acetic acid concentrations decrease to near zero - the bed level at Zero acids concentration defines the upper limit of this zone; NH_3-N concentration remains near constant and soluble organic nitrogen decreases to minimum; pellet break up commences in this zone. The utilization hydrogen by the methanogens is such that the hydrogen partial pressure falls to such a low value that the acetogens can convert the propionic acid to acetic acid, hydrogen and carbon dioxide.

iii) An upper inactive zone: this zone extends above the upper zone to the top of the bed; no overt biokinetic reactions are observed except for pellets breakup, the debris being discharged as organic fines into the suspended blanket above the bed.

The behavior of the system with respect to the acid transformation and methane generation conforms to established fermentation process behavior. However, Sam Soon et. al. (1987) identified responses in the lower active (high hydrogen partial pressure) zone that are not consistent with normal fermentation process behavior: i) disappearance of NH_3-N and generation of organic nitrogen ii) a volatile solids generation greater than that associated with COD utilization for cell synthesis iii) pellets break up into fines in the upper active and upper inactive zones. These abnormal responses led Sam Soon et. al. (1987) to propose an hypothesis to describe pellet formation. His hypothesis states that: In the high hydrogen partial pressure region a methanoorganism develops, presumably methanobacterium strain AZ (M. Strain AZ) which uses hydrogen only as its energy source. This organism can produce all its amino acids, for cell synthesis, except cysteine (Zehnder and Wurhmann, 1977). Due to the high hydrogen partial pressure, the M. Strain AZ is induced to produce all its amino acids (except cysteine) at a high rate but its growth is limited by availability of cysteine from external sources e.g. from death of organisms or Cysteine supply in the feed - the excess production of amino acids induces the organism to form extracellular long chain polypeptides - these polypeptide chains bind the species and others into pellets.

2.5 Kinetics of Growth:

Process kinetics play a central role in the development and operation of anaerobic treatment system. Based on the biochemistry and microbiology of the anaerobic process, kinetics provide a rational basis for process analysis, control and design. In addition to the quantitative description of the rates of waste utilization,process kinetics also deal with operational and environmental factors affecting these rates. A sound knowledge of kinetics allows for the optimization of performance, a more stable operation, as well as better control of the process (Pavalostathis and Giraldo, 1991).

Biological treatment processes have been successfully described by the theory of continuous cultivation of microorganisms and process kinetics have been used for the mathematical description of both aerobic and anaerobic biological treatment Process (Lawrence & McCarty, 1970; Lawrence , 1971; Metacalf & Eddy Inc., 1991). Biological growth kinetics are based on two fundamental relationships; growth rate and substrate utilization rate. The effect of the growth limiting substrate (i.e. the essential nutrients) concentration on the rate of microbial growth has been described by various mathematical models (Monod, 1949; Mosser, 1958; Contois; 1959; Grau et. al., 1975).

The following models have been developed in anaerobic treatment by using fundamental kinetic relationships applying mass balances for the biomass and the rate limiting substrate.

1. First order:

$K_o = K_{omax}\ S_e/(S_o - S_e) - b,\ -dS_e/dt = K_{omax}S_e$

$S_e = S_o/(1 + K_{omax}T_x)$

2. Lawrence & McCarty (1970):

$X = T_xY(S_o - S_e)/T_d(1 + bT_c)$

3. Grau et. al. (1975):

$K_o = K_{omax}\ S_e/S_o - b,\ -ds_e/dt = K_{omax}S_e/Ys_o$

$S_e = S_o(1+bT_x)/(KomaxT_x)$

4. Monod (1949):

$K_o = K_{omax}S_e/(K_s + S_e) - b,\ -ds_e/dt = K_{omax}S_e/Y(K_s + S_e)$

$S_e = K_s(1+bT_x)/[T_x(Komax - b) - 1]$

5. Chen & Hashimoto (1978):

$K_o = K_{omax}\ S_e/KS_o + (1-K)S_e - b,\ ds_e/dt = K_{omax}XS_e/(KX + YS_e),$

$S_e = KS_o(1+bT_x)/[(K-1)(1+bT_x) + K_{omax}T_x]$

where:

K_o = observed specific rate of substrate removal g COD/gvss.d)

S_e = Soluble substrate concentration (gCOD/l) in digester effluent

K_s = Half-saturation constant (g COD/l)

K_{omax} = Maximum observed specific rate of substrate removal (g COD/g Vss.d)

b = Specific microorganism decay (d^{-1})

Y = True growth yield (g Vss/gCOD)

S_o = Feed soluble COD concentration (gCOD/l)

T_x = Solids residence time (d^{-1})

T_d = Hydraulic residence true (d^{-1})

X = biomas concentration in the digester (gVss/l)

As previously described, the anaerobic treatment of complex organics is a multi step process. Most of the early attempts to kinetically describe the anaerobic treatment process relied upon the so-called rate limiting step. Generally speaking, when a process is composed of a sequence of reactions, one step is usually very much slower than the other steps. The last slow step in a sequence of reactions has been called the rate-controlling, rate limiting or rate-determining step (Hill, 1977).

Lawrence (1971) proposed that in anaerobic digestion process the rate limiting step be defined as "that step which will cause process failure to occur under imposed conditions of kinetic stress". In the context of a continuous culture, kinetic stress refers to the imposition of a continually reducing value of the solids retention time until it is lower than its limiting value and results in washout of the micro-organisms. In anaerobic treatment, washout-type failure leads to near cessation of methane production, decreased substrate destruction and build up in the concentration of long and short chain fatty acids (Andrews and Pearson, 1965; Lawrence, 1971).

In their effort to model anaerobic digestion kinetics, various investigators have considered only some of the steps outlined in figure 2.2 to be relevant to their work. For example, O'Rourke (1968) looked at steps such as hydrolysis, fermentation, acidogenesis, and methanogenesis, but his kinetic formulation was based on the conversion of long and short chain fatty acids. Others have pointed out that the hydrolysis step is also very important (Ghosh, 1981; Eastman and Ferguson, 1981; Gosset and Besler, 1982; Pavlostathis and Gosset, 1986). It is increasingly clear that the type of waste being digested (e.g. soluble , Vs particulate; or it's chemical composition; toxicity) dictate which step need to be considered, thus explaining why different investigators dealing with different wastes have arrived at quite diverse model formulations. In anaerobic digestion, the rate limiting step is related to the nature of the substrate, process configuration, temperature, and loading rate (Speece, 1983).

Pavalostathis and Giraldo (1991) reported that whenever the kinetic of the hydrolysis step were studied they were found to be the rate limiting-step in the overall reaction. Even in cases where acidogenesis and methanogenesis are considered to be the limiting step, hydrolysis may affect the overall process kinetics, a point too often over looked. According to Pavalostathis and Giraldo (1991) the most commonly applied model for description of hydrolysis is the 1st order model with the exception of the hydrolysis step, all other sub process of anaerobic treatment (Acidogenesis, methanogenesis, Acetogenesis) have successfully been modeled by following Monod (1949) kinetics.

Studies of the methanogenesis process, in particular, using individual volatile fatty acids (VFA) such as acetic acid, propionic acid, or butyric acid have been reported else where (Monod, 1949; Contois, 1959; Lawrence & McCarty, 1970). The following equations have been successfully used in analyzing process kinetics for methanogenesis in anaerobic digestion (Lawrene and McCarty, 1969; change <u>et. al.,</u> 1982).

$k_o = K_{omax}S_e/(K_s + S_e)$ --------------(1)

or $S_e/K_o = K_s/K_{omax} + S_e/K_{omax}$ --------------(2)

where parameters were as defined before.

An equation has also been used for determining the values of y and b:

$K_o = [1/Y]D + b/Y$ --------------(3)

Where: D = dilution rate = 1/HRT

HRT = Hydraulic retention line

The kinetics values K_{omax}, K_s, Y, and b can be determined by using the least square method to plot S_e/K_o Vs S_e and k_o V_e D according to equations 2 and 3.

Combining equations 1 and 3, the effluent substrate concentration can be predicted from the kinetic constants obtained (Metacalf and Eddy, 1979).

$S_e = K_s\ (D + b)/[Y\ K_{omax} - (D+b)]$ --------------(4)

The minimum sludge retention time (SRT) for bacteria in a bioreactor, such as UASB, upflow anaerobic filter, etc., is the retention time at which the bacteria exhibit their maximum growth rate (Noike <u>et.</u> <u>al.</u>, 1985). The bacteria will be washed out from the reactor if the hydraulic dilution rate exceeds the maximum bacterial growth rate (Noike <u>et.</u> <u>al.</u>, 1985). Minimum SRT can be calculated from equations 5 and 6:

$$SRT_{min} = 1/U_{max} \quad \text{--------------} (5)$$

$$U_{max} = Y - K_{omax} - b \quad \text{--------------} (6)$$

Where:

SRT_{min} = Minimum solids retention time (day)

U_{max} = Maximum specific growth rate (1/day)

Hence using the calculated values of Y, b, K_{omax}, the minimum SRT of the methanogens can be determined.

No particular modeling for UASB reactor performance has been reported. However, Stukey (1981) indicated that the kinetics of anaerobes within the UASB system appear to lie somewhere between those for suspended growth (Conventional or contact), and those for a fixed film system, Upflow Bed Filter (UBF). Modeling of UBF reactor performance has been reported by (Guoit, 1986). Guiot, based his study on Monod (1949). The model system was the standard UBF reactor treating 1% synthetic soluble sugar waste.

Because of the nature of the UBF system design, the reactor accumulates part of the biomass produced. Biomass saturated or being operated at critical dilution rate D_c (when $D>U_{max}$, D and U_{max} as defined before). That would result in biomass washout.

Assuming completely stirred tank reactor as far as soluble components are concerned, mass balance equations:

$\frac{dX}{dt} = UoX - DX_e$ --------------(7)

$\frac{dS_e}{dt} = DS_o - DS_e - K_oX = 0$ --------------(8)

$W\frac{dX}{dt} = DS_o - (DS_e + WDX_e + zQ_{CH4})$ --------------(9)

$YK_o = U_o + b$ --------------(10)

Where:

U_o = Observed specific growth (d^{-1})

X_e = Solids concentration in the effluent (gVss/l)

W = Biomass conversion factor into COD(g COD/gvss)

z = conversion factor of methane volume into COD (gCOD/l)

Q_{CH4} = Volumetric flowrate of methane (Vol/Vol.d)

Other symbols meaning as defined before.

Substitution of equations 7 and 8 into 9 yields equation 11 which enables indirect measurement of growth from the substrate utilization rate and methane production. This allows the assessment of growth yield and growth deficit while avoiding biomass measurement.

$zQ_{CH4} = D(S_o - S_e) - WU_oX$ --------------(11)

from Monod model

$K_o = K_{omax}S_e/(K_s + S_e)$ --------------(12)

with: $K_o = (U_o + b)/Y$ --------------(13)

$K_{omax} = U_{omax}/Y$ --------------(14)

Where:

U_{omax} = Maximum observed specific growth rate (d^{-1})

In the case of non inhibitory substrate, simultaneous solutions of equation 12 and 8 relates the effluent soluble COD concentration and to the influent COD concentration. The resulting expression is a quadratic equation which has two solutions, the only real solution being positive.

$$S_e = 1/2[S_o-K_s-K_{omax}X(HRT)+1/2[(S_o-K_s-K_{omax}X(HRT))^2+4k_sS_o]^{1/2}$$

--------------(15)

When K_s is very small relative to S_o the predictive zero order solution is

$S = So - K_{omax}X(HRT)$ --------------(16)

Solving for U_o by combining equations 8 and 13 then substituting into and rearranging equations 11 and 15 the methane production rate can expressed as a function of the HRT, biomass concentration and influent concentration.

$$Q_{CH_4} = (W/z)bX + 1 - WY/2zHRT[S_o - K_s - K_{omax}X(HRT)]$$

$$- [(S_o - K_s - K_{omax}X(HRT))_2 + 4k_sS_o]^{1/2} \qquad \text{--------------(17)}$$

Hence knowing the energetic parameters, y and b, the kinetic parameters K_{omax} and k_s as well as the influent concentration S_o, the residual concentrations of the substrate in the effluent (hence process efficiency and the methane productivity) can be predicted as a function of the HRT and active biomass concentration. Effluent soluble COD concentration may be used as the value of S_e in equations 8 to 17. This assumes that the COD is completely biodegradable (Guiot, 1986). Many authors (Andrews, 1968; Hill and Barth, 1977; Morries <u>et. al.</u>, 1977; Pfeffer, 1981, Moletta <u>et. al.</u>, 1986) have established the inhibitory effect in methane fermentation of undissociated volatile fatty acids (VFAs), but have used them in the kinetic equation as both inhibitory and an energy source limiting term. However, whereas only undissociated VFAs are inhibitory, all VFAs are an energy-limiting source (Haldane, 1930). The Haldane, 1930 inhibitory model has been developed to describe the specific substrate utilization.

$$K_o = K_{omax}\ S_e/(K_s + S_e + \delta Se^2/k_i) \qquad \text{--------------(18)}$$

Where δ = the fraction of unionized VFAs given by

$$\delta = 1/(1+ 10^{(PH-4.83)}) \qquad \text{---------------(19)}$$

K_1 = inhibition constant (gCOD/L)

One can note that equation 18 reduces to equation 12 (Monod, 1949, model) when δ is very small value (PH over 7). The kinetic constants can be identified using non linear regression procedure. When the substrate is inhibitory, equation 18 is simultaneously solved with equation 8. The derived solution is cubic equation.

$$S_e^3 + (K_1/\delta - S_o)S_e^2 - K_1(S_o - K_s - K_{omax}XT_d)S_e/\delta$$
$$- K_1K_sS_o/\delta = 0 \qquad \text{---------------(20)}$$

Only one real solution with physical meaning exists which yields the value of S_e. The value of Q_{CH4} can be predicted at a given PH by plugging the value of $S_e(T_d)$ predicted from equation 20 into 11 and 13 and rearranging.

Hence in inhibitory substrate case, knowing the macro-energetic parameters y and b, the kinetic parameters, K_{omax}, K_s and K_1 and the concentration of the influent S_o, the efficiency of substrate removal and the methane productivity can be predicted as a function of HRT, biomass concentration and PH.

Predictive equations can yield critical value useful for reactor design and operation. Considering that the control of PH in a neutral range is a must in the anaerobic digestion, the critical values assessment will be limited to non-inhibitory equation (because ♪ is a mall value) (Guiot, 1986).

The minimum attainable soluble COD in the effluent S_{emin}, is given by equation 12, set up with the lower limit of the specific substrate utilization rate, which is b/Y (U_o = 0, in equation 10. Hence,

$S_{emin} = K_s b/(Y\ Komax - b)$ --------------(21)

The critical sludge residence time (SRT), Q_{xc} is the reciprocal of the maximum attainable specific growth rate (U_o^*), which depends upon the influent concentration of substrate, according to the Monod model as:

$Q_{xc} = 1/U_o^* = (K_s + S_o)/\ U_{omax} S_o$ --------------(22)

providing that $1/U_o^*$ is larger than the average doubling time of the bacterial group controlling the kinetic of the overall process.

A critical value of RT (Q_c in hr) is yielded by the critical SRT (Q_c) as:

$Q_c = 24\ (Xe/X)Q_{xc}$ --------------(23)

where: X & Xe as defined before.

The Xe/X ratio is a washout factor, which may vary as a function of the operational conditions of the reactor. In first approximation, the ratio Xe/X could be retained as relatively constant under operation at constant waste strength. (Guiot and Van Den Berg, 1985). The HRT (T in hrs) is also related to the liquid up flow velocity (m/hr), which raises a critical value (Vc), when causing such an expansion of the granular sludge bed which would lead to a net loss of the biomass. The liquid velocity is a function of D (i.e. 1/Td or 24/T), the effluent recycled to feed ratio (R) and the height of the reactor (H in m). Hence the value of Q_c provided by equation 23 must be consistent with the Vc as

$Q_c > (1+R)\ H/Vc$ --------------(24)

Otherwise, the value (1+R) H/Vc would be the value to consider ultimately for critical HRT (Guiot, 1986).

Substrate diffusion limitations across the depth of the sludge bed should not significantly affect the kinetics of substrate utilization. The microorganisms affinity for acetate is presumably more limiting than diffusion (williamson & McCarty 1976).

Henze and Harremoes (1983) combined data based on enriched pure culture of acid-formed and methane formers to estimate kinetic constants for anaerobic mixed culture to find K_{omax} of approximately 1 g COD/gvss.d and U_{omax} of $0.15d^{-1}$. Anderson and Duarte (1980) using glucose as substrate reported $0.16d^{-1}$, 0.75 gCOD/gVss.d and 0.2 gCOD/l and chin (1981) on glucose plus peptone, $o.27d^{-1}$, 1.4 g COD/gvss.d and 3 gCOD/l for U_{omax}, K_{omax} and K_s respectively. Table 2.4 below gives typical kinetic coeficients for anaerobic digestion of various substrate at 20°c.

Table 2.4: Typical kinetic coefficients for anaerobic digestion of various substrate at 20°c. (Metacalf, 1979)

SUBSTRATE	COEFFICIENT	
	Y	b
Domestic Sewage	0.06	0.03
Fatty acid	0.05	0.04
Carbohydrate	0.024	0.03
Protein	0.075	0.014

2.6 Criteria for the Utilization of UASB reactors:

Generally, UASB reactors are used for the treatment of waste water in which the main pollutant is organic material and consequently for the production of biogass from these residues. For instance, domestic sewage and waste water from the production of beers and soft drinks, sugar cane alcohol, instant coffee, citric juices, paper, etc. (Souza, 1986).

2.6.1 Suspended solids:

Suspended matter (or potentially precipitating matter) present in waste water can affect the anaerobic systems (such as UASB) in the following way: (Lettinga and Hulshoff, 1991).

(I) It reduces the specific methanogenic activity of the sludge (when expressed on the basis of organic sludge present). In the case when the SS is poorly biodegradable or non-biodegradable, it accumulates in the sludge bed either by a mechanism of mechanical entrapment or physical adsorption. This action causes a drop in the volumetric methanogenic activity of the suldge.

(ii) It may lead to the formation of scum layers consisting of floating substrate ingredients together with entrapped or attached active sludge. Particularly, the presence of suspended fats and lipids will heavily promote the tendency for sludge floatation, both flocculent and granular. This scum layer formation may result in a more significant washout of active matter, as well as in the production of considerable quantities of poorly stabilized excess scum layer sludge.

(iii) Attachment of newly generated bacterial matter to the surface of suspended particles will, in the case when flocculent seed sludge is used, slow down or even may completely counteract the formation of granular sludge. When the suspended matter consists of colloidal or of poorly settleable matter, a considerable part of newly formed bacterial matter will leave the reactor together with this suspended solids fraction. This particularly will occur when the suspended solids consists of fibrous matter.

When granular seed sludge is used, the presence of ss in the influent may perhaps in specific cases also negatively affect the stability (e.g. strength) of the granular sludge.

(iv) A Prolonged continuous entrapment of voluminous suspended solids in a granular sludge bed may lead to spontaneous and sudden washout of almost the complete sludge bed, e.g. initiated by an imposed organic shock load. This phenomenon has been observed both in full scale reactors and in laboratory (bench) scale experiments.

A part from the characteristics of the ss, also the concentration of the dispersed matter is of a big importance. Lettinga and Hulshof (1991) indicated that beyond a certain SS-concentration, depending on the characteristics of the SS,an anaerobic treatment system like the UASB reactor will become less feasible. They have suggested some characteristics with respect to the possible effects of the insoluble matter (or various fraction of ss) which should be looked at when designing a high rate anaerobic system like a UASB reactor. These are:

-biodegradability and/or rate of degradation under the prevailing operational condition.

-size and surface area of SS.

-affinity of bacterial matter to attach to the material.

-affinity of the SS-matter to coalesce.

-tendency of SS-matter to be adsorbed to the sludge.

Souza (1986) recommended a maximum acceptable ss concentration depending on the total concentration of contribute decisively to the applicability of the UASB reactor (Souza, 1986). Lettinga and Hulshof (1991) reported that, application of granular sludge UASB reactors becomes doubtful at TSS concentrations in influent exceeding 6-8 g/l, because at high TSS concentration accumulation of flocculent sludge occurs between the granular sludge. Segregation and washout of this flocculent sludge (by applying, occasionally, for a period of 0.5 to 1 hr, a high superficial velocity in the reactor) from the bed does not proceed sufficiently rapidly. In that case it is recommended to apply Preclarification. For high strength waste waters with a high insoluble fraction (i.e. exceeding 15%), generally conventional digesters are in favor over UASB and other high rate systems. (Lettinga and Hulshoff, 1991).

2.6.2 Toxic Compounds:

Toxins inhibits the growth of anaerobes leading to a stressed situation and eventual process failure, especially so on the last two stages of anaerobic digestion (i.e. Acetogenesis and Methanogenesis). Heavy metals, however, seem to affect all four stages of anaerobic digestion (Hydrolysis, Acidogenesis, Acetogenesis, and Methanogenesis) (Mosey, 1976).

In general toxins seem to fall into two categories, organic and inorganic, at high or low concentrations. Organics that are toxic at low concentration include the methane analoos,; carbon tetrachloride (CCl_4), chloroform ($CHCl_3$) and methane chloride (CH_2cl_2) (Kirsch, 1971; Thiel, 1969; Stuckey et. al., 1980), azides, amines and hydrazines (Bannink and Muller, 1951), ethylene dichorides and Vinyl chloride (Stuckey et. al., 1980).

Many inorganics are not toxic except at high levels relative to organic compounds. However, a few like cyanide (Bannink and Muller, 1951) and hydrogen ions (Clark and Speece, 1970) are toxic at very low levels. Inorganics toxic at higher levels include sulphide, salt cations, ammonium, calcium, sodium, magnesium and potassium (Kugelmann and Chin 1971; Van Velsen, 1979) and heavy metals (Kugelmann and Chin, 1971; Mosey, 1976).

Owen and Co-workers (1979) have developed a simple, quick and inexpensive bioassay technique to determine the toxicity (Anaerobic toxicity Assay ATA) of wastes under anaerobic conditions. The toxicity of the waste of interest is incubated in a sealed serum bottle with nutrient media and anaerobic seed, together with an acetate-propionate "spike" which provides a radial utilizable substrate for bacterial of the second and the third steps. The percent of waste converted to methane is followed by measuring gas production and methane composition with time by means of syringe inserted into the gas phase through a rubber serum cap. Ratios of gas production versus time in comparison with uninhibited control (Maximum Rate Ratio - MRR) are determined and ratios less than one indicate toxicity waste strengths can be varied to determine the toxicity threshold. Data from this bioassay can also be used to determine whether the anaerobes will acclimate to the toxin present, and after what time. Under toxic conditions analysis of the liquid contents by gas chromatography (G.C) can help to ascertain the pathways of inhibition.

An important issue that can make the treatment of waste water in a UASB reactor impossible is the presence of these toxic compounds at concentrations which can not be tolerated by the bacteria. There are so many papers on this subjected, mainly related to the effect of heavy metals, alkaline and alkaline earth metals, sulphates, sulphites, chloroform, cynides, phenols, chlorides, nitrates, oxygen, etc. (McCarty, 1964a; Mosey, 1976, Yang <u>et. al.</u>, 1981; Souza, 1982). Even for wastes containing powerfully inhibitory toxic compounds, some techniques may be used in order to make the anaerobic treatment possible such as, dilution of waste, digester effluent recirculation mixture with other waste, pre-acidification. etc. (Souza, 1986).

Sulphur compounds in particular, are of concern due to their presence in many wastes. Sulphur compounds act as terminal electron acceptors for sulphate reducing bacteria which may compete the methane producing bacteria for the available substrate:

$$So_4^{=} + \text{organic matter} \ \underset{\text{Bacteria}}{\underline{\text{Anaerobic}}} \text{ ----> } S + H_2o + Co_2$$

This may result in low loading rate potentials and shift the population to sulphate reducing bacteria. Sulphate below 1600 mgS/l (Karhadakar <u>et. al.</u>, 1987) do not inhibit the methane producing bacteria whereas sulfite (Eis <u>et. al.</u>, 1983; Puhakka <u>et. al.</u>, 1985) and dithionite (Puhakka <u>et. al.</u>, 1985) at 100 mgS/l may be inhibitory. The free hydrogen sulphide which is produced by the reduction of sulphur may be higher toxic to bacteria.

$$S^{=} + 2H^{+} \text{ <====> } H_2S$$

Free hydrogen sulphide at 50 mgS/l decreased the methanogenic activity by 10-50% (Kroiss and Plahl-Wabnegg, 1983; Karhadkar <u>et. al.</u>, 1987); Koster <u>et. al.</u>, 1986). On the other hand, an increase of methanogenic activity of about 60% was reported when free hydrogen sulphide concentration was increased from 0-50 mg S/l (Speece <u>et. al.</u>, 1986). The inhibition observed in different studies varies because of the different biomass growth history, waste water composition, environmental conditions and different experiments set up.

It was recently established that to avoid such problems, it was necessary that COD/$So_4^{=}$ ratio in the waste has to be higher than 7-10 (Lettinga, 1981). However, the presence of low concentrations of sulphate (0.00015 to 0.0003 moles) in the reactor influent found to be beneficial to the growth of methanogens and fatty acid degrader. Alab-scale UASB experiment using a VFA mixture as feed (containing 0.3 mm Feso4 to replace Na_2S enhanced acetate and propionate degradation rates by 100% (Thiele et. al., 1990).

Moreover, sulphate has been shown to play an important part in PH regulation in a UASB system via the biological sulphate reduction process which consumes acidity. If sulphate were excluded from the waste the requirements for alkalinity addition, and then the operating costs of the process, possibly would be increased. (Russo and Dold, 1988).

2.6.3 Temperature:

Temperature is important for economic feasibility of the process. The optimum temperatures for mesophillic range is 37°c (Metacalf et. al., 1979). The process occurs at acceptable rate between 15 and 25°c and at a relatively high rate between 30° to 40°c(Gray, 1989). In all circumstances, it is essential to avoid sharp variation in temperature (Lettinga et. al., 1984). A study was carried out , by Lettinga et. al., (1984), to assess the effect of short term temperature variation on the treatment efficiency and methane production of UASB reactors working at temperature of 37-39°c. Shocks of 5-24 hrs of temperature variation led to a sharp decrease of the different microbial populations as a result of elevated decay rate. The methanogenic bacteria was found to be the most sensitive to temperature variation while acidogenic bacteria were least affected (Van Lier et. al., 1990). The automatic control of the temperature, and sometimes even the thermal insulation of the biodigester is unnecessary (Souza, 1986). In this case, reduction of costs is remarkable and the use of UASB reactors is much more desirable.

In a pilot plant research performed in colombia on treating domestic sewage using UASB system at ambient temperature, averaging 24°c, a COD removal of 68-79 percent was achieved at a hydraulic retention time of 4 hrs (Louwe Kooijmans et. al., 1985). However, for diluted wastes, like domestic sewage, the question of temperature is much more important because the quantity of methane is low in relation to the waste water volume to be heated, and, consequently, where heating is necessary an external source would have to be used. (Souza, 1986).

For wastes with a high concentration of organic material, the flow velocity of the waste through the reactor is relatively low. Consequently, the influence of ambient temperature on the reactor temperature is greater, and efficient systems of thermal insulation and even controlled heating may be necessary, depending on the intensity of the fluctuation in the local ambient temperature (Souza 1986).

When the waste water is generated at high temperatures (above 50°c), treatment in the thermophilic range may be viable (Lettinga et. al., 1991). This will generally bring about a higher reaction rate and higher efficiency when compared to mesophilic range according to Metacalf (1979). However, available information on the thermophilic process is still limited (Souza, 1986). Besides, Souza (1986) indicated that it is not advisable to heat waste produced under mesophilic conditions to operate in the thermophilic range, because the increase in efficiency and rate would probably not compensate for the difficulty and cost increase related to heating and temperature control. The above mentioned information indicates that the UASB process can be utilized at low ambient temperature but higher temperature is preferable. And that the concentration of organic matter in the waste is also a factor in the determination of the UASB reactor performance, when operated at ambient temperature. Therefore, adequate information about ambient variation, intensity of variation, the temperature at which the waste water is generated, characteristic strength is normally required for the operation of a UASB system at ambient temperature.

2.6.4 Organic Loading and Flow Variation:

The UASB reactor may be used for waste presenting significance variations in organic material concentration or flow. Some extra precautions may be taken in these cases, such as the use of initial equalization tanks. The cost increase may be compensated for by an increase in the efficiency, stability and safety during the operation of the UASB reactor (Souza, 1986). Recirculation of digester effluent may also contribute to equalization as well as will help in the dilution of highly concentrated waste (>5000mgCOD/L), enhance mixing which would foster contact between micro-organism and substrate. Lab-scale experiments indicated that increase in recycling enhanced COD removal by 3% when a moderate strength VFA medium was fed at loading rates of 33.6 $kg/m^3/day$ (Lettinga et. al., 1983). In case where large variation in flow rate may occur, the use of several UASB reactors operating in parallel could be a solution. The first units would operate with continuous flow which would guarantee greater efficiency, stability and safety, while the last units would operate with a variable flow determined by the quantity to be treated (Souza, 1986).

An important UASB reactor advantage is it's potential use for waste generated seasonally. It has already been demonstrated (Craveiro et. al., 1982) that, for a UASB reactor having operated satisfactorily during a determined harvest time, after some months without operation or feeding, operational conditions may be re-established during the next harvest time rapidly (in some weeks) and without difficulties. In the interim period, it is not necessary to feed the reactor or to control the system temperature. This ability to maintain the anaerobic viability in a UASB reaction does not occur similarly in aerobic processes and is more problematic in other anaerobic processes. Controlling of loading rate to the UASB reactor during start-up period is important and this is discussed in subsequent sections.

Loading rates applied to a UASB reactor are somehow dictated by the required removal efficiency of TSS from waste water. Lettinga and Hulshoff (1991) indicated that, low space loading rates are recommended when a high total suspended solids removal efficiency should be accomplished. This will allow excess flocculent sludge to accumulate between the granular sludge, which can then be segregated and washed out by applying, occasionally, for a period of 0.5-1 hr, a high superficial velocity in the reactor.

Another important reason for applying relatively space loads when a high TSS removal efficiency is pursued, is to achieve a satisfactory stabilization of the accumulated solid substrate ingredients. Particularly when operated under lower ambient temperature conditions, it is necessary to maintain a sufficiently long sludge detention time for that purpose (Sayed, 1987).

In the case where little if any TSS removal is pursued in the anaerobic treatment step, i.e. when this is delegated to a clarifier placed in series with the anaerobic reactor, the applicable space loading rates for the granular sludge bed reactor are significantly higher as compared to flocculent sludge bed UASB's (Lettinga and Hulshoff, 1991).

2.6.5 Nutrients and Environmental Factors:

Nutrients rather than organic or inorganic substrates principally nitrogen and phosphorous are very essential for cell synthesis and growth (Gray, 1989). These may not always be present in sufficient quantities as in case of high carbohydrate content industrial wastes. Nutrients may be provided by adding chemicals (KHPO4,NH4cl) or by mixing with domestic waste water (Souza, 1986).

In fresh waste water, nitrogen is primarily present as proteinaceous matter and urea. This organic nitrogen is rapidly decomposed by bacterial action in the case of protein, or by hydrolysis in the case of urea, to the form of ammonia (NH_3-N)(Ammonia Nitrogen) (Gray, 1989).

Organic nitrogen is normally measured separate from ammonia although occasionally they are expressed together as kjeldahl nitrogen. Soluble organic nitrogen is determined by the kjeldahl method. The aqueous sample (filtered) is first boiled to drive off the ammonia, and then is digested (bacteria). During the digestion the organic nitrogen is converted to ammonia. Total Kjeldahl nitrogen is determined in the same manner as organic nitrogen , except that the sample is not filtered and not boiled. Total kjeldahl nitrogen is therefore the total of organic and ammonia nitrogen. Soluble kjeldahl nitrogen is the kjeldahl nitrogen in the filtered sample (Metacalf, 1979).

The oxidized forms of ammonia, nitrate and nitrite are normally absent from fresh waste water as they are products of the biological oxidation process within the treatment plant. Therefore, as the total nitrogen includes all chemical forms of nitrogen, the total Kjeldahl nitrogen can be assumed to be equivalent to the total nitrogen in raw waste water, and soluble Kjeldahl nitrogen to be equivalent to soluble nitrogen in the waste water (Gray, 1989).

For anaerobic digestion the COD:N:P ratio of 100:5:1 is to be maintained (Gray, 1989). It should be noted that effluents from forest industry are always deficient in basic nutrients such as P and N (Datta and Rao, 1987). Several micro-nutrients are also necessary for optimal digestion. Trace elements (such as Ni,Co,Mo) are found to enhance methanogenic activities in lab-scale digesters (Takashima and Speece, 1988), increase biomass in anaerobic filters (Murray and Van den berg, 1981) and stimulate granule formation in UASB reactors (Guiot _et. al._, 1988). In a laboratory-scale experiment using a UASB system for treatment of waste water from recycled paper industry Russo and Dold (1988) reported that, when addition of a solution of trace elements containing Cu, Mn,Fe,Ni,Mo,Na was stopped from the feed after few days from the beginning of the experiment, the COD removal efficiency was not affected. This information gives a good indication that waste water from recycled paper industry might, in general, be rich in these micronutrients. This would, if true, contribute to the ease of treating these waste waters in a biological system such as a UASB reactor.

The optimum range of PH for anaerobic digestion being 6.6-7.6 PH below 6.5 or above 7.5 may be harmful to the bacteria, mainly the methanogens (Gray, 1989). Metacalf (1979) reported that, methanogenic activity will be very much inhibited at PH less than 6.2. However, Souza (1986) indicated that waste waters with very low PHs may be easily treated in a UASB reactor because of the buffering capacity of anaerobic process for most wastes.

In anaerobic digestion units that are operating in a stabilized conditions, two groups of bacteria work in harmony to accomplish the destruction of organic matter. The saprophytic organisms carry the degradation to the acid stage, and then the methane forming bacteria complete the conversion into methane and carbon dioxide. When sufficient population of methane forming bacteria present and environmental conditions are favorable, they utilize the end products produced by the saprophytic bacteria (mainly volatile acids) as a result, acids do not accumulate beyond the neutralizing ability of the natural buffers present, and the PH remains in a favorable range for the methane bacteria. Under such condition, McCarty (1964b) indicated that, the volatile acid content of digesting sludges usually runs in the range of 50-250 mg/l as a acetic acid. According to Gray (1989) the methane forming bacteria appear to be more susceptible to changes in environmental conditions and food load. They are affected much more rapidly by changes in PH and temperature than the acid forming bacteria (Syprohytic bacteria). The saprophytic bacteria are not inhibited until PH levels fall to 5 (McCarty, 1964b). Inhibitions to methane forming bacteria caused by either of these factors result in a decreased rate of destruction of volatile acids and consequently volatile acids begin to accumulate in the system (McCarty, 1964b).

The major natural buffering materials in digesting sludge which tend to prevent a drop in PH are bicarbonates, which are formed by the reaction of carbon dioxide from biogas with the natural mineral alkalinity in the waste water. The bicarbonates which in equilibrium with carbonic acid tend to regulate the hydrogen ion concentration. The PH in bicarbonate buffer system is calculated as: (McCarty and Mosey,1991).

