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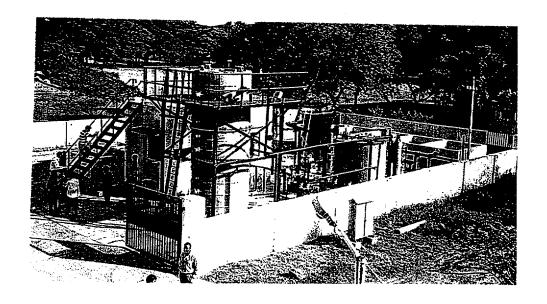
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APPLICATION OF FLESHINGS TO UPFLOW ANAEROBIC SLUDGE BLANKET (UASB) REACTOR WITH TANNERY EFFLUENT FOR BIOGAS GENERATION AT CLRI, CHENNAI, INDIA

UNIDO Contract No.P.97/200 US/RAS/92/120/PDU-3



FINAL REPORT



DEPARTMENT OF ENVIRONMENTAL TECHNOLOGY CENTRAL LEATHER RESEARCH INSTITUTE, CHENNAI, INDIA



UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANISATION, VIEWNA

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SPECIFICATION FOR STIRRER, STAND AND FRP TANK PROCURED UNDER THIS PROJECT

List of symbols and abbreviations

Average Avg **Common Effluent Treatment Plant CETP** Carbon, Hydgrogen and Nitrogen analyser CHN Central Leather Research Institute **CLRI Chemical Oxygen Demand** COD Chromium Crd day diameter dia dry solids DS **Effluent Treatment Plant ETP** Filtrate to Total F/T gram g gram per gram g/g gram per litre g/L hour(s) h High density polyethylene **HDPE** HP **Horse Power** IRS **Indian Rupees** kilogram kg kilometer km kWkilowatt L litre m^3 cubic meter (1000 litres) me/L milli equivalent per litre milligrams per litre mg/L min. minutes millilitre ml MLSS **Mixed Liquor Suspended Solids MLVSS** Mixed Liquor Volatile Suspended Solids NP Nitrogen passed °C degree Celsius negative logarithm of hydrogen ion concentration pН ppm parts per million Regional Programme for Pollution Control in the Tanning RePO Industry seconds sec. Sulfur Recovery Unit SRU Suspended Solids SS tonne (1000 kg) T/T **Total to Total TNO** The Netherlands Oraganisation TS Total solids TVS Total volatile solids **UASB Upflow Anaerobic Sludge Blanket** UNIDO **United Nations Industrial Development Organisation** VSS **Volatile Suspended Solids**

APPLICATION OF FLESHING TO UPFLOW ANAEROBIC SLUDGE BLANKET (UASB) REACTOR WITH TANNERY EFFLUENT FOR BIOGAS GENERATION AT CLRI, CHENNAI INDIA

1. INTRODUCTION

In India 700,000 tonnes of raw hides and skins are processed per annum. During the process after sulfide liming excess fleshing from the hides & skins are removed and it is estimated that 70,000 to 100,000 tonnes of wet fleshing with about 85% moisture is generated per year. The fleshing operations are carried out either manually or mechanically. At present, part of fleshing is used for manufacturing of glue and animal protein but some quantity of fleshing is dumped as a waste due to high moisture content. Such fleshing is dumped as land fill or disposed of along with other solid wastes. The unutilised fleshing containing high concentration of lime and sulfide putrefy and produce obnoxious odour, cause groundwater pollution, attract flies, rodents and stray dogs causing public nuisance. Tamil Nadu Pollution control Board (TNPCB) is yet to identify the site for safe disposal of solid wastes. Due to high moisture content handling and transportation of such fleshing become difficult. To solve the disposal problem of fleshing, one of the options being estimated is biomethanation. One tonne of wet fleshing with 85% moisture is estimated to generate 20-30 m3 of biogas gas. According to rough estimation, about 15000-18000 tonnes of wet fleshing (85% moisture) is dumped as waste in Tamil Nadu, signifying a potential loss of 375000 to 450000 m³ of biogas gas and resultant organic manure. The quantity of fleshing generation and expected biogas production from tanneries in Tamil Nadu is given in Table 1.

Table 1. Quantity of fleshing generation and expected biogas production from Tanneries in Tamil Nadu

SL No	Description	Value
1	Number of tanneries in Tamil Nadu	900
2	Processing capacity per annum	300000 tonnes
3	Quantity of fleshing generated per annum	36000 tonnes
4	Quantity of fleshing unutilised	18000 tonnes
5	Biogas generation expected from unutilised fleshing	0.45 million m ³

The fleshing can be anaerobically digested in closed digesters and digested sludge used as manure. For efficient anaerobic digestion in UASB reactor, the fleshing has to be reduced in size. Though the biogas generated in the process can be recovered and used as energy, one of the major problems faced in biomethanation of fleshing is pulverisation for easy feeding and better digestion.

Pulverisation of the fleshing can be achieved either mechanically or biologically. Mechanical pulverisation involves high investment and operation and maintenance cost. It may not be feasible for small tanneries processing up to 5 tonnes of rawhides or skins per day to adopt mechanical pulverisation. Implementation and maintenance of treatment systems separately for solid and liquid wastes may be cumbersome and expensive. UNIDO under the programme US/RAS/92/120/PDU/3 subcontracted to CLRI a pilot scale experiment to apply fleshing in the 12.5 m³ capacity Upflow Anaerobic Sludge Blanket (UASB) pilot plant installed under TNO-CLRI co-operation programme.

One of the methods studied was liquefaction of fleshing and then biomethanation of the liquefied fleshing in UASB reactor. For this purpose initially fleshing was characterised and bench scale studies were taken up for liquefaction and anaerobic digestion. After successful completion of the bench scale studies pilot scale studies were taken using the 12.5 m³ pilot UASB reactor at CLRI.

1.1 Present Mode of Disposal

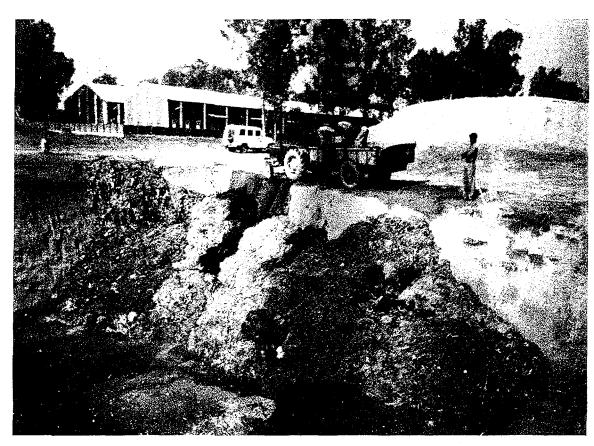
At present, part of the fleshing produced is taken for making glue and animal protein. The rest is dumped as waste due to high sulfide and moisture content. Moreover the demand for animal glue is diminishing day by day.

The fleshing is dumped on the riverbanks along with other garbage. In some areas fleshing is buried in the tannery premises it self. This leads to leachate problem and pollution of ground water. Palar river in Tamil Nadu has impervious soil below 20 m depth. Therefore subsurface water which is used for imigation and human consumption gets contaminated rapidly. Nearly 90% of the imigation in North Arcot District is done by lift imigation. Safe land fill sites for the disposal of sludge and solid wastes are yet to be identified by local pollution control bodies.



DUMPING OF WETLIMED FLESHING IN OTHER PARTS OF THE WORLD





DISPOSAL OF WETLIMED FLESHING IN UNLINED PITS



2. OBJECTIVES

The main objectives and terms of reference of the UNIDO, PDU/3 of US/RAS/92/120 carried out by CLRI as subcontractor are:

- To characterise the fleshing from different sources of hides and skins.
- To develop the appropriate method for making the fleshing into slurry or liquid fit for feeding into UASB system.
- Composition of fleshing and wastewater to be fed into the reactor for efficient bio degradation.
- To study the feasibility for biomethanation of fleshing.
- To optimise organic loading rate to the UASB system.
- To optimise of solid and hydraulic loading rates.
- To determine the effectiveness of biomethanation of the fleshing in UASB system.
- To evaluate the performance of UASB with variation of fleshing load and composite tannery wastewater.
- · To quantify and qualify biogas generated.
- To convert biogas into energy.