H_2CO_3 <----> $HCO_3^- + H^+$

$H^+ = K_c\ [H_2CO_3]/[HCO_3^-]$

$K_c = 4.45 \times 10^{-7}$ at 25°c

$[H_2CO3] = 0.000267 * (Co_2)$ Henery's law

Where:

CO_2 = The concentration of carbon dioxide in the gas (% by vol.)

(HCo_3^-) = total alkalinity

On the basis of Henry's law, an equilibrium also exists between the partial pressure of carbon dioxide in the gas phase and the carbonic acid concentration. The effect of this equilibrium and that expressed by the equations above indicated that the higher the bicarbonate concentration and the lower the percent carbon dioxide in the digestion gas, the higher the PH (McCarty, 1964b).

As volatile acids accumulate in a digester, they destroy the bicarbonate buffer and increase the carbon dioxide concentration.

$R\text{-}COOH + HCO_3^-$ ----> $R\text{-}COO^- + H_2o + Co_2$

Acetic acid as well presents a buffering capacity for it is a weak acid and dissociates as: (McCarty, 1964b)

$CH_3COOH \text{ ----> } CH_3COO^- + H^+$

$[H^+] = K_{ac}[CH_3COOH]/[CH_3OO^-]$

Concentrations of "acetic acid", determined by chemical analysis, are the total concentrations of free and saline "acetic acid" which is usually present almost entirely as acetate. At low PH where this buffer operates, significant concentrations of free, undissociated, acetic acid will be also present. It's concentration can be calculated from

$[CH_3COOH] = [AT] - [CH_3COO^-]$

Where: [AT] = Total concentration of free and saline acetic acid in solution

$[CH_3COO^-]$ = calculated by electroneutrality equations.

Ammonium ions produced from degradation of protein in the raw sewage also normally presents buffering capacity in anaerobic digesting sludge systems especially with wastes which contain high concentrations of protein (Souza, 1986). In the absence of carbon dioxide in the biogas, the value of PH of the digester contents increases to very high values that are controlled by the dissociation of ammonium ions (if present) (McCarty & Mosey, 1991).

$NH4^{+} \longleftrightarrow NH_3 + H^{+}$

$[H^{+}] = Kamm[NH4^{+}]/[NH_3]$

$Kamm = 5.69 \times 10^{-10}$ at 25°c

$[Amm] = [NH_3] + [NH4^{+}]$

[Amm] = total concentration of free and saline ammonia

$[NH4^{+}]$ = calculated from electroneutrality equations.

Gray (1989) notes that, PH above 7.5 leads to an increasing percentage ammonium ions being converted to toxic dissolved ammonia which inhibits the process. It is necessary to maintain buffer capacity by adding basic materials from outside sources or to exercise some control over the rate of VFAs formation if PH conditions favorable to methane-forming bacteria are to be maintained (Gray, 1989). External control of PH includes addition of alkali (lime or sodium bicarbonate).

With wastes with high PH, it is advisable to conduct previous digestibility tests. The adoption of PH control system (for example the additions of hydraulic acid) may be necessary(Souza, 1986).

2.6.6 Treatability level:

Even if all previous conditions were satisfied for a certain waste, it may not be possible to treat it anaerobically at the desirable level, unless this possibility has already been proven by practical experience. Otherwise, it is very important to conduct treatability tests (Souza, 1986).

For instance, establishment of COD/BOD correlation for a certain waste water gives a useful guide to know the proportion of organic material that is biodegradable in that waste water. The COD will always be higher that the BOD as the former estimates substances that are chemically as well as biologically oxidized in the waste whereas the BOD estimates only substances that are biologically oxidized. However some aromatic compounds such as, benzene, pyridine, and toluene are either unaffected or partially oxidized during a COD test (Gray, 1989). On the other hand, some polysaccharide cellulose can only be degraded anaerobically and will not be included in the BOD estimation since the test is based on aerobic conditions (McCarty, 1964a). Furthermore, some compounds, such as, lignin (from forest industry) takes quite sometime to be oxidized and could hardly be included in the BOD estimation since it is usually based on 5 or 7 days (Lettinga, et. al., 1991). In general, the COD/BOD relationship varies between 1.25 to 2.5 depending on the waste analyzed (Gray 1989). The relationship remains fairly constant for a specific wastes, although the correlation is much poor when the COD values are <100 mg/l (Aziz and Tubutt, 1980). This correlation can be expressed by simple linear regression equation:

$BOD_5 = aCOD + b$

Where a and b are constants, the value of which depends on wastewater. For instance, the COD/BOD correlation for domestic waste has been established by Ademoroti (1986) as:

$BOD_5 = 0.6COD - 6.9$

It is important to note that if one observes the above mentioned restriction, the UASB reactor (Souza, 1986) with the present level of knowledge, may be used for the treatment of waste water with any concentration of organic material, even the most dilute or the most concentrated ones.

Owen and Co-workers (1979) have developed simple, quick and inexpensive bioassay technique to determine the biodegradability (Biochemical Methane Potential B.M.P.) of wastes under anaerobic conditions. To determine biodegradability, the waste of interest is incubated in a sealed serum bottle with nutrient media and an anaerobic seed. The percent of waste converted to methane is followed by measuring the gas production and the methane composition with time by means of a syringe inserted into the gas phase through a rubber serum cap.

2.7 Design and Construction of UASB Reactor:

With the present pace of innovation in anaerobic waste water treatment systems, the understanding of basic microbiology and biochemistry can greatly help in the design and operation of these advanced reactors. From experience, the criteria for the design of these reactors has been found to rest on hydraulic and organic loading rates together with laboratory and pilot scale experimentation (Souza, 1986; Lettinga and Hulshoff, 1991).

2.7.1 Required Reactor Volume:

The reactor volume depends on a number of factors including:

(Lettinga and Hulshoff 1991).

- The maximum total daily COD-load.
- The admissible liquid surface load.
- The minimum temperature of waste water.
- The strength of the waste water (e.g. complexity, polluting compounds, biodegradability, presence of proteins in the waste water, etc).
- The permissible space loading rate at a specific sludge hold up.

- The required treatment efficiency.
- The required extent of sludge stabilization (the sludge stabilization that can be accomplished dependents on the biodegradability of the entrapped, sorbed and/or precipitated substrate ingredients, on the operational temperature and the average sludge hold-up time)

The admissible maximum superficial velocity (based on the wet surface area in the settler) for granular sludge UASB reactors can be set at approximately 3m/hr average over a day for soluble wastewater and at 1-1.25m/hr for partially soluble waste waters (Lettinga and Hulshoff , 1991). Souza (1986) suggests maximum superficial velocity of 1.2 to 1.5m/hr for reactor preceded by equalization, pretreatment (e.g. clarification) etc. Lettinga and Hulshoff (1991) suggest that, temporarily, for a few hours per day, velocities up to 6m/hr and 2m/hr can be tolerated for soluble and partially soluble wastewater respectively. Under these conditions most of the granular sludge will be retained in the reactor. The high superficial velocities may result in the washout of poorly settleable (smaller) granular particles, but generally this will not be accompanied by any serious problems. For voluminous flocculent types of sludge lettinga and Hulshof (1991) suggested maximum admissible superficial velocities of 0.5m/hr, with temporarily (2-4 hrs) admissible peaks upto approximately 2m/hr .

For dilute types (partially soluble like domestic sewage) of waste waters (COD levels below 1000mg/l) and for operational temperatures exceeding 25°c, the reactor volume generally will be determined by the admissible hydraulic retention time, rather than by the applicable organic space load (i.e. by the superficial velocity) (Lettinga and Hulshoff, 1991). In this particular , Souza (1986) suggests that, the reactor has to have the minimum possible height in order to increase the surface area per unit of volume and, consequently, to reduce the hydraulic retention time as much as possible. At the present level of knowledge, Souza (1986) advised to have a height of about 4.5m whereas Lettinga and Hulshoff (1991) recommended a height of 3-5m. When the superficial velocity is a limiting design factor, the allowable hydraulic retention time (Ta) is determined by the surface area and the height of the reactor, according to the equation: (Lettinga and Holshoff, 1991).

$$Ta = A\,H/Q \qquad \text{---------------}(25)$$

in which

Ta = allowable hydraulic retention time (hr)

A = surface area of the reactor (m^2)

H = reactor height

Q = average flow rate at most continuous flow (m^3/h)

The admissible superficial velocity will ultimately determine the hydraulic retention time for a given reactor height.

$$Va = H/Q \qquad \text{--------------(26)}$$

Hence the reactor volume can be calculated by

$$Vr = Ta\ Q \qquad \text{--------------(27)}$$

The allowable hydraulic retention time will depend also on the type of sludge present in the reactor (flocculent or granular) and the quality of the gas-solids separator (Letting and Hulshoff, 1991).

For concentrated waste waters (e.g. industrial waste water), the limiting design parameter is the applied organic load (in terms of biodegradable COD). The maximum safe laod is 15-20kg COD/m^3 /d (Souza, 1986). To use these limits, the availability (or formation) of biological sludge with good characteristics of settlement and methanogenic activity, preferably granular sludge, is taken for granted. Lettinga and Holshoff (1991) have established a relationship between the waste water strength and the required reactor volume(Vr) (Fig 2.3).

It can be seen beyond a specific waste concentration range, the reactor volume will depend on the waste strength (c) and the applicable space loading rate(Bv), according to the equation.

$$Vr = \frac{24\ C\ Q}{Bv} \qquad \text{--------------(28)}$$

The space load greatly depends on the sludge activity, and thus the temperature and the treatment efficiency perused for the various polluting fractions on the composition and the nature of the pollutant, the sludge concentration, the quality of the feed distribution system (will be discussed in subsequent sections) and the desired safety factor.

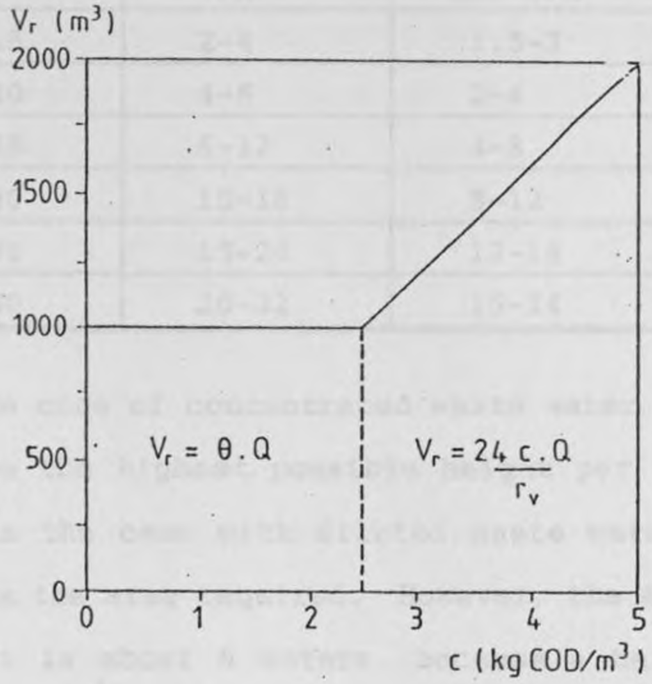


Fig 2.3: Relationship between pollution strength and reactor volume (Lettinga and Hulshoff, 1991). (Assumptions Ta = 4h, Q = 250m^3/h, Bv = 15kgCOD/m^3/d)

Table 2.5 which has been provided by Lettinga and Holshoff (1991), gives guidelines for admissible organic space loading rates in relation to the operational temperature (assuming an average granular sludge concentration of 25 kg Vss/m^3).

Table 2.5: Applicable organic loads in relation to operational temperatures for UASB reactors containing an average sludge concentration of 25kg VSS/m^3)(Lettinga and Hulshoff, 1991)

Temp.	Organic Loading rate (Kg/m^3.d)		
	VFA	NON VFA	30% SS-COD
15	2-4	1.5-3	1.5-2
20	4-6	2-4	2-3
25	6-12	4-8	3-6
30	10-18	8-12	6-9
35	15-24	12-18	9-14
40	20-32	15-24	14-18

In the case of concentrated waste water it is advisable to use the highest possible height per unit of volume, unlike the case with diluted waste water, in order to reduce the area required. However, the advisable useful height is about 6 meters, because a height above this value may cause some problems such as difficulty in the solids and gas separation, foaming, etc. (Souza, 1986).

In both cases, the settler height does not need to be higher than approximately 1.5m, bearing in mind its specific settling function. The remaining part of the reactor height will correspond to the digester itself

(Souza, 1986).

Finally, According to Letting et. al., (1983), the design criteria of UASB rector can not be limited. As one acquires experience with UASB reactors in full scale, design criteria must change accordingly. In full scale reactors, often the designed organic loading rates have been exceeded without much effect on conversion efficiencies.

2.7.2 The Reactor Shape and Materials for Construction: For concentrated wastes since the necessary area for the settling is small, the reactor may have a uniform section, thereby making design and construction easier, it may be circular or rectangular. For dilute waste, since the largest settling area is needed, it can be advantageous to adopt a uniform section at the lower part of the reactor (digestion compartment) and an increasing section area in the settling region so that the available area will be larger at the top of the settler than that at the lower part of the reactor and result in a large superficial area per unit volume. The following combination for settler and digester compartments may be used: (Souza, 1986).

- Circular digester, circular settler
- Circular digester, rectangular settler
- Rectangular digester, rectangular settler

The rectangular shape facilitates influent distribution at the bottom of the reactor, and the modularization of the system. Choice of shape is mainly depended on cost, availability of materials and other local conditions (Souza, 1986).

The most commonly used construction materials for UASB reactors have been steel and concrete. The use of steel generally implies easier construction/installation for shapes with circular sections. While for concrete, the rectangular section is simpler. (Souza, 1986).

Lettinga and Hulshoff (1991) reported that, from experience with full-scale reactors in the Netherlands, corrosion can present a major problem. All reactors constructed at the end of seventies and beginning of the eighties appeared to be severely damaged by corrosion after 5 or 6 years of operation. The biggest problem occurs in the upper part of the reactor, where hydrogen sulfide is oxidized to sulphate by air oxygen. This can lead to very low local PH conditions. Both concrete and shell will be affected by this. Corrosion by dissolved carbon dioxide will occur under the water level; calcium monoxide from concrete will dissolve as a result of the presence of carbonic acid. Depending on the construction material used some corrosion of the settler plates may occur as a result of the presence of carbon dioxide. Full scale practice showed that settlers constructed from seawater-resistant aluminum-alloy became severely perforated by this phenomenon.

However, due to severe corrosion problems, nowadays, some constructors use poly-propylene coated concrete for the reactor body, and material consisting of plastic covered with impregnated hardwood for the settler. Plastic fortified plywood (e.g. for effluent weirs) and ferrocement have also been recently used. (letting and Holshof, 1991).

In order to prevent nuisance problems caused by the escape of hydrogen dioxide from the effluent to the air, it is necessary to cover the anaerobic reactor. By covering the reactor settler compartment also the occupance of corrosion can be reduced, because the entrance of air (oxygen) can be greatly avoided in this way. Moreover, it is of major importance to avoid mixture of air (oxygen) with the gases (e.g. carbon dioxide, methane, hydrogen sulphide) for safety purposes (Lettinga and Hulshoff, 1991).

2.7.3 Internal Settler/Gas Collectors:

The main objective of the settler/Gas collector (or gas solids separator, GSS) in a UASB reactor are: (Souza, 1986)

1. To separate and discharge biogass from the reactor
2. To prevent the washout of bacterial matter
3. To enable the sludge back into the digester compartment
4. To serve as a kind of barrier (Stopper) for rapid excessive expansions of sludge (which is mainly composed of flocculent sludge) into the settler
5. To provide a polishing effect
6. To provide the washout of floating granular sludge.

Relatively a lot of research has been spent in recent years for the design of new, more exclusive GSS system. The last word on the design of the GSS-device certainly has not been said. However, in principle the design of the GSS device can be fairly simple, i.e. it does not necessarily constitute a very expensive part of the reactor (Lettinga and Hulshoff, 1991).

Souza (1986), indicated that, several settling units may be necessary, depending on the reactor size, due to the fact that their height is limited (1.5m) as has been pointed out. There are, at least, two options for the positioning of the gas collection region at the top of the reactor, between two settling units or on the settler rim (Fig 2.4).

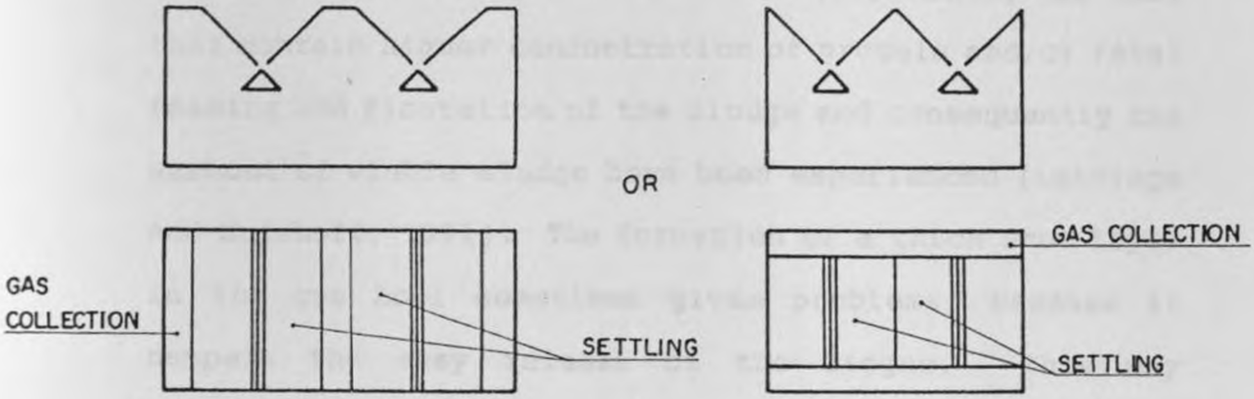


Fig 2.4: Position of the settling and gas collection unit (Souza, 1986).

The choice of the number and disposition of the settler and gas collectors also depends on the necessary surface area for the release of the gas to be produced. As an estimate for this area, the recommended minimum superficial gas release rate should be $1m^3/m^2/h$ and the maximum, 3 to 5 $m^3/m^3.h$. The gas release should be high enough to avoid the formation of a scum layer but low enough for the ready release of the gas, thus avoiding the excessive build up of sludge in the regions and pipes of the gas exist. (Souza, 1986).

To avoid the washout of viable sludge or dispersed solids (especially with dilute waste waters) from the reactor, Lettinga and Hulshof (1991) recommended that, a baffle should be incorporated to the Gss system by placing it in front of the effluent weir.

In treating industrial waste waters (especially the ones that contain higher concentration of protein and/or fats) foaming and floatation of the sludge and consequently the washout of viable sludge have been experienced (Lettinga and Hulshoff, 1991). The formation of a thick scum layer in the gas bowl sometimes gives problems, because it hampers the easy release of the biogas. This may occasionally result in partial escape of biogass via the settler, which obviously is quite detrimental for settling out the sludge and consequently increase the concentration of ss in the effluent. In these cases measures should be taken to remove the floating matter from the reactor (Lettinga and Hulshoff, 1991).

At a certain fixed space load, the specific gas production rate (m^3/m^2/d) increases proportionally with the reactor height (Lettinga and Hulshoff, 1991).

Lettinga and Holshoff (1991) provided a general guidelines for the construction of GSS systems

1. The slope of the settler bottom (i.e inclined wall of the gas collector) should be between 45°-60°c.
2. The surface area of the apertures between the gas collectors should be between 15-20% of the reactor

surface area.

3. The height of the gas collector should be between 1.5-2m at reactor height of 5-7 m.

4. A liquid-gas interface should be maintained in the gas collector in order to facilitate the release and collection of gas bubbles and to compact scum layer formation.

5. The overlap of baffles installed beneath the apertures should be 10-20 cm in order to avoid upward flowing gas bubbles to enter the settler compartment.

6. Generally scum layer baffles should be installed in front of the effluent weirs.

7. The diameter of the gas exhaust pipes should be sufficient to guarantee the easy removal of the biogas from the gas collection cap, particularly also in the case of foaming.

8. In the upper part of the gas-cap, anti-foam spray nozzles should be installed in case the treatment of the wastewater is accompanied by heavy foaming.

2.7.4 Gas Deflection/Passage to the Settler:

The gas deflection system may be of a very simple design. It takes advantage of the tendency of a gas to flow vertically in a liquid. The deflectors should have an adequate slope so as not to hinder the return of sludge from the settlers. The aperture of the passage to the settler for the liquid containing a portion of sludge may be used as a passage for the return sludge. The velocity of flow must thus be sufficiently low, and should not exceed 3-5m/h (Souza, 1986).

Regulation of velocity of flow in pilot and full-scale plants would be of great help for the proper operation of the system. Prediction of the critical liquid upflow velocity has already been discussed in section 2.7.1.

2.7.5 Feed Inlet System:

Mixing in the UASB reactor is accomplished by the biogas produced during anaerobic digestion and/or the liquid upflow velocity. For utilizing the retained reactor sludge, it is important to ensure an optimal contact between sludge and waste water i.e channeling of the waste water through the sludge bed or the formation of dead corners in the reactor should be avoided. The danger of channelling becomes bigger at lower gas production rates, less than $1m^3/m^3.d$ for a 4-6m tall reactors (Lettinga and Hulshoff, 1991).

The gas production obviously remains low when the imposed organic loading rate has to be kept low e.g. when very dilute waste water are treated and the temperature is in the psychrophilic or low sub-mesophilic range. However, for soluble types of wastes, even in that case, a fairly good contact between sludge and waste water can be accomplished by applying taller reactors and taller sludge bed (Lettinga and Hulshoff, 1991). For diluted wastes, like domestic sewage, a good influent distribution point should be used for each 1-2m^2 whereas for concentrated wastes, where good mixing is obtained from high gas production, it is not necessary to have a vigorous inlet distribution system. One distribution point for each 7-10m^2 being sufficient (Souza, 1986). Excess mixing may cause rupture of flocs or granules, thus damaging the system performance. The inlet system should be easy to clean because clogging of inlet pipes particularly when treating partially soluble waste may occur and consequently would result in an uneven distribution of the waste water over the reactor bottom (Lettinga and Hullshoff, 1991).

2.7.6 Effluent Withdrawal/Removal of Excess Sludge:

The effluent withdrawal system at the top of the settler should be designed to permit as uniform an upflow as possible. Effluent removal can be accomplished through weirs, for example, as it is normally done in conventional settlers. The weirs can be located in the center or on the rim of each settler unit (Souza, 1986).

Regarding the excess sludge removal, when the main purpose of a UASB system is the production of biogas, there are no scientifically established reasons for the removal of the digester sludge i.e. the sludge can leave the reactor naturally, together with the liquid effluent. When the main purpose of the system is the treatment of wastewater, in this case a portion of the sludge accumulated in the digester must be directly removed from time to time to avoid negative effect on effluent quality. This direct removal of the sludge is almost obligatory (Souza, 1986).

Generally a good place for discharging excess sludge is at one half the height of the reactor, it is also recommended to equip the reactor, near the bottom, and approximately half a meter beneath pipes with some other inserted sludge discharge pipes. For assessment of the total quantity of sludge in the reactor it is recommended to install a number (5-6) of valves over the height of the reactor to enable sludge sampling and profiling. (Lettinga and Hulshoff, 1991).

2.7.7 Required Post Treatment/Pretreatment:

Anaerobic treatment is merely efficient for removing biodegradable organic matter, generally not for phosphate, pathogens, ammonia and certainly not for sulphide. Therefore, depending on the restriction set for the effluent quality, some adequate post treatment has to be applied for removing organic pollutants and dispersed solids. Some systems have been considered or researched for improvement of effluent quality such as settlement, floatation, sand filtration, stabilization ponds, air stripping, aerobic biological processes also equipment has to be installed for handling and storing excess sludge or for dewatering and/or drying excess sludge. As the excess sludge production in the anaerobic treatment of soluble waste water is very low, particularly for waste water which contains a considerable VFA concentration, generally little if any problems are encountered in sludge handling and disposal (Lettinga and Hulshoff, 1991).

A pretreatment unit may be required for the purpose of equalization of flow, supply of alkalinity to enhance the waste water buffering capacity, removal of suspended particles for insoluble waste waters, etc. (Lettinga and Hulshoff, 1991).

2.7.8 Costs:

It is impossible to make a general forecast on the cost of the UASB system. An estimate of costs depends on many factors such as nature of the wastewater, pre-treatment, temperature control, pumping requirement, sludge disposal, utilization of biogass etc. The UASB reactors themselves represent the greater part of the installation costs. Pre-treatment (e.g. screening and grit chamber), the sludge dewatering (e.g. drying bed) and the effluent post-treatment (e.g. chlorination, sand filtration) systems may be very simple and relatively inexpensive. In addition, heating and temperature control systems (especially for tropical regions, e.g. (Sudan) is not necessary. In these cost considerations, the cost of the land can represent a reasonable amount of saving due to use of the UASB reactor which requires a small area in relation to other conventional systems.

The possibility of modularising UASB units may represent an economy in the sewage collection and transportation systems because it dispenses with the construction of large and expensive collectors, interceptors etc. The costs related to the O&M of UASB rectors tend to be satisfactorily reduced compared to the conventional anaerobic process, particularly in terms of elimination of the oxygen supply (Souza, 1986).

2.8 Start-up Operation and Control:

2.8.1 Start-up:

Once the treatment system in UASB reactors has been adequately designed and constructed, the start-up is a determining factor in the unit performance (Zeeuw and Lettinga, 1983). It may be considered that the start-up begins with the reactor inoculation and ends when a sufficient quantity of active high settlement-velocity biological sludge which is adapted to the waste and is maintainable in the reactor. Under these conditions, the system can already be exposed to high applied organic loads or high superficial velocities without hindering the efficiency (Souza, 1986).

Selection of a suitable inoculum material is essential to successfully start-up an UASB reactor. Inoculum material should posses micro-organisms that can degrade the organic compounds in the target waste water, and induce the formation of granules(or develop sludge with good settling properties). The inoculum can be granular sludge from an existing UASB reactor; or Non granular material such as anaerobic digested sludge, waste activated sludge, cow manure, etc. (Hickey <u>et.al.</u>, 1991).

Utilization of granular sludge as inoculum has the advantage of being well defined, and is probably a function of both the type of waste and granular sludge source available. The range of 10-30% of the reactor volume can be considered to be the range of inoculum volume required (Sam Soon <u>et.</u> <u>al.</u>, 1984; Sax, 1985 and Hickey <u>et.</u> <u>al.</u>, 1991).

The amount of inoculum of non-granular materials needed for start-up has been discussed by several investigators (Lettinga <u>et.</u> <u>al.</u>, 1984; Wu <u>et.</u> <u>al.</u>, 1987; de Zeeuw, 1988). The use of digested sewage sludge with relatively high solids concentration (i.e. 60-75 g Vss/l) rather than lower strength materials (<40gvss/l) is recommended to develop well setting granular sludge with little washout (Lettinga <u>et.</u> <u>al.</u>, 1984, 1985; de Zeeuw, 1984). Inoculated digested sludge concentration of 10-20 gvss/l in the reactor region is recommended (Lettinga <u>et.</u> <u>al.</u>, 1983; 1984; Wu et. al., 1987). The larger the quantity of sludge used for inoculation, the faster the start-up will be completed (Souza, 1986). Addition of a small amount of granules even 1% to no granular inoculum can simulate the granulation process (Hulshoff et. al., 1983; Alibhai and Foster, 1986).

After inoculation, different procedures should be adopted to enhance microbial utilization, in accordance with the concentration of organic material in the waste water to be treated. The lower the strength of waste water, the faster the granulation. However the strength should be sufficiently high to maintain good condition for bacterial growth (Lettinga and Hulshoff, 1991). If the residue is highly concentrated it is recommended to start the operation by applying a maximum volumetric organic load of 0.5kg COD/m^3/d, a maximum organic load to the sludge of 0.05-0.1 kgCOD/kgvss.day (Souza, 1986). The feeding flow rate should only be increased if the gas production and composition is satisfactory (See estimates in section 2.8.4) and if the concentration of volatile acids in the sludge is low (<500mg acetic acid/l) or with clear tendency to decrease (Souza, 1986). A tendency towards a rapid increase in the concentration of VFA in the sludge should be immediately avoided by reducing the feeding flow rate (Souza, 1986). Relatively high flow velocity in relation to the designed value through the sludge exerts a "washout" effect, avoiding an accumulation of organic material around the bacteria. This condition should be taken into consideration especially with diluted waste to avoid on excessive loss of sludge (Hulshoff et. al., 1983).

For start-up and operation of UASB reactor, the environmental factors should always be under control. The PH of the sludge should be maintained between 6.5 and 7.5 by adding chemical products if necessary. Sufficient nitrogen and phosphorous should also be maintained. The ratio COD:N:P for anaerobic treatment is 100:5:1 (Gray, 1989). High concentration of ammonium (>1000mg/l NH_4-N) should be avoided because it will inhibit granulation in UASB reactor (Hulshoff et. al., 1983). Concentration of sodium (greater than 5 to 10g/l) inhibits acetate utilizing methanogens growth in both digested sludge and granular sludge (Lui et. al., 1985; Rinzema et. al., 1988). Sufficient trace elements (e.g. Fe,Ni,Co) should be present in sufficient amounts in available form (Lettinga and Hulshoff, 1991). Temperature control of the reactor content during start-up period is necessary. Granular sludge can be developed using granular inoculum materials at mesophilic (38-40°c), thermophilic (50-60°c) as well as ambient temperatures conditions for a number of waste waters (Hickey et. al., 1991).

2.8.2 Operation and Control:

In order to correctly evaluate the operational conditions of a UASB reactor, it is necessary to know or to estimate the efficiencies of the organic material removal and gas production possible to be obtained for the specific situation as well as the probably sludge production. Microbial kinetics and stoichiometry (covered in sections 2.3 and 2.5) can be used as a useful guide to estimate these parameters in a UASB reactor (Souza, 1986).

2.8.3 COD Removal:

The more adapted and active the biological sludge, and the more below the maximum permissible limits the applied organic load and the superficial velocity are, the more efficient the COD removal for a certain waste will be. On the other hand, among the several wastes, the one which contains less toxic compounds and less non-biodegradable organic materials will have a higher COD removal. For dilute wastes, the contributions to the total COD of the reactor effluent, due to the concentration of the suspended solids in the effluent and to the methane gas dissolved in it (20 to 50ml CH_4/l waste, depending on the temperature), may be significant, thereby, hindering the COD removal efficiency in the reactor. For concentrated wastes, these factors are generally not important, thereby bringing about a greater total COD removal efficiency. In these cases, even with high removal efficiencies the reactor effluent will still contain high COD concentrations (Souza, 1986). Lettinga and Hulshoff (1991) indicated that it is advisable to apply effluent recycle or dilution at influent COD>5000mg/l.

2.8.4 Gas Production and Composition:

In order to estimate the possible gas production to be obtained from a waste, at least three factors should be considered : (Souza, 1986).

- In a steady state, the theoretical methane production is proportional to the quantity of COD consumed in the reactor.
- part of the gas produced is dissolved and lost with the effluent
- part of the COD is transformed into biomass.

The composition of gas produced during anaerobic digestion varies somewhat with the environmental condition of the digester. The ratio of the carbon dioxide to methane varies radically with the character of the substrate undergoing decomposition.

Because of the wide variety of organic substances (usually of unknown composition) that are subjected to methane fermentation, it is advisable to analyze the gases produced using any gases analytical method to determine its fuel value and maintain a check on the behavior of the digestion unit (McCarty, 1964b).

According to Souza (1986), the free gas production in concentrated wastes is high in relation to the part which remains dissolved. In this case, one will remain in practice a production of about 0.3 litre CH_4/gCOD consumed, and a content of methane in biogas of about 55 to 65% (the remaining being constitute mainly of carbon dioxide). For diluted wastes, the portion of the gas which is lost with the effluent is greater and thus the recoverable production of gas is smaller with domestic waste, for instance, it has been obtained, in practice, a production of about 0.15 CH_4/gCOD consumed. In this case, the methane content in the biogas is about 75% and the biogas may contain high concentration of nitrogen, the remaining part consisting mainly of carbon dioxide. The hydrogen sulfide concentration in the biogas is generally low and depends on the sulphate concentration in the waste and on the COD/SO_4 relationship. The gas production rate and composition changes rapidly during the period that digestion is being initiated, and when normal digestion is inhibited. For digesters operating in a routine manner and being fed a given substrate regularly, the composition and rate of the biogas produced is fairly uniform.

2.8.5 Sludge Production:

It is also possible to estimate the sludge accumulation from stoichiometry (as explained in section 2.3) considering mainly the following factors: (Souza, 1986)

- Formation of biological sludge
- Suspended solids in the influent which will be retained in the reactor and will not undergo biogasification
- Suspended solids which will leave the system in the effluent.

Lettinga and Hulshoff (1991) indicated that, a good place for discharging excess sludge is at one half of the reactor height. They also advised that, excess sludge should be kept with the objective of using it to replace the reactor sludge in case of the system failure and also to inoculate other new UASB reactors. It is also indicated by Lettinga (1991)that, washed out dispersed sludge should not be returned to the reactor.

CHAPTER THREE

TREATMENT OF PULP AND PAPER WASTEWATERS

3.1 Pulp and Paper Industry:

Pulp and paper industry is one of the biggest industries in the world. In 1985 the world production of paper and paper board was around 165 million tones (UNEP, 1985). Table 3.1 shows a break down of paper and board production in the world.

Paper is produced from a number of raw material (containing cellulose) like wood, esparto, straw, rag, jute and hemp, bamboo, bagasse, cotton linters, flax, textile waste and waste paper (FAO, 1990).

Wood is the most favorable raw material because different softwoods and hardwoods give paper makes a variety of strength, texture and weight. The total world production of wood pulp, according to UNEP (1985), was around 26.5 million tones, of mechanical wood pulp, 6.5 million tones, of semi-chemical wood, and 83 million tones of chemical wood pulp. Table 3.2 shows a break down of wood pulp production in the world.

Table 3.1: Paper and board production (UNEP, 1985).

	PRODUCTION (TONNE)	% OF TOTAL WORLD PRODUCTION
North America	67,471,000	40
Western Europe	43,384,000	26
Japan and others	18,681,000	10
Australia/New Zealand	2,197,000	1
Africa	359,000	0.002
Latin America	7,697,000	4
Near East	649,000	0.003
Far East	3,977,000	2
Asia	6,467,000	3.9
Eastern Europe	14,479,000	8.7

Table 3.2: Wood pulp production (UNEP, 1985)

	MECHANICAL PULP (TONNE)	SEMI-MECHANICAL PULP (TONNE)	CHEMICAL PULP
North America	11436000	3611000	45753000
Western Europe	8222000	1184000	15059000
Australia	855000	249000	783000
Japan/others	1664000	677000	653200
Africa	266000	9000	408000
Latin America	410000	292000	382400
Near East	116000	1000	156000
Far East	199000	25000	609000
Asia	945000	-	1419000
Eastern Europe	2453000	604000	8433000

There are three main stages in production of paper. These are; manufacture of pulp; treatment of pulp; and manufacture of paper from pulp.

The raw materials are turned into paper pulp in a mechanical or chemical process. In the mechanical process, the raw materials are reduced to pulp by cutting and grinding them under certain temperature. In the chemical process the raw materials are reduced to pulp by cutting and grinding which is then cooked in a chemical liquor to separate out the fibres. There are three chemical processes; sulphite process, sulphate process, and soda process. In the sulphite process the cooking liquor is prepared by burning sulphur and absorbing sulphurous acid gas either in milk or lime or in towers filled with limestone over which the water is sprayed. In the sulphate process (Kraft mills) the cooking liquor contains caustic soda and sodium sulphate. In the soda process the cooking liquor is a solution of caustic soda. After being prepared, pulp is passed through a number of refining, washing and bleaching operations to enhance it's quality and hence the quality of the produced paper (Husain, 1976).

Waste paper processing has recently given a lot of attention all over the world as a consequence of the high cost of producing paper from wood and the global environmental campaign against deforestation.

Consumption figures in 1985 are quoted in table 3.3.

Table 3.3: Paper consumption, utilization rate, and recovery rate (UNEP, 1985)

	Group of countries utilization recovery		
	Tonnes	Rate % *	Rate % **
Total for Europe	17654000	31	31
EEC	10666000	45	32
Noradic	980000	7	30
Other Western	2407000	41	38
Eastern Europe	3604000	25	25
North America	14413000	22	25
Asia	13079000	46	38
Australia	636000	29	27
Latin America	3450000	47	37
Africa	607000	36	26
World total	49860000	31	31

* Waste Paper consumption as proportion of total paper and board production.

** Waste paper recovery as proportion of total paper and board consumption

3.2 Pulp and Paper Waste Water Characteristics:

Pulp and Paper industry generates effluents of variable characteristics depending on the type of the manufacturing processes used. The following is a brief reflecting the quality of waste that is commonly produced by each process:

3.2.1 Wood Preparation Effluents:

These waters result from transporting, washing, and debarking wood, and contain both course and fine particles of bark, wood slivers, and silt (Harry, 1980). In wet debarking process the suspended solids load before external treatment is in the range of 3-12 kg/m^3 of wood depending on wood species. The discharge of dissolved substances is determined by wood species, the size of bark particles and contact time of the wood with water. The BOD$_7$ lies between 2-7 kg/m^3 wood. The COD lies between 5-20 kg/m^3 (UNEP, 1985). Effluents from screening and pulp cleaning contain wood debris, pulp, fines and grit (Harry W. G., 1980).

3.2.2 Mechanical and Chemi-Mechanical Pulping Effluents:

The mechanical and chemi-mechanical pulping processes can be classified in the following way:

- conventional stone ground wood (SGW)
- pressurized ground wood (PGW)
- refiner mechanical pulp (RMP)
- thermo-mechanical pulp (TMP)
- chemi-mechanical pulp (CMP,CTMP, etc.)

The main sources of water pollution in mechanical pulping are:(UNEP,1985)

- rejects from pretreatment (e.g. chip washer)
- rejects from final stage cleaners
- filtrates from thickener.

The dissolved organic substance, and the BOD_5, COD and suspended solids discharged from mechanical pulping process are shown in table 3.4.

Table 3.4: Dissolved organic substances, BOD_5, COD and suspended solids from mechanical pulping processes (UNEP, 1985).

Process	Dissolved Organic substance (%)	BOD_5 Kg/tonn	COD Kg/tonn	TSS Kg/tonn
Stone ground Wood (SGW)	1 - 2	10 - 22	22 - 50	10 - 50
Refiner mechanical Pulp (RMP)	2	12 - 25	23 - 55	10 - 50
Thermo-mechanical pulp (TMP)	2 - 5	10 - 30	25 - 60	10 - 50

3.2.3 Chemical Pulping Effluents:

Chemical pulping effluent are produced by the preparation of Kraft, soda, sulphite, sulphate, or semi chemical pulps. All such effluents are relatively low in suspended solids, the bulk of the impurities being in solution in the form of lignin, tanins, carbohydrates, salts of fatty acids, and other cooking chemicals (Harry W. G., 1980). Tables 3.5 and 3.6 show the characteristics of effluents from sulphate and sulphite pulping processes.

Table 3.5: Effluent discharge from sulphate pulp mills UNEP, 1985).

Types of Mills	Water consum. m3/tonn	BOD_7 Kg/tonn	ColorKg pt/tonn	Suspen. solids Kg/tonn
<u>Old mills</u>				
Unbleached pulp	50-250	35-50	165-250	20-30
Bleached pulp	110-260	40-65	310-400	25-35
<u>Modern mills</u>				
Unbleached pulp	40-60	8-20	20-40	10-20
bleached pulp	60-90	20-40	200	10-40
Oxygen bleached pulp	60-90	12-20	50-100	10-40

Table 3.6: Characteristics of effluents from sulphite pulp mills (UNEP, 1985).

Parameter	Concentration
BOD_7 (kg/tone)	20 - 120
TSS (kg/tone)	10 -60
SO_2 (gaskgl/tone)	70 - 145
PH	1 - 8

3.2.4 Bleaching Wastes:

All types of pulp can be bleached to improve brightness. Most of the bleaching chemicals employed are oxidizing agents, including chlorine, chlorine dioxide, hypochlorite, peroxides, and hydrosulfites. Bleaching wash waters are generally colored by the presence of lignins and tannins removed from the pulp; in addition, they contain a small amount of fiber fines and hydrolysis products. The type of pulp bleached, degree of bleaching, and process employed determine the pollution load carried by these effluents (Harry W. Gehm, 1980).

3.2.5 Paper Machine Wastes:

In general, paper machine wastes contain mainly fiber fines and fillers, but may also contain a considerable amount of dissolved solids from sizing and filler materials and special additives of both organic and inorganic materials (Harry w. Gehm, 1980). Table 3.7 shows typical water consumption and pollution loads in modern paper and board mills.

Table 3.7: Typical water consumption and pollution loads in modern paper and board mills (UNEP, 1985).

Paper mill	Water consumption m3/tonne	Suspended solids m3/tonne	BOD_5 Kg/tonne
News print	20-30	8-20	2-4
Magazine paper	20-30	10-20	2-4
Wood free printing paper	10-20	12-25	3-6
Kraft paper	10-20	8-15	1-3
Folding box board	20-40	2-8	2-5
Food board	20-40	2-8	2-5
Corrugated medium	10-20	10-25	1-3

3.2.6 Effluents from Recycled Paper Industry:

Waste paper processing does not in general give rise to significantly more pollution than the processing of virgin pulp in a paper mill. Naturally, waste paper is often dirtier and will contain more contraries such as paper clips, pieces of plastics, filler materials, etc. But these present no great problem in terms of environmental pollution.

The characteristics of effluents emitted during the manufacture of paper product vary considerably according to; the processes involved to produce specific type and grade of paper for instance, printing and writing, sugar, ticket and board, newsprint, Tissue, and packaging papers. The age of the paper mill; production sequence; percentage of virgin pulp used; quality of the waste paper used; degree and method of white water recirculation and fibre recovery adopted also considerably determined the quality of effluent generated. In general upto half of waste paper input by weight can end up as effluent (Julius G., 1978). Tables 3.8,3.9,3.10, and 3.11 show typical waste water characteristics at different recycled paper mills.

Table 3.8: Waste Water characteristics after primary sedimentation at a Paper Mill (Kroiss, et. al., 1992).

Parameter	Concentration
COD	2000-2800 mg/l
Flow	4000-5000m^3/d
COD load	8000-14000 kg/d
COD/BOD$_5$	1.8-2.0
TSS (0.4um)	Approx. 400 mg/l
Total Nitrogen	Approx. 20 mg/l
Dissolved Nitrogen	Approx. 5 mg/l
Temperature	Approx. 35°C
Total Phosphorous	Approx. 3 mg/l

Table 3.9: Raw Waste water characteristics from a Deinking Paper Mill (Russo and Dold, 1988)

Parameter	Concentration
COD	4500 mg/l
TKN	20 - 30 mg/l
P	5 mg/l
SO$_4$	150 - 750 mg/l
PH	5 - 7

Table 3.10: Waste water characteristics of a recycled paper mill (Hulshoff Poll and Lettinga, 1986).

Parameter	Concentration
COD	1000 mg/l
BOD_5	500 mg/l
TSS	16 - 60 mg/l
VFAs	Approx. 5 mg/l
Temperature	26 - 28°C
Flow	9600 m^3/day

Table 3.11: Waste water characteristics of a Deinking Paper Mill (John Gullichsen, 1993)

Parameter	Concentration
COD	3000 mg/l
BOD_7	1500 mg/l
TSS	85000 mg/l
P	5 mg/l
Nitrogen	20 mg/l
Flow	1500 mg/l

An average BOD_5/COD ratio of 0.52 has been reported by Mobius and Baumgarten (1985) for different recycled paper mills producing different types of paper in Germany.

The strength of effluents from recycled paper industry can increase enormously as the load imported with waste paper increases. This has been found, for instance, in the COD concentrations in German recycled paper mills effluents, that have risen almost trebled on the average between the years 1970 and 1990 (Huter et. al., 1991). (Fig 3.1).

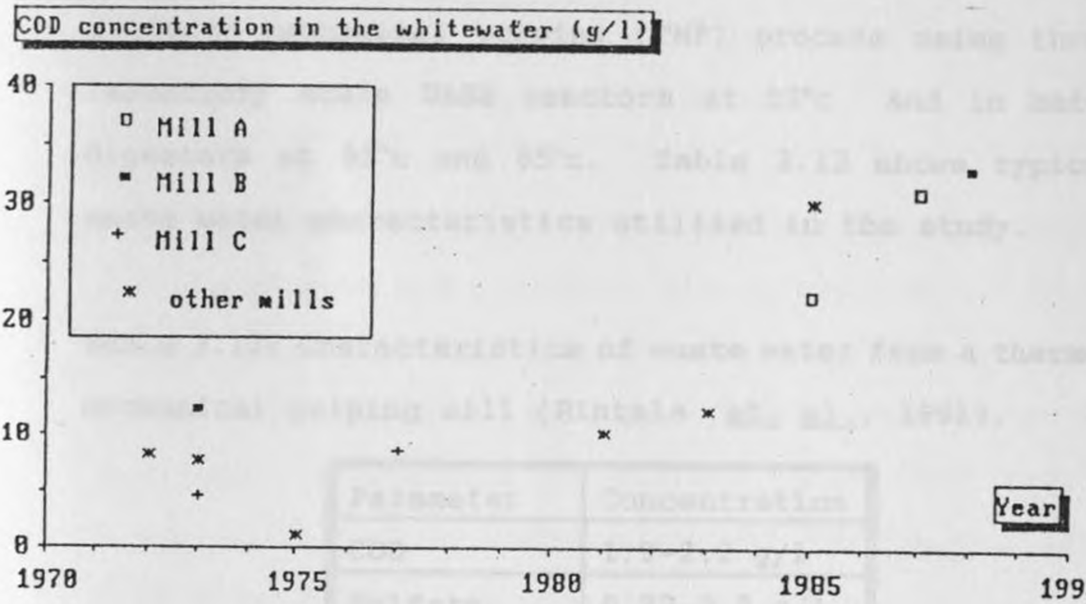


Fig 3.1: Development of the COD concentration in completely closed white water circuits at selected German recycled paper mills (Huter et. al.,1991)

3.3 Treatment of Pulp and Paper Effluents by UASB Process:

The UASB system is one of the treatment systems currently receiving attention in the pulp and paper industry (S.L. Russo and Dold, 1988). Recent researches have given realistic attention to the use of UASB system in the treatment of pulp and paper waste water.

For instance, high process temperatures and relatively closed water circuits in pulp and paper manufacturing generate several concentrated warm process waters, which are potentially suitable for thermophilic anaerobic treatment. Rintala <u>et. al.</u>,2 (1991) studied the treatability of sulfate-rich clarified white water from a thermo-mechanical pulping (TMP) process using three laboratory scale UASB reactors at 55°c and in batch digesters at 55°c and 65°c. Table 3.12 shows typical waste water characteristics utilized in the study.

Table 3.12: Characteristics of waste water from a thermo-mechanical pulping mill (Rintala <u>et. al.</u>, 1991).

Parameter	Concentration
COD	1.9-2.2 g/l
Sulfate	0.33-0.5 g/l
COD/Sulfate	1.4-2.1
PH	5.0

They concluded with the following results:

i) The highest COD removal efficiency (effluent sulfide stripped) achieved was approximately 65% in the UASB reactors. About 55% COD removal efficiency was obtained at loading rate of about 41 kg COD/m^3 day in one of the UASB reactors seeded with thermophilic sludge cultivated with volatile fatty acids (VFAs).

ii) Sulfate reduction was almost complete in the batch digester, whereas 24-64% of sulfate was reduced in the UASB rectors.

Thermophilic anaerobic treatment of pulp and paper industry waste waters using UASB reactor has also been investigated (Takeshita et. al., 1981; Brune et. al., 1982; Salkinoja-Salonen et. al., 1983; Salkinoja-Salonen et. al., 1987) on laboratory and pilot scale, but extensive reports are not available.

The effluents from CTMP mills are on one hand too dilute for evaporation and recovery, and on the other hand too highly polluted for conventional aerobic secondary treatment. Habets and de Vegt, (1991) investigated the anaerobic treatability of effluent from CTMP process using two full-scale UASB reactors of 3500m^3 each. Table 3.13 shows typical waste water characteristics utilized in the study.

Table 3.13: Characteristics of waste water from a CTMP industry (Habets and de Vegt, 1991).

Parameter	Concentration
BOD	3100 mg/l
COD	200 mg/l
TSS	400 mg/l
VFA	20 meg/l
Peroxide	50-100 mg/l
Sulphur	300 mg/l
PH	7-8
Temperature	35-40 c
Resin Acids	50-550 mg/l

They concluded with the following results:-

i) The BOD and COD removal rates were 45-65% and 30-40% respectively.

ii) The VFAs removal averaged between 80-90%

iii) Weekly average loading rates varied between 8 and 15 kg COD/m^3.day. with daily loading rates of as high as 18 kg COD/m^3.day.

iv) The sulphur levels in the effluent were relatively high, but resulting sulfide levels were not toxic to methanogens and COD/Sulphur ratios were high enough to achieve acceptable removal efficiencies.

Habets and Knelissen (1985) studied the performance of a full-scale UASB reactor treating a paper industry (Papierfabriek Roermond, the Netherlands). The UASB was a part of an integrated anaerobic aerobic waste water treatment. Part of the former aerobic treatment unit was used as an equalization tank for the UASB reactor. The reactor volume was 100m^3. Table 3.14 shows typical waste water characteristic utilized in the study.

Table 3.14: Characteristics of waste water from a paper industry (Habets and Knelissen, 1985).

Parameter	Concentration
COD	3000 mg/l
BOD_5	1500 mg/l
Flow	2400 - 3000 m^3/day
Temperature	30 - 40°C

Urea and phosphoric acid were added upto COD:P:N = 350:1:5. The following conclusion was made:-

i) COD reduction = 75%

ii) Volumetric loading = 10.5kg/m^3/d

ii) Remarkable improvement of the performance of the aerobic activated sludge plant

iv) Good quality granular sludge was developed.

Hulshoff and Lettinga (1987) reported the performance of a full scale UASB reactor treating a recycled Paper Mill (Industrial water, Eerbeek, the Netherlands) effluents. The reactor volume was 2200m^3 with a height of 5.5m. The operating temperature of the reactor was ranging between 26 to 30°c. Table 3.15 shows typical waste water characteristics utilized in the study.

Table 3.15: Characteristics of waste water from a recycled paper mill (Hulshoff and Lettinga, 1987).

Parameters	Concentration
COD	Approx. 1000 mg/l
BOD$_5$	Approx. 500 mg/l
TSS	160 - 600 mg/l
VFAs	Approx. 5 mg/l
Flow	9600 m^3/day
Temperature	26 - 28°C

The following conclusion was made:

i) The COD reduction = 70 - 72%

ii) The BOD$_5$ reduction = 75 - 83%

iii) The reactor temperature = 30°c

iv) After the removal of the hydrogen sulfide, electricity production in a 150 KW generator, was upto 400 kwh/day.

v) HRT = 5.5 hrs

The discharge of a mechanically treated waste water of an Austrian waste paper mill to a region sewer system served by a biological treatment plant, caused several environmental problems. Typical waste water characteristics after primary sedimentation are as shown in table 3.16.

Table 3.16: Characteristics of waste water from a waste paper mill (Kroiss <u>et. al.</u>, 1991).

Parameter	Concentration
COD	2000-2800 mg/l
Flow	4000-5000 m^3/d
COD Load	8000-14000 kg/d
COD/BOD	1.8-2.0
SS (0.45 um)	400 mg/l
Dissolved Nitrogen	5 mg/l
Total Phosphorous	3 mg/l

It was decided to erect a biological pretreatment plant on site of the paper mill. Several labscale and Pilot investigations have been carried out by Kroiss <u>et. al.</u>, (1991) of the technical university of Vienna, Institute of Water Quality to compare the three different processes

- Activated Sludge
- Trickling filter
- Anaerobic up flow reactor + Activated Sludge post-treatment

Satisfying results were obtained by the investigation with both the activated sludge process as well as anaerobic - aerobic treatment but not with the trickling filters process. Mainly because of lower total costs, anaerobic - aerobic pretreatment plant with UASB reactor has been erected. In the investigation with anaerobic process, three labscale plants with a reactor volume of 4, 4, and 2 liter were installed. The two 4 liter reactors were filled with digested sludge from the regional treatment plant, the 2 liter reactor was seeded with granular sludge from a full scale anaerobic treatment plant of a sugar factory. The aim of the experiment was to receive knowledge concerning the following items:

- COD removal efficiency
- PH value for a stable process
- Nutrient requirement
- Possibility to use lime for neutralization.

The results of the study are shown in table 3.17.

Table 3.17: Results of treatability study of activated sludge, trickling filter, and UASB processes.

	Reactor 1	Reactor 2	Reactor 3	Units
Reactor Vol	4	4	2	Liter
COD Load	4.5	2.7	8.8	kg/m3.d
COD rem.	78	70	79	%
PH	6.8-7.0	6.7-7.0	6.9-7.1	-
NaOH	0.3	-	0.3	g/l
Ca(OH)2	-	0.8	-	g/l

The following conclusion was made:

i) The two reactors neutralized with caustic soda were more stable.

ii) The nutrient requirements were evaluated as

COD:N:P = 100:1.0:0.35

iii) The specific methane production from reactor (1) and (2) was about 0.32 ml/g COD removed, from reactor (3) it was only 0.1 ml/g COD removed due to leakage in the gas measuring system.

iv) The concentration of carbon dioxide in the digester gas of reactor (1) and (3) was about 13% while in the gas of reactor (2) was about 7%.

v) The concentration of hydrogen sulphide in the digester gas of all reactor was lower than 0.5%.

vi) Concerning the post-treatment of the effluent from the anaerobic reactors, no operational problems like bulking sludge occurred.

Russo and Dold (1988) studied the sludge character and role of sulphate in UASB System Treating a Paper Plant effluent. Effluent from a recycled paper plant, having the characteristics shown in table 3.18 , was treated in 9 liter labscale UASB reactors operated at 25°c and 35°c.

Table 3.18: Characteristics of waste water from a recycled paper mill (The role of sulphate in UASB process) (Russo and Dold, 1988).

Parameter	Concentration
COD	4500 mg/l
Sulphate	250 mg/l
TKN	20 - 30 mg N/l
Phosphorous	5- 10 mg/l
PH	5
VFAs	45% (COD base)

The following results were obtained:

i) organic loading rates of approximately 25 kg COD/m^3.d were attained at both 25 and 35°c. This corresponds to hydraulic retention time of 5 hrs. The loading rate was not constrained by limitations in the biological treatment capacity. Rather, difficulties associated with settleability of sludge and blockage of under-designed laboratory reactor occurred.

ii) Average COD removal efficiency attained over a period 8 months operation ranges between 85% to 90%.

iii) The biological sludge bed formed had a granular, well flocculated form.

iv) Complete removal of sulfate was recorded. Nevertheless, it has been demonstrated that sulfate plays an important role in the treatment with respect to sludge pelletization and PH regulation.

CHAPTER FOUR

CASE STUDY

4.1 Introduction:

In Kenya there is only one integrated wood pulp and paper mill, Panafrican paper mill ltd, with a production capacity of 56200 mt/yr of chemical pulp (sulphite) and 15000 mt/yr mechanical pulp. Production is about 55000 mt/yr of pulp and 60000 mt/yr of paper . One wheat straw pulp and paper mill located in the wheat producing district of Nakuru is producing 3000 mt/yr and plans double production. (Kahuki., 1986).

Production of paper by recycling of waste paper is a new practice not only in Kenya but in all African countries.

Currently in Kenya there are three recycled paper mills: Chandaria paper mills ltd; Madhu paper mills ltd; and thicka paper mills ltd. In this study, Chandaria paper mill was selected as a case study.

Chandaria Paper Mill which is one of the largest paper mills in East Africa located on the Eastern side of Nairobi town (Kenya) and about 6 km from the town center. It was founded in 1985 as a privately owned. The mill occupies an area of 3000 m^2 in a rapid growing industrial area where many investors are acquiring plots to erect their investments.

The mill produces an average of 8000 tones per year of different grades of tissue paper and machine glazed paper (abbreviated MG). The raw material used is almost 100% waste paper. However, virgin wood pulp is sometimes used, mixed with waste paper in certain proportions, to improve the quality of the paper produced. The wood pulp used is namely bleached sulphite pulp imported from paper mills in Sweden.

Paper is manufactured by two paper machines working in parallel. These two paper machines are recognized as, paper machine number one (abbreviated PM1) and paper machine number two (abbreviated PM2). The PM1 operates at a speed of 400 m/min and produces only (MG) paper at a rate of 13 tones per 24 hours. The PM2 operates at a speed of 300 m/min and produces only tissue paper, at a rate of 10 tones per 24 hours.

Each of the two paper machines is supplied with stock (prepared pulp) from a separate 'stock preparation processes line'. The 'stock preparation processes line' embodies a number of operations. These are; pulping (or defibring), blending, cleaning and refining operations. Each of these operations are discussed in details in section 4.5.

As far as water consumption waste water generation are concerned, the factory has reduced its water consumption by closing the process water circuit. The white water generated from each of the two paper machines is partly recycled for pulping and partly treated, in a separate treatment work, to recover fibres and other useful materials lost during the formation of the paper web (known as machine broke). The discharge from this water circuit and all other waste water streams are combined together in a big manhole to form one main effluent stream which is allowed to flow directly to the nearest city sewer.

Fig. 4.1 shows a schematic flow diagram for the two production lines at Chandaria Paper Mill.

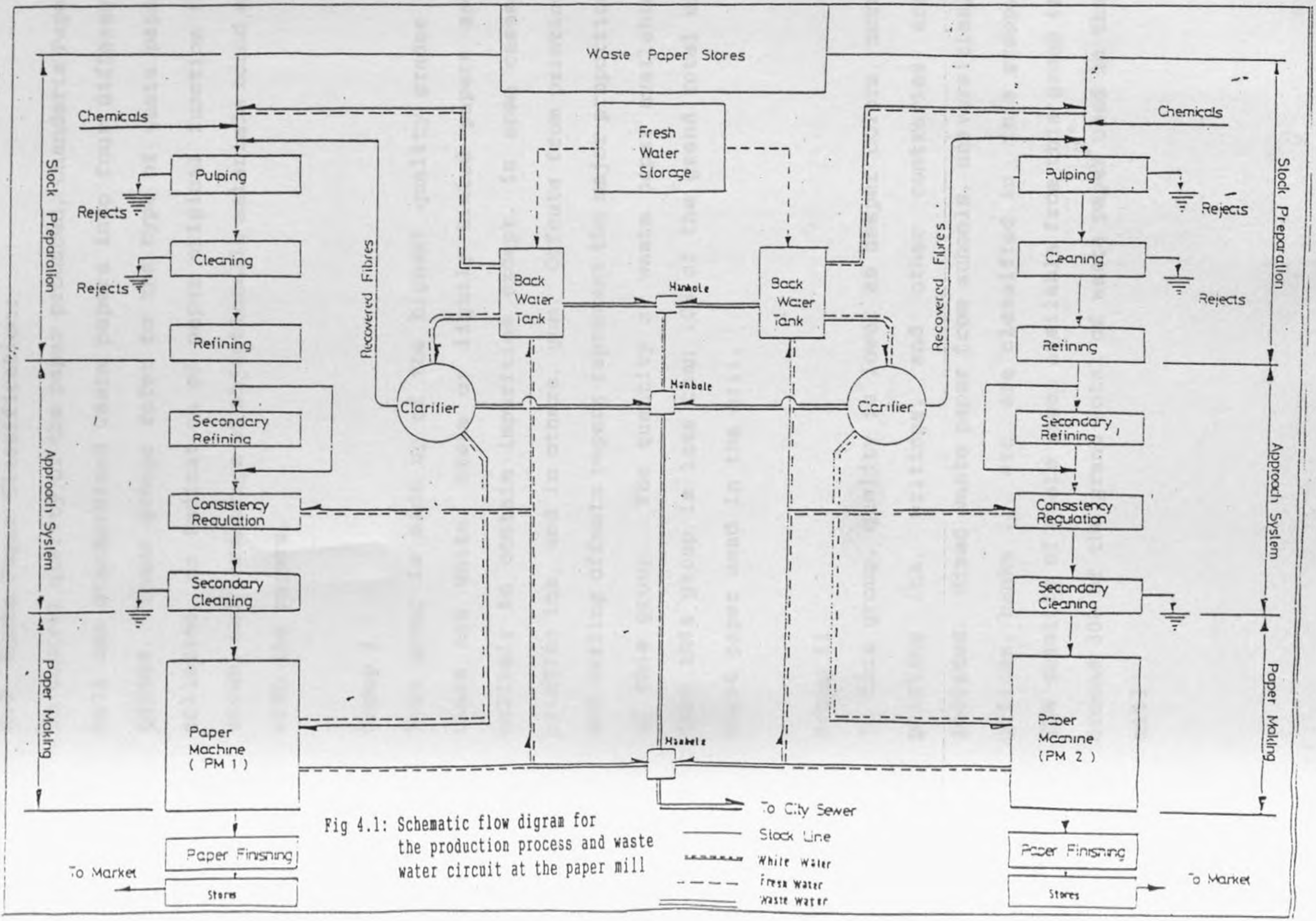


Fig 4.1: Schematic flow digram for the production process and waste water circuit at the paper mill

4.2 Waste Paper Classification:

To control quality of the paper produced, Chandaria Paper Mill has standardized waste papers into four different groups. These groups refer to the type of waste paper collected, an indication of paper original function if known, and percentage of objectionable materials bound up with the papers.

Group I

This group is made up of the highest quality grades - these are white, cream or lightly tinted papers and unlikely to contain impurities except, in some cases, printing ink, and in others, gum. Offcuts from printing and writing offsets papers represent the major proportion of this group. The quantity of waste paper available from this group is less than 10% of the grand total of waste paper used in the mill.

Group II

In this group, quality is lower as deeper colors, more printing ink, writings, and other contraries are included. Mixed waste paper from schools, universities, offices, banks ... etc. are classified in this group. The quantity of waste paper available from this group is around 30% of the grand total of waste paper used in the mill.

Group III

This group contains mixed brown waste paper and board-corrugated containers, used cases or sheets of corrugated board with or without kraft liners and a fluting of straw or waste paper. Supermarkets, shops, offices and case manufactures are the main sources of this group of waste paper. This group constitutes about 50% of total waste paper usage in the mill.

Group IV

This is mostly higher gramage paper, made originally from mechanical pulp. Corrugated-kraft cases, sheets and shavings of corrugated medium in kraft or semi-chemical pulp. The quantity of waste paper available from this group is about 15% of the grand total of waste paper used in the mill.

4.3 Type and quality of paper produced:

Different types and grades of tissue paper and machine glazed paper are produced at Chandaria Paper Mill. These are:

1. Tissue Production

Tissue paper is produced mostly from waste paper classified in Group I and/or group II. 4-5 tones of waste paper yields an average of 3.5 tones of tissue paper. The types of tissue paper produced are:

(a) Toilet Tissue

The majority of waste paper classified in Group II is used for the production of this type of tissue. It is produced in different colors and made in double ply by means of a slitter machine. The substance weight of this type of tissue ranges between 17 gsm to 22 gsm (gsm = grams per square meter).

(b) White Serviette Tissue

This is normally white in color. The stock for this product is prepared by mixing 75% white waste paper (Group I) with 25% bleached sulphite pulp. Softener, wet strength resin and optical brightener chemicals are added during the stock preparation. The substance weight of this type ranges between 24 gsm to 25 gsm.

(c) Hand Toweling tissue

This can be white or colored, normally heavily crept during drying process with wet strength resin chemical. It is made from 85% white waste paper (Group I) and 15% bleached sulphite pulp. Softener and optical brightener are also added during the stock preparation. The substance weight of this type ranges between 48 gsm to 50 gsm.

(d) Facial Tissue (or Hankie)

This is very white tissue with very fine and good looking formation. It is made from 80% bleached sulphite pulp and 20% white waste paper (Group I). Softener and optical brightener are also added to the stock. The substance weight of this type ranges between 15 gsm to 16 gsm.

2. Machine glazed (MG) paper production

Machine glazed (MG) paper is produced mostly from waste paper classified in Group III and/or Group IV. 4-5 tones of waste paper yield an average of 4 tones of the (MG) paper. The (MG) paper is made by allowing it to dry with one side in contact with a polished, heated cylinder. The side in contact with the heated cylinder receives a bright glossy finish, whilst the other side remains rough.

The (MG) paper is useful for making paper bags, envelopes, and book covers ; the high gloss of one side makes it easier to print, and the roughness of the other provide a key for adhesive used. The substance weight of the (MG) paper produced ranges between 30 gsm to 100 gsm.

4.4 Collection, transportation and storage of waste paper:

4.4.1 Collection and transportation of waste paper:

Chandaria Paper Mill has given a considerable interest to 'collection' and 'transportation' because they are the main components which dominate the supply price of waste paper. It has also built up a long standing links with all paper converters (e.g. card manufacturers, printers, binders, and box board makers), big offices (governmental and private), institutions, shops and supermarkets within and outside Nairobi town to secure continuous supply of waste paper to the mill.

Street boys (small vendors) play a principal role in collecting waste paper from these origins as well as from domestic solid waste dumping areas (mixed waste paper), within and outside nairobi town. They work in groups to collect as much waste paper as possible in big sacks which they sell together to central depots in Nairobi town at a rate of 4 kenyan shillings per kg waste paper.

At the central depots the waste paper is sorted out, packed and then transported to the mill. The aim of collecting and packing the waste paper at these central depots is to keep always collection and transportation costs to minimum.

Most of the transportation services are carried out by vehicles owned by the mill itself, only few private transporters are sometimes hired for this purpose.

4.4.2 Storage of waste paper:

Good storage of waste paper is most essential to protect the fibres from being destroyed by sunlight, fires and moisture or from being contaminated with objectionable materials such as rejected oil from the mill.

Rapidly increasing quantity of waste paper being received in the past few years and space restriction at Chandaria, has dictated the mill administration to put some effort in developing the waste paper stores, as well as the storage facilities in the mill. As a result: (1) new extension to the stores has been built; (2) materials and equipment for bailing and packing has been supplied; (3) continuous inspection to the stores has been done; (4) and proper handling and neat storage of waste paper in the mill has been encouraged.

Waste paper received at the mill is first weighed, classified and then stored with waste paper which belong to its group.

4.5 Paper Making (Production Process):

Paper making processes at Chandaria embodies three main operations: stock preparation; approach flow system; and the paper machine.

4.5.1 Stock Preparation:

Stock preparation covers the processes for producing 'stock' which is a suspension of fibres and other additives in water. The stock has to be in the right condition and of the right composition for the production of a sheet of paper on the paper making machine. These processes are embody defibring of waste paper (pulping), stock blending and stock additives, cleaning of stock, and refining of fibres.

1. **Defibring of waste paper or pulping**

This represents the 1st stage in stock preparation. It entails separating of bonded fibres by wetting, followed by mechanical action (pulper).

Waste paper in bale form (about 400 kg) is carried by squeeze clamp truck from waste paper stacks and placed on to the pulper conveyor belt. The pulper consists of a large circular chest, 3.5m in diameter, having at the bottom, one ridged rotor running at high speed. This circulate the waste paper, and at the same time separate the fibres. A cleaning device known as 'ragger' is provided for removing contraries which most likely exist in low-grade waste paper such as, bale wire, strings, thin plastic sheets, textiles, tapes, book scrims, and any other material which can wrap itself round the collecting wire suspended in the pulper. The wire is gradually withdrawn, and provided there are sufficient spinnable contraries in the incoming waste paper, the self generating 'rope' will continue to grow. It seems very simple but very effective cleaning device.

Hot steam from boilers is also supplied to the pulper to heat up the stock in order to aid separation of fibres and cleaning of stock. Moreover, the pulper is usually operated under low consistency (about 2.5%) to ease cleaning operation. Upto 900 kg waste paper can effectively be pulped in this machine while maintaining low consistency.

Fresh water from a bore hole, supplemented with backwater from the paper machine and recovered water from drying the rejected impurities is used in pulping. The average quantity of fresh water used for pulping is (40 m3/tone waste paper). This figure has been observed over along period of time for different production processes.

2. **Stock blending and stock additives**

Blending as a term, means, mixing of two or more different pulp (or waste paper) qualities, and may also add recovered 'machine broke' that is, fibre which escape from the paper machine, to the stock, as required to produce the correct furnish for the paper making machine.

Blending at Chandaria is carried out at the pulping stage where waste paper from different groups or waste paper and virgin wood pulp (i.e. bleached sulphite pulp) are mixed together in certain proportions to produce a stock of a given properties.

For instance: (1) 75% waste paper (Group I) mixed with 25% virgin wood pulp (bleached sulfite pulp) to prepare a stock used for the production of a given grade of serviette paper (tissue paper); (2) mixing of 80% virgin wood pulp (bleached sulphite pulp) with 20% white waste paper (Group I) to prepare a stock for the production of facial tissue; (3) or mixing papers from Group III and IV to prepare a stock for the production of a specific gramage of the (MG) paper.

Furthermore, mixing of 'machine broke', with the incoming waste paper in the pulper is also done by recycling part of the white water to the pulper.

Several other materials besides fibre are also added either at the pulping stage or at any later stage to make paper of the desired proportion. These materials are: sizing agents; auxiliary sizing materials; wet strength agents; pH-adjusting agents; filler (or loadings); and dye.

Sizing agents: Paper made from untreated fibre will possess a degree of absorbency dependent on the origin of the fibre and the degree of beating (grinding). Absorbent papers are clearly unsuitable for water-based writing inks which will spread or 'feather' from the point of contact.

Sizing agents are added particularly in making the (MG) paper to prevent this and make such paper suitable as a writing substrate. The sizing agents used for this purpose are Rosin and Alum. They are mixed together and added to the stock at the pulping stage where thorough mixing is provided.

Rosin is a brown, brittle substance, originating from wood through a number of processes 'gum rosin'. In chemical terms, 'Rosin' is a mixture of organic acids, mainly abietic acid, which is water insoluble.

Alum used at Chandaria, is aluminum sulphate and not the double salt so-named by chemists. The one used at Chandaria, is the one which is having minimum iron content, in order to maintain a low color level for high quality of paper produced. It is added with rosin to form a finely-dispersed hydrophobic precipitate on the cellulose fibres.