3. CHARACTERISTICS OF WETLIMED FLESHING

The fleshing generated from buffalo, cow, buffcalf, cowcalf, goat and sheep was brought from different tannery clusters and were analysed. Liming operation is carried out in pits and paddles. The quantity and quality of lime and sodium sulfide used vary from tannery to tannery. Many tanneries use lime stone with very low purity which leads to more ash content in fleshing/spent lime liquor. Tanneries are adopting both hair saving & hair pulping process. Some tanneries are reusing the lime/lime liquor in the process. COD (g/g of dry solid) and ash percentage of fleshing is varying from sample to sample and tannery to tannery based on the raw material quality, quantity and purity of chemical used in the process, type of process adopted in the tannery, quantity of water used, moisture content and freshness of the fleshing etc. Many tanneries are washing the materials before fleshing operation. The characteristics of fleshing collected from tanneries processing different types of Hides/Skins are given in Table 2. The variations observed in the characteristics are due to above reasons.

Table 2. Characteristics of Fleshing collected from Tanneries processing different types of Hides/Skins

SL Parameters . Raw material				
No		Buff and Cow hide	Buff and Cow calf	Skins (Sheep and goat)
1	рН	12.0-12.4	12.0-12.3	11.8-12.2
2	Moisture	81-90	82-90	74-90
3	Ash content	0.18-0.47	0.16-0.37	0.22-0.7
4	Volatile solids	0.53-0.82	0.63-0.84	0.3-0.78
5	COD Total	0.57-1.02	0.7-1.4	0.66-1.08
6	Calcium as Ca (Total)	0.07-0.15	0.06-0.2	0.11-0.17
7	Sulfate as SO ₄ (Total)	0.001-0.007	0.0005-0.0054	0.001-0.008
8	Sulfide as S	0.0004-0.003	0.0003-0.002	0.0003-0.0004
9	Phosphorous as P	0.0002-0.0019	0.00015-0.00045	0.0002-0.0015
10	Ammonia nitrogen as N	0.0017-0.0036	0.002-0.0045	0.001-0.0023
11	TKN	0.06-0.12	0.09-0.14	0.03-0.09
12	Oil & Grease	0.05-0.12	0.07-0.2	0.06-0.6

Note: All values except pH and moisture are expressed in w/w on dry basis. Moisture content expressed in percentage.

The samples were also analysed using CHN analyser for carbon, hydrogen and nitrogen and results are reported in Table 3.

Table 3. Nitrogen, Carbon and Hydrogen analysis for dried fleshing using CHN analyser

SL	Parameters	Parameters	Unit			Place and Samp	ole Source	
No			Ranipet Buffalo	Ranipet Cow	Vaniyambadi Skin	Melvisharam Buff calf	Melvisharam Cow calf	
1	Nitrogen	%	10.09	6.48	9.01	9.07	8.67	
2	Carbon	%	32.85	27.45	37.07	30.77	40.07	
3	Hydrogen	%	5.31	4.36	5.85	4.97	6.38	

3.1 Analytical Procedure

Fleshing samples were analysed after drying it in oven for removal of moisture. Only dried fleshing samples were powdered and taken for analysis. The fleshing samples were analysed for the parameters as per the Standard Methods for the examination of water and wastewater (17 and 19th Edition). Analytical procedures followed are given briefly in Annexure – I.

4. HOMOGENIZATION AND LIQUEFACTION OF WETLIMED FLESHING

The analytical results established that volatile solid content in fleshing is above 50% and the moisture is above 75%. COD is in the range of 0.57-1.4 g/g of dried solids. These basic parameters were indicative of the feasibility of biomethanation of fleshing and lab scale studies were undertaken to determine the biodegradability of fleshing. As efficiency of biodegradation can be increased by pulverising the fleshing, various methods of pulverisation as described below were estimated:

- a. Mechanical homogenisation using homogeniser
- b. Homogenisation after dipping the fleshing in hotwater for few minutes
- c. Biological liquefaction of fleshing

The various methods adopted for liquefaction of wetlimed fleshing is given in Fig 1.

4.1 Mechanical Homogenisation of Fleshing

Fleshing collected from the tanneries varied in size from 30-45 cm long and 2 to 10 cm in width. Due to its fibrous and slippery nature handling of wet fleshing was very difficult. Long pieces of fleshing were cut into small pieces of 1 cm or below using scissors and then homogenised using Kinematica make homogeniser along with tap water at room temperature. Homogenisation was not adequate as the fleshing got stuck into the pores of homogeniser. The fibres in the fleshing got jammed on the shaft of the homogeniser. This led to inadequate homogenisation of the fleshing.

4.2 Mechanical Homogenisation of Fleshing after Soaking in Hotwater

Wetlimed fleshing was soaked in hot water of about 70-80°C for 15 min. and then homogenised. In the process, the homogenisation was almost complete, but it needed heat energy. Therefore biological liquefaction of fleshing was tried using treated tannery effluent from UASB reactor.

4.3 Biological Liquefaction of Fleshing

Various combinations of biological liquefaction of fleshing were tried

- a. Liquefaction of fleshing with sludge from UASB reactor in different ratios
- b. Liquefaction of fleshing with sludge and anaerobically treated tannery wastewater.
- Liquefaction of fleshing with anaerobically treated tannery wastewater with different ratios.

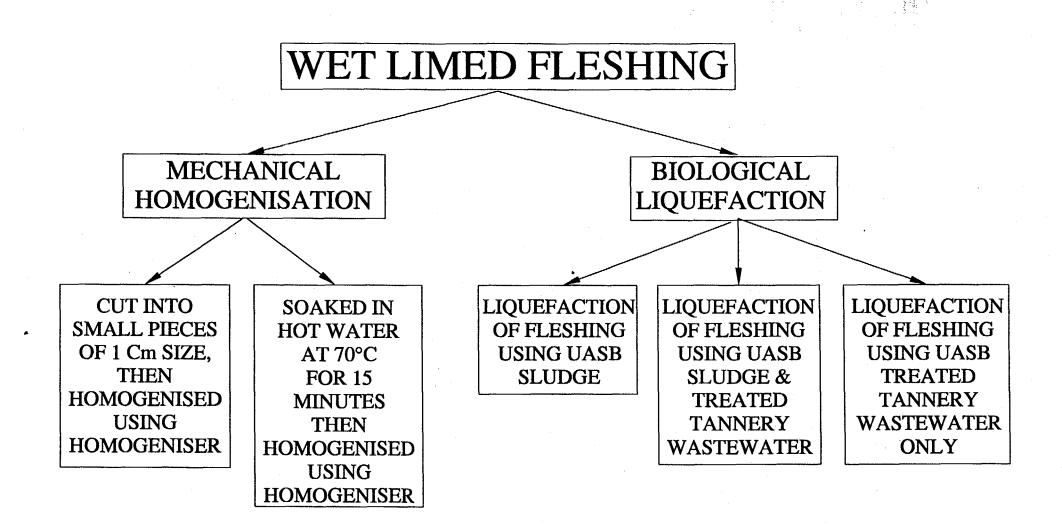


FIG 1 VARIOUS LIQUEFACTION METHODS OF WET LIMED FLESHINGS

- d. Liquefaction of fleshing with anaerobically treated tannery wastewater with pH adjustment
- e. Liquefaction of fleshing with anaerobically treated tannery wastewater without pH adjustment.

From the above studies it was observed that with all the above mentioned five methods, fleshing could be liquefied. But the methods of liquefaction of fleshing with sludge from UASB reactor in different ratios and liquefaction of fleshing with sludge and anaerobically treated tannery wastewater were dropped as frequent withdrawal of bio sludge from UASB reactor required for liquefaction would affect the UASB performance as required MLVSS cannot be maintained in the reactor.

The method of liquefaction of fleshing with anaerobically treated tannery wastewater with pH adjustment was discontinued as hydrogen sulfide was liberated from fleshing during the addition of HCI.