Although emulsion sizes could be used, which need no alum, but it has been observed by the factory operators that none appears to have as great a sizing effect as alum. Moreover, alum fulfills other functions besides sizing. These include PH control, fixation of acid, direct and pigment colors, assistance in filler retention and foam control acid catalysis of wet-strength resin (will be discussed later), pitch and slime control, and water and effluent treatment.

Alum-rosin ratio varies depending on the required degree of sizing, but is usually in the range of 2:1 to 3:1 for the production of all grades of (MG) paper. For instance, in the production of 60 gsm (MG) paper, 16 kg of alum and 8 kg of rosin are added per tone of waste paper.

Auxiliary sizing materials: This is mainly starch, which is added to the pulper to confer other properties on final paper, e.g., dry strength. It is derived mainly from corn (maize) or potatoes. It is also cheap and available in the local market.

Starch is mainly used in the production of the (MG) paper to improve the sheet strength (burst and tensile), pick resistance, quantity of sizing agents, handle, rattle and physical characteristics in general. An average of 8kg/tone waste paper is usually used for this purpose.

Wet-strength agents: These are chemicals used (added to the pulper) to improve the wet strength properties of the paper produced. Urea formaldehyde, which requires curing on the machine and running under acid condition, is used in the production of all grades of the (MG) paper particularly grades such as wrapping, paper and sacks.

For tissue grades, polyamide resin which requires running under neutral conditions (i.e. PH around 7) is used. An average of 1 liter/tone waste paper of wet-strength agent is usually used.

PH - adjusting agents: Regulation of PH is one method of controlling paper properties. At common alum levels, PH of the system is 4-5, but this does not always give the desired properties, so adjustments are sometimes made. Lower PH values are produced simply by adding more alum, whilst for higher PH values lime is added.

Lime is usually added to the pulper in order to raise the PH of the returning backwater temporarily to a level which will aid the efficiency of the other additives.

Fillers (or Loadings): These are essentially water-insoluble, white inorganic materials added to the stock to improve paper printability, brightness, opacity, smoothness, softness of handle and dimensional stability as well as to reduce the cost. The cheapest fillers namely, China clay and chalk are used. They are added to the stock at the pulping stage.

China clay is formed naturally from the feldspar component in granite deposits. Chemically, china clay is hydrated aluminum silicate.

As a filler, it has the advantage of chemical inertness in the paper furnish. It is therefore in its natural state is used in the production of all grades of the (MG) paper. The quantity added ranges between 200 to 250 kg/tonne waste paper depending on the grade of paper being produced.

Chalk is calcium carbonate. It is coarser particle size than china clay, and hence it gives a more matt surface to the paper. Because chalk reacts with acidic alum used in sizing, the so-called 'protected chalk', which is coated with starch, is used. Chalk is considerably cheaper than china clay and it is used in the production of high quality of the tissue paper (serviette) and the (MG) paper. The average quantity added is 200 kg/tone of waste paper.

Dye: Basic, acid and direct dyes are used for coloring purposes. The quantity and type of dye used depends on the type and the grade of paper produced.

The basic dyes are salts of a complex organic amine with acetic acid. They are used for coloring both tissue and the MG paper.

The acidic dyes are typically alkali metal salts of sulphuric acid. They are used for coloring the tissue grades.

The direct dyes are essentially a special group of acid dyes, originally so-called because their molecular configuration gives them some degree of direct affinity for cellulose. They are used for coloring both tissue and (MG) papers.

3. Cleaning of stock

This entails removing of the impurities or contraries and converting others into an acceptable form. The stock at Chandaria paper mill is passed through a number of cleaning stages. The cleaning method used in each stage depends on the nature of the contraries to be removed. Contraries are classified as follows:

Contrary	Examples
1. High density relatively large in size (Class I).	Tin cans, stones, small pieces of bailing wire, nails, nuts, bolts, large staples.
2. High density, small in size. (Class II)	Grit, sand, paper clips, pins, balls of aluminium foil.

3. Spinnable contraries in sheet or string form (Class III)	Plastic films, wet strength or waxed paper, bailing wire, string, textiles, tape, scrim form book spines
4. Low density (Class IV).	Wood, polystyrene foam, small pieces of low density plastic.
5. Density and size comparable with cellulose fibres (Class V).	Small pieces of plastic films, small pieces of wet strength paper, hair, long fibres from sisal, string, synthetic fibres, agglomerates of latex and other "sticky" materials agtomorates of wax and bitumen, printing ink.

The mixed waste paper (Group II), which is collected from shops, offices, and household, is the most difficult raw material for stock preparation as far as cleaning is concerned. Contraries arise from this group of waste paper include: staples from magazines, office paper clips, textile, scrim and plastics strips from the spines of magazines, catalogues and books, metal foil from foil/paper composites, waxed and wet-strengthened paper from wood wraps, bitumen and polythene-lined papers from waterproof wrappers, carbon copying paper, latex and similar type materials from pressure sensitive seals on envelopes, cement .... etc. left in the bottom of used paper sacks, tin cans, wood splinters, polystyrene drinking cups, polystyrene foam and wood wool from packaging waste, grit from shop sweepings, strings and wire from bundles and bales.

Removal of Class I contraries: These are high density heavy enough to fall through the waste paper stock in the pulper, are collected at the bottom of the pulper and passed to an automatic extraction device called 'Junker'. Pulpermen at Chandaria are occasionally rewarded by finding such things as coins and penknives in the 'Junker' rejects.

Removal of Class II contraries: These are small and can be carried along and removed from the pulper with the accepted pulp, because of their high density, they are removed by centrifugal cleaner. Two centrifugal cleaning stages are provided for this purpose. In the 1st stage the Class II contraries are removed under a condition of high consistency (4-4.5%) of stock i.e. immediately after pulping stage. the 2nd stage accepts stock which has already been refined and diluted i.e. of low consistency (0.8%-1.0%).

Removal of Class III contraries: These are removed from the pulper by means of a 'ragger' (described before under Defibring of waste paper).

Removal of Class IV contraries: Because of their low density, they float on the surface of the pulper and a system exists to scoop them off.

Removal of Class V contraries: These are the most difficult to remove, because their density and size are of the same order as those of cellulose fibres, and gravitational methods are ineffective. They are separated by screening, using plates with small holes (2.0 mm diameters) under high pressure and low consistency (0.8-1.0%) of stock. These screens are called high pressure screens.

Bitumen which occurs mainly in 'mixed waste', in corrugated case/container waste and in multi wall sack waste grades is not removed from waste paper pulp but is dispersed into such a fine form that it can not be seen in the finished paper.

In addition to the above mentioned cleaning mechanisms, vibration screens are also provided to recover the water bound with the rejects.

4. Refining of stock

Though pulping is an essential first stage, it is not necessarily the most economical means of defibring; hence it is used to break down incoming waste paper bales and bundles into small pieces of paper or clumps of fibre, which then pass on to a more economical defibring equipment known as 'deflaker' or 'disintegrator'. It applies shear forces to fibre clumps and slot to any coating flakes, shear forces to fibre clumps and also to any coating produces a more homogeneous, defibred, 'speck-free' pulp. A number of 3 primary deflakers (supplied with stock from a clean stock chest) and one secondary deflaker (supplied with stock from machine stock chest) are used. They are optionally operated depending on the degree of stock refining required.

4.5.2 Approach Flow System

The stock preparation process described above is designed to produce a stock with the fibres correctly treated and with the correct non-fibrous additives in the correct proportions. This stock however, is still not ready for supply to paper making machine for making the web of paper. It has first to be transported down the pipeline system to the paper machine and during the passage a number of other operations, explained below, are carried out, so that the stock shall be in the right condition for papermaking.

The part of the paper mill system between the stock preparation plant and the paper machine is known as the approach system. The approach system operations embody: regulation of consistency; supply of stock; control of flow rate; additional refining; and additional cleaning.

Regulation of consistency: This operation is extremely important to control the rate of flow of fibre to the paper machine. Consistency is controlled by controlling the volume of stock flowing. Mixed water (fresh water + backwater) is added to attain low consistency (Fig 4.1).

Supply of stock: From a constant head to the flow control valve. This is important because the volume of flow through the valve at any given setting depends upon the pressure behind the valve as well as on the stock consistency

Control of flow rate: The flow is controlled in the system by using a constant head overflow chest to give the required rate of flow in kg/min of fibre going to the paper machine.

Additional refining: This is an or alternative to the refining carried out during stock preparation to control the sheet formation and the drainage rate on the paper machine wire.

Additional cleaning: This is an additional to the cleaning carried out during the stock preparation. Pressure screens which always work under low consistency is part of this additional cleaning process.

4.5.3 The Paper Machine:

The two paper machines PM1 and PM2 are working in parallel and produce almost 8000 tone/year of different grades of tissue and MG paper. The principle of operation of these machines are as described below.

The paper machine consists of two sections; these are the wet end and the dry end. In the wet end of the paper machine, water is removed from the sheet by natural drainage, by forced drainage over vacuum boxes and by squeezing in presses. In the dry end the paper is dried completely as it passes through a steam heated drying cylinders.

The Paper Machine wet end: The wet end consists of (a) a flow box and slice (b) a wire part and (c) a press part.

(a) The flow box and slice

The main function of the flow box is to provide the necessary gravity head of stock to give the correct discharge velocity through the slice opening on the wire, and to even out the flow of stock across the width of the box, thereby giving a uniform consistency of stock on the wire, avoiding any channelling from the inlets that would result in an uneven gramage (wt per square meter) across the width of the paper machine web. The stock is projected from the slice onto the wire in the form of a wide jet. The thickness of the jet is controlled by adjusting the slice opening.

(b) **The wire part arrangement**

For every tone of paper made on the paper machine, between 300-500 tones of water are put onto the machine at the slice. The basic function of the paper machine is to remove this water and upto 97% of it has to be extracted on the wire part.

The process of water removal on the paper machine is accomplished; (1) by free drainage; (2) by suction on wire part; (3) by pressing on the press part; and (4) by evaporation in the dry part. Of the total water removed on the machine, upto 97% is taken out on the wire part, upto 2% on the press part and 1% on the dry part.

The effective length of the wire is from the breast roll to the couch pit; this is divided into two main sections, the forming section and the suction section. The width of the wire is fixed in relation to the trimmed width of the finished web. To this, allowances have been added for the strips removed at the edges on the winder, shrinkage in the dryers, wet strips removed from the edges at the couch, and the amount allowed at each side between slice opening and the edge of the wire.

The wire is made of plastic fabric which is resilient, flexible and not subject to fatigue failures, stock jams, pimples or edge crack. It is non-corrodible but still liable to contamination by bitch or bitumen. Units related to the wire part are: Breast Roll; Forming Board; Hydrofoils; Suction Boxes; Flooding Showers and High Pressure Needle showers; Save-all Troughs and Trays; and Couch Pit.

- The Breast Roll

The stock passes from the lip of the slice onto the endless wire that carries it from the breast roll to the couch. The breast roll is made relatively large, as it is the returning point of the wire and too sharp a turn is detrimental to the wire life.

- The Forming Board

The main functions of the forming board are: (1) to retard drainage by allowing a layer of stock to form on the wire surface, long enough to obtain even distribution, before drainage commences; and (2) to support the wire.

- The Hydrofoils

The basic functions of the hydrofoils is to remove the film of water from the underside of the wire. this prevents the water from being carried forward to the nip of the next roll where it might be detrimental to the formation of the web.

- **The Suction Boxes**

The suction boxes are an important section of the wire part, as they can remove upto one third of the total water removed on the paper machine. At the suction boxes, the water is extracted by the difference in pressure between the atmosphere around the web and the vacuum maintained inside the box.

- **The Flooding showers and high pressure needle showers**

These are used mainly for cleaning and conditioning the wire and the rollers. the high pressure needle showers are supplied with fresh water from the fresh water tank via a 25 ATE (Atmospheric Pressure) pump. The flooding showers are supplied with treated white water from the treatment work (after being clarified) via a 5 ATE pump.

- **The Save-all troughs and trays**

These are used for collection of the water, removed from the stock on the wire part, for recirculation. If this water was allowed to fall directly into the pit under the wire, it would have to pass through the returning wire and the fibres present might clog the wire and damage it.

- The Couch Pit

This is a quite big pit, underneath the paper machine, used for the collection of white water and water from other points on the paper machine for recirculation.

(c) The Press part arrangement

These are essentially two plain press rolls used, with a reverse press action, to squeeze out excess water in the web and also help to hold the paper during transfer from the machine wire to the drying felt.

Paper machine dry end: The main characteristic of the sheet formation are produced in the wet end section of the paper machine but the paper still contains upto 70% water as it enters the dryer section.

The dry end consists of:

(a) A big steam heated cylinder (known as MG dryer). It is 1.2m in diameter and 1.5m in length. It is heated by steam from a boiler system working at 180C.

(b) A press roll, working in a reverse press action with the MG dryer.

(c) A doctor blade, for crepping and removal of paper from the MG dryer.

(d) Hood, to remove water vapor and speed-up drying.

It accomplishes 40% of the drying.

(e) Suction boxes to speed-up drying operation.

(f) Drying felt to carry the paper sheet through the drying units.

4.6 Water Uses:

4.6.1 Fresh water system:

Fresh water is one of the principle factors which control papermaking process. The demand for fresh water for recycled paper processing in particular is quite high.

At Chandaria Paper Mill 2000 m3 to 3000 m3 is required per 24 hours to supply the two production lines (i.e. PM1 and PM2). Of the total quantity of fresh water used, 92% is consumed in the pulping process (average 40 m3/tone waste paper). The remaining 8% is used for other different purposes, such as supply of the high pressure showers for reconditioning and cleaning the return run of the wire, felt and rolls which carry the wire, domestic use, cleaning the factory floor, cooling system, boilers, dilution of stock, etc.

Before 1987, the only source of fresh water to the mill was the municipal water supply. In 1987 two bore holes for fresh water supply were sunk within the factory; (1) to cut down the water cost by reducing the quantity of water pumped from the municipal water; (2) and to secure continuous supply of water to the mill. The fresh water from the bore holes is received in a large over head tank from which it is distributed for different uses in the two production lines. (Fig 4.1).

The quantity of fresh water added to the pulper is controlled by the quantity of water which has been lost from the water circuit during the process through; (1) evaporation, (2) overflows, (3) and effluent discharge. The fresh water is mixed with the back water from the paper machine in a large tank called the backwater tank, before being added to the pulper (Fig 4.1).

The proportion of fresh water used for cleaning purposes is drawn from the over head tank by two different types of pumps, these are:

(1) 25 ATE (Atmospheric pressure) pump, to supply the high pressure showers for cleaning the returning wire and felt.

(2) 3 ATE pump, to supply water for dilution of stock, cooling system, cleaning of the factory floor.

The municipal water is strictly used for domestic purposes as well as for steam generating boilers.

4.6.2 White water recirculation:

The water which is drained from the wire of the paper machine during formation of the sheet and other water discharged from other points on the wet end is known as 'white water' or 'backwater'. This water is assumed to contain some valuable materials especially fibre, filler and possibly chemical additives. It is, therefore, collected, partly recovered, partly purified, and re-used. Moreover, recirculation of this water would reduce the high demand for the fresh water as well as would reduce the effluent discharge from the mill.

The two production lines (i.e. PM1 and PM2) have the same origins of water for recovery, white water treatment process, points of re-use and effluent discharge points. However, the volume of white water generated from the (PM1), which is mainly used for the production of the (MG) paper is higher than that generated from (PM2) which is mainly used for the production of the tissue paper. The following is a description of the white water origins, recovery, purification and re-use form the (PM1) production line.

(a) **White water origins and recovery**

1. **Wire part table rolls, foils and vacuum boxes**

This is the greatest volume of water (approximately 75 % of total white water volume generated) and contains the highest proportion of solid (i.e. fibre, filler, chemicals, and other impurities.

2. **Presses**

Water removed here has a smaller volume and a lower content of papermaking fibre than water from wire part, but it may contain textile fibre, from the felts.

3. **Spray water**

This is the water used for cleaning the return run of the wire, felt and rolls that guide, tension and carry the wire. This water has a small amount of fibre washed off the wire; for example it usually carries the deckle trim. But it has quite high volume.

The white water from points (1), (2) and (3) mentioned above is collected with aid of 'save-all trays and troughs', underneath the top run of the wire, into the 'couch pit'. In the couch pit, this water is agitated continuously by means of 'a mechanical agitator' to prevent settling of the useful materials (i.e. fibres, filler, chemical additives .... etc.) and then pumped back to the back water tank where it is mixed with fresh water from the fresh water tank and reused directly for pulping. Excess water in the back water tank is let to flow to a treatment plant called 'krofta' for purification and hence recovery of fibres. Excess white water in the couch pit is always allowed to overflow intentionally to the effluent stream to avoid high concentration of dissolved organic material which can act as nutrients for growth of microorganism in the closed white water circuit. This rejected part of white water is compensated by supplying fresh water to the system during pulping operation.

(b) **White water purification and re-use**

'Krofta' treatment plant is a system where solids in white water is recovered by floating them to the surface and skimming off. It consists of: a receiving tank; air dissolving tube; cylindrical clarifier (flotator); 25 ATE feed pump; and two 3 ATE pumps for dosing flocculent and floatation agents.

The receiving tank: This tank is 5m in length, 4m in width and 2.5m in depth. It is used for holding the influent and controlling of its flow to the treatment work.

The air dissolving tube: This is used for supplying air bubbles to the white water to enhance the floatation of fibres and filler particles.

The cylindrical clarifier (floatator): This is 2.5m in diameter, and 1m in depth. It is located at a higher level; 3m above the ground level. The principle of its operation is that, the air bubbles supplied by the air dissolving tube attach themselves to the fibre and filler particles and cause them to float. The floating fibres and filler particles are then skimmed off by a skimming equipment rotating at the top of the floatation and discharged to the pulper.

The clarified white water is discharged from the bottom of the clarifier to a treated water storage tank then, from there, is pumped to the mill via a 5 ATE pump to be used for cleaning and reconditioning the machine wire and rollers, dilution of stock, cleaning of high density cleaners, and pumps gland sealing water.

Sediment materials are also collected by means of a rotating scraper at the bottom of the clarifier and discharged in a form of slurry to the waste water stream every one hour under normal operation conditions of PM1 and PM2.

The 25 ATE feed pump: To take untreated white water from the holding tank to the clarifier.

The 3 ATE pump for dosing flocculent agents: Since the optimum PH valve for efficient fibres and filler particles floatation is PH5, adjustment of white water PH is always carried out.

PLATE 4.1 PM1 and PM2 Clarifiers
(Krofta Treatment Plant)

White water from tissue paper processing is normally having PH varying between 7-10. In such a case, alum is dosed into the suction side of the krofta feed pump (to PH 5) to bring the fibres as well as filler particles together and hence enhance their floatability. However, the PH of white water from MG paper processing varies between 4.5 and 5 therefore lime (ca Co3) sometimes is added at the same point to maintain the PH at PH5.

The 3 ATE pump for dosing floatation agents: Polymin SK (liquid) or superfloc C573 (liquid) is also dosed at an average rate of 6 liters per hour via a 3 ATE pump.

Finally, although the treatment plants for the (PM1) and the (PM2) are working for a large extent efficiently for useful material recovery, but their capacities are under estimated, that, they are not capable of accommodating the flow of white water from the mills even under normal operation conditions, therefore, uncontrolled over flows from the clarifiers, storage tanks, couch pits to waste water stream usually take place. This in turn leads to loss of large quantities of useful materials (fibrous and non-fibrous materials) in the discharged white water and in the meantime increases the volume and strength of the final effluent from the factory.

4.7 Waste water generation and discharges:

The two production lines (i.e. PM1 and PM2) have the same origins and discharge points of effluent. However, their discharges varies in volume and strength depending on the quantity and grade of paper being produced in each line.

Waste water streams originating in each of the two production lines can be classified as follows:

(a) **White Water Stream (stream I)**

This contains pure white water discharged from the couch pit of the paper machine, and it contributes the largest volume of waste water generated (approximately 50 %) to the final effluent from the mill.

(b) **Treated white water stream (stream II)**

In this stream, the volume is smaller (approximately 30 %) and constitutes clarified white water from the 'Krofta' treatment plant, mixed with sediment materials (in form of slurry) in the clarifier.

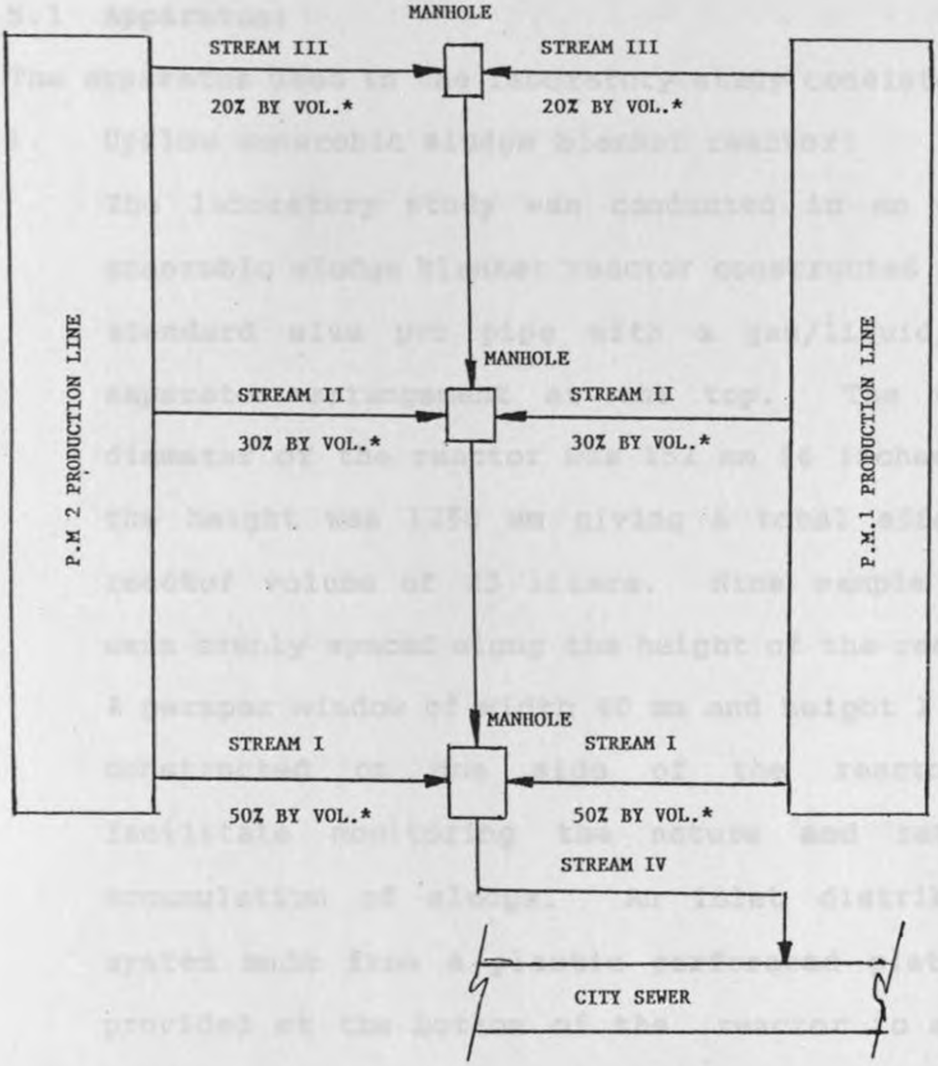
(c) **Untreated waste water stream (stream III)**

This stream contains untreated water discharged from the 'Krofta' treatment plant to reduce excess overloads on the clarification system (contains approximately 20% by volume).

(d) **Final effluent stream (stream IV)**

The flows in the above mentioned streams, from each of the two production lines, are combined together into one common stream which is let to flow to the main city sewer.

Other discharges, from the factory floor washing or overflows from the processing units and the treatment works are diverted directly to the common stream. The waste water streams are shown diagrammatically in fig 4.2.



* Percentage by volume calculated based on the total volume of waste water produced by a production line

FIGURE 4.2: Waste Water Streams at Chandaria Paper Mill

CHAPTER FIVE

EXPERIMENTAL INVESTIGATION

5.1 Apparatus:

The apparatus used in the laboratory study consisted of:

1. Upflow anaerobic sludge blanket reactor:

   The laboratory study was conducted in an upflow anaerobic sludge blanket reactor constructed from a standard size pvc pipe with a gas/liquid/solid separator arrangement at the top. The inside diameter of the reactor was 152 mm (6 inches) and the height was 1250 mm giving a total effective reactor volume of 23 liters. Nine sample ports were evenly spaced along the height of the reactor. A perspex window of width 40 mm and height 1 m was constructed on one side of the reactor to facilitate monitoring the nature and rate of accumulation of sludge. An inlet distribution system made from a plastic perforated plate was provided at the bottom of the reactor to ensure uniform distribution of flow throughout the cross section of the sludge bed. The reactor was also provided with a tap at the bottom for sludge removal.

2. Gas Collection Unit:

The method used for collecting and measuring the gas produced by the reactor was the water seal method. The gas collection unit was consisting of a plastic basin and a calibrated measuring cylinder supported on a stand. The water used for sealing was acidified with hydrochloric acid to PH 2 to prevent dissolution of the produced methane gas (CH_4) and dyed with Rhodamine B dye to facilitate reading on the measuring cylinder.

3. Variable Speed Pump:

This was used for supplying the reactor with substrate. The speed of this pump was adjustable to a flow rate between 0 to 3 liters per minute.

4. Substrate storage tank

Fig 5.1 shows a schematic diagram of the apparatus

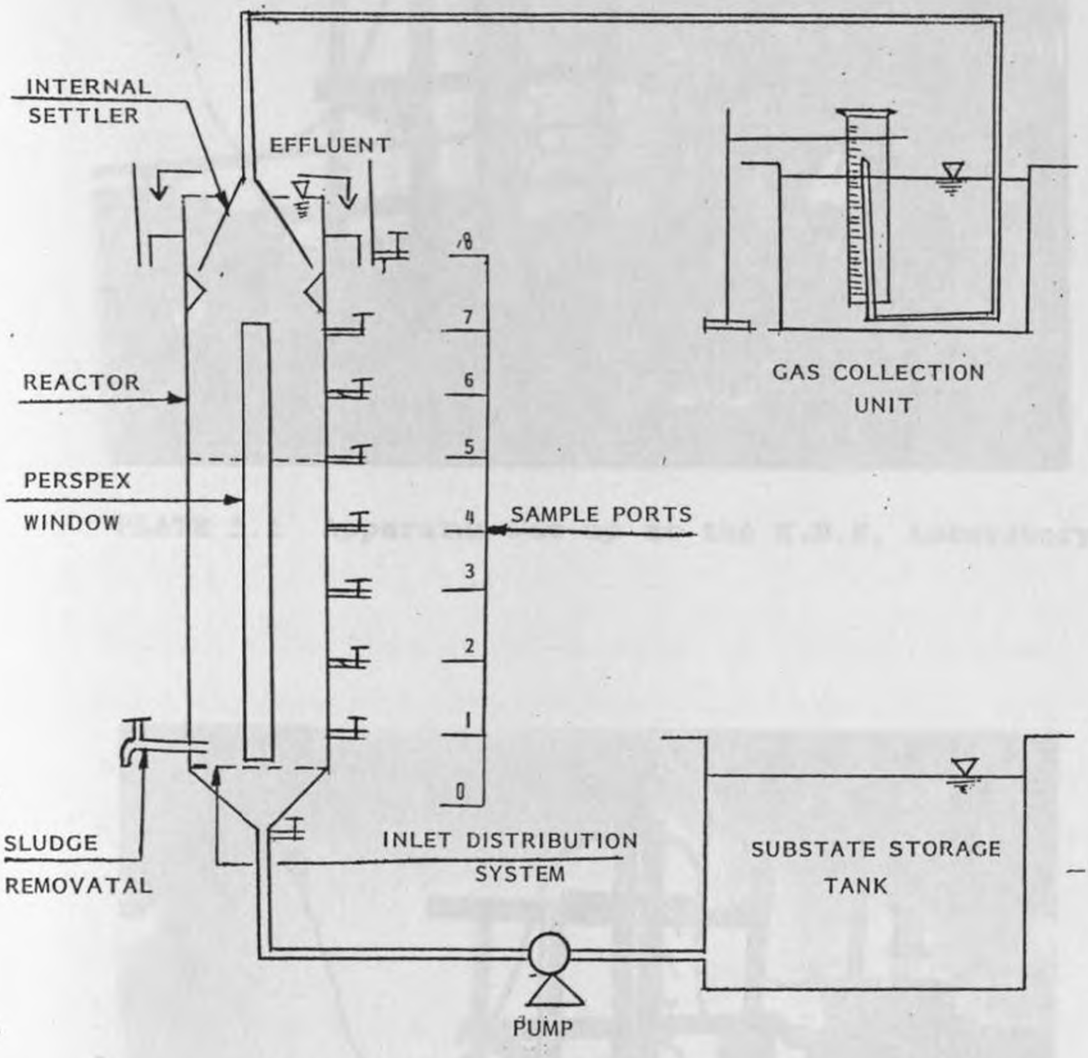


FIGURE 5.1: SCHEMATIC DIAGRAM OF THE APPARATUS

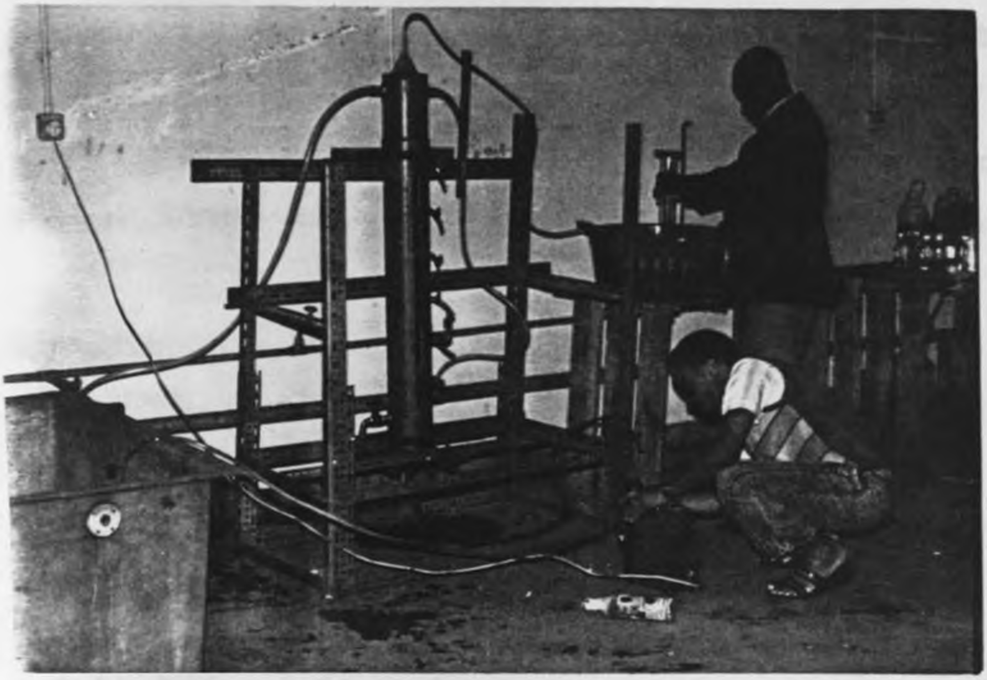


PLATE 5.1 Apparatus Set-up at the E.H.E. Laboratory

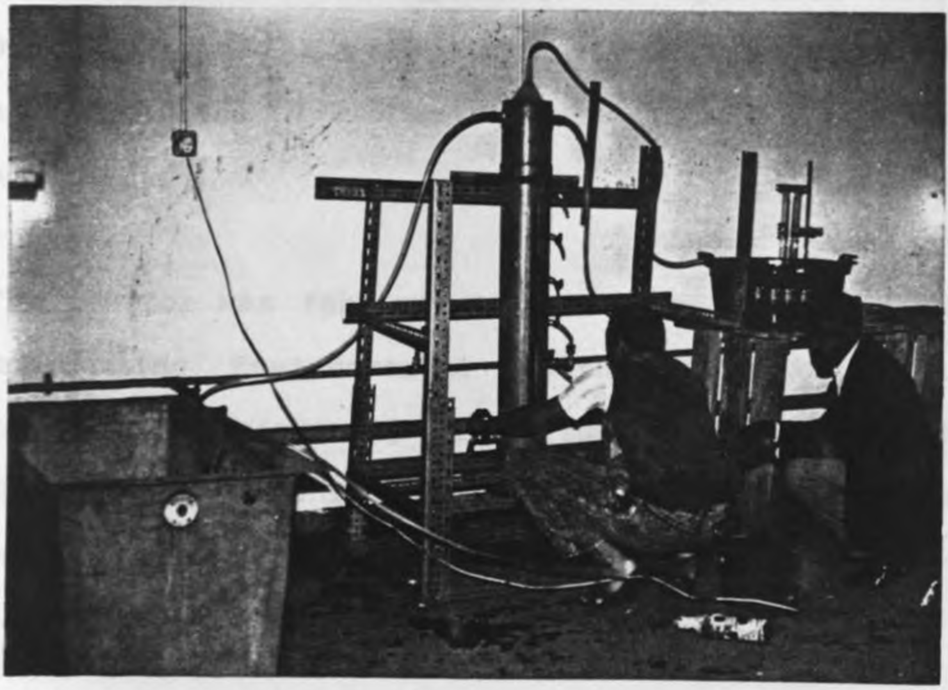


PLATE 5.2 Testing the Hydraulic Parameters

Using the criteria stated by Souza (1987) (Section 2.7.1) for peak loading condition, with feed COD concentration 2100 mgCOD/l, which corresponds to the average COD of the waste water used, the maximum organic load rate 20kgCOD/m^3/day corresponds to a hydraulic rate (Q) of:

$$Q = \frac{20kg(COD/m^3/day)x23x10^{-3}(m^3)}{2100x10^{-3}(kg/m^3)} = 0.219(m^3/day)$$

the corresponding superficial velocity (Vr)

$$Vr = \frac{0.219(m^3/day)}{0.152^2 x\pi/4(m^2)} = 12.068(m/day)$$

$$= 0.5(m/hr) < 1.2(m/hr)$$

Hence, upto organic load rate of 20kgCOD/m^3/day, at concentration of 2100mgCOD/L, and hydraulic rate of 0.219m^3/day could be applied to the reactor without exceeding the limiting values of the superficial velocity.

The reactor was fabricated in the Department of Civil Engineering, Environmental Health Engineering (E.H.E.) laboratory, University of Nairobi and transferred to Kariobangi Sewage Treatment Plant where the experiment was tested and run.

5.2 Preliminary Tests:

The waste water streams originating from different processing phases of the PM1 and PM2 production lines at Chandaria Paper Mill were identified, quantified and analyzed with the objective of demarcating the contribution of each stream as well as the combined final flow that is discharged to the main city sewer. The analysis and measurements were carried out under different production process conditions (i.e. when the mill was producing different types and quality of paper) to ensure the stability of the waste water characteristics. The strength of each waste water stream was determined in terms of the average total chemical oxygen demand (COD). The COD of each stream, at a certain production conditions, was measured twice at a difference of 3 hours and the average was taken to cater for any possible variation in strength. The volume of the discharged waste water in each stream was determined in terms of the average hydraulic flow rate (Q) in each stream. The method used for the determination of the hydraulic flow rate (Q) was the floating body method:

1. A floating body was dropped into a waste water stream at a known point and allowed to travel with the flow upto a predetermined distance (varied between 5-10m depending on the accessible length of

the stream channel) while observing its travelling time.