The method of liquefaction of fleshing with anaerobically treated tannery wastewater without pH adjustment was selected for application of pilot scale studies as only equal amount of treated tannery wastewater is required and this method was the simplest of all.

5. BIOLOGICAL LIQUEFACTION OF WETLIMED FLESHING AT CONTROLLED TEMPERATURE

Quantity of wet limed fleshing and UASB effluent taken for liquefaction study at controlled temperature is given in Table 4.

Table 4. Quantity of wet fleshing and UASB effluent taken for liquefaction studies at 30 °C

Parameter	Reactor I	Reactor II
Reactor capacity	2 L	2 L
Wet limed fleshing	780 g	820 g
UASB effluent	780 ml	820 ml
Temperature	30 °C	30 °C

Moisture content, COD (Total), Volatile & Total Solids were measured for the wet limed fleshing and UASB effluent. The characteristics of fleshing and UASB effluent are given in Table 5.

Table 5. Characteristics of fleshing and UASB effluent

Parameter	Fleshing	UASB effluent
Moisture	87%	
Total solids		18468 mg/L
Total volatile solids	0.618 g/g of dry solids	1080 mg/L
COD (total)		1236 mg/L
COD (soluble)		690 mg/L

Liquefaction of fleshing studies were carried out in 2 litre capacity double jacketed bench scale reactors at 30 °C. Two reactors were taken up for the study. Both the reactors content were maintained at 30°C by circulating water at the outer jacket.

Due to logistic reasons the sampling and analysis were done 4 to 5 days in a week. After mixing the reactor contents thoroughly samples were taken for analyses of COD (Soluble). Samples were centrifuged at 5000 rpm for 5 min. COD (Soluble) and pH of the samples were determined and are given in Table 6. Graphical representation is given in Graph 1. Analytical result of the liquefaction at 30°C temperature is given in Table 7.

Table 6. COD (Soluble) and pH of the liquefaction studies at 30°C temperature

Days	pH Reactor I	pH Reactor II	Reactor I Soluble COD (mg/L)	Reactor II Soluble COD (mg/L)
0	11.61	10.51		
1	12.10	11.22	5781	4414
2	12.14	11.58	7988	5017
3	11.90	11.52	11403	6306
6	11.77	11.55	21931	10300
7	11.48	11.40	28587	15882
8	11.32	11.57	34193	20039
9	11.06	11.78	34753	26065
10	10.85	10.68	36435	31951
13	11.12	10.81	41620	38257
14	11.03	10.7	47295	40358
16	11.12	10.49	54477	48872
17	10.91	10.58	55073	52129

LIQUEFACTION OF LIMED WET FLESHING AT 30 DEG.CELCIUS TEMP

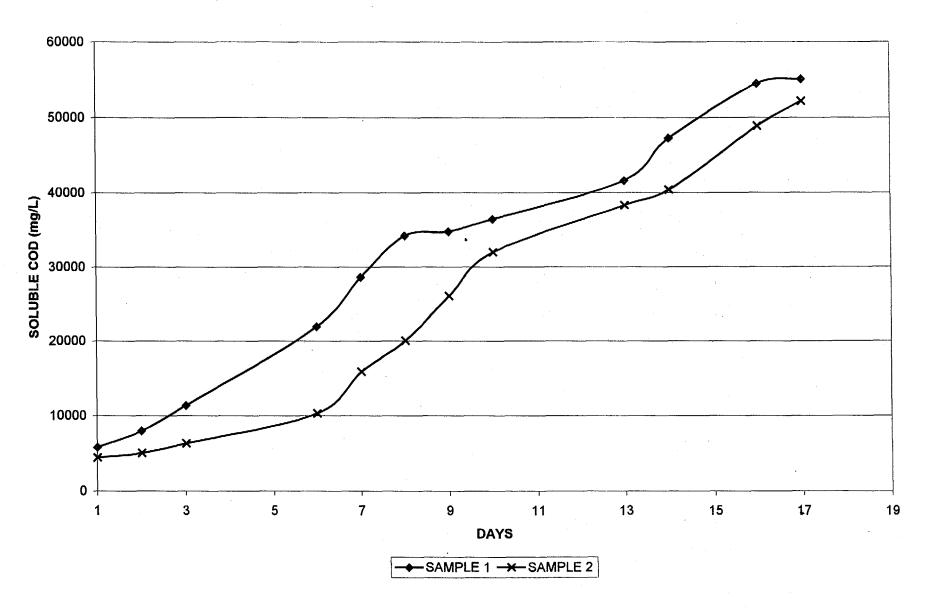


Table 7. Analytical results of the liquefaction at 30 °C temperature

Parameters	Reactor I	Reactor II
Reactor volume	2 L	2 L
Weight of fleshing in g	780	820
UASB effluent in ml	780	820
Ratio of fleshing vs Wastewater	1:1	1:1
Study period (days)	17	17
Temperature	30 °C	30 °C
Total COD in g	88.9	93.45
COD soluble in g measured after 17 days	55.07	52.12
COD in soluble state after 17 days	62%	55%

From the above study it was observed that nearly 60% of the total COD got converted into soluble COD.

After liquefaction the liquefied fleshing was screened through a 5 mm sieve and the quantity of solids retained in 5 mm sieve is given in table 8.

Table 8. Quantity of solids retained in 5 mm sieve

Parameter	Value
Weight of wet-limed fleshing taken before liquefaction	780 g
Dry solids in wet-limed fleshing	101.4 g
Volatile solids in wet-limed fleshing	62.25 g
Quantity of dry solids retained in 10mm sieve after liquefaction	20.49 g
Quantity of volatile solids retained in 10mm sieve	14.73 g
Percentage of volatile solids liquefaction	76.3

The advantages and disadvantages of the mechanical and biological homogenisation of fleshing are presented in the Table 9.

Table 9. Advantages and disadvantages of mechanical homogenisation & biological liquefaction of fleshing

SL No	Parameter	Homogenisation using Homogeniser	Homogenisation using Homogeniser after soaked in hot water at 70°C for 15 min.	Liquefaction of fleshing using UASB treated tannery wastewater only
1	Manual cutting of fleshing	Needed	Not needed	Not needed
2	Heating	Not needed	Needed	Not needed
3	Time requirement	About 1 hr	About 30 min.	About 10-15 days
4	Observation	After homogenisation still some fibres are present	No fibres were observed after homogenization	No fibres were observed after liquefaction
5	pH adjustment	Not needed	Not needed	Not needed
6	Mechanical equipment	Mechanical homogeniser	Mechanical homogeniser	Container with stirrer assembly

From the above table it may be seen that biological liquefaction is an appropriate and easy technique for liquefaction of fleshing and application to anaerobic reactor for biomethanation for small scale installation though the time required for biological liquefaction is more.

6. BIOMETHANATION OF HOMOGENISED AND LIQUEFIED FLESHING USING BATCH SCALE ANAEROBIC REACTORS

6.1 Experimental set up of bench scale bio reactor

Double jacketed bench scale reactors of 2 litre capacity each were taken for the study. The reactor is provided with airtight lid, a stirrer, a gas out let, a sample port and an online pH meter. The stirrer is connected to a timer so that stirring interval and duration of the stirring can be controlled. In addition to this, to achieve good mixing of the reactor contents, stirrer rpm also can be adjusted. Gas outlet from the reactor is connected to a Marriot flask containing 6N NaOH solution with indicator. The sodium hydroxide solution absorbs CO₂

and H₂S from the biogas. NaOH volume equivalent to methane volume generated is displaced into a measuring cylinder.

6.2 Biomethanation of Mechanically Homogenised Fleshing

Wetlimed fleshing was collected from tannenes and homogenised for biomethanation studies by two different methods:

- 1. Mechanical homogenisation with tap water at room temperature.
- Mechanical homogenisation with tap water after soaking fleshing in hot water.

6.2.1 Biomethanation of Mechanically Homogenised Fleshing at ambient Temperature

Wetlimed fleshing of 200 g were cut into small pieces of 1 cm and below and mixed with known amount of tap water and homogenised at ambient temperature using GK-A model Kinematica AG make homogeniser. The pH of the homogenised fleshing was in the range of 11.0 to 12.9. Methanogenic bacteria will perform best in the pH range of 6.5 to 8.0. Hence pH of the homogenised fleshing was adjusted to 7.5 using 6 N HCI.