2. The procedure in (1) was repeated 4-5 times for each flow over a period of three hours to cater for any possible variation in flow rate and the average of the observed travelling times was taken.

3. Knowing the average travelling time (Tav), the travelled distance (L), the depth of flow, and the width of the stream channel (Wd) (the flow channels of all wastewater streams are open channels with rectangular cross sections), the average hydraulic flow rate in the stream was approximated by:

$$Q = \frac{L}{Tav} . (Wd) \qquad \text{-------------(29)}$$

assuming that

$\frac{L}{Tav}$ = The average surface flow velocity in the steam ≈ the average flow velocity across the depth of flow in the stream.

The results of the preliminary tests are illustrated in table 5.1. The final effluent (Stream IV) was found to be contributing the highest pollutional load. Therefore, it was chosen as a source for waste water utilized in the laboratory study.

TABLE 5.1: Results of the Preliminary Tests

PRODUCTION LINE	WASTE STREAM	PARA-METER	SAMPLING DATES			
			16 OCT-1992	6TH NOV. 1992	17TH NOV. 1992	4TH DEC. 1992
PM1	I	$Q(m^3/d)$	570.0	686.0	276.0	559.0
		COD (mg/l)	2286.67	1806.0	2048.56	2278.36
	II	$Q(m^3/d)$	342.0	405.0	196.6	334.0
		COD (mg/l)	2215.13	1718.21	1969.32	2191.77
	III	$Q(m^3/d)$	228.0	250.0	149.0	214.0
		COD (mg/l)	2249.52	1756.32	1969.44	2234.54
PM2	I	$Q(m^3/d)$	338.0	320.0	544.0	503.0
		COD (mg/l)	2216.0	1781.90	2124.14	2187.37
	II	$Q(m^3/d)$	232.0	220.0	270.0	148.0
		COD (mg/l)	2124.58	1681.61	2086.21	2101.74
	III	$Q(m^3/d)$	190.0	200.0	232.0	68.0
		COD (mg/l)	2165.77	1712.11	2013.83	2123.18
	IV	$Q(m^3/d)$	1940.0	2121.0	1699.0	1856.0
		COD(mg/l)	2248.36	1773.61	2098.52	2231.97

PM1 = Paper Machine number one production line which produces mainly machine glazed grades (MG)

PM2 = Paper machine number two production line which produces mainly tissue grades.

STREAM I = Discharged white water from the paper machine

STREAM II = Discharged white water after clarification, (floatation) mixed with sediment materials in the clarifier

STREAM III = Discharged white water before clarification (Paper Machine white water mixed with fresh water)

COD = Average total chemical oxygen demand of two grab samples, collected at interval of 3 hrs in (mg/l)

Q = Approximate average hydraulic flow rate of 4-5 measurements take over a period of approximately 3 hrs (m^3/day).

5.3 Sampling and Sample Handling:

The waste water utilized in the laboratory study was collected in batches from the final effluent of the paper mill (Stream IV). The batches were collected at times such that they represent the quality of the mill effluent under different production process conditions. They were handled carefully in a well sealed plastic containers from the mill to Kariobangi sewage treatment plant (in Nairobi) where the study was carried out. New batches were collected at intervals of approximately one week. The temperature of the waste water generated was measured on site at each time of sampling. The required size of a batch was determined before collection according to the required feed flow rate into the reactor and the required dilution factor. The concentrations in different batches as collected of chemical oxygen demand (COD), biological oxygen demand (BOD), sulphate (SO_4^-), total Kjeldahl Nitrogen (TKN, free and saline ammonia (NH_3-N), phosphorous (P). Total suspended solids (TSS) and the PH were measured. The results of such measurements are listed in appendix (A).

5.4 Experimentation:

5.4.1 Start-up and Inoculation Procedure:

The reactor was operated at ambient temperature (average 22°c) and was seeded with a non-pelletized sludge of 64g Vss/l. The sludge was collected from a municipal anaerobic digester treating primary sewage sludge at 35°c, at the Kariobangi Sewage Treatment Plant. Approximately 30% of the reactor volume was filled with the sludge (approximately 8 liters).

The waste water was deficient in the principal inorganic nutrients required for biological growth (Nitrogen and Phosphorous). These were supplemented by addition of chemicals. NH_4Cl and K_2HPO4 were used as nutrients supplements.

The required quantities of the nutrients supplements were determined as follows:

required COD:N:P = 100:5:1 ------------(30)

= 1000:50:10 ------------(31)

1- <u>Nitrogen (N)</u>

1 mole of NH_4Cl weighs (14) + 4(1) + (35.5) = 53.5 gms ------------(32)

Therefore, The amount of NH_4Cl to provide 5 mg N is:

$\frac{53.5 \times 5}{14}$ = 19.1 mg NH_4Cl ------------(34)

From equations 31 & 34, 191.0 mg NH_4Cl is required per 1000 mgCOD

2- <u>Phosphorous (P)</u>

The initial available phosphorous content in the waste water per 1000 mgCOD is:

$\frac{(P_o)x1000\ (mg)}{(COD)}$ ------------(35)

Where: (P_o) = Concentration of phosphorous measured in the raw waste water in (mg/l).

COD = Chemical oxygen demand concentration measured in the raw waste water in (mg/l).

Using equations 2 & 35, the remaining required amount of phosphorous per 1000 mg COD is:

$$[10 - \frac{(P_o)x1000}{(COD)}] \text{ (mg)} \quad \text{------------(36)}$$

1 mole K_2HP04 weighs 2(39) + (1) + (31) + 4(16) = 174.2 gms

Therefore the amount of K_2HP04 to provide

$[10 - \frac{(P_o)x1000}{COD}]$ (mg) is:

$\frac{174.2}{31} x [10 - \frac{(P_o)x1000}{(COD)}]$ mg

For instance, for the batch number 12 (Appendix A), (P_o) = 4.12 mg/l & COD = 1989.23 mg/l. Hence, the initial available phosphorous content in the batch per 1000 mg COD is:

$\frac{4.12x1000}{1989.23}$ = 2.07P.

Therefore, the remaining required amount of phosphorous per 1000 mgCOD is:

10 - 2.07 = 7.92 mgP

The amount of K_2HP04 to provide 7.92 mgP is:

$\frac{174.2x7.92}{31}$ = 44.55 mg K_2HP04

44.55 should be added per 1000 mg COD

But the waste water COD concentration is 1989.23 mg/l.

Therefore, the amount of K_2HP04 to be added per litre

$$= 44.55 \times \frac{\underline{1989.23}}{1000} = 88.6 \text{ mg } K_2HP04/l$$

The average pH of the waste water was in the region of pH 5.275 (5.3) This necessitates addition of alkalinity to the feed to adjust the pH to a value close to neutral, a requirement for successful operation of the anaerobic process (see section 2.6.5) The alkalinity source of the study was through the addition of $NaHCo_3$. Each waste water batch when brought to the laboratory was mixed thoroughly and a sample of 100 ml was tested for the pH. $NaHCo_3$ was added to the sample slowly until its pH was brought to pH 7. Accordingly, the amount of $NaHCo_3$ required to neutralize the feed was calculated. For instance, for a raw waste water of pH5 (batch No.9), approximately 0.199mg $NaHCo_3$ was required to bring the pH of a 100ml sample to pH7 Consequently, 1.99mg $NaHCO_3$/l would be added to bring the feed pH to pH7. In addition to N,P and alkalinity a trace metal solution (2ml/L) as suggested by Zehnder and Wuhrmann (1977) (Section 2.6.5) for enrichment of cultures of methanogenic bacteria, was added to the feed over the initial period of operation. The addition of this solution was later stopped due to shortage of chemicals. The constituents of the trace metal solution are shown in table 5.2.

Table 5.2 : Constituents of the trace metal solution

COMPOUND	QUANTITY
Ferric chloride ($FeCl_2 4H_{20}$)	2000 mg/l
Boric acid (H_3BO_3)	50 mg/l
Cupper chloride ($CuCl_2.2H_2O$)	40 mg/l
Manganeze chloride ($MnCl_2.4H_2$)	500 mg/l
Aluminuim chloride ($AlCl_3$)	30 mg/l
Nicle chloride ($NiCl_2.6H_2o$)	500 mg/l
Conc. HCl	1 ml
Distilled Water	To make 1 Lit

The first 4 waste water batches were required to be diluted for the sake of acclimatizing the bacteria to the substrate. Meanwhile, the amount of chemicals added were determined according to the adopted dilution factors.

To acclimatize the sludge to the substrate, the feed was applied initially at low COD concentration 500 mgCOD/l (as recommended by Souza, 1987 (Section 2.8.1) of diluted

PLATE 5.3 Reaction Operation at the Kariobangi Sewage Treatment Works

waste water at a flow rate of 0.63 l/hr (corresponds to 24 hours hydraulic retention time). Thereafter, the feed rate was maintained at 0.63l/hr and the feed concentration increased step wise from 500 mgCOD/l through 1000, 1500 to 2100 mgCOD/l. These concentrations were corresponding to organic loading rates (O.L.R) of 0.5, 1, 1.5 and 2.1 kg COD/m^3/day respectively. The COD concentration 2100 mg/l corresponds to the average COD concentration of the final effluent from the mill, therefore, it was assumed to be the design feed concentration. The required feed concentration was obtained by diluting the batches of strong waste with tap water. At each step of loading the feed concentration was held constant for approximately two weeks. The reactor performance was monitored through the measurement of the influent COD, effluent COD, gas production rate, reactor temperature as well as observing the settleability of solids above the sludge bed through the reactor perspex glass window. This was done every two to three days throughout the reactor operation period.

5.4.2 Reactor Loading and Profiling:

Once the design feed concentration had been reached i.e. 2100mg/l the hydraulic retention time was decreased stepwise to increase the loading on the rector from 24 hrs through 20,15,10,7,5,4,3 and ultimately to 2.5 hrs by increasing the hydraulic flow rate. These retention times were corresponding to organic loading rates (O.L.R) of 2.1, 2.56, 3.28, 4.93, 6.93, 9.54, 11.71, 15.17 and 19.02 kgCOD/m^3/day respectively. The reactor retention time and consequently the organic loading rate was changed once a steady state condition of the reactor performance had been reached. The steady state condition was assumed to have been reached when the COD removal efficiency and the gas production rate were approximately near-constant.

Fig 5.2 shows the time organic loading sequence. The slow rate of increase in load over the initial period should be noted in particular.

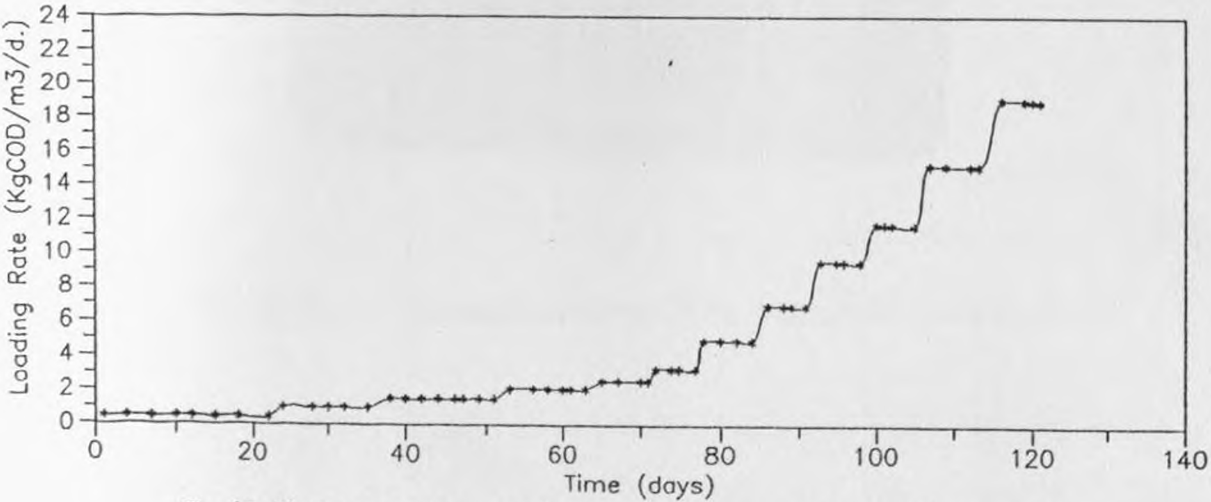


Fig (5.2) Sequaence of increase in organic loading rate for the reactor.

AT steady state conditions of the last five steps in load (i.e. which corresponds to 7,5,4,3 and 2.5 hrs retention times) the concentrations of different parameters were measured along the reactor height (reactor profiling). At each step of the loads 6.93, 9.54, 11.71, 15.17, and 19.02 Kg/m3/day the analysis of filtered COD, short chain volatile fatty acids VFAs (Acetic and Propionic Acids), sulphate (SO_4^-), pH organic nitrogen (Org.N) and free and saline Ammonia (NH_3-N) and total suspended solids (TSS).

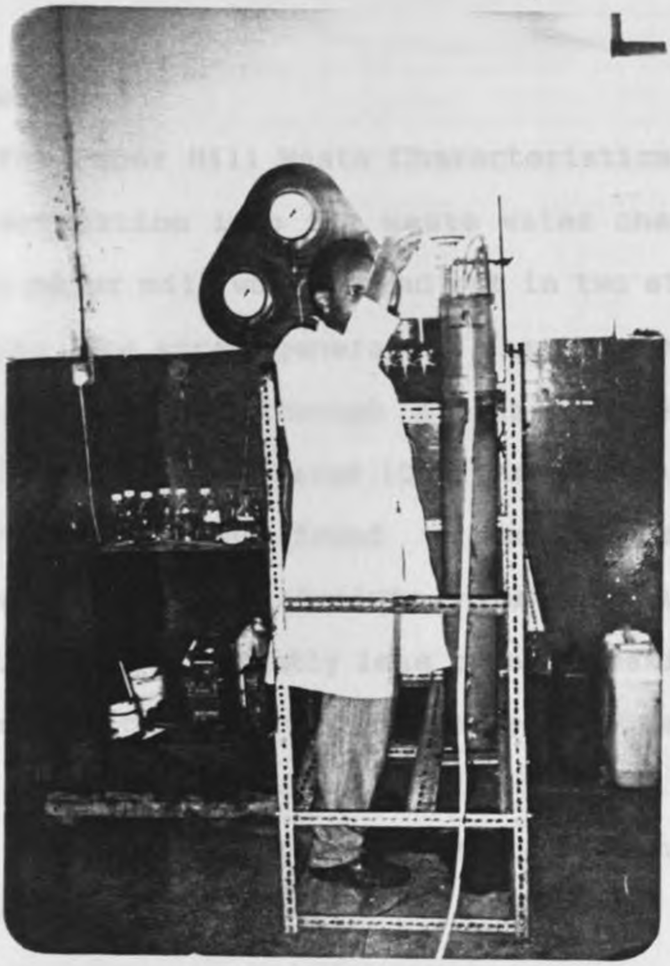


PLATE 5.4 Measurement of the Reactor Temperature

CHAPTER SIX

RESULTS AND DISCUSSIONS

6.1 Results:

6.1.1 The Paper Mill Waste Characteristics:

The investigation into the waste water characteristics from the paper mill was carried out in two steps. In the first step, the stream generating the maximum pollutional load was identified through preliminary tests for the total COD and the discharge (Q). As a result, the final effluent stream was found to be the stream which generates the largest absolute volume and always have a COD concentration slightly less than the maximum absolute COD concentration. It was, therefore, selected as a source for the waste water utilized in the study. The results on the preliminary tests are presented in table 5.1 (Section 5.2).

In the second step, the waste water batches collected for the laboratory study were analyzed to determine the characteristics of the waste water in terms of the COD, BOD_5, $SO_4^{=}$, TKN, NH_3-N, P, TSS concentrations and the pH. The results of such analysis are presented in appendix A.

A summary of the results showing the range of variation of different waste water parameters is shown in table 6.1.

Table 6.1: Characteristics of the mill final effluent (stream IV).

Parameter	Concentration
COD	Approx. 1900-2300 (mg/l)
BOD_5	Approx. 1100-1300 (mg/l)
$SO^{=}_4$	Approx. 87-164 (mg/l)
TSS (0.4 um)	Approx. 500-900 (mg/l)
TKN	Approx. 11-26 (mg/l)
P	Approx. 3-5 (mg/l)
Flow	Approx. 1700-2100 (m^3/d)
pH	Approx. 4-5
Temperature	Approx. 22-28°c
NH_3-N	0.0 (mg/l)

It should be noted that, these results covers all possible variations in the characteristics of the mill effluent over a period of approximately 4 months.

Analysis to determine the VFAs (acetic and propionic acids) concentration in the reactor influent was carried out later to ascertain their variation along the reactor length at steady state conditions. The results showed that the acids comprise approximately 43 percent of the COD. Fig 6.1 shows a COD/BOD_5 correlation of the mill effluent. The COD/BOD_5 relationship is represented by the best fit line equation:

$$BOD_5 = 0.59COD + 2.24$$

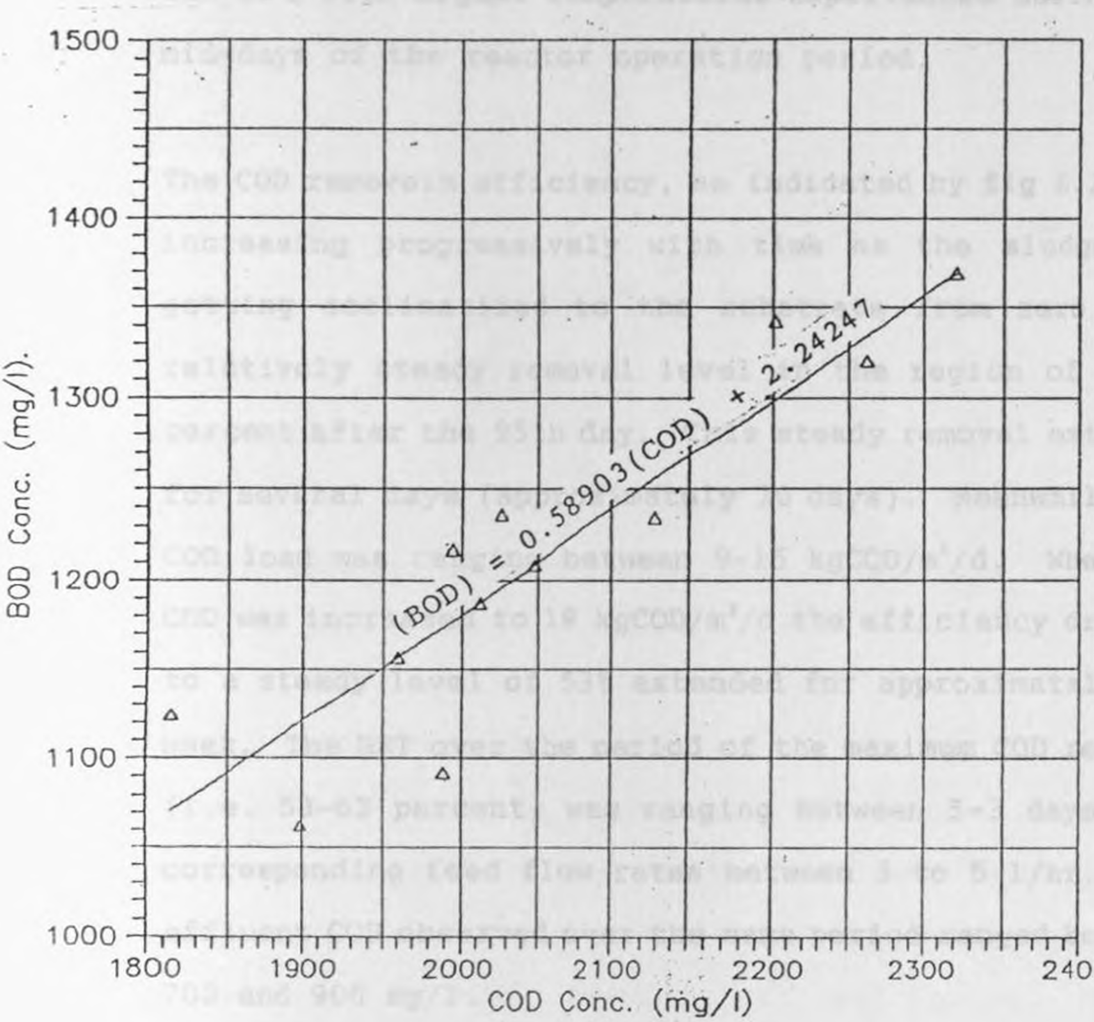


Fig 6.1: COD/BOD5 Correlation result of the paper mill effluent

6.1.2 Reactor Conversion Efficiency:

The reactor performance was assessed in terms of the soluble COD removal potential in the waste which could be attained if a post separation of suspended solids is implemented. The percentage COD removal was observed over a period of approximately 4 months (reactor operation period) during which the COD load was increased stepwise from 0.5 to 19 kgCOD/m^3/d. The hydraulic retention time (HRT) was correspondingly reduced from 24 to 2.5 hrs. The reactor temperature ranged between 19 and 22°c with higher temperatures experienced during the mid-days of the reactor operation period.

The COD removals efficiency, as indicated by fig 6.2, was increasing progressively with time as the sludge was getting acclimatized to the substrate from zero to a relatively steady removal level in the region of 58-63 percent after the 95th day. This steady removal extended for several days (approximately 20 days). Meanwhile the COD load was ranging between 9-15 kgCOD/m^3/d. When the COD was increased to 19 kgCOD/m^3/d the efficiency dropped to a steady level of 53% extended for approximately one week. The HRT over the period of the maximum COD removal (i.e. 58-63 percent) was ranging between 5-3 days with corresponding feed flow rates between 3 to 5 l/hr. The effluent COD observed over the same period ranged between 700 and 900 mg/l.

The results of the percentage COD removal together with the operating conditions over the period of the reactor operation are presented in fig 6.2 and Appendices B-1, B-2, B-3, and B-4.

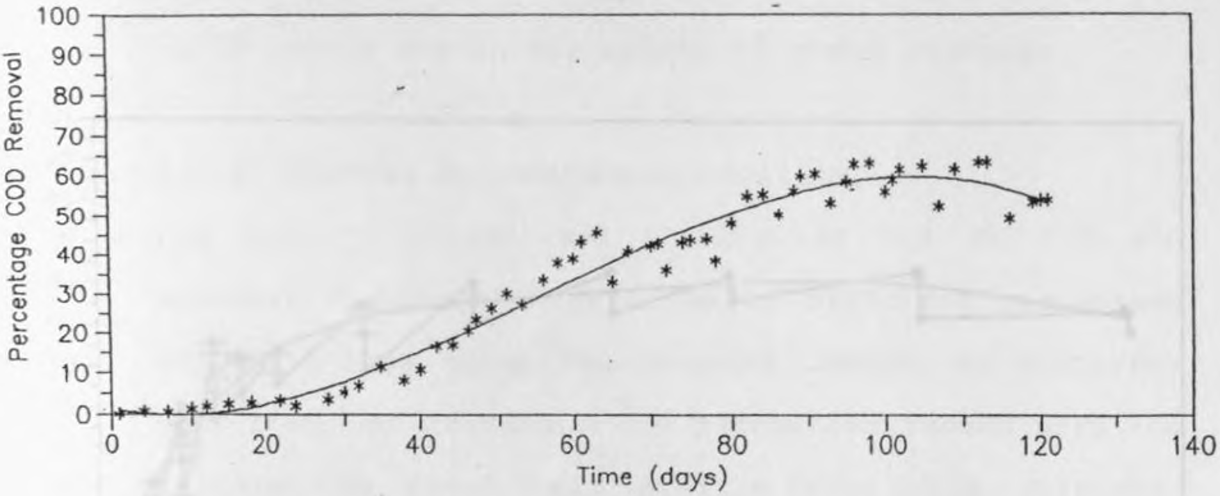


Fig 6.2 : Percentage COD removal observed in the reactor

6.1.3 Maximum Loading Rate:

The maximum reactor organic loading rate (OLR) was assessed in terms of the maximum COD load (expressed as $kg/m^3/day$) which could be applied to the reactor without causing any adverse effect in its performance. During the first period of the reactor operation (up to 63rd day) the COD load was increased (stepwise) via increasing the COD concentration in the feed upto 2100mg/l (average COD of the mill final effluent). Thereafter, the feed concentration was kept constant at 2100 g/l and the (O.L.R) was increased by increasing the feed flow rate.

The data on the COD removals efficiency versus the (O.L.R) are presented in appendix B and fig 6.3.

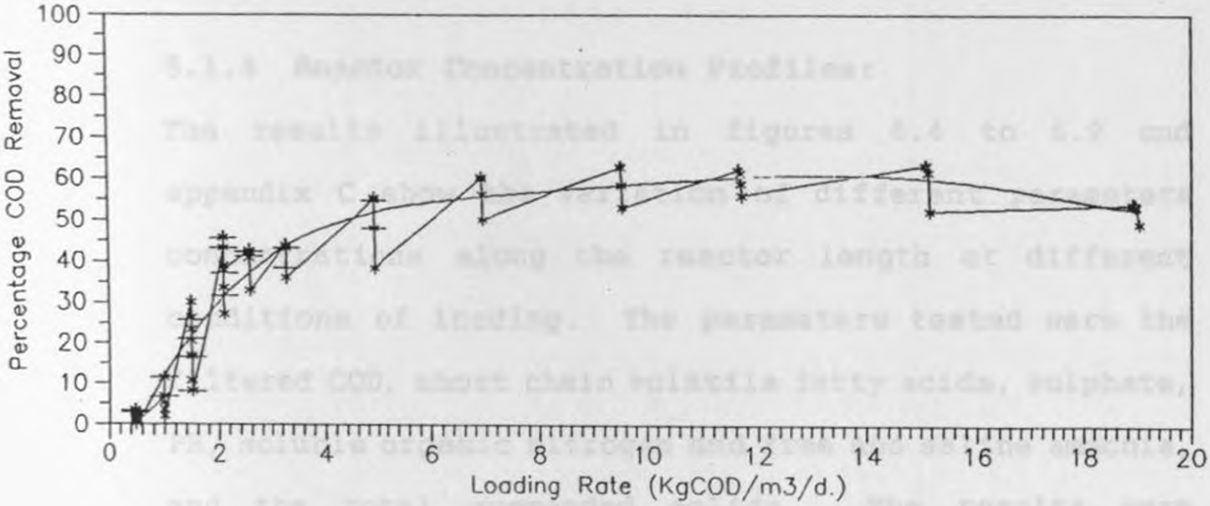


Fig 6.3 : Percentage COD removal plotted versus organic loading rate

Fig 6.3 above comprises of two graphs, a best fit curve and a step graph. The best fit curve shows that the COD removal rate was generally increasing progressively with the increase in the (O.L.R) upto a level of around 58 percent attained under a load 9 kg/COD/m^3/day. Thereafter, the removal rate was steady between 58 and 63 percent at loads upto 15 kg COD/m^3/day. When the OLR was increased to around 19 kgCOD/m^3/day, the removal rate dropped to 53% at steady state.

Therefore, it can be concluded that the most desirable optimum load range is around 12-15 kgCOD/m^3/day (HRT = 3 hrs). The data also shows that, as indicated by the step graph in fig 6.3, over the period of each step in load the COD removal rate was initially decreasing for a while and then was increasing again up to a steady level. This is obviously due to the effect of shock loading.

6.1.4 Reactor Concentration Profiles:

The results illustrated in figures 6.4 to 6.9 and appendix C show the variation of different parameters concentrations along the reactor length at different conditions of loading. The parameters tested were the filtered COD, short chain volatile fatty acids, sulphate, PH, soluble organic nitrogen and free and saline ammonia, and the total suspended solids. The results were obtained at steady state conditions of the loads 6.9, 9.5, 11.6, 15 and 19 kgCOD/m^3day on the 91st, 58th, 105th, 113th, and 121st days respectively. The steady state conditions were assumed when the daily gas production and the COD removal efficiency reached an almost constant level.

6.1.4.1 The Filtrate COD:

The data on the filterate COD profiles at the different loading conditions mentioned above are presented in figs 6.4.1 to 6.4.5 and appendix C-1

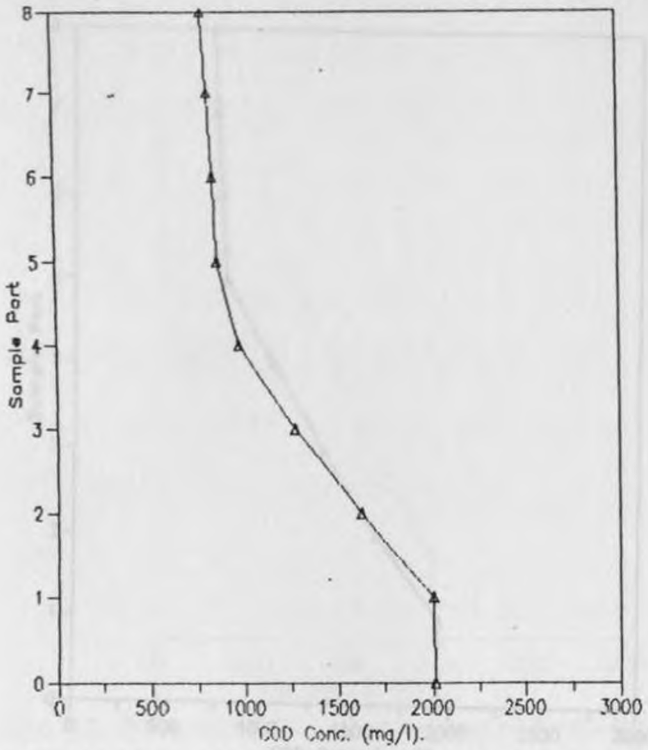


Fig 6.4.1 : Filtered COD concentration profile on the 91st day.
O.L.R. = 6.907 KgCOD/m3/d.

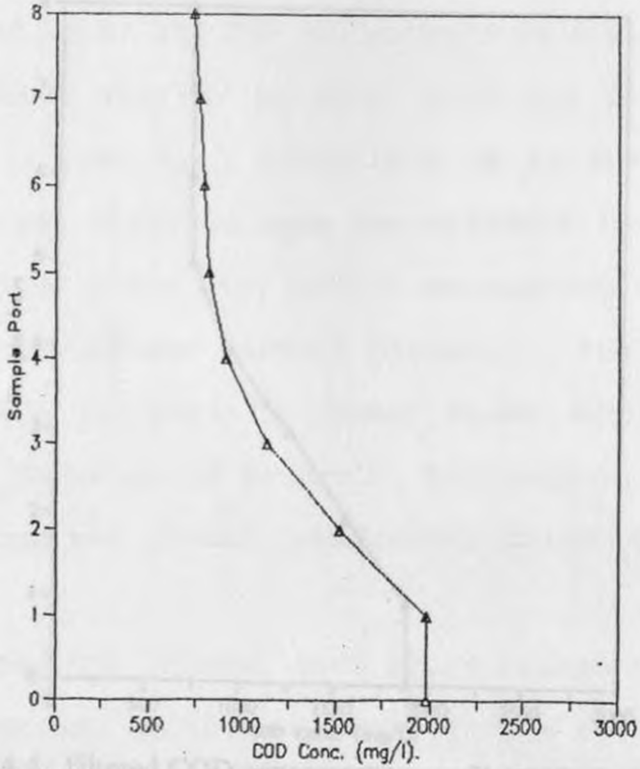


Fig 6.4.2 : Filtered COD concentration profile on the 98th day.
O.L.R = 9.497 Kg/m3/d.

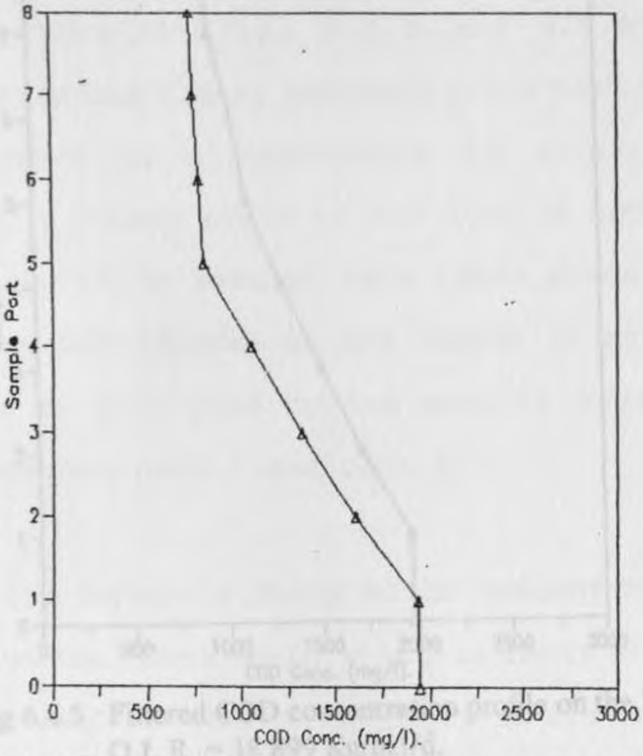


Fig 6.4.3 : Filtered COD concentration profile on the 105th day.
O.L.R. = 11.641 kgCOD/m3/d.

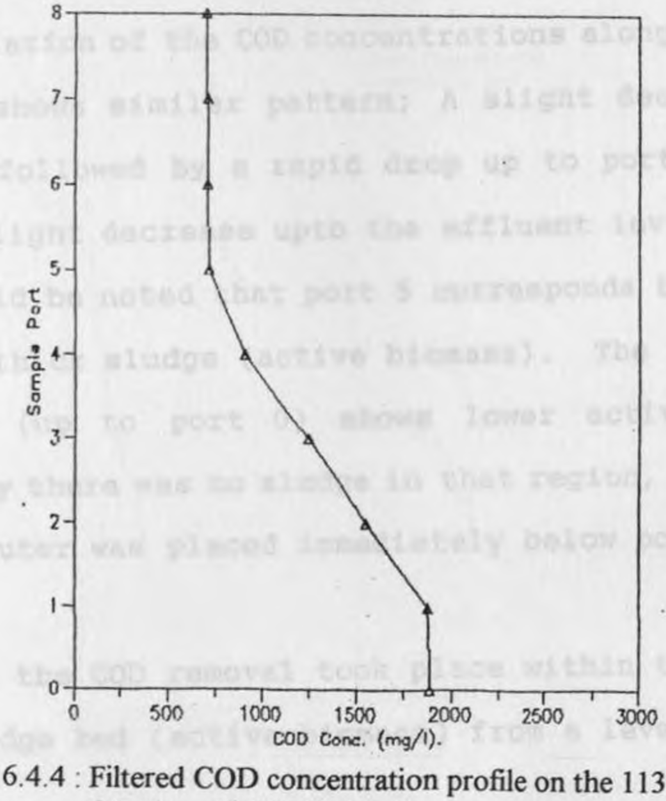


Fig 6.4.4 : Filtered COD concentration profile on the 113th day.
O.L.R. = 15.092 Kg/m3/d.

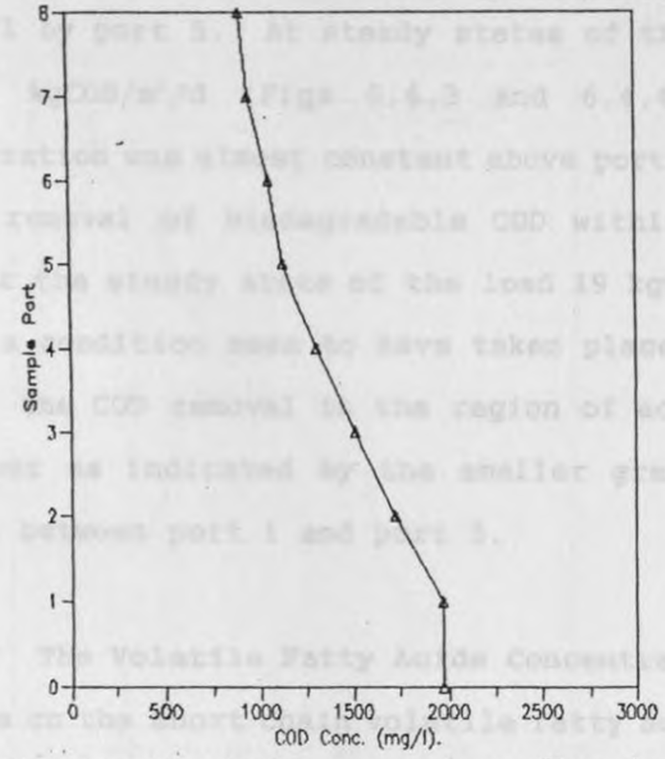


Fig 6.4.5 : Filtered COD concentration profile on the 121st day.
O.L.R. = 18.899 Kg/m3/d.

The data show clearly that within the range of load used the variation of the COD concentrations along the reactor length shows similar pattern; A slight decrease up to port 1 followed by a rapid drop up to port 5 and then again slight decrease upto the effluent level (port 8). It should be noted that port 5 corresponds to the height of the thick sludge (active biomass). The region below port 1 (up to port 0) shows lower activity because actually there was no sludge in that region, the influent distributer was placed immediately below port 1.

Most of the COD removal took place within the height of the sludge bed (active biomass) from a level of between

1950 and 2000 mg/l at port 1 to a value between 700-1000mg/l by port 5. At steady states of the loads 11.6 and 15 kgCOD/m^3/d (Figs 6.4.3 and 6.4.4) the COD concentration was almost constant above port 5 indicating higher removal of biodegradable COD within the sludge bed. At the steady state of the load 19 kgCOD/m^3/d (Fig 6.4.5) a condition seem to have taken place because the rate of the COD removal in the region of active biomass was lower as indicated by the smaller gradient of the profile between port 1 and port 5.

6.1.4.2 The Volatile Fatty Acids Concentration:

The data on the short chain volatile fatty acids (acetate and propionate) concentration profiles are presented figs 6.5.1 to 6.5.5 and appendices C-2 and C-3.

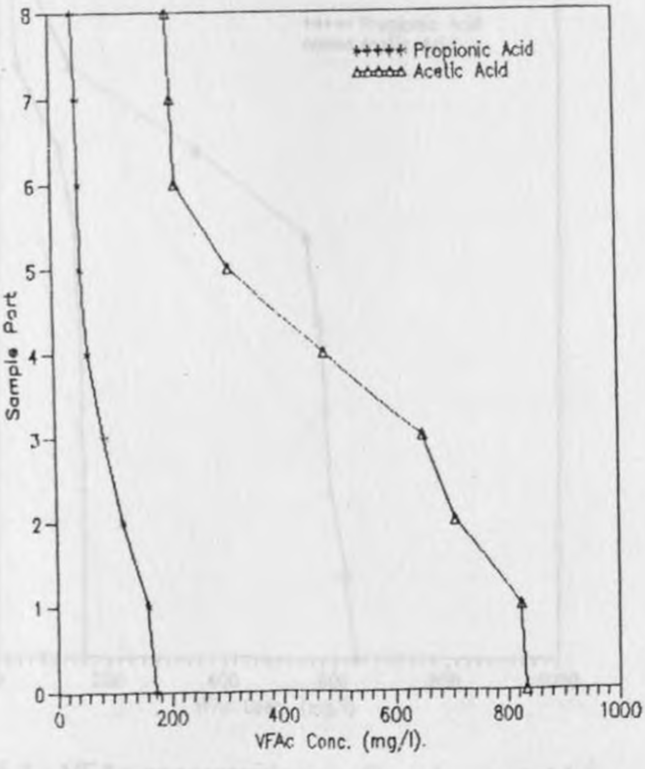


Fig 6.5.1 : VFAs concentration profile - Acetic Acid & propionic Acid on the 91st day. O.L.R. = 6.907 KgCOD/m3/d.

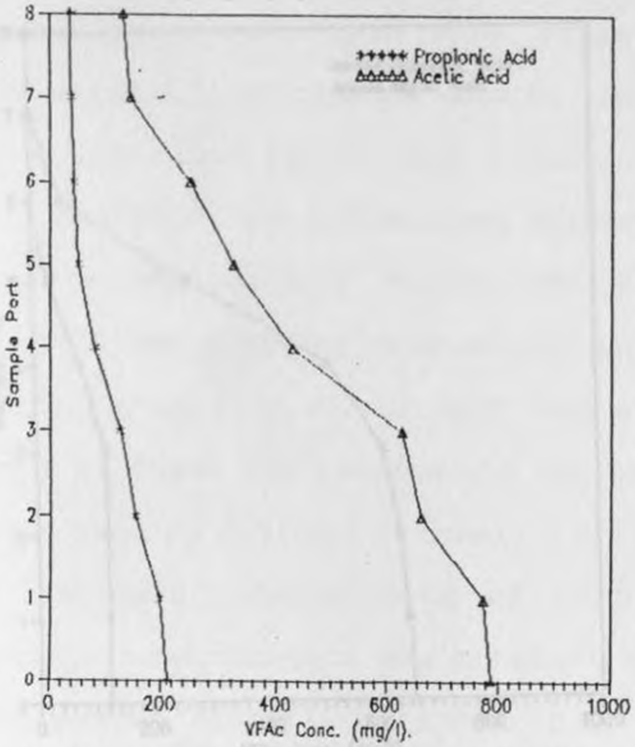


Fig 6.5.2 : VFAs concentration profile - Acetic Acid & propionic Acid on the 98th day. O.L.R. = 9.497 KgCOD/m3/d.

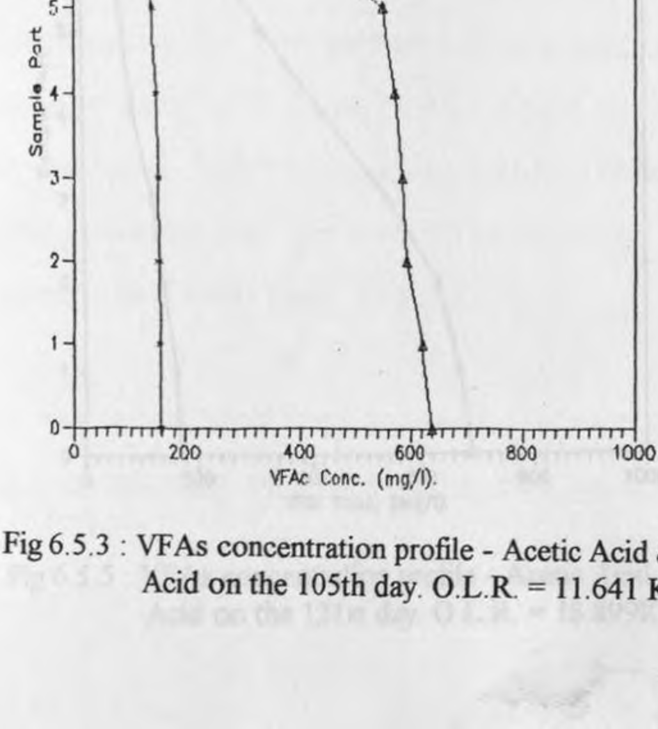


Fig 6.5.3 : VFAs concentration profile - Acetic Acid & propionic Acid on the 105th day. O.L.R. = 11.641 KgCOD/m3/d.

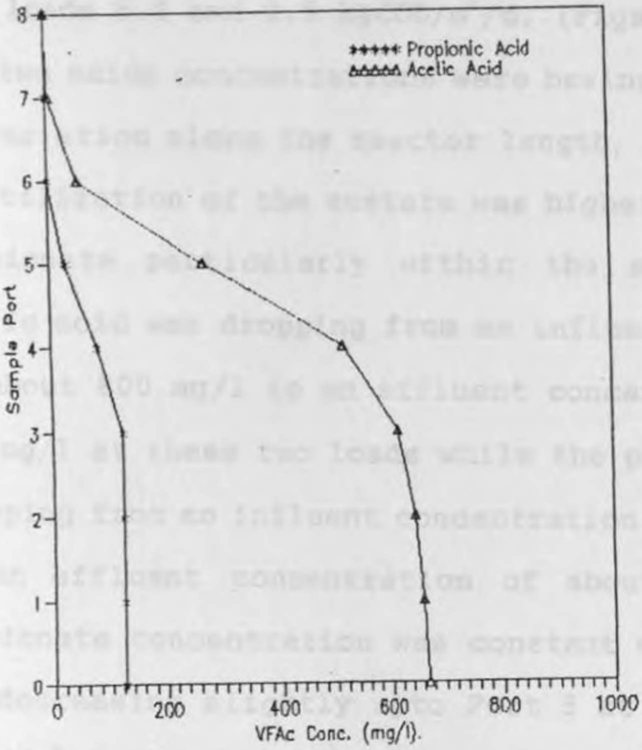


Fig 6.5.4 : VFAs concentration profile - Acetic Acid & Propionic Acid on the 113th day. O.L.R. = 15.092 KgCOD/m3/d.

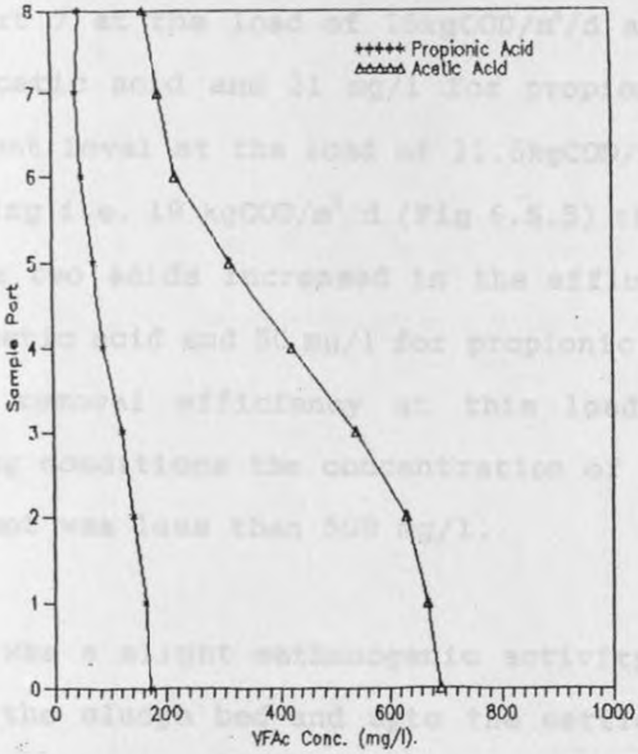


Fig 6.5.5 : VFAs concentration profile - Acetic Acid & propionic Acid on the 121st day. O.L.R. = 18.899KgCOD/m3/d.

The acetic and the propionic acids comprise approximately 43 percent of the COD in the feed. At steady state of the loads 6.9 and 9.5 kgCOD/m^3/d. (Figs 6.5.1 and 6.5.2) the two acids concentrations were having the same pattern of variation along the reactor length, however, the rate of utilization of the acetate was higher than that of the propionate particularly within the sludge bed. The acetic acid was dropping from an influent concentrations of about 800 mg/l to an effluent concentration of about 180 mg/l at these two loads while the propionic acid was dropping from an influent concentration of about 200 mg/l to an effluent concentration of about 40 mg/l. The propionate concentration was constant while the acetate was decreasing slightly upto Port 5 at the load of 11.6 kgCOD/m^3/d (Fig 6.5.3) and upto port 3 at the load of 15 kgCOD/m^3/d (Fig 6.5.4). Then both acids dropped to zero by port 7 at the load of 15kgCOD/m^3/d and upto 56 mg/l for acetic acid and 21 mg/l for propionic acid at the effluent level at the load of 11.6kgCOD/m^3/d. At higher \loading i.e. 19 kgCOD/m^3/d (Fig 6.5.5) the concentration of the two acids increased in the effluent, 167.5 mg/l for acetic acid and 50 mg/l for propionic acid indicating lower removal efficiency at this load. At all the loading conditions the concentration of the VFAs in the effluent was less than 500 mg/l.

There was a slight methanogenic activity at the region above the sludge bed and upto the settler indicated by the acetate utilization in that region under the different loading rates. This activity was minimal at the load of 19 kgCOD/m^3/d.

6.1.4.3 The Sulphate Concentration:

The data on sulphate concentration profiles are illustrated in figs 6.6.1 to 6.6.5 and appendix C-4 .

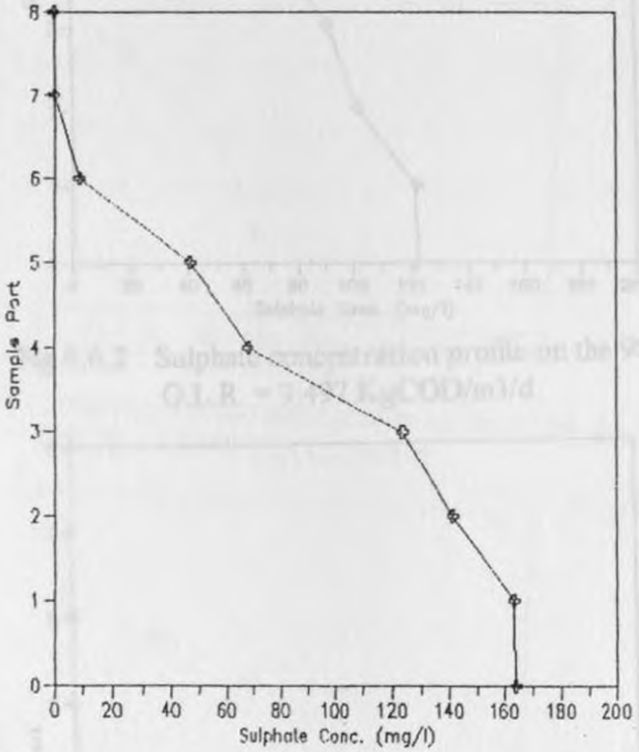


Fig 6.6.1 : Sulphate concentration profile on the 91st day.
O.L.R. = 6.907 KgCOD/m3/d.

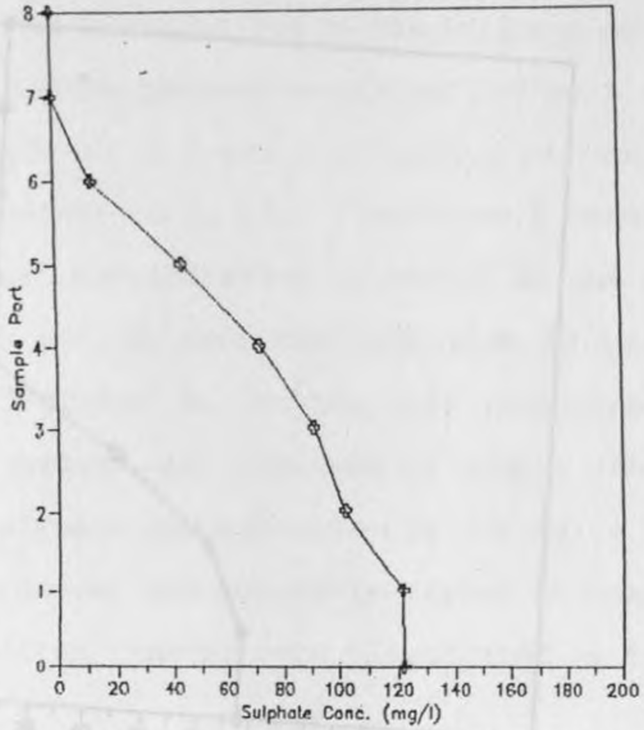


Fig 6.6.2 : Sulphate concentration profile on the 98th day.
O.L.R. = 9.497 KgCOD/m3/d.

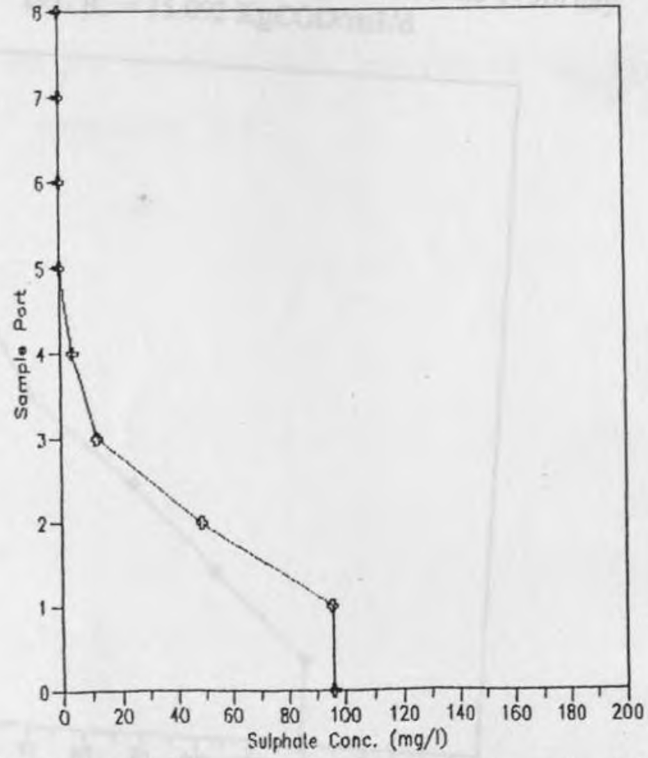


Fig 6.6.3 : Sulphate concentration profile on the 105th day.
O.L.R. = 11.641 KgCOD/m3/d.

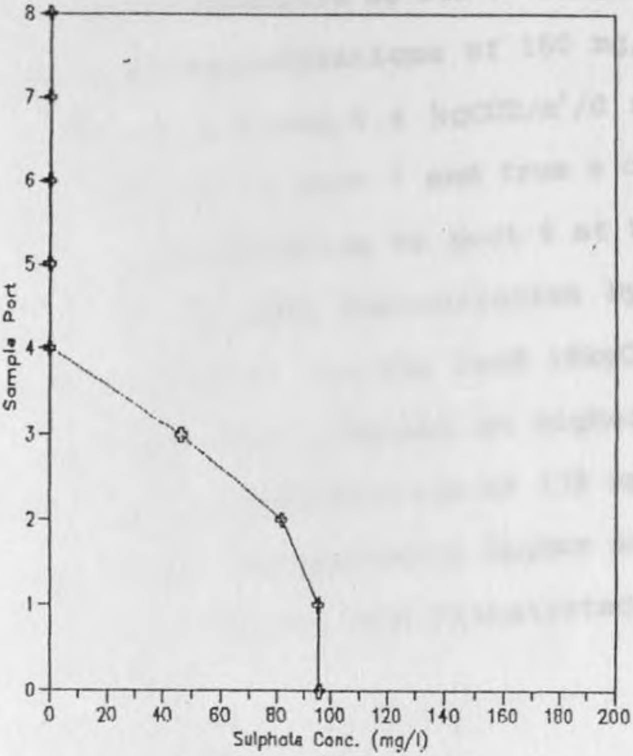


Fig 6.6.4 : Sulphate concentration profile on the 113th day.
O.L.R. = 15.092 KgCOD/m3/d.

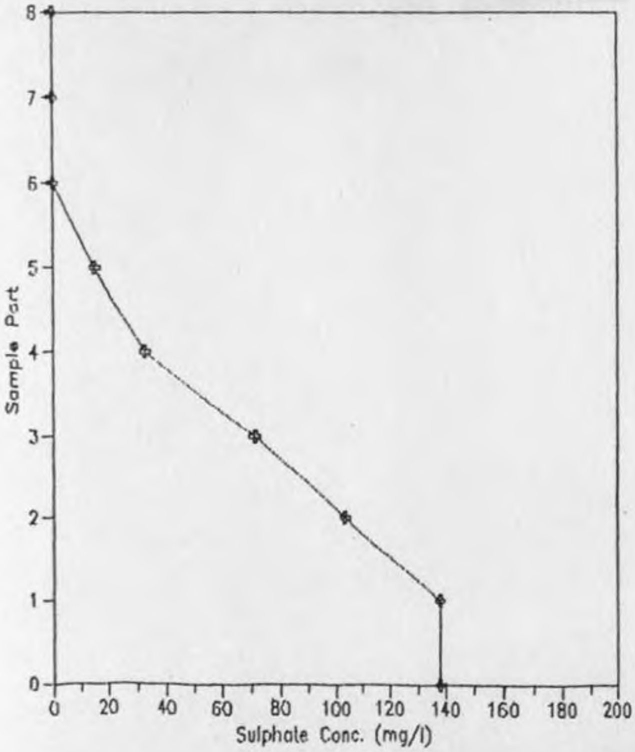


Fig 6.6.5 : Sulphate concentration profile on the 121st day.
O.L.R. = 18.899 KgCOD/m3/d.

As it can be observed, the sulphate was completely removed at steady state conditions of the different loading rates irrespective of its influent concentration. It dropped from concentrations of 160 mg/l and 120 mg/l at the loads of 6.9 and 9.4 kgCOD/m^3/d respectively to zero concentration by port 7 and from a concentration 96 mg/l to zero concentration by port 5 at the load of 11.6 kgCOD/m^3/d and to zero concentration by port 3 at the load of 15kgCOD/m^3/d. At the load 19kgCOD/m^3/d complete sulphate removal was attained at higher level (port 6) from an influent concentration of 139 mg/l. The rate of sulphate removal was generally higher as compared to the volatile acids removal rate illustrated in figs 6.5.1 to 6.5.5.

6.1.4.4. The pH :

The data on pH profile are presented in figs 6.7.1 to 6.7.5. and appendix C-5.

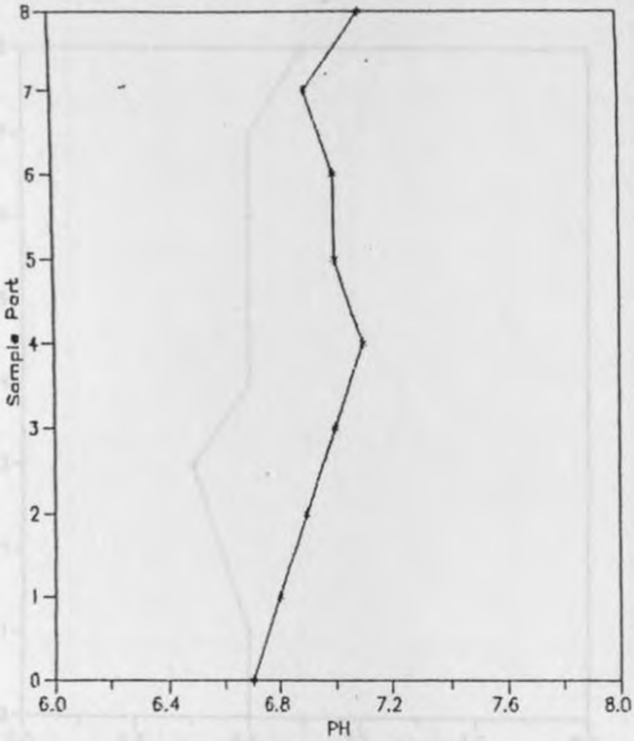


Fig 6.7.1 : pH profile on the 91st day.
O.L.R. = 6.907 Kg/m3/d.

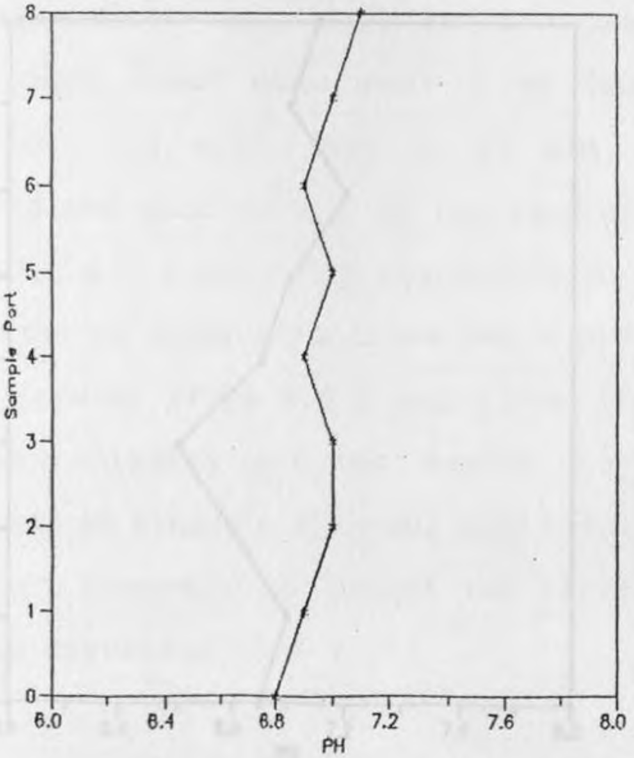


Fig 6.7.2 : pH profile on the 98th day.
O.L.R. = 9.497 KgCOD/m3/d.

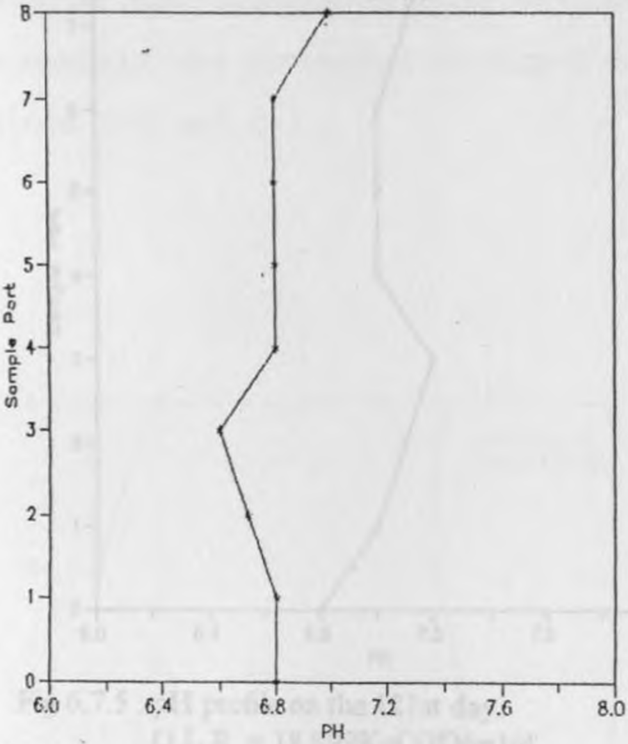


Fig 6.7.3 : pH profile on the 105th day.
O.L.R. = 11.641 KgCOD/m3/d.

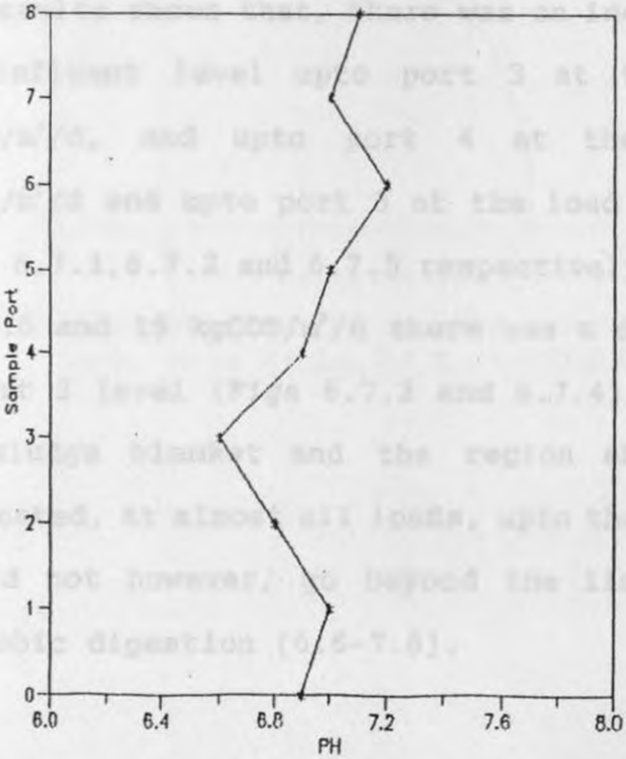


Fig 6.7.4 : pH profile on the 113th day.
O.L.R. = 15.092KgCOD/m3/d.

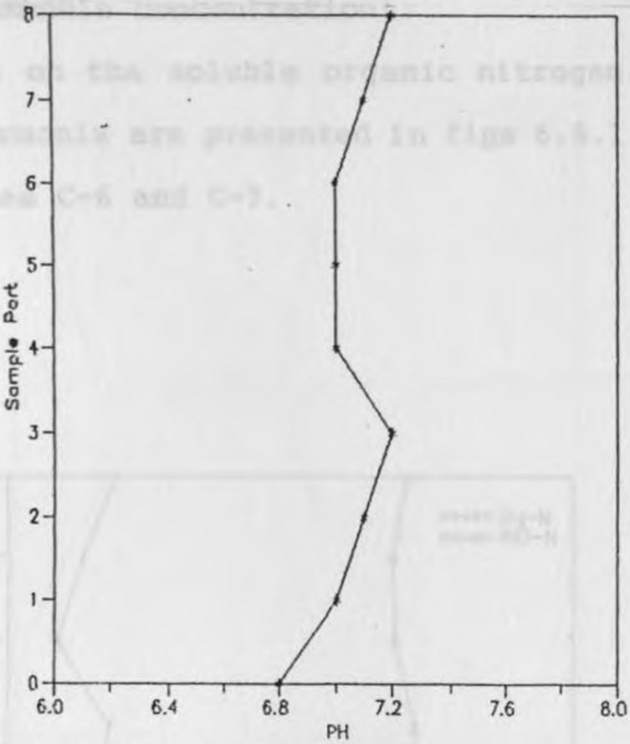


Fig 6.7.5 : pH profile on the 121st day.
O.L.R. = 18.899KgCOD/m3/d.

The results shows that, there was an increase in PH from the influent level upto port 3 at the load of 6.4 kgCOD/m^3/d, and upto port 4 at the of load 9.46 kgCOD/m^3/d and upto port 3 at the load of 19kg COD/m^3/d (Figs 6.7.1,6.7.2 and 6.7.5 respectively). At the loads of 11.6 and 15 kgCOD/m^3/d there was a decrease in PH up to port 3 level (Figs 6.7.3 and 6.7.4). At the top of the sludge blanket and the region above it, the PH fluctuated, at almost all loads, upto the effluent level. It did not however, go beyond the limits optimum for anaerobic digestion (6.6-7.6).

6.1.4.5 The Soluble Organic Nitrogen and Free and Saline Ammonia concentration:

The data on the soluble organic nitrogen and free and saline ammonia are presented in figs 6.8.1 to 6.8.5. and appendices C-6 and C-7.

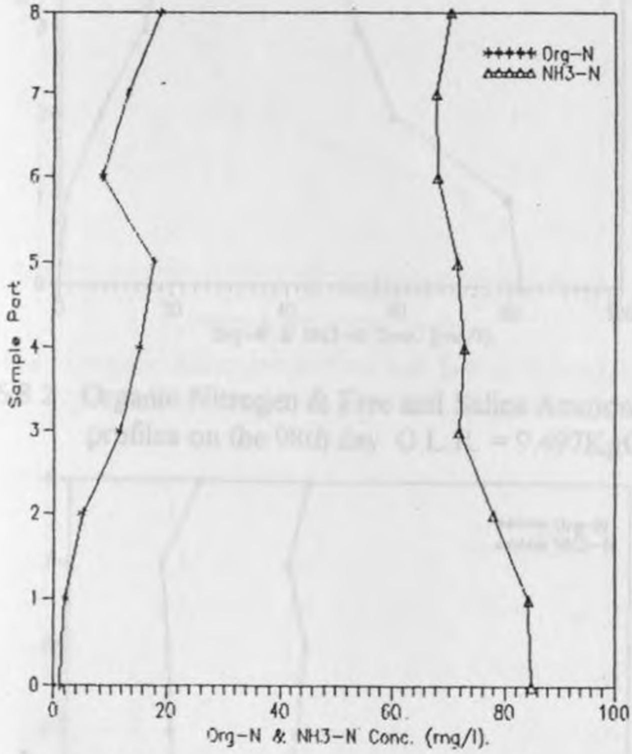


Fig 6.8.1 : Organic Nitrogen & Free and Saline Ammonia concentration profiles on the 91st day. O.L.R. = 6.907KgCOD/m3/d.

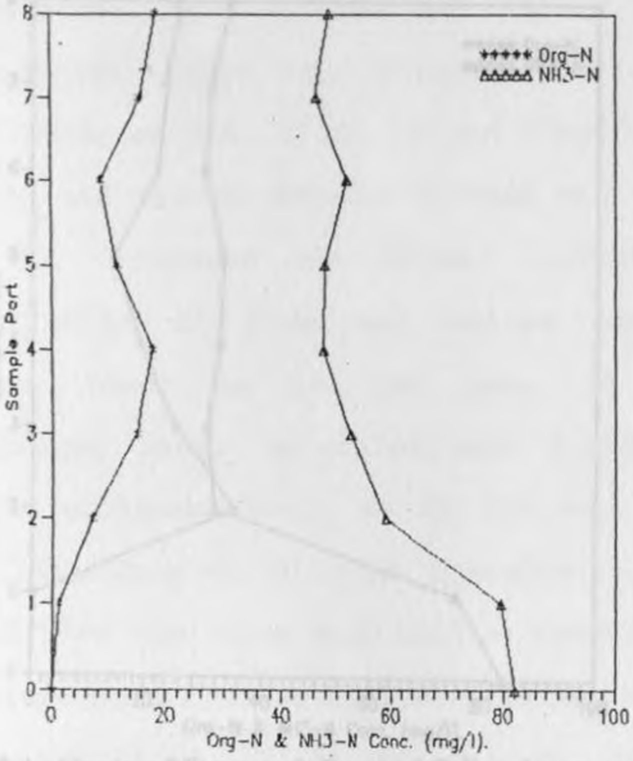


Fig 6.8.2 : Organic Nitrogen & Free and Saline Ammonia concentration profiles on the 98th day. O.L.R. = 9.497KgCOD/m3/d.

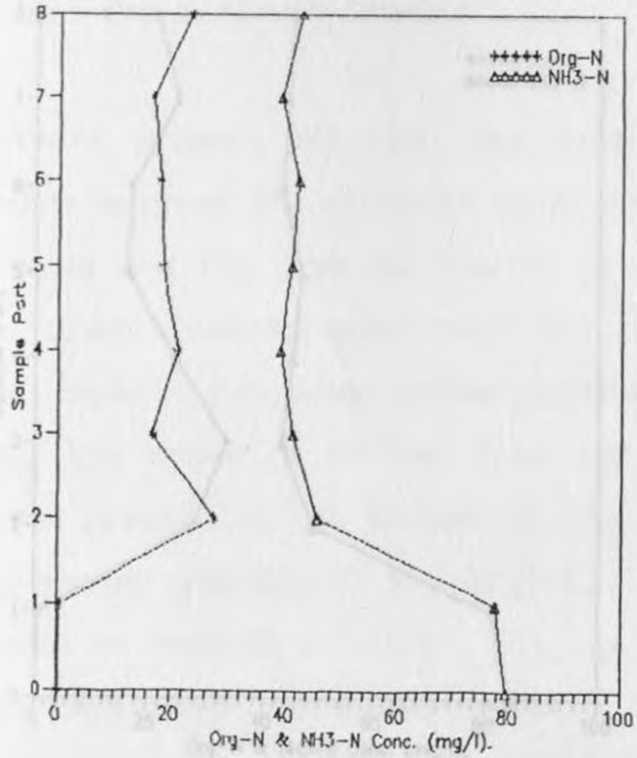


Fig 6.8.3 : Organic Nitrogen & Free and Saline Ammonia concentration profiles on the 105th day. O.L.R. = 11.641 KgCOD/m3/d.