For biomethanation studies the reactor was seeded with 300 ml of biosludge from UASB pilot plant treating tannery wastewater. The volatile solids content of the seed sludge was 60 g/L. Percentage of volatile solids was 35%.

Methane production was measured daily by the displacement of NaOH solution kept in a Marriot bottle. Reactors were intermittently stirred using a timer. The quantity biogas produced from homogenised fleshing was observed daily.

6.2.2 Biomethanation of Mechanically Homogenised Fleshing Soaked with Hot Water

Fleshing was prepared as per procedure described above. 2 Nos of 2 L capacity reactors were fed with around 200 g of homogenised wet fleshing after adjusting the pH to 7.0 using HCl. Reactor was seeded with UASB sludge of volatile solids 15 g. The reactor contents were stirred for 60 seconds for every 12 min. Methane generated from fleshing was measured by displacing 5% NaOH solution in Marriot bottle. By this method of collection hydrogen sulfide and carbon-di-oxide are absorbed and only methane is measured and the methane production results are reported in Graph 2. Details of sample preparation for uncut, cooked and cut & homogenised fleshing is given in Table 10.

Table 10. Sample preparation data

SL No	Parameter	Reactor-I	Reactor-II
1	Description of the sample and sample preparation	Uncut, cooked & homogenised fleshing	Cut & homogenised fleshing
2	pH of the sample	7.5	7.5
3	Reactor volume	2 L	2 L
4	Wet fleshing weight	200 g	200 g
5	Dry solids	52 g	52 g
6	Volatile solids	42 g	42 g
7	Volume of seed sludge taken	300 ml	300 ml
8	Volatile solids in seed sludge	6 %	6 %
9	Study period	36 days	36 days
10	Methane produced	. 38 L	32 L

Based on the results obtained on the methane production for the uncooked and cooked fleshing, it was observed that cooked fleshing degraded more quickly for obvious reasons. Initially protein, carbohydrate etc were degraded by the microorganisms. After that a lag period was observed in both the reactors. During the lag period the methane production in both the reactors was low. Degradation of fats started after the lag period in both the reactors. Rate of generation of methane production was higher in cooked fleshing.

Volume of methane production was also higher by 15% for the cooked fleshing. This study was continued till the gas production in both the reactors ceased. The daily gas production is shown in Graph 2.

From the results it is observed that in cooked fleshing 0.90 L of methane was produced per gram of volatile solids but for uncooked fleshing 0.70 L of methane was produced per gram of volatile solids introduced in the reactor. More than 90% of methane production was observed within a period of 30 days. The results are given in Table 11. Good homogenisation was obtained for the cooked fleshing and also rate of methane production was more in the cooked fleshing when compared with uncooked fleshing.

BIOMETHANATION OF LIQUIFIED FLESHING

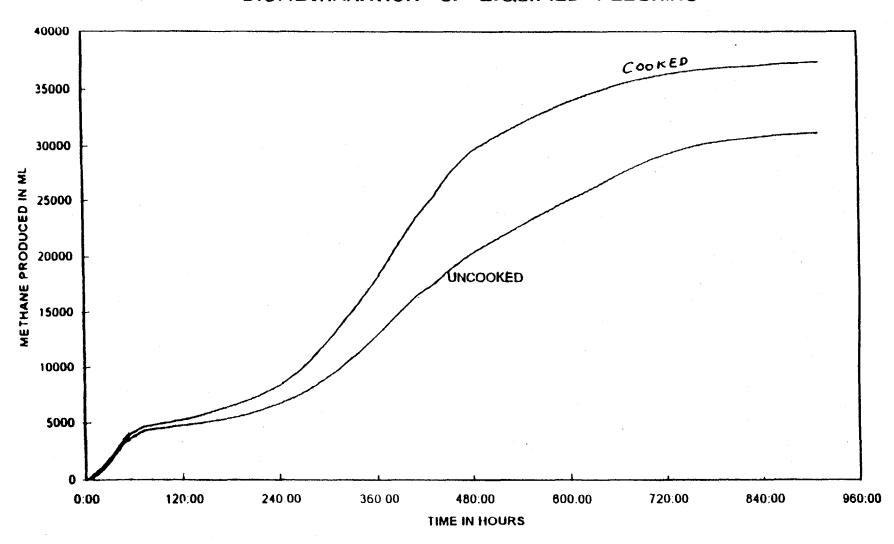


Table 11. Gas production observed

Sl No	Parameter	Reactor-I	Reactor-II
1	Weight of wetlimed fleshing	200 g	200 g
2	Period	30 days	30 days
3 - 2	Methane produced over a period of 30 days	36 L *****	29 L: 3.54
4	Methane produced per kg of wet fleshing	180 L	145 L
5	Methane produced per kg of dry fleshing	700 L	560 L
6	Methane produced per kg of volatile matter	900 L	725 L

From the above study it was established that fleshing can be anaerobically biodegraded and biogas can be generated. Quantity of gas generated from cooked fleshing is slightly more than the gas generated from uncooked fleshing.

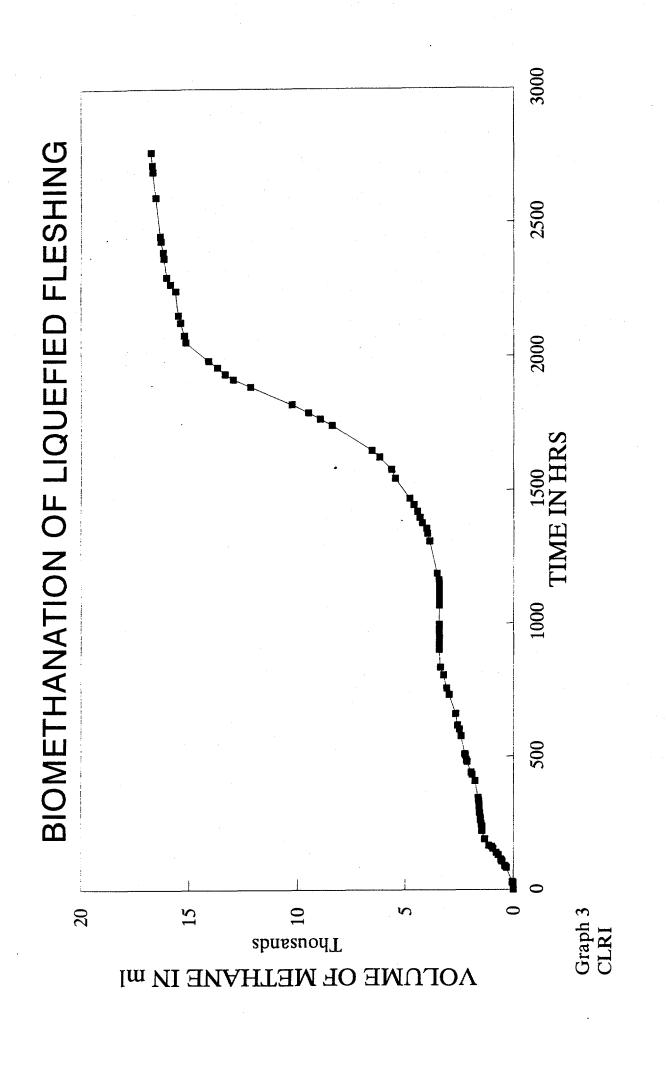
6.3 Bench Scale Study for Biomethanation of Liquefied Fleshing using UASB Effluent

For this study 2 litre bench scale reactor was used. 250 ml of seed sludge was taken along with 500 ml of liquefied fleshing and 1250 ml of UASB effluent. The characteristics of the liquefied fleshing and seed sludge are given in Table 12. The daily gas production is shown in Graph 3.