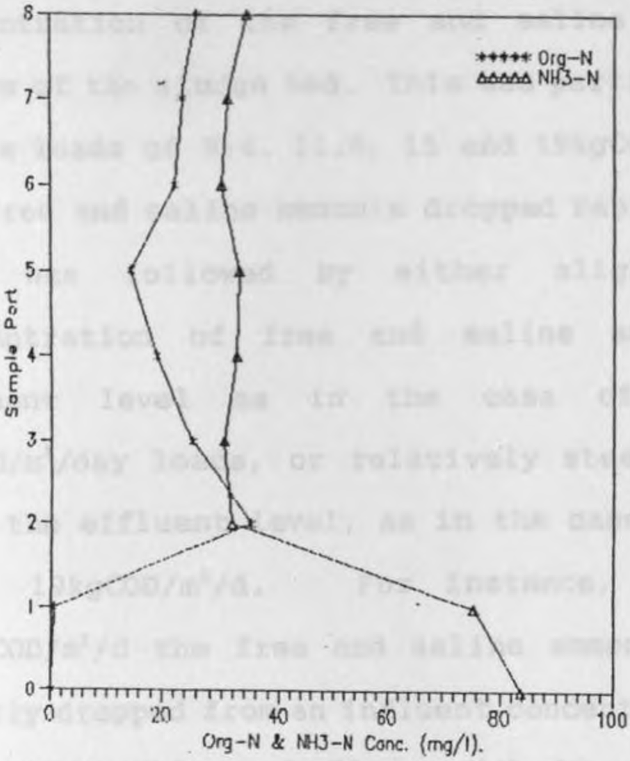


Fig 6.8.4 : Organic Nitrogen & Free and Saline Ammonia concentration profiles on the 113th day. O.L.R. = 15.092 KgCOD/m3/d.

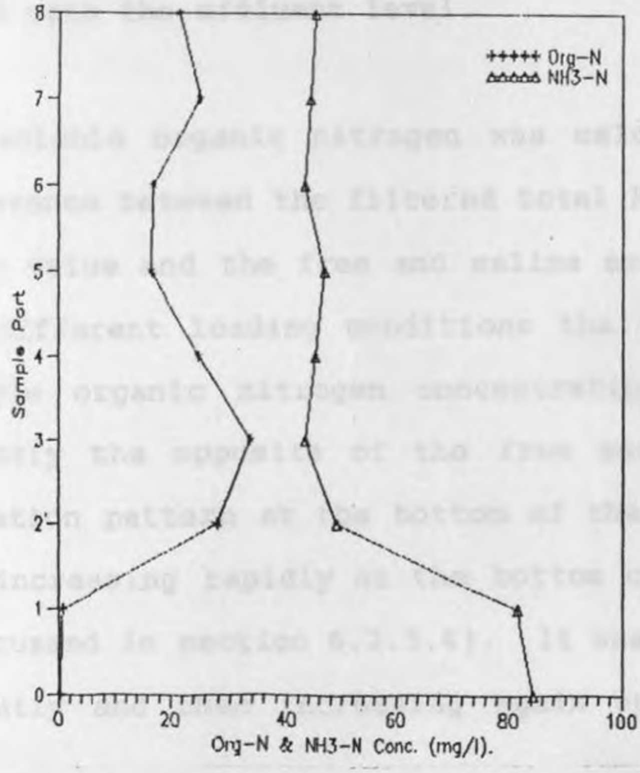


Fig 6.8.5 : Organic Nitrogen & Free and Saline Ammonia concentration profiles on the 121st day. O.L.R. = 18.899 KgCOD/m3/d.

It can be observed at the different loading conditions that there was a rapid drop in the steady state concentration of the free and saline ammonia at the bottom of the sludge bed. This was particularly apparent at the loads of 9.4. 11.6, 15 and 19kgCOD/m^3/day whereas the free and saline ammonia dropped rapidly upto port 2. This was followed by either slight decrease in concentration of free and saline ammonia upto the effluent level as in the case of the 6.9, 9.4 kgCOD/m^3/day loads, or relatively steady concentration upto the effluent level, as in the case of the 11.6, 15 and 19kgCOD/m^3/d. For instance, at the load of 15kgCOD/m^3/d the free and saline ammonia concentration firstly dropped from an influent concentration of 83mgN/L to concentration of 31 mg N/L by part 2 then the concentration was relatively steady at a value between 30 to 33 upto the effluent level.

The soluble organic nitrogen was calculated from the difference between the filtered total Kjeldahl nitrogen (TKN) value and the free and saline ammonia value. At the different loading conditions the variation in the soluble organic nitrogen concentration was following directly the opposite of the free and saline ammonia variation pattern at the bottom of the reactor i.e. it was increasing rapidly at the bottom of the sludge bed (discussed in section 6.2.3.4). It was then decreasing slightly and then increasing again upto the effluent level. For instance, at the load of 15kgCOD/m^3/d, the concentration of the soluble nitrogen increased rapidly from zero concentration in the influent to a concentration of 35 mg N/L by port 2 then it decreased to a concentration of 14 mg N/L by port 5 then increased again upto a concentration of 26 mg/l at the effluent level.

It should be noted that, the rate of change in the free and saline ammonia and the soluble organic nitrogen concentrations (decrease in saline ammonia and increase in the organic nitrogen) at the bottom of the sludge bed was increasing with increasing organic load upto a maximum recorded at the load of 15kgCOD/m^3/d. When the load was further increased i.e. to 19kgCOD/m^3/d the rate decreased, indicating, a conditions of over loading.

6.1.4.6. The Total Suspended Solids Concentration:

The data on the suspended solids concentration profiles are illustrated in figs 6.9.1 to 6.9.5. and appendix C-8.

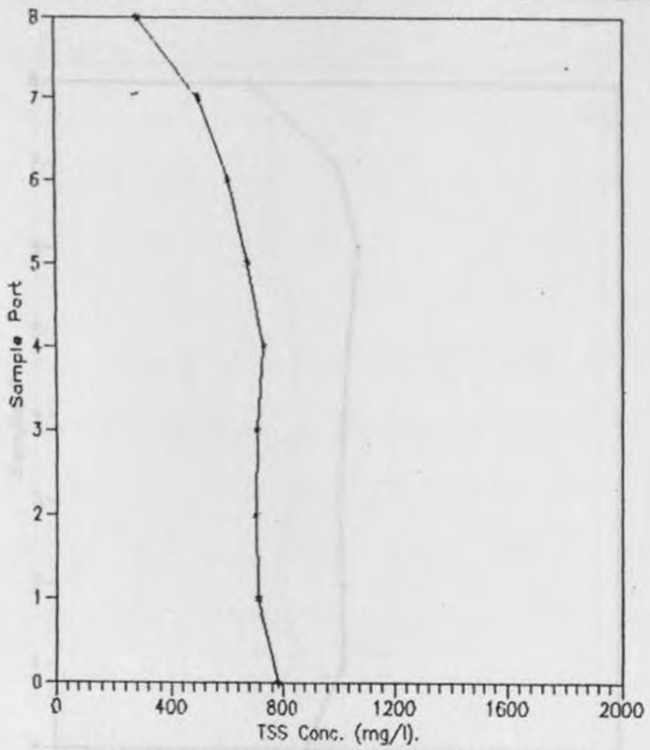


Fig 6.9.1 : Total Suspended Solids concentration profile on the 91st day. H.L.R. = 52.56 L/d.

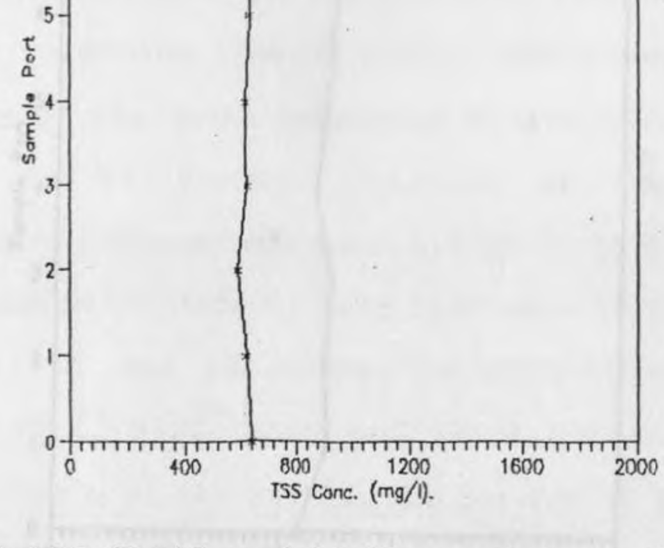


Fig 6.9.2 : Total Suspended Solids concentration profile on the 98th day. H.L.R. = 73.44L/d.

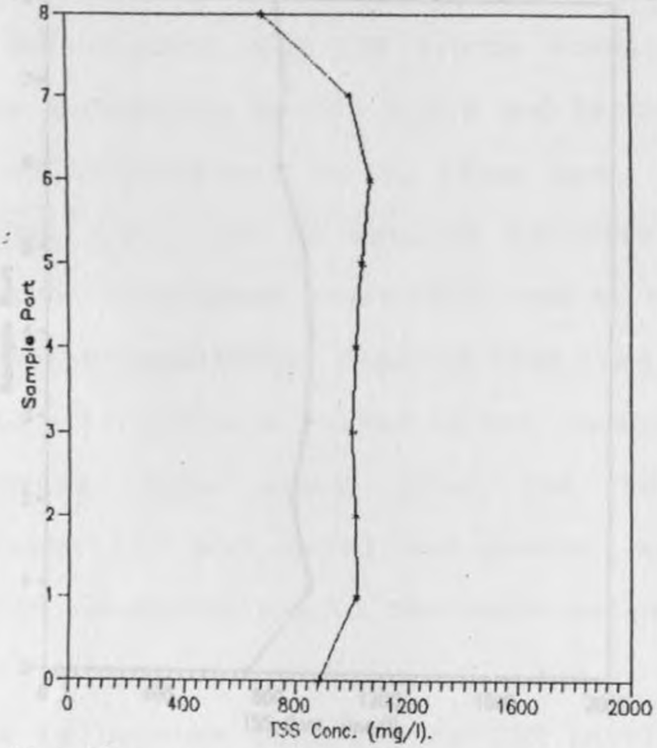


Fig 6.9.3 : Total Suspended Solids concentration profile on the 105th day. H.L.R. = 91.68 L/d.

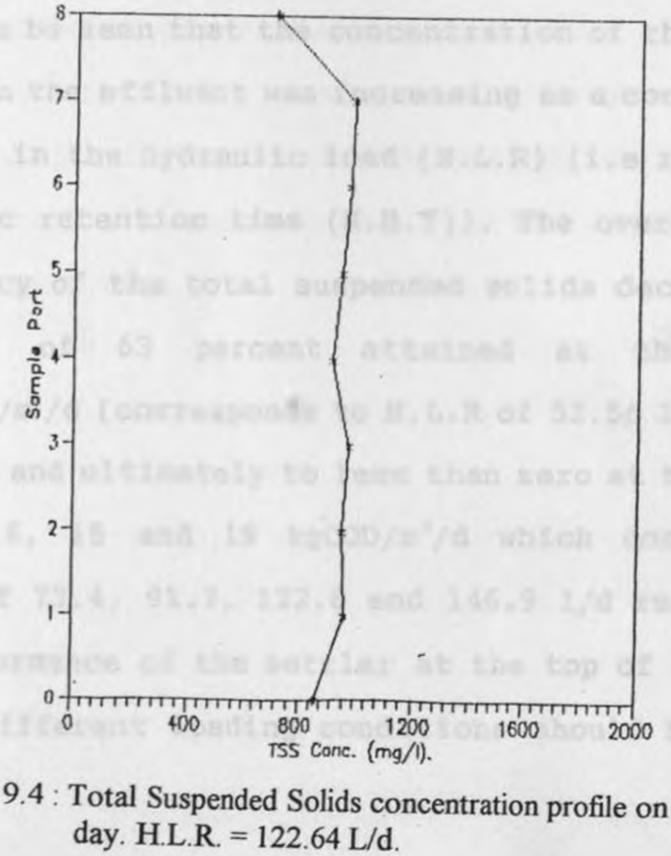


Fig 6.9.4 : Total Suspended Solids concentration profile on the 113th day. H.L.R. = 122.64 L/d.

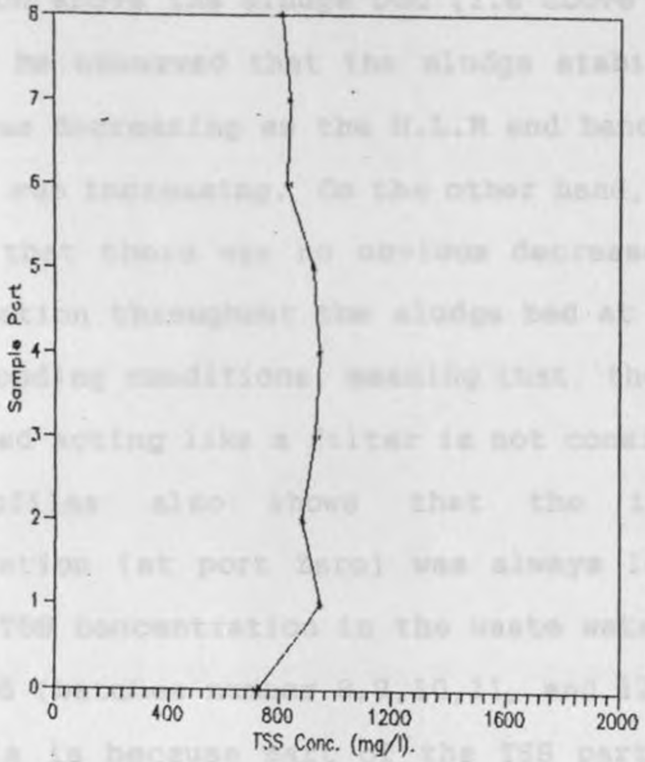


Fig 6.9.5 : Total Suspended Solids concentration profile on the 121st day. H.L.R. = 146.88L/d.

As it can be seen that the concentration of the suspended solids in the effluent was increasing as a consequence of increase in the hydraulic load (H.L.R) (i.e reducing the hydraulic retention time (H.R.T)). The overall removal efficiency of the total suspended solids decreased from a value of 63 percent attained at the load of 6.9kgCOD/m^3/d (corresponds to H.L.R of 52.56 l/d) through 60,21,18 and ultimately to less than zero at the loads of 9.4, 11.6, 15 and 19 kgCOD/m^3/d which correspond to H.L.Rs of 73.4, 91.7, 122.6 and 146.9 l/d respectively. The performance of the settler at the top of the reactor at the different loading conditions should be noted as there was an obvious decrease in the TSS concentration in the region above the sludge bed (i.e above port 5). It can also be observed that the sludge stability in that region was decreasing as the H.L.R and hence the upflow velocity was increasing. On the other hand, it should be noticed that there was no obvious decrease in the TSS concentration throughout the sludge bed at steady state of all loading conditions, meaning that, the role of the sludge bed acting like a filter is not considerable. The TSS profiles also shows that the influent TSS concentration (at port Zero) was always less than the initial TSS concentration in the waste water batches as collected (batches number 8,9,10,11, and 12 in appendix A). This is because part of the TSS particularly the settleable ones were separated in the feed holding basin.

6.1.5 The Total Gas Production:

The data on the daily average total biogas production (expressed in l/day) over the period of the reactor operation are presented in fig 6.10 and appendices B-1, B-2, B-3, and B-4.

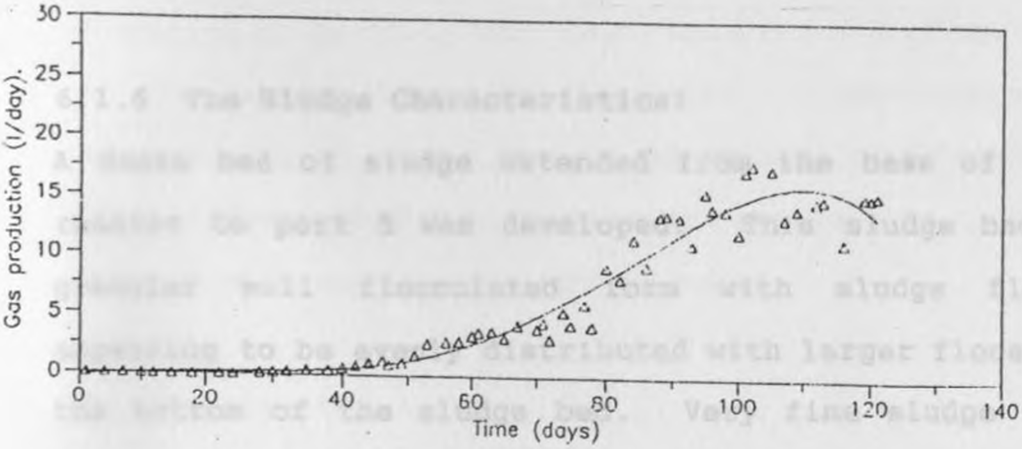


Fig 6.10 : Observed gas production rate plotted versus time.

The data shows that, the gas production rate was increasing as the sludge was getting acclimatized to the waste and the organic loading rate was increased. As indicated by the best fit curve in fig 6.10, the rate of the total biogas production over the initial period of the reactor operation (up to the 40th day) was very low, almost less the 1 l/day. After the 40th day and upto the 80th day the rate was increasing slowly and in a uniform pattern upto a relatively steady level of approximately 4 l/day, which is equivalent to 0.25 l/g COD removed. After the 107th day up and to the end of the experiment the rate slightly decreased to a value between 11 to 15 l/day corresponding to 0.12 to 0.17 l/gCOD removed respectively. Disappearance of biogas from the reactor through the reactor settler was observed. This was indicated by a smell of H_2S at the top of the reactor as well as fine gas bubbles noticed at the surface of the liquid.

6.1.6 The Sludge Characteristics:

A dense bed of sludge extended from the base of the reactor to port 5 was developed. This sludge had a granular well flocculated form with sludge flocs appearing to be evenly distributed with larger flocs at the bottom of the sludge bed. Very fine sludge was observed within the sludge bed. A small number of big sludge granules were also observed particularly at the base of the reactor. The region above the static bed i.e from port 5 to the settler was occupied by finely, divided sludge kept in suspension by turbulence caused by gas rising bubbles. A decrease in concentration from immediately above the static sludge to the reactor settler was noticeable. This was indicated by the suspended solid profiles presented in figs 6.9.1 to 6.9.4 (Section 6.1.4.6). Erosion of granules and suspension of fine sludge above the sludge bed was observed when the load was increased to around 19kgCOD/m^3/d which was corresponding a feed flow rate 146.8 liter/d and liquid flow velocity of 0.33 m/hr. This can be seen clearly in fig 6.9.5 (Section 6.1.4.6) as the suspended solids concentration was not decreasing above the static sludge bed towards the settler. During the first period of the reactor operation (up to the 21st day) expansion of the sludge bed and washout of the flocs and fines was also experienced. However, this behavior disappeared gradually as the sludge settleability was improved. The formation of granules was observed obviously at the base of the reactor after the 52nd day. Some sludge was accumulating at the surface of the liquid in the reactor. This sludge caused some operational problems by blocking the effluent and gas collection tubes.

6.2 Discussion:

6.2.1 The Paper Mill Waste Water Characteristic:

In comparing the waste water qualities in the different streams at the paper mill, table 5.1 (Section 5.2) the results show that the strength (in terms of COD) of the waste water generated from the PM1 production line is always higher than that generated from the PM2 production line. This is attributable to the nature and quality of the paper produced by PM1 production line. In the sense that, the types and grades of paper produced by the PM1 which mainly comprise machine glazed papers (MG), require more cleaning operations and more additives during the stock preparation stage. The higher speed and production capacity of the PM1 production line also contribute considerably to the higher strength in it's waste stream. According to the machines operators at the mill, overflow and spillage of stock and white water has been experienced more often from the PM1 processing units.

Comparing the COD of effluent before and after clarification (stream III and II in table 5.1 respectively). It can be seen that the COD does not decrease considerably after clarification as should be expected. However, this should not necessarily indicate poor efficiency of the mill clarification system because sediment materials in the clarifier (in form of slurry), which could also be a highly oxygen demanding materials, are continuously discharged into the clarified water stream (i.e stream II).

As indicated by the results in table 5.1, stream I of the PM1 production line is the stream which has the highest COD concentration. However, in terms of volume it contains much less volume than the final effluent. Moreover, in comparing the COD of this stream with that of the final effluent, it can be observed that there is only a slight difference.

It should be noted that the values of the hydraulic flow rates shown in table 5.1 should be higher than the actual flows because they were calculated based on the superficial velocity (as explained in section 5.2) (i.e. neglecting the effect of frictional drag forces exerted by the channels beds). This effect is, however, assumed to be common in all streams and hence the result are acceptable for comparison purposes.

In view of table 6.1 (Section 6.1.1), the COD concentration of the mill effluent ranges between 1900 and 2300 mg/l. Comparing these results with the COD concentration of the mill effluent reported over the year 1990, which was ranging between 1200 and 1800 mg/l (Reported by industrial waste water monitoring team, Nairobi municipality, 1990), it can be concluded that the strength of the mill final effluent is increasing with time. The increment in strength can mainly be attributed, on one hand, to recycling of white water and, on the other hand, to the increase of contaminants imported with waste paper particularly the one from domestic refuse (mixed paper) as a consequence of the continuing public awareness to reuse waste paper. For instance, writing or printing on both sides of paper and reduce margins, use of newsprints for wrapping, use of packaging and wrapping paper many times before being disposed, ..etc. The use of different qualities of printing and writing materials (ink, colors, etc) as well contribute to this. This assertion is supported by the results obtained in the literature. In this regard, Huter <u>et. al.</u> (1990) have found that, the COD concentration is some of the German recycled paper mills have risen almost trebled on the average between the years 1970 and 1990 (Fig 3.1 in section 3.2.6). They have attributed this increase in strength mainly to the increase in load imported with waste paper.

The main sources of the COD in the mill effluent could be residual of fibres which are difficult to recover, dissolved organic substances which may present in the waste paper originally, products of decomposition of fibres during the paper making and treatment additives used in the process. For instance, an average yield of 3.5 tones of tissue is produced out of 4.5 tones of waste paper i.e. 25% by weight of fibres, contraries, additives etc is rejected as 70% of fibres are recovered, assuming 5% as an additive for furnish preparation.

The COD/BOD5 correlation illustrated in fig 6.1 shows that, the waste water is considerably a high strength organic type waste and hence can be treated anaerobically. The relationship is represented by the best fit curve equation.

$BOD_5 = 0.59COD + 2.24$

This is comparable to the result (average $BOD_5/COD = 0.52$) observed by Mobius and Baumgarten (1985) for a recycled paper mill effluent.

On the other hand, The results on VFAs concentration shows that they comprise approximately 43% of the COD. This of course confirms the results obtained regarding the waste organic content as indicated by the equation above. However, there is a deficiency in the basic inorganic nutrients (phosphorous and nitrogen) necessary for anaerobic digestion as indicated by the results of P and N in table 6.1 . The COD:N:P of the raw waste is approximately 100:0.0:0.2 whereas the optimum ratio for anaerobic treatment is 100:5:1 (Gray, 1989). This deficiency could be supplemented either by addition of chemicals such as NH_4Cl, K_2HPo_4 or mixing the waste water with domestic waste. In this connection, if this waste water were to be treated in a UASB system , it would be most suitable to erect the UASB system somewhere down stream of the domestic city sewer into which these waste water is discharged. As far as the PH is concerned, the results shows that the water is acidic and hence can not be treated directly in anaerobic system. This acidity is obviously caused by the chemicals added in the process such as alum (sizing process). For anaerobic treatment, this might require addition of chemicals such as $NaHco_3$ to raise the PH to the range 6.6 - 7.2. Alternatively, complete or partly replacement of alum used in sizing process by emulsion sizes, might change the PH level to a better condition. An added advantage of alum replacement by emulsion sizes, is the reduction of toxic sulphates concentration in the waste. However, alum has been found to be cheaper in price and fulfills other functions in the process besides sizing such as, fixation of acid, direct and pigment colors, assistance in filler retention and foam control etc. Therefore, its replacement by emulsion sizes in the process is controversial and it's replacement by the industrialist for environmental consideration should not be expected unless under strongly forced legislation.

The sulphate concentration at normal operational conditions is of low toxicity. As can be observed from table 6.1 it is in the range of 87 to 164 mg/l, giving, an average $COD/SO_4^{=}$ ratio of approximately 14 which is above the minimum defined for toxicity 7-10 (Lettinga, 1981). However, this might not be the case under abnormal conditions of operation. For instance, if the PM1 production line is operating at full capacity, where larger amount of alum is used, while the PM2 production line is down or operating below its production capacity.

The TSS concentration in the waste water is below the concentration which makes the waste water treatability in a UASB system is problematic. As indicated by the results in table 6.1 the TSS concentration ranges between 500 and 900 mg/l which is less than 1000mg/l and gives TSS/COD ratio between 0.2 and 0.4 i.e. less than 0.5. The criteria for assessing the treatability of waste water in a UASB reactor in terms of TSS was given by Souza (1986) as TSS<1g/l and SS/COD<0.5) (Section 2.6.1).

The waste water flow variation as indicated by the results in table 6.1 is not steady, which of course should be expected in an industry having two production lines with different production capacities and different quality of products. Therefore, bearing in mind that, the anaerobic treatment is of high resistance to shock loads and environmental stress, treatment of these waste waters anaerobically can highly be feasible.

The temperature of the waste water ranges between 22-28°c which is slightly higher than the average ambient temperature. This result is actually expected because the larger proportion of waste water is generating from the paper machines wires where no heat energy is applied. Although the machines dry ends are operating at high temperature, about 80°c (the MG dryer), however, the water removed at these ends is negligible.

During the first start-up of the reactor operation in the laboratory, a solution containing trace metals was added to the feed, after some days when the addition of this solution was stopped due to shortage of chemicals, no change in the reactor performance was observed this would mean that the waste water is rich in trace metals nutrients required for bacterial growth. Similar result has also been observed in the literature (Russo and Dold, 1988). The waste water characteristics results is comparable to the results reported by (Kroiss <u>et. al.</u>, 1991) for a recycled paper mill producing corrugated paper from 100 percent waste paper (Section 3.2.6).

In general, by comparing the results of the effluent characteristics in this study with the results reported for the same industry in literature (Section 3.2.6). It can be seen that there is always a difference in the concentration of the different waste water parameters and volumes even between the results reported in literature. This can be referred to the difference in; materials used; production processes; degree of white water recirculation; quality and quantity of paper produced; quantity and quality of fresh water used; production sequences; and other environmental factors.

6.2.2 Reactor Conversion Efficiency and The Maximum Load:

The results obtained in connection with the substrate removal efficiency (Fig 6.3) clearly show that, the substrate removal efficiency in terms of COD is affected by the organic loads of more than 12-15kgCOD/m3/d., meaning, therefore, that the reactor removal capacity has been reached. This removal capacity ranged between 58 and 63 percent COD removal at a load of between 12-15kgCOD/m^3/d and HRT of about 3 hours. However, at the load of 19kgCOD/m^3/d the removal rate dropped to 53 percent whereas the liquid upflow rate was 146l/d which is equivalent to an upflow velocity of only 0.33 m/hr. Recalling the maximum limits for the COD load and the upflow velocity from literature, 15-20 kgCOD/m^3/d and 1.2 - 1.5 m/hr respectively (Souza, 1986). It can be seen that the reactor has reached it's full removal capacity at a corresponding upflow velocity much less than the maximum flow velocity. It should also be noted that at this flow velocity (i,e 0.33m/hr) no expansion of bed was observed, however, only that the concentration of the suspended particles at the region above the sludge bed and up to the settler increases as indicated by the suspended solids profile at the load of 19kgCOD/m^3/d (Fig 6.9.5). Therefore, it can be concluded that the criteria for the liquid upflow velocity and the COD load might not be attained simultaneously especially with concentrated waste whereas the maximum COD load could most likely be removed at low upflow velocity. This assertion is supported by results reported in literature . For instance, a COD load of 25kgCOD/m^3/d has been reached at an up-flow velocity of less than o.3m/hr in treating a waste of 4500 mgCOD/l in a UASB reactor (Dold and Russo, 1991). Eventually, this would mean that, in treating a highly concentrated waste in a UASB reactor, there is an advantage of applying high organic loads at low upflow velocity which consequently enhance proper passage of settled sludge on the settler surface and hence reduce concentration of suspended solids in the reactor effluent. According to Souza (1986), the velocity of flow through a UASB reactor should be sufficiently low to permit the return of sludge portion contained in the liquid leaving the reactor. Moreover, application of influent at low upflow velocity would make zone or hindered settling of the concentrated suspension at the top of the sludge bed possible. This phenomenon was observed clearly during the period of the experiment. From the results shown in appendices B-1, B-2, B-3, and B-4 it can be seen that at maximum COD removal efficiencies (i. e. 58-63%), the COD concentration in the effluent is still high (700-900mg/l). These results confirms the proposal by Souza (1986) that in treating concentrated waste in a UASB reactor, even with high COD removal efficiencies, high COD concentration may be obtained in effluent due to the contribution of suspended solids and the dissolved methane gas to the effluent COD. therefore, post treatment might be required depending on the effluent standards targeted.

In view of fig 6.2 it can be seen that the COD removal efficiency remain fairly constant between day 99 and day 108 at an average of 58 percent. Therefore, the start-up of the digester can be said to have been completed by day 99. Ideally, start-up is complete when gas production rate, COD removal efficiency and volatile acids concentration in the effluent remain fairly constant over a period of time (Barbosa and Sant'Anna, 1989). Duration of start-up period depends to a considerable degree on the quantity and quality of the seed biomass, and the environmental and operational parameters.

6.2.3. Reactor Concentration Profiles:

6.2.3.1 The COD and Volatile Fatty Acids concentration:

In view of the COD concentration profile at the load of 15kgCOD/m3/d. (Fig 6.4.4), it can be observed that the COD concentration decreased to 700 mg/l by port 5 and remained at that concentration up to the effluent level. In the mean time and at the same loading rate, complete removal of short chain volatile fatty acids took place by ports 6 and 7 for propionate and acetate respectively as indicated by fig 6.5.4. Bearing in mind that the short chain volatile fatty acids comprise approximately 43% of the COD, this result, therefore, indicates that the effluent COD contains a large proportion of unbiodegradable materials.

The volatile fatty acids and sulphate concentrations are major factors which determine the hydrogen partial pressure and hence the degree of sludge pelletization in a UASB reactor (Russo and Dold, 1988). According to Zehnder and Wurhmann (1977), in the high H_2 partial pressure region a methano-organism develops, presumably methanobacterium strain AZ (M.Strain AZ), which uses hydrogen only as it's energy source. This organisms can produce all it's amino acids, for cell synthesis, except cystine. The excess production of amino acids induces the organisms to form extracellular long chain polypeptides. These polypeptide chains bind the species and others into pellets. In this connection and in view of fig 6.5.4 it can be seen that the concentration of propionic acid remains constant upto port 3, and only started declining thereafter. This constant concentration of propionic acid indicates that the hydrogen partial pressure is high up to port 3, despite the rapid hydrogen removal by sulphate reducing bacteria, indicated by the rapid decrease in sulphate concentration shown in fig 6.6.4. Under this condition it would be expected that the hydrogen partial pressure is sufficient to allow generation of excess amino acids by methano-organisms; this in turn should lead to sludge pelletization according to Zehnder and Wurhmann, 1977) proposal. This generation of amino acids is confirmed in fig 6.8.4 by the rapid increase of soluble organic nitrogen upto port 2. Therefore, the large sludge pellets observed at the bottom of the reactor were to be expected.

At the load 6.9 and 9.4 kgCOD/m^3/d (Figs 6.5.1 and 6.5.2) respectively, there is an immediate decrease in the propionic acid concentration upto port 5. This would indicate a low hydrogen partial pressure upto that level. The reason for this low hydrogen partial pressure appears to relate to the higher concentration of sulphate in the feed (120-164 mg/l) at these two loads compared to 95 mgSO$_4$/l in the feed at the loads 11 and 15kgCOD/m^3/d.

The reduction of hydrogen partial pressure in the reactor in one hand has an advantage in motivating the reaction of the oxidation of reduced co-enzyme Niacinamide Adenine Dinocleolide (NADH) back to (NAD^+) with the production of hydrogen.

NADH + H^+ <----> H_2 + NAD^+ G = 18kJ

The reaction is essential for fermentation to continue since there are only small quantities of NAD^+ present in the bacterial cell (Thauer et. al., 1977). This reaction is endothermic and will shift to the right at low hydrogen partial pressure. In this study since there is no heat applied to the reactor, presence of sulphate in the influent, which means presence of efficiently metabolizing hydrogen-utilizing bacteria (sulphate reducing bacteria), is necessary for this reaction to continue to the right.

On the other hand, Some researchers (Lettinga, 1981, Russo and Dold, 1988; Thiele et. al., 1990) have indicated that the presence of sulfate at low concentrations in the reactor influent enhances it's performance.

In contrast, presence of sulfate plays a role in reducing the hydrogen partial pressure in the reactor which means reduction of the available hydrogen for methanogenic bacteria and this would result in low generation rates of amino acids and hence sludge pellets according to Sam Soon <u>et. al.</u> (1987) proposal.

The COD concentration profiles show that there is a slight activity in the region above the sludge bed (above port 5), indicated by the slight decrease in the COD concentration at the loads 6.9, 9.4 (Figs 6.4.1 and 6.4.2). This activity increased at the load 19kgCOD/m^3/d, indicated by higher decrease in the COD concentration above port 5 (Fig 6.4.5), meaning, therefore under this load some of the active fine sludge left the sludge bed as a consequence of increasing the liquid upflow velocity to remain in suspension upto the settler level.

According to Young and McCarty (1969)in anaerobic digestion as the rate of acid formation becomes greater than the rate of acid conversion to methane, the equilibrium VFAs concentration in the effluent increases with increasing the organic load. In this study, the rate of acid conversion to methane appear to decrease with increasing the organic load. This is indicated by the decrease in the rate of biogas production after the 105th day at a load between 11 and 15kgCOD/m3/d. (fig 6.10). this assertion is confirmed by the appearance of short chain VFAs in the reactor effluent at steady state of a load of 19kgCOD/m3/d. (Fig 6.5.5). On the other hand, at low loading rates, 6.9 and 9.4 kg/COD/m^3/d (Figs

6.5.1 and 6.5.2 respectively), there is higher utilization of acetic acid than propionic acid especially within the sludge bed which indicates higher activity of methanogens in converting this acid to methane, despite the high competition imposed by sulphate reducing bacteria in the available substrate. This high methanogenic activity is attributable to the greater retention time provided for methanification at these two loads.

6.2.3.2 The Sulphate Concentration:

It was recently established that to avoid sulphate toxicity, it is necessary that the COD/$SO^{=}_{4}$ ratio in the waste has to be higher than 7-10 (Lettinga, 1982). In this study, the concentration of sulphate in the waste ranged between 87 and 164 giving a COD/$SO^{=4}$ ratio of approximately 14. Therefore, it can be said that sulphate had no inhibitory effect to the methanogens in the experiment. Moreover, sulphate seem to have, at this concentration, contributed to the pH regulation in the reactor. As can be observed in the pH profiling results in figs 6.7.1 to 6.7.1 the PH level remains relatively steady within the range of 6.6 to 7.2 which is the optimum for anaerobic digestion. In this connection, Russo and Dold (1988), reported that, sulphate has an important role in pH regulation in a UASB system, that, via the biological sulphate reduction process acidity will be consumed. If sulphate were excluded from the waste, the requirements for alkalinity addition and then the operating costs of the process, possibly would increase.

Moreover, low concentration of sulphate (below toxicity level) in the reactor influent found to be beneficial to the growth of methanogens and fatty acid degraders (Thiele et. al., 1990). On the other hand an increase of methanogenic activity of 60% was reported when free hydrogen sulphide concentration was from 0-50 mg/l. (Speece et. al., 1986). In this study, low concentration of sulphate in the influent seem to have improved the methanogenic activity via production of hydrogen sulphide at low concentration. This is supported by the observation of the progressive increase in the total gas production (Fig 6.10) due to the high rate of acetic acid utilization in the reactor by methanogens.

The utilization of hydrogen and acetic acid by sulphate reducing bacteria to produce sulphide (principally HS^- and H_2S at the prevailing pH) is favored thermodynamically over use by methanogens (Souza, 1986). Sulphur compounds act as terminal electron acceptors for sulphate reducing bacteria which may compete methane producing bacteria for available substrate.

$$SO_4^{-} + \text{organic matter} \ \underset{\text{Bacteria}}{\underline{\text{Anaerobic}}} \ S^{-} + H_2O + CO_2$$

In this study, The rapid decline in sulphate concentration and then its's complete removal in the reactor at all loading conditions (Fig 6.6.1 to 6.6.5) indicates the high activity of the sulphate reducing bacteria and hence high ability to compete with methanogens in the available substrate, particularly, hydrogen and acetate. This high affinity for hydrogen utilization would indicate the high tendency of sulphate reducing bacteria to reduce the hydrogen partial pressure in the reactor. This in turn would lead to lowering the rate of sludge pelletization in the reactor according to Sam Soon <u>et. al.</u> (1987) proposal (Section 2.4.2).

6.2.3.3 The pH :

The optimum pH for anaerobic digestion is of the range 6.6-7.6. pH below 6.5 or above 7.8 may be harmful to the bacteria, mainly the methanogens (Gray, 1989). In this study the pH profiles show that despite the pH fluctuation in the reactor, it never exceeded the optimum values for anaerobic digestion, which in turn indicates the high natural buffering capacity developed in the system to maintain optimum digestibility by the microorganisms particularly the methanogens which are the most susceptible to PH variation (McCarty, 1964b).

The PH in anaerobic digestion usually drops when the methane forming bacteria are not capable of utilizing the end products of the acidogenesis (mainly volatile acids)

McCarty, 1964b). The main natural buffering in anaerobic digestion which tend to balance a drop in pH are bicarbonate which formed by the reaction of carbon dioxide from the biogas with the natural mineral alkalinity. (McCarty, 1964b).

Examining the pH profiles at the loads of 6.9, 9.4 and 19kgCOD/m^3/d in figs 6.7.1, 6.7.2 and 6.7.5 respectively, it can be observed there is an increase in pH upto port 3 level (Fig 6.7.1) and upto part 4 level (Fig 6.7.2) and upto port 3 level (Fig 6.7.5). This pH increase is caused by high rate of sulphate reduction and acetic and propionic acids utilization upto the same levels at the same loading conditions as illustrated by the sulphate (Figs 6.6.1, 6.6.2, and 6.6.5) and acetic and propionic acids concentration profiles (Figs 6.5.1, 6.5.2 and 6.5.5). This consequently means that the rate of acidogenesis (production of long chain VFAs), up to those levels , at the same loads, was low enough to interfere with the increase in the PH. On the other hand, in view of the same figures, it can be seen that, above those levels, the reduction of sulphate and acetic and propionic acids concentration continue at relatively lower rates while the pH keeps on varying unsteadily upto the effluent level. This can be referred to, since there is a continuation in the reduction of the sulphate and acetic and propionic acids concentrations, a fluctuation in the rate of the VFAs production.

At the loads 11.6 and 15 kgCOD/m^3/d (Figs 6.7.3 and 6.7.4 respectively) the pH decreases in the region between port 1 and port 3. This is probably due to high rate of VFAs production in that region at these two loads. This assertion is also supported by the observation that the short chain VFAs (propionic and acetic acids) concentrations were almost constant upto port 5 at the load 11.6 kgCOD/m^3/d (Fig 6.5.3) and upto port 3 at the load 15kgCOD/m^3/d (Fig 6.5.4).

6.2.3.4 The Organic Nitrogen and Free and Saline Ammonia concentration:

Nutrients rather than organic or inorganic substrates principally nitrogen and phosphorous are very essential for cell synthesis and growth (Gray 1989). In this study the waste water before chemical addition contained no free and saline ammonia. All the total kjeldahl nitrogen (TKN) present in the waste water is organic nitrogen associated with particulate matter at a concentration of approximately 11 to 26 mg/l. To supply nitrogen for cell synthesis NH_4Cl was added to the influent to provide a soluble ammonia concentration such that the ratio of COD:N = 100:5 was obtained (Section 5.3).

According to Sam Soon <u>et. al.</u> (1987), at high hydrogen partial pressure zone in the UASB rector, free and saline ammonia (NH_3 - N) concentration reduces to minimum and soluble organic nitrogen concentration increases to a maximum; pellet growth is restricted to this zone as a result of polypeptide formation as precursor to sludge pellet formation. In this study the free and saline ammonia shows a rapid drop at the bottom of the reactor at the different loads used (Figs 6.8.1 to 6.8.5). In terms of Sam Soon et. al. (1987) proposal, this could be associated with polypeptide formation and hence pellet formation. This assertion is supported by the observation of large sludge pellets at the bottom part of the reactor.

The soluble organic nitrogen (same figures) shows a rapid increase at the same region where decrease of the free and saline ammonia (NH_3 -N) occurs. Two possible sources for this material can be identified. Firstly, as a result of over production of soluble organic nitrogen during pelletization. The second source would be from hydrolysis of particulate organic nitrogen in the feed.

At the load 15kg/m3/d. the free ammonia decreased rapidly to a concentration of 31.7 mg/l which is less than the organic nitrogen concentration at that level (35 mg/l). This result reflects the high affinity of the organisms to use ammonia as a source of nitrogen.

6.2.3.5 The Total Suspended Solids Concentration:

According to Souza (1986), there are two criteria which, if occurring simultaneously (SS<1g/l and SS/COD<0.5) will not impede the treatment of waste water in a UASB reactor (Souza, 1986). In this study, the TSS concentration in the feed ranged between 500 and 900, giving a TSS/COD ratio of 0.2 to 0.4. Therefore, the waste, in terms of Souza (1986) proposal, is not problematic for treatment in a UASB reactor. However, problems like blockage of inflow pipes; blockage of the gas/liquid/solid separator due to formation of scum layer at the liquid surface were encountered during experimentation. This can be attributed to the nature of the suspended solids in the feed which mainly comprise paper fibres. The settleable proportion of the TSS was separated in the feed storage basin but the paper fibres were observed to be always in suspension. Moreover, if this waste were to be treated in full-scale UASB system, continuous accumulation of paper fibres within the sludge bed might lead to spontaneous and sudden washout of the complete sludge bed especially at shock loading. This problem has been experienced in full scale UASB reactors treating wastes containing voluminous suspended solids (Lettinga and Hulshoff, 1991).

On the other hand, the TSS removal efficiency at the optimum loading rate, 12-15kgCOD/m^3/d, is very small, approximately 21% as compared to that achieved by Barbosa and Sant Anna (1989) (72%) with domestic sewage (Section 2.6.1). This would make application of pretreatment and post treatment necessary for these waste waters.

Another important feature in the TSS concentration profiles is that, the TSS removal decreases rapidly with increasing the hydraulic load until it reaches a value of less than zero at the load 19kgCOD/m^3/d, meaning, that at the load 19kgCOD/m^3/d, despite the low upflow velocity (o.33m/hr), some of the sludge bed materials started to disappear. Therefore, the optimum load which could be applied for successful treatment is between 12 and 15kgCOD/m^3/d

6.2.4 The total gas Production:

The value of the maximum observed rate of total biogas production in the reactor at steady state condition, 17 l/d which is equivalent to 0.2 l/g COD removed is much less than the values reported in the literature. The theoretical methane production alone is assumed as 0.35 l/g COD removed (Lawrence and McCarty 1969; Souza, 1986). The low value of the observed rate of biogas production can mainly be attributed to the disappearance of the evolved biogas through the reactor settler. This assertion is justified by the following observations.

1. high rate of short chain fatty acids utilization which means high rate of methane and carbon dioxide gases production according to (Gray 1989)

$CH_3COOH \text{ ----> } CO_2 + CH_4$ (acetic acid)

$CH_3CH_2COOH + 0.5H_2O \text{ ----> } 1.25CO_2 + 1.75CH_4$

2. Complete removal of sulphate which means production of H_2S gas:

$So_4^{=} + 2H_2 \text{ ----> } H_2S + H_2o$

3. Low biomass production rate indicated by low sludge accumulation rate in the reactor, which means small proportion of the COD removed is transformed into biomass, and this in turn means large proportion of the COD removed is transformed into methane, carbon dioxide, hydrogen and H_2s gases for instance,

Carbohydrate $C_3H_{12}O_6 + H_2 \text{ ----> } CH_4 + Co_2$

4. The smell of the H_2s gas observed at the top of the reactor as well as the gas bubbles observed at the liquid surface.

5. Even size distribution of sludge granules developed in the reactor, larger particles being at the bottom of the sludge bed. According to Hickey et. al. (1991) high biogas flux rates in the reactor result in an even size, distribution and a smaller mean sized granules. This is assumed to be due to higher sheer exerted by the higher gas flux rates.

On the other hand, very high rate of biogas was not expected because of; the temperature fluctuation, which, according to Souza (1986), mostly affect methanogenesis especially at low upflow velocity and hence methane and CO_2 production rates; tendency of methane to dissolve in water; the transformation of some of the CO_2 generated into bicarbonate alkalinity according to (Gray, 1989).

$CO_2 + HOH \longleftrightarrow H_2CO_3 \longleftrightarrow HCO_3^- + H^+$

$H_2CO_3 + OH^- \longleftrightarrow HCO_3^- + HOH$

The bicarbonate alkalinity produced played a big role as a natural buffer, in maintaining the pH in the reactor within the range desirable for anaerobic digestion (6.6-7.2) indicated by the pH profiles.

Analysis of the produced biogas composition is not embodied in the objective of this study. However, the biogas composition can be predicted based on the waste composition and results reported in previous studies.

According to Souza (1986), the content of methane produced in treating a concentrated waste is about 55 to 65 percent, the remaining being constitute mainly of CO_2. The concentration of H_2S in biogas is generally low and depends on the sulphate concentration in the waste and on the $COD/SO_4^=$ ratio. N_2 is generally produced from wastes which constitute mainly proteins. For instance, with domestic sewage, the CH_4 content in the biogas is about

72% and the remaining may contain high concentration of N_2 (Souza, 1986). For digesters operating in routine manner and being fed with substrate regularly, the composition and rate of the biogas produced is fairly uniform.

In this study, the rate of biogas produced was more or less not regular, as indicated by the graph in fig 6.10. This would mean that, the biogas composition is not also uniform. However, the biogas produced can be said, according to the waste composition, to constitute mainly of CH_4, H_2S, CO_2 and probably H_2.

6.2.5 The Sludge Characteristics:

Development of well settling sludge biomass is a prerequisite for successful operation of a UASB system (Souza, 1986). In this study, development of sludge with well settling characteristics seem to have played a big role in improving the reactor conversion efficiency. On the other hand, due to the high COD concentration of the waste, all organic loading rates used corresponded to relatively low upflow velocities (maximum was 0.33 m/h). These low up flow velocities played a role in improving the sludge granules settleability by exerting low up-lift force on them. According to Souza (1986), keeping the velocity of the flow sufficiently low, should not surpass 3 to 5 m/h, will permit the return of sludge granules on the reactor settler.

Sam Soon et. al. (1987) noted that sludge pellets formation is related to the hydrogen partial pressure available in the reactor. The higher the available hydrogen partial pressure the larger size of pellets develop in the reactor. In this regard, the presence of sulphate in the feed seems to be working against sludge pelletization in the UASB system. Because the sulphate reducing bacteria utilizes the available hydrogen and hence reduces its's partial pressure in the reactor. The low sulphate concentration in this particular waste water (87-164mg/l) seem to have little effect in the sludge pelletization.

On the other hand, the waste composition of high concentration of short chain fatty acids (approximately 43% of the COD), in terms of Sam Soon et. al. (1987) proposal, will also limit the sludge pelletization in the reactor. Because, this would mean that the remaining substrate available for acidogenesis with it's associated hydrogen production, is limited and consequently the possibility of creating a high hydrogen partial pressure is also limited.

CHAPTER SEVEN

CONCLUSION AND RECOMMENDATIONS

7.1 Conclusion:

The study conducted on the characteristic strength and treatability of waste water from a recycled paper mill provided information on wide range of factors. The following conclusions may be itemized from the results obtained in this study:

1. The mill waste water is of high organic strength and can successfully be treated using anaerobic means. The COD concentration ranges between 1900 and 2300 mg/l and the BOD concentration ranges between 1100 and 1300 mg/l. The COD/BOD_5 correlation is represented by:

   $BOD_5 = 0.59COD + 2.24$

   The total suspended solids concentration is in the range of 500-900 mg/l. The waste water is acidic, PH between 3 and 5, and deficient in basic inorganic nutrients, Phosphorous 3-5 and NH_3-N 0.0. Approximately all the total kjeldahl nitrogen (TKN) is associated with organic matter at a concentration of 11-26 mg/l. The sulphate content is between 87 and 164 mg/l. The waste water temperature is between 22-28°C.

2. The mill waste water flow variation is not steady (between 1700-2100 m^3/d), which of course should be expected in an industry having two production lines that require different quantity of water inputs and produce different products.

3. In comparing the results of the waste water characteristics obtained in this study with the results reported in the literature. It can be concluded that there is always a difference in the concentration of the different waste water parameters and volumes even between the results reported in the literature. This can be referred to the difference in materials used, production processes, degree of white water recirculation, quality and quantity of paper produced, quantity and quality of the water used, production sequences, and other environmental factors.

4. COD removals of approximately 63 percent were attained by using UASB system at ambient temperature (average 22°C) at organic loading rate between 12-15kg $COD/m^3/d$. This corresponded to hydraulic retention time of approximately 3 hours and influent COD concentration of 2100 mg/l. Under this condition, no difficulties associated with sludge settleability were encountered. However, blockage of the influent pipe and the gas

collection pipe at the reactor settler occurred.

5. The time required for the anaerobic biomass to acclimatize to the waste water was approximately 99 days.

6. A dense bed of sludge extend from the base to approximately half the reactor length was formed. This sludge had a well-flocculated form with the flocs appearing to be evenly distributed, according to their size, with larger flocs at the bottom of the sludge bed. Very fine sludge was also observed within the sludge bed. No sludge removal was required throughout the experimentation period

7. Problems encountered, associated with biogass collection, resulted in low value of the average total biogass measured which was equivalent to 0.2 liter/gCOD removed.

8. The sulphate contents of the waste water (87 to 164 mg/l) is of low toxicity to micro-organism. However, from the results obtained by the sulphate and short chain volatile fatty acids (propionate and acetate) concentration profiling, it can be concluded that the sulphate reducing bacteria has higher biological activity and hence higher affinity to hydrogen than the methanogens. This

higher affinity of sulphate reducing bacteria to hydrogen appear to reduce the possibility of creating high pressure of hydrogen within the sludge bed and hence limit the degree of sludge pelletization.

9. The results from the total suspended solids (TSS) profiles indicate that, the TSS removals appear to relate to the liquid upflow velocity. The higher the liquid upflow velocity the lower the TSS removal efficiency. The low TSS removals, only around 20% removals attained at optimum loading conditions, necessitate application of post treatment to the reactor effluent.

10. The results from the pH profiles indicate that the UASB anaerobic system has high natural buffering capacity to pH variation.

11. The results from the organic nitrogen and free and saline ammonia concentration profiles indicate; decrease in the free ammonia which appear to relate to long chain amino acids polypeptide formation as precursor to sludge pellet formation; and increase in organic nitrogen as a result of hydrolysis of particulate organic nitrogen in the feed and over production of soluble organic nitrogen during pelletization.

7.2 Recommendations:

1. Application of UASB system in the developing countries especially tropical countries (e.g sub-saharan) can highly be feasible. Because the system could be operated successfully at ambient temperature and hence the cost of heating the system will be omitted. Moreover, the methane gas produced by such systems can contribute considerably to solving the problems associated with energy availability in these countries. On the other hand in countries like Sudan where the average temperature is higher than 37°C, higher performance of the UASB system would be anticipated.

2. The mill waste water characteristics; high COD concentration, large volume and high flow variation, high biodegradability, low toxicity; make it's treatment in an anaerobic system quite feasible. However, adjustments of the PH, basic inorganic nutrients namely, nitrogen and phosphorous are necessary.

3. If this waste water were to be treated in a UASB system, a pilot scale study is recommended. The pilot plant study will aim, for instance, at; determining the feasibility of using domestic sewage, with which the mill effluent is mixed, as a

source to provide inorganic nutrients (nitrogen and phosphorous) and adjusting the PH; providing guide lines for full scale plant design construction and operation; monitoring and overwhelming the mill effluent variation for longer period of time; determining the feasibility of using the biogas produced as a source of energy in the mill; determining the feasibility of reusing the waste water, after being treated, in the mill etc.

4. In treatment of the mill effluent in a UASB system, separation of suspended solids, which mainly comprise paper fibres, prior to the UASB system is necessary to; omit the problems associated with the flow of water into the system, such as blockage of influent pipe, blockage of influent distribution system, etc; contribute to the system removal efficiency; reduce the possibility of formation of scum layer which might be entrapped or attached to active sludge and cause blockage of the reactor settler; reduce the possibility of spontaneous and sudden washout of almost the complete sludge bed, caused by a prolonged continuous entrapment of suspended solids particularly paper fibres in the sludge bed e.g. initiated by an imposed shockload. A flotation system could be used for this purpose to remove both paper fibres and sediments.

5. Application of efficient post treatment system, sedimentation system, for the separation of the remaining suspended solids in the reactor effluent is highly recommended, the results obtained in the study indicated low suspended solids removals at optimum organic loading rates. Post treatment will also add to the COD and BOD reduction in the waste water as well as other pollutants such as pathogens, sulphide, etc.

6. Proper design and construction of the reactor settler, is important, the results obtained from the TSS concentration profiles showed that the reactor settler plays a big role in prohibiting active sludge from leaving the reactor with the effluent. Proper design and construction of influent distribution system is as well necessary to ensure uniform distribution of the feed across the sludge bed.

7. The reactor should be handled with a lot of care during the first period of start up; start with low loading rates < 0.5 kg COD/m^3/d; close inspection; avoid start-up during very cold seasons; increase loading rate stepwise; provide enough time for sludge to acclimatize to the waste.

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APPENDIX A: CHARACTERISTIC STRENGTH OF WASTE WATER BATCHES

BATCH NO.	CONCENTRATIONS (mg/l)							
	COD	BOD_5	$SO_4^{=}$	TKN	NH_3-N	P	TSS	PH
1	2012.18	1187.08	87.22	18.00	0.00	4.00	789.5	5.8
2	2320.20	1368.81	94.14	26.00	0.00	5.33	890.36	5.7
3	1814.61	1124.37	107.62	13.77	0.00	3.21	601.53	5.1
4	2128.60	1234.24	148.00	21.58	0.00	4.11	940.33	4.9
5	2201.37	1342.61	159.42	24.69	0.00	5.00	752.14	4.7
6	2048.09	1208.37	84.53	14.07	0.00	3.71	505.96	5.7
7	2261.55	1320.42	98.12	24.68	0.00	5.16	815.14	5.5
8	2026.17	1235.86	164.95	19.18	0.00	4.20	910.00	4.6
9	1994.36	1216.55	122.21	15.41	0.00	3.01	774.13	5.0
10	1960.17	1156.40	97.07	17.41	0.00	3.50	915.31	5.7
11	1898.63	1062.88	96.37	11.36	0.00	3.30	849.37	5.7
12	1989.23	1091.96	139.08	18.37	0.00	4.12	764.54	4.9

APPENDIX B-1: REACTOR PERFORMANCE MONITORING

SAMPLING DAY	Influent COD (mg/l)	Effluent COD (mg/l)	Feed Flow Rate (l/hr)	O.L.R (Kg COD/m3/d)	Retention Time (hrs)	Reactor Temp.(°C)	COD Removal Rate (%)	Average Daily Gas Prod.(l/d)
2nd	498.38	498.12	0.63	0.498	24	19.2	0.05	0.000
4th	495.55	491.11	0.63	0.496	24	19.0	0.89	0.000
7th	493.69	490.20	0.63	0.494	24	19.1	0.70	0.000
10th	489.22	482.33	0.63	0.489	24	19.5	1.41	0.000
12th	488.32	478.55	0.63	0.488	24	19.5	2.00	0.000
15th	486.52	474.35	0.63	0.486	24	19.7	2.50	0.000
18th	484.71	470.65	0.63	0.484	24	19.8	2.90	0.000
22nd	481.36	464.99	0.63	0.481	24	19.9	3.40	0.000
24th	999.20	978.21	0.63	1.000	24	19.9	2.10	0.000
28th	995.11	958.29	0.63	0.996	24	21	3.70	0.120
30th	993.01	940.38	0.63	0.994	24	21	5.30	0.189
32nd	991.62	923.15	0.63	0.992	24	20.8	6.90	0.250
35th	989.03	875.29	0.63	0.990	24	20.9	11.50	0.382
38th	1498.22	1375.36	0.63	1.499	24	20.6	8.20	0.400
40th	1496.37	1334.70	0.63	1.497	24	20.6	10.80	0.600
42nd	1495.11	1246.92	0.63	1.496	24	21.2	16.60	0.810
44th	1493.75	1239.81	0.63	1.494	24	21.7	17.00	1.010

O.L.R. = Organic Loading Rate

APPENDIX B-2: REACTOR PERFORMANCE MONITORING CONT.

SAMPLING DAY	Influent COD (mg/l)	Effluent COD (mg/l)	Feed Flow Rate (l/hr)	O.L.R (Kg COD/m3/d)	Retention Time (hrs)	Reactor Temp.(°C)	COD Removal Rate (%)	Average Daily Gas Prod.(l/d)
46th	1491.31	1184.10	0.63	1.492	24	21.9	20.60	1.210
47th	1490.00	1139.85	0.63	1.491	24	22	23.50	0.920
49th	1487.25	1096.10	0.63	1.488	24	21.8	26.60	1.100
51st	1484.91	1037.95	0.63	1.485	24	22	30.10	1.710
53rd	2098.78	1527.91	0.63	2.100	24	21.9	27.20	2.670
56th	2094.66	1390.85	0.63	2.096	24	22.2	33.60	2.800
58th	2092.10	1299.19	0.63	2.094	24	22.1	37.90	2.910
60th	2090.00	1274.90	0.63	2.092	24	22.3	39.00	3.370
61st	2087.63	1185.77	0.63	2.089	24	21.9	43.20	3.650
63rd	2085.67	1132.51	0.63	2.087	24	21.3	45.70	3.750
65th	2097.94	1405.61	0.77	2.566	20	21.1	33.00	3.210
67th	2095.36	1240.45	0.77	2.563	20	20.8	40.80	4.300
70th	2092.82	1213.80	0.77	2.559	20	20.9	42.00	4.000
71st	2089.10	1199.14	0.77	2.556	20	20.8	42.60	4.500
72nd	2045.22	1308.94	1.01	3.280	15	20.4	36.00	3.170
74th	2043.11	1164.57	1.01	3.278	15	20.5	43.00	5.400
75th	2041.92	1151.64	1.01	3.275	15	20.2	43.60	4.320

O.L.R. = Organic Loading Rate

APPENDIX B-3: REACTOR PERFORMANCE MONITORING CONT.

SAMPLING DAY	Influent COD (mg/l)	Effluent COD (mg/l)	Feed Flow Rate (l/hr)	O.L.R (Kg COD/m3/d)	Retention Time (hrs)	Reactor Temp.(°C)	COD Removal Rate (%)	Average Daily Gas Prod.(l/d)
77th	2038.79	1143.76	1.01	3.270	15	19.7	43.90	6.050
78th	2098.63	1292.75	1.50	4.930	10	19.4	38.40	4.220
80th	2095.31	1089.56	1.50	4.923	10	19.6	48.00	9.120
82nd	2092.11	945.63	1.50	4.916	10	20.0	54.80	8.120
84th	2088.91	933.74	1.50	4.907	10	20.1	55.30	11.600
86th	2022.37	1007.14	2.19	6.938	7	20.4	50.20	9.310
88th	2019.71	884.27	2.19	6.927	7	20.4	56.21	13.500
89th	2017.93	811.20	2.19	6.920	7	20.3	59.80	13.630
91st	2013.77	799.47	2.19	6.907	7	20.1	60.29	13.420
93rd	1990.93	933.74	3.06	9.540	5	19.9	53.10	11.130
95th	1987.18	826.67	3.06	9.526	5	20.2	58.39	15.520
96th	1985.12	740.40	3.06	9.516	5	20.2	62.70	14.230
98th	1981.27	734.95	3.06	9.497	5	20.1	62.90	14.000
100th	1957.30	861.21	3.82	11.713	4	20.0	56.00	12.110
101th	1954.88	805.41	3.82	11.694	4	19.9	58.80	17.370
102nd	1952.01	753.47	3.82	11.682	4	19.8	61.40	17.930
105th	1946.23	735.67	3.82	11.641	4	19.8	62.20	17.580

O.L.R. = Organic Loading Rate

APPENDIX B-4: REACTOR PERFORMANCE MONITORING CONT.

SAMPLING DAY	Influent COD (mg/l)	Effluent COD (mg/l)	Feed Flow Rate (l/hr)	O.L.R (Kg COD/m3/d)	Retention Time (hrs)	Reactor Temp.(°C)	COD Removal Rate (%)	Average Daily Gas Prod.(l/d)
107th	1895.44	904.12	5.11	15.171	3	19.6	52.30	13.370
109th	1892.54	728.42	5.11	15.147	3	19.6	61.51	14.190
112th	1887.63	696.33	5.11	15.112	3	19.4	63.11	14.780
113th	1985.94	693.73	5.11	15.092	3	19.6	63.21	15.800
116th	1984.44	1008.09	6.12	19.024	2.5	19.6	49.20	11.370
119th	1978.63	924.02	6.12	18.966	2.5	19.8	53.30	15.220
120th	1975.87	912.83	6.12	18.937	2.5	19.7	53.80	15.150
121st	1971.37	908.80	6.12	18.899	2.5	19.7	53.90	15.370

O.L.R. = Organic Loading Rate

APPENDIX C-1: REACTOR PROFILING RESULTS - COD.

SAMPLING		FILTERED COD CONCENTRATION (mg/l)								
DAY	O.L.R. Kg CDO/m^3/d	Influent	Sample Port (1)	Sample Port (2)	Sample Port (3)	Sample Port (4)	Sample Port (5)	Sample Port (6)	Sample Port (7)	Effluent
91st	6.907	2013.77	2002.40	1627.14	1278.12	975.33	869.19	854.53	826.36	799.47
98th	9.497	1981.27	1976.31	1518.00	1131.75	907.56	818.67	794.59	764.93	734.95
105th	11.641	1946.23	1934.93	1612.15	1321.92	1063.43	799.49	774.58	751.44	735.67
113th	15.092	1885.94	1878.17	1554.19	1246.63	898.41	709.37	701.91	698.11	692.73
121st	18.899	1971.37	1968.37	1731.58	1514.61	1312.13	1138.87	1058.17	948.81	908.80

O.L.R. = Organic Loading Rate

APPENDIX C-2: REACTOR PROFILING RESULTS - PROPIONIC ACID

SAMPLING DAY	O.L.R Kg CDO/m^3/d	PROPIONIC ACID CONCENTRATION (mg/l)								
		Influent	Sample Port (1)	Sample Port (2)	Sample Port (3)	Sample Port (4)	Sample Port (5)	Sample Port (6)	Sample Port (7)	Effluent
91st	6.907	172.52	161.04	119.93	90.55	65.34	53.71	50.77	48.92	43.48
98th	9.497	212.52	198.10	152.71	124.39	79.54	51.22	42.50	39.93	37.63
105th	11.641	156.34	155.68	152.21	150.22	147.42	139.39	109.56	34.59	21.79
113th	15.092	122.91	122.52	122.15	121.87	80.38	29.69	1.44	0.00	0.00
121st	18.899	172.61	165.56	141.72	123.10	90.32	73.19	51.26	42.77	49.77

O.L.R. = Organic Loading Rate

APPENDIX C-3: REACTOR PROFILING RESULTS - ACETIC ACID

SAMPLING DAY	O.L.R Kg CDO/m^3/d	ACETIC ACID CONCENTRATION (mg/l)								
		Influent	Sample Port (1)	Sample Port (2)	Sample Port (3)	Sample Port (4)	Sample Port (5)	Sample Port (6)	Sample Port (7)	Effluent
91st	6.907	834.44	825.33	706.41	652.15	478.81	309.03	218.15	210.44	206.33
98th	9.497	786.16	772.59	664.14	629.49	428.21	323.28	250.09	144.37	131.34
105th	11.641	639.52	622.72	593.52	584.22	569.57	547.21	350.01	129.44	55.98
113th	15.092	667.94	659.75	644.05	615.13	517.52	274.22	52.53	6.14	0.00
121st	18.899	691.32	670.14	631.00	538.18	422.17	312.25	220.97	191.30	167.50

O.L.R. = Organic Loading Rate

APPENDIX C-4: REACTOR PROFILING RESULTS - SULPHATE

SAMPLING DAY	O.L.R Kg CDO/m^3/d	SULPHATE CONCENTRATION (mg/l)								
		Influent	Sample Port (1)	Sample Port (2)	Sample Port (3)	Sample Port (4)	Sample Port (5)	Sample Port (6)	Sample Port (7)	Effluent
91st	6.907	164.17	163.74	141.50	123.73	68.33	46.95	8.84	0.00	0.00
98th	9.497	121.94	121.34	102.11	91.06	72.15	43.90	13.03	0.00	0.00
105th	11.641	96.48	96.03	48.72	12.06	4.11	0.00	0.00	0.00	0.00
113th	15.092	95.92	95.55	81.76	45.94	0.00	0.00	0.00	0.00	0.00
121st	18.899	138.11	137.97	103.68	71.09	32.44	15.29	0.00	0.00	0.00

O.L.R. = Organic Loading Rate

APPENDIX C-5: REACTOR PROFILING RESULTS - PH

SAMPLING DAY	O.L.R Kg CDO/m^3/d	PH								
		Influent	Sample Port (1)	Sample Port (2)	Sample Port (3)	Sample Port (4)	Sample Port (5)	Sample Port (6)	Sample Port (7)	Effluent
91st	6.907	6.7	6.8	6.9	7.0	7.1	7.0	7.0	6.9	7.1
98th	9.497	6.8	6.9	7.0	7.0	6.9	7.0	6.9	7.0	7.1
105th	11.641	6.8	6.8	6.7	6.6	6.8	6.8	6.8	6.8	7.0
113th	15.092	6.9	7.0	6.8	6.6	6.9	7.0	7.2	7.0	7.1
121st	18.899	6.8	7.0	7.1	7.2	7.0	7.0	7.0	7.1	7.2

O.L.R. = Organic Loading Rate

APPENDIX C-6: REACTOR PROFILING RESULTS - ORGANIC NITROGEN

SAMPLING DAY	O.L.R Kg CDO/m^3/d	ORGANIC NITROGEN CONCENTRATION (mg N/l)								
		Influent	Sample Port (1)	Sample Port (2)	Sample Port (3)	Sample Port (4)	Sample Port (5)	Sample Port (6)	Sample Port (7)	Effluent
91st	6.907	1.03	2.07	4.93	11.62	15.21	17.87	8.51	13.09	18.85
98th	9.497	0.00	1.09	6.95	15.00	17.83	11.56	8.66	15.79	18.69
105th	11.641	0.21	0.57	27.39	16.87	21.05	18.55	18.00	16.74	23.17
113th	15.092	0.00	0.52	35.09	25.00	18.87	14.43	22.29	23.56	25.91
121st	18.899	0.38	1.02	27.73	33.41	24.89	16.75	16.98	25.03	21.43

O.L.R. = Organic Loading Rate

APPENDIX C-7: REACTOR PROFILING RESULTS - FREE AND SALINE AMMONIA

SAMPLING DAY	O.L.R Kg CDO/m^3/d	AMMONIA CONCENTRATION (mg N/l)								
		Influent	Sample Port (1)	Sample Port (2)	Sample Port (3)	Sample Port (4)	Sample Port (5)	Sample Port (6)	Sample Port (7)	Effluent
91st	6.907	84.93	84.37	78.00	71.71	72.54	71.36	68.10	68.00	70.31
98th	9.497	82.17	79.53	59.11	52.55	47.92	48.13	51.91	46.76	48.88
105th	11.641	79.56	77.61	45.77	41.07	38.85	41.00	42.14	39.00	42.52
113th	15.092	83.77	75.38	31.73	30.22	32.62	33.10	30.07	31.05	34.50
121st	18.899	84.15	81.59	49.10	43.07	45.21	46.68	43.11	44.24	45.21

O.L.R. = Organic Loading Rate

APPENDIX C-8: REACTOR PROFILING RESULTS - TOTAL SUSPENDED SOLIDS

SAMPLING DAY	O.L.R Kg CDO/m^3/d	TOTAL SUSPENDID SOLIDS CONCENTRATION (mg/l)								
		Influent	Sample Port (1)	Sample Port (2)	Sample Port (3)	Sample Port (4)	Sample Port (5)	Sample Port (6)	Sample Port (7)	Effluent
91st	6.907	786.56	714.37	708.46	712.54	733.37	680.15	613.54	502.00	285.50
98th	9.497	642.11	621.56	588.46	624.21	617.47	632.21	638.15	487.15	254.61
105th	11.641	882.71	1022.36	1018.47	1009.22	1024.37	1047.00	1072.11	1004.52	695.16
113th	15.092	856.34	961.44	951.21	972.42	912.03	944.41	971.31	986.12	701.53
121st	18.899	721.76	944.53	878.21	932.15	945.16	922.43	832.14	841.15	812.11

O.L.R. = Organic Loading Rate