Table 12. Characteristics of the sludge and liquefied fleshing

SI No	Parameter	Liquefied fleshing	UASB Sludge
1	рH	8.74	
2	Sulfide filtered	75	-
3	Chloride filtered	4416	-
4	COD total	18938	
5	COD filtered	13446	-
6	Total solids	22340	57544
7	Total volatile solids	11104	21972
8	Suspended solids	13676	47668
9	Volatile suspended solids	6204	21264
10	VFA	140 me/L	-
11	Bicarbonate Alkalinity	11.2 me/L	

Note: All values except pH, VFA and bicarbonate alkalinity are expressed in mg/L. VFA and bicarbonate alkalinity are expressed in me/L



7. RESULTS OF LAB SCALE STUDIES

From the laboratory studies the following observations were made

Fleshing has to be cut into small pieces before it is homogenised. Raw uncut fleshing could not be homogenised using mechanical homogeniser.

Fleshing dipped in hotwater at 70-80°C temperature for about 15 min. could be easily homogenised.

CH₄ production of 0.7-0.9 L per g of volatile solids was observed over a period of 30 days.

Biologically fleshing can be liquefied by mixing with UASB effluent.

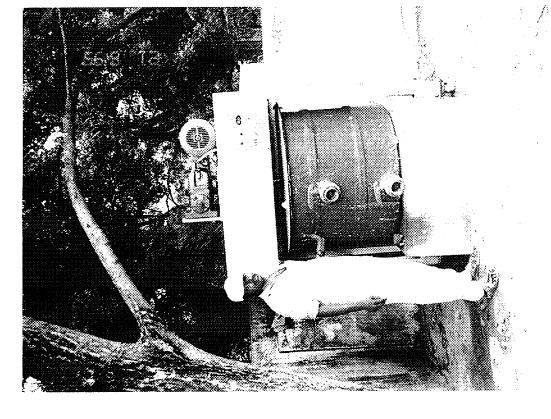
8. CONCLUSION OF LABSCALE STUDIES

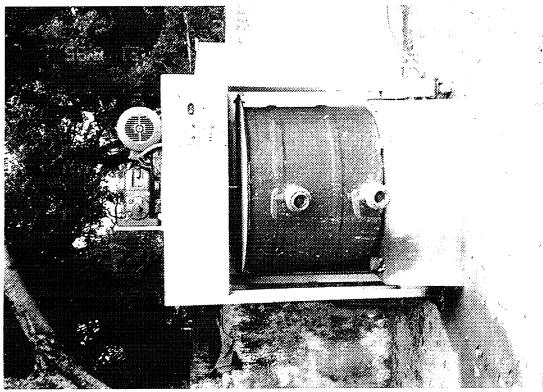
Based on the lab scale and batch experiment results of the various liquefaction methods, liquefaction of limed fleshing using UASB treated tannery effluent without pH adjustment was found to be more appropriate particularly with reference to field application in conditions prevailing in India and therefore adopted for the pilot scale study of biomethanation of fleshing with tannery composite wastewater in pilot scale UASB reactor.

During the pilot plant studies the wetlimed fleshing was mainly brought from tanneries in Pallavaram. They process both cow and buff hides. The pH of the wetlimed fleshing was in the range of 11.5-12.2. Moisture content of the fleshing was 82% to 90%. The volatile solids content were 0.5-0.8 g/g of dry solids.

9. PILOT SCALE STUDIES OF LIQUEFACTION AND BIOMETHANATION

For the purpose of biological liquefaction FRP tank of 550 litres capacity with timer control and stirrer arrangement had been fabricated and installed near the 12.5 m³ capacity UASB pilot plant. Background information of the pilot scale UASB plant is given in Annexure-II. The details of the liquefaction tank are given in Annexure-III.





9.1 Liquefaction of Fleshing

Wetlimed fleshing was collected from commercial tanneries for the pilot plant studies. For liquefaction of fleshing equal amount of fleshing and UASB treated effluent was mixed at ambient temperature. Ten to fifteen days were required for fleshing to get liquefied as per data from different samples. After liquefaction the liquefied fleshing was screened through a 10 mm sieve and mixed with tannery wastewater in the equalisation tank. Characteristics of the wetlimed fleshing brought from tanneries are given in Table 13.

Table 13. Characteristics of wet limed fleshing collected from tanneries in Pallavaram, Chennai for liquefaction and biomethanation studies

SI No			Samples							
	Parameters	1	2	3	4	5	6	7	8	9
1	Moisture content (%)	83.0	82.7	84.7	83.6	87.1	89.5	90.0	89.1	86.7
2	COD g/g of dry solid	O.58	0.72	0.73	0.75	0.95	1.68	0.95	0.8	0.79
3	Volatile solids g/g of dry solid	0.51	0.58	0.54	0.57	0.76	0.80	0.64	0.70	0.67
4	Ash content g/g of dry solid	0.49	0.42	0.46	0.43	0.24	0.20	0.36	0.30	0.33
5	Total nitrogen g/g of dry solid	0.056	0.074	0.068	0.072	0.091	-	0.104	0.11	

9.2 Characteristics of Liquefied Fleshing

Liquefied fleshing was analysed for COD (total and soluble), VFA, TS, TVS, SS and VSS. Liquefied fleshing was homogenised and analysed for total COD. The total and soluble COD of liquefied fleshing were 41-75 g/L and 23-40 g/L respectively. The volatile fatty acids content range from 150-340 me/L. Total solids content were in the range of 24-71 g/L and total volatile solids were 10-29 g/L. The total suspended solids were 13-42 g/L and its volatile solids content were 6-18 g/L. Characteristics of liquefied fleshing fed in to the reactor are given in Table. 14.

Table 14. Characteristics of liquefied fleshing

DATE	COD (Total) mg/L	COD (Soluble) mg/L	VFA me/L	TS mg/L	SS mg/L	TVS mg/L	VSS mg/L
05-Aug-98	32760	23410	157	24830	13205	10488	6300
30-Aug-98	48671	32700	242	44296	21220	19470	8965
10-Sep-98	45900	28224	248		32400	16760	8650
14-Sep-98	59584	36064	285	31900	19488	15760	9136
21-Sep-98	55000	32720	260		37600		16230
24-Sep-98	51744	30576	240	49268	25676	21248	11824
07-Oct-98	45472	23328	236	32180	19088	19400	12000
11-Oct-98	41230	24304	205		27400		9800
20-Oct-98	46700	23520	210		34100		18230
22-Oct-98	75260	40376	343	62070	34256	28960	16750
30-Oct-98	36200	25224	217		29328		13501
5-Nov-98	46000	24540	206		41550		17340
11-Nov-98	47560	33088	234				
18-Nov-98	66700	35670	294	71300	41670	23400	17940
24-Nov-98	48000	28470	252				

10. BIOMETHANATION OF FLESHING IN UASB PILOT PLANT

About 30,000 litres of wastewater and 150 kg of wetlimed fleshing are generated during the process of one tonne of hides/skins from raw to finish. During the first phase 30 kg of wetlimed fleshing was liquefied and mixed with 15000 L of tannery composite wastewater and fed in the UASB reactor. The quantity of addition of liquefied fleshing to tannery wastewater gradually increased to 100 kg (200 L) for 15000 L of composite tannery wastewater. Flow diagram for biomethanation of fleshing is given in Fig.2

The period and the quantity of liquefied fleshing added into tannery wastewater are given in Table 15.



LIQUEFIED FLESHINGS READY FOR FEED



Table 15. Details of liquefied fleshing added into tannery wastewater

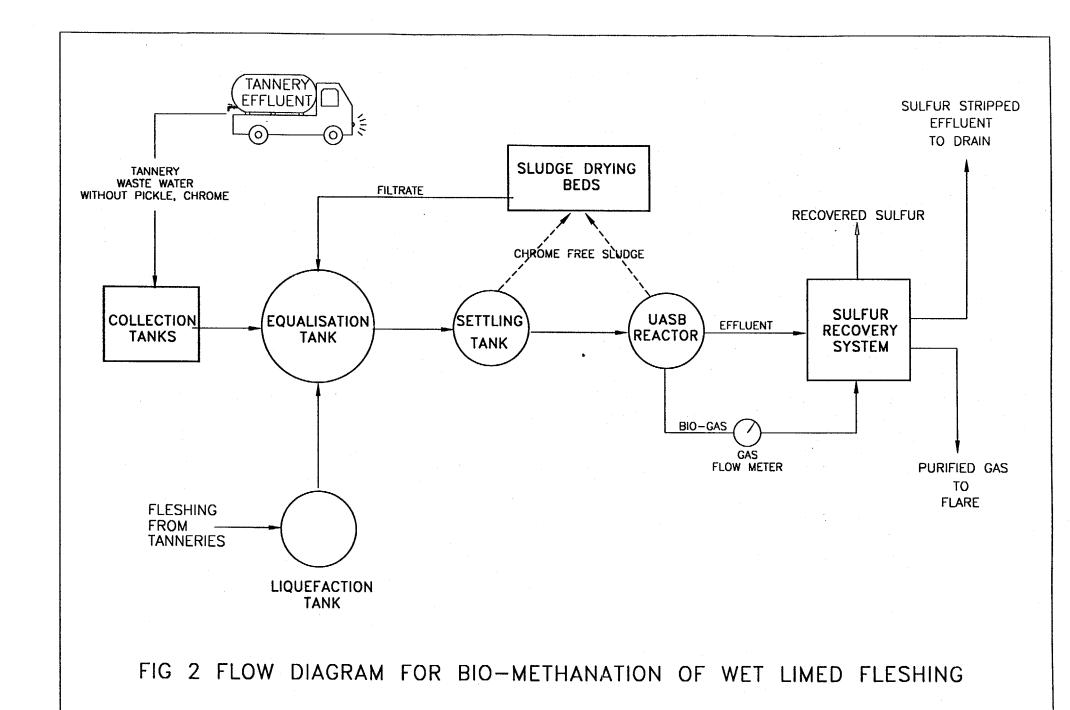
SL No	(Period) Days	Qty of Wetlimed Fleshing in kg	Qty of Liquefied Fleshing added in L for 15000 L of Tannery Wastewater
1	15 May'98-10 Jun'98	30	60
2	11 Jun'98-17 Aug'98	50	100
3	18 Aug'98-09 Sep'98	65	130
4	10 Sep'98-31 Oct'98	75	150
5	01 Nov'98-28 Feb'99	100	200

Tannery composite wastewater with liquefied fleshing was used as the influent for UASB reactor. The characteristics of liquefied fleshing is given in Table 16.

Table 16. Characteristics of liquefied fleshing

Sl No	Parameter	Value			
		Min.	Max.	Avg.	
1	COD (Total)	32760	75260	49750	
2	COD (Soluble)	23330	40370	29500	
3	Total Solids	24830	71300	45100	
4	Suspended Solids	13205	41670	29000	
5	Total Volatile Solids	10500	28960	19430	
6	Volatile Suspended Solids	6300	18230	12800	

Note: All values are expressed in mg/L.



11. RESULTS AND DISCUSSION ON PERFORMANCE

Influent Quality to UASB after mixing with Liquefied Fleshing

Not much variation was observed in the influent characteristics due to the addition of liquefied fleshing except COD, VFA and Nitrogen. The characteristics of the influent has changed when the UASB fed with 15000 L of composite tannery wastewater mixed with 150 L of biologically liquefied fleshing (75 kg of wetlimed fleshing with average 85% moisture) as given in Table 17.

Table 17. Percentage increase in the tannery composite wastewater due to the addition of liquefied fleshing

SI No	Parameter	Percentage Variation due to the Addition of Liquefied Fleshing into the Composite Wastewater
1	Flow (L/day)	1.0
2	COD	10.0
3	VFA as me	12.0
5	Sulfate as SO ₄	0.4
6	Sulfide as S	1.3
8	Total Dissolved Solids	1.6

Hydraulic Retention Time (HRT)

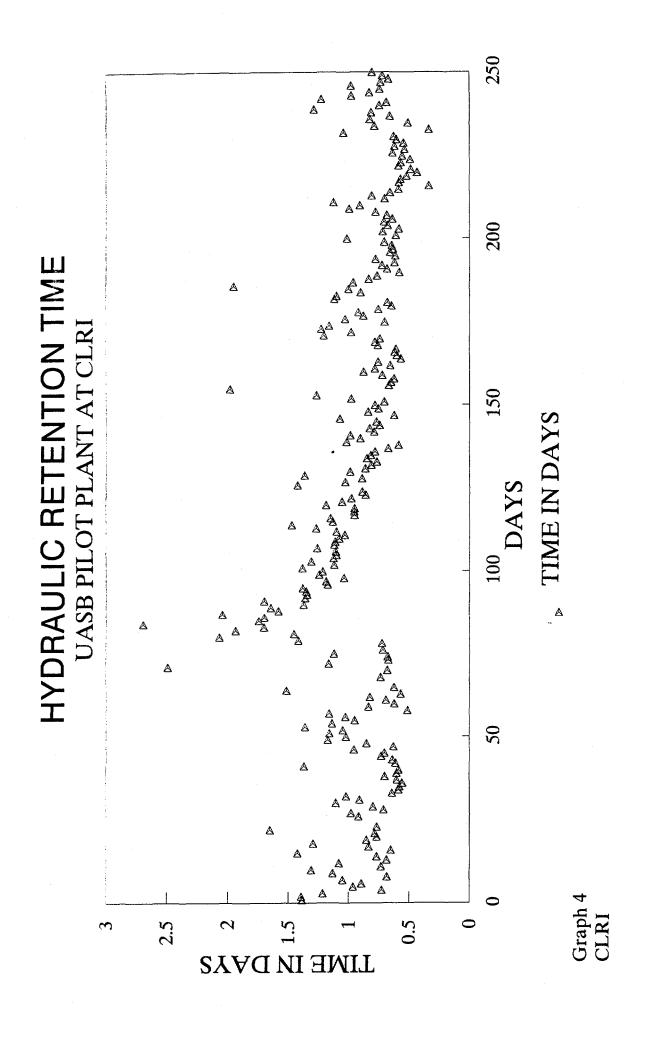
Average HRT during the study period was about 21 hrs. The detention time of the UASB reactor has not been changed during the study period due to the addition of liquefied fleshing. Details of HRT maintained is given in Graph 4.

COD Load & Removal Efficiency

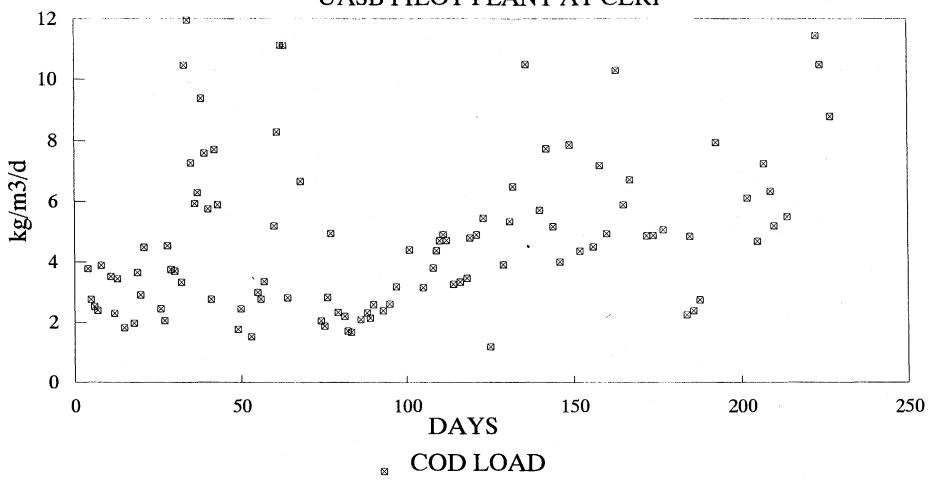
During the study period the average COD (F/T) removal efficiency observed was about 63%. Maximum COD loading rate applied was 11.5 kg/m 3 /d. COD loading rate is given in Graph 5 & COD (T/T) & COD (F/T) estimated after stripping H₂S is given in Graph 6 & 7 respectively.

H₂S and CO₂ Content in Biogas

The maximum biogas production was 14500 Litre /day. Daily biogas production is given in Graph 8. The concentration of H_2S and CO_2 in the biogas was measured using drager tubes and the results are given in Table 18. The biogas from UASB reactor was cleaned in sulphur recovery system. After cleaning the biogas in SRU the maximum concentration of H_2S was 0.06%.



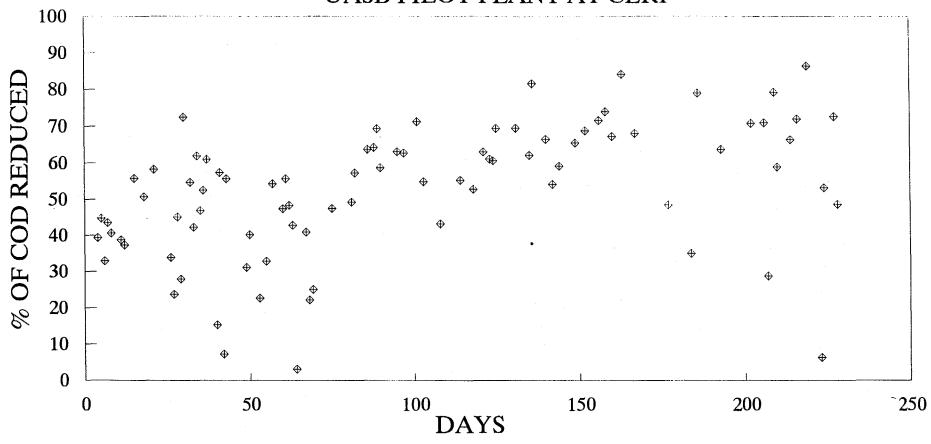
COD (TOTAL) LOAD UASB PILOT PLANT AT CLRI



Graph 5 CLRI

PERCENT COD REDUCTION

UASB PILOT PLANT AT CLRI

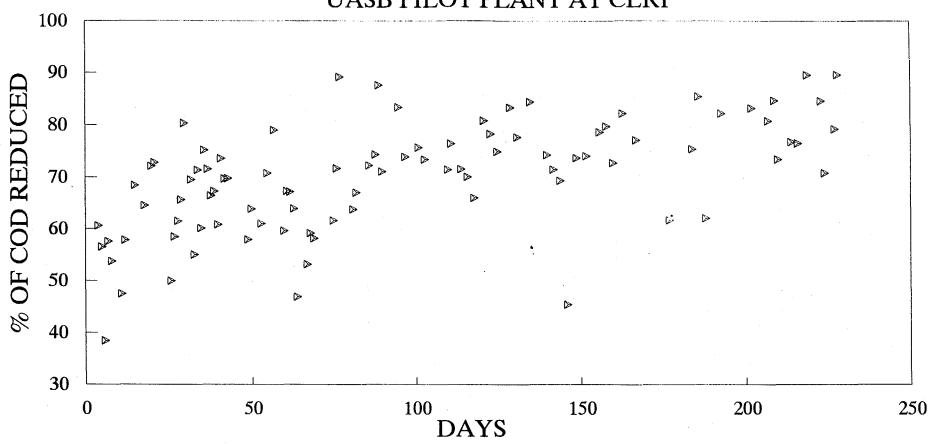


COD (T/T)NP (Nitrogen passed for sulfide stripping)

Graph 6 CLRI

PERCENT COD REDUCTION

UASB PILOT PLANT AT CLRI

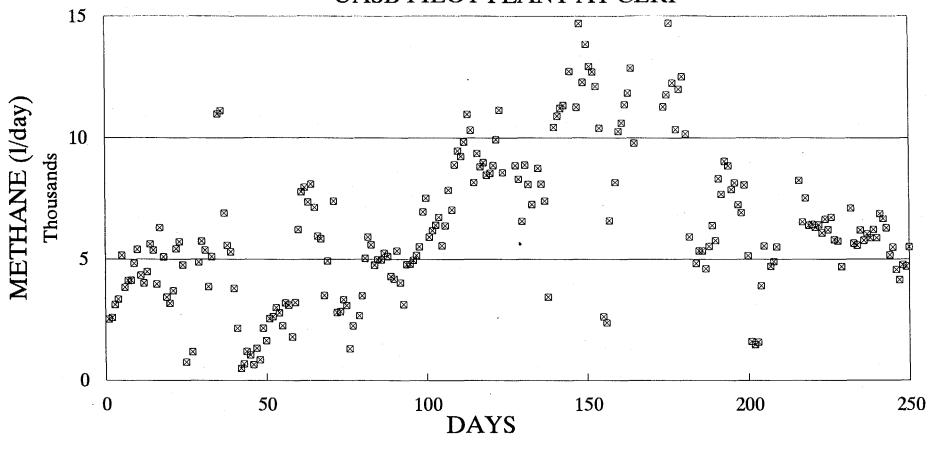


COD (F/T) NP (Nitrogen passed for sulfide stripping)

Graph 7 CLRI

METHANE PRODUCTION IN LTS/DAY

UASB PILOT PLANT AT CLRI



METHANE PRODUCED I/day

Graph 8 CLRI Therefore the cleaned biogas is suitable for use in the dual fuel engine to convert it into electrical energy. No change in methane content in the biogas was observed when compare to the period when only wastewater was treated in the reactor. The COD increase due to the addition of liquefied fleshing for 15000 L of tannery wastewater is given in Graph 9.

Table 18. Hydrogen sulfide and CO₂ content in biogas

SL No	Parameter	Value
1	Methane	75-85%
2	Hydrogen sulfide in biogas (v/v)	0.8-3.25%
3	Carbon-di-oxide	6-15%
4	Hydrogen sulfide in cleaned biogas (v/v)-max.	0.06%

12. UASB SLUDGE CHARACTERISTICS

Before the introduction of liquefied fleshing studge content in the UASB reactor was

Total solids : 500-585 kg

Percentage of volatile suspended solids : 36-45

Percentage of Ash : 55-64

After introduction of fleshing the solids content in the reactor was

Total solids : 503-816 kg

Percentage of the volatile solids : 31-59

Percentage of Ash : 41-59

From the results it was observed that volatile suspended solids content in the reactor increased. The increase was due to more organic loading rate applied in the reactor. The sludge characteristics are given in Table 19.

COD INCREASE DUE TO ADDITION OF LIQUEFIED FLESHING FOR 15000 LIT OF TANNERY WASTEWATER

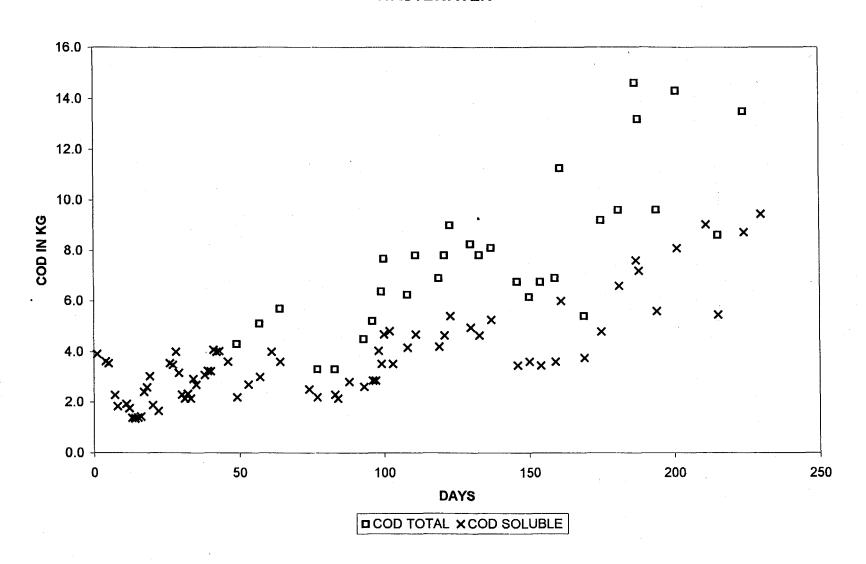


Table 19. Characteristics of sludge in UASB reactor

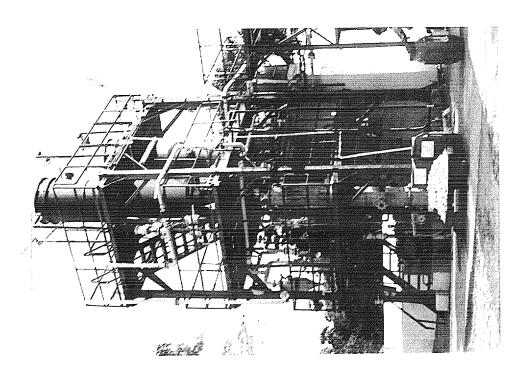
Date	Total Solids (kg)	Suspended Solids (kg)	Volatile Solids (kg)	VSS %	ASH %
4.6.98	816	733	229	31.24	68.76
9.6.98	768	637	238	37.36	62.64
16.6.98	631	532	207	38.91	61.09
18.6.98	521	456	191	41.89	58.11
24.7.98	551	418	175	41.92	58.08
27.08.98	503	434	234	53.92	46.08
07.09.98	523	459	203	44.23	55.77
11.09.98	568	517	224	43.33	56.67
18.09.98	515	416	219	52.64	47.36
07.10.98	544	497	294	59.15	40.85
15.10.98	574	501 .	264	52.69	47.31
03.11.98	526	437	210	48.05	51.95
26.11.98	513	476	223	46.85	53.15
16.12.98	529	445	222	49.90	51.10

No considerable variation in sludge quality was observed during the study period. The average sludge content in the UASB reactor was about 684 kg. The volatile and ash content of the sludge were about 37.4% & 62.6.

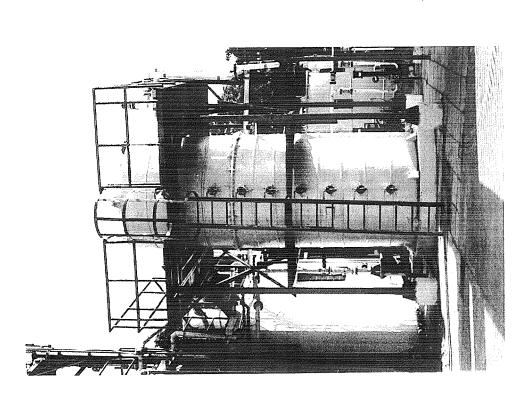
The overall performance of UASB reactor is given in Table 20.

Table 20. The overall performance of the UASB reactor

SI No	Parameter	Value
1	Study period (15 May – 30 Dec '98)	230 days
2	Quantity of wetlimed fleshing added for 15000 L of wastewater	30-100 kg
3	Tannery wastewater flow (avg)	14,800 L
4	HRT (avg)	23 hrs
5	COD loading rate (avg)	5.2 kg/m ³ /d
7	COD removal efficiency (F/T)	70 %
8	COD removal efficiency (T/T)	53 %
10	Biogas produced per kg of COD (T/T) removed	250 L
11	Quantity of volatile solids in UASB reactor	224 kg
12	VSS content in sludge	45.8%
13	Ash content in sludge	54.2%
14	Hydrogen sulphide content in biogas v/v (max)	3.25 %
15	Hydrogen sulphide content in cleaned biogas v/v (max)	0.06 %
16	Maximum allowable limit for Hydrogen Sulfide content in biogas for duel fuel engines (v/v)	0.15%



SULFUR RECOVERY UNIT



UASB PILOT PLANT

13. INVESTMENT AND O&M COST FOR ETP

Cost analysis for a tannery processing about 3 tonnes of raw hides and skins is given below.

The tannery will generate about 90 m³ of wastewater and 375 kg of wet limed fleshing.

1.	Processing Capacity	3 tonnes per day
2.	Wastewater generation	90 m³ per day
3.	COD load from wastewater	315 kg
4.	Wet limed fleshing generated	375 kg
5.	Volume of liquefied fleshing	750 L
6.	COD load from liquefied fleshing	37 kg
7.	Biogas generated from fleshing and wastewater	57 m³ per day
8.	Percentage of methane in biogas	75
9.	Quantity of methane generated	42 m³ per day
10.	Capital investment towards construction of effluent treatment plant consisting of equalisation tank, physio-chemical treatment system, UASB followed by extended aeration system, solar evaporation pans and sludge drying beds and liquefaction tank	4 million IRS
11.	Energy requirement for operating ETP	13.0 KW
12.	Energy recovery from biogas	5.2 KWe
13.	Operation and maintenance cost per month including power, manpower and chemicals	40,000 IRS
14.	Energy recovery from biogas per month at Rs. 3 per unit	11,250 IRS
Note :	One m^3 of Biogas = 0.7 m^3 of methane	

One m³ of methane = 8580 k.cal Power cost = Rs. 3 Per unit

14. CONCLUSIONS

From the results the following conclusions were drawn.

- 1. From the pilot scale studies conducted at CLRI it was established that biogas can be generated from wetlimed fleshing after liquefying the fleshing biologically by mixing with treated tannery wastewater in 1:1 ratio and digesting it in UASB reactor.
- 2. About 250 L of biogas was produced per kg of COD removed in the reactor.
- 3. Wet limed fleshing can be liquefied using treated tannery wastewater from UASB between 10-15 days. For design purpose a minimum of 15 days retention time should be considered. For a typical tannery processing 3 tonnes of hides and skins per day will require a liquefaction tank of capacity 12 m³ and stirrer of about 2 HP.
- 4. Up to 85% of liquefaction of fleshing could be achieved by mixing with treated tannery wastewater in 1:1 ratio with retention time of 15 days.
- No considerable variation in the characteristics of sludge was observed in the UASB reactor.
- 7. Variation in the influent quality due to addition of liquefied fleshing was observed only in COD, VFA and Nitrogen concentrations.
- 8. Biogas generated can be used as a fuel after scrubbing the hydrogen sulfide from the biogas in the sulfur recovery system.
- 9. Disposal problem of fleshing wherever it exists can be solved when the anaerobic system is used for treating liquefied fleshing.
- 10. From the data it is seen that nearly 40% of the energy required for operation of the effluent treatment plant can be recovered by treating wastewater and wet limed fleshing in addition to solving the problem of disposal of fleshing.
- 11. The process can be applied in tannery by additionally providing only liquefaction tank and stirrer with timer control in the effluent treatment plant for liquefaction of fleshing.
- For the purpose of liquefaction of fleshing and treating with tannery wastewater no addition of chemicals is required.

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ANNEXURE - I

BRIEF DESCRIPTION OF ANALYTICAL PROCEDURE FOLLOWED FOR ANALYSIS OF FLESHING SAMPLES

Moisture

Known weight of wet fleshing sample was taken and dried at 103 °C to 105 °C for the removal of moisture. After removal of moisture weights were taken for the dried samples after cooling in the desiccator. The same procedure was repeated till concordant values are obtained. Results are expressed in percentage.

Volatile Solids

The dried fleshing were (5-10 g) taken in a crucible and ignited in a muffle furnace at a temperature of 550°C. It is estimated as per the procedure given in Standard Method, Edition 19, Section 2540-E, Page 2-77.

Calcium

Known weight of samples were taken and pH was adjusted using diluted HCl to pH 2. Using Orion make ion selective electrode calcium was estimated. Results are expressed in w/w on dry weight basis.

Sulfate

Known weight of sample was taken and acidified. Sulfate was estimated using barium chloride as per the procedure given in Standard Method, Edition 19, Section 4500-E, Page 4-136 (Turbidimetric method). Results are expressed in w/w on dry weight basis.

Sulfide

For the purpose of analysis sulfide WET samples were taken and analysed using iodometric method as per the procedure given in Standard Method, Edition 19, Section 4500-F, Page 4-127. Results are expressed in w/w on dry weight basis.

Phosphorous

Known weight of dried samples were taken and analysed as per the procedure given in Standard Method, Edition 19, Section 4500-PC Vanadomolybdophosphoric Acid Colorimetric Method, Page 4-111. Results are expressed in w/w on dry weight basis.

Ammonia - Nitrogen

Ammonia - Nitrogen was estimated by distilling with alkali and collecting it in boric acid. Borate was titrated against standard H₂SO₄ as per the procedure given in Standard Method, Edition 17, section 4500-NH₃ E Titrimetric Method, Page 4-121. Results are expressed in w/w on dry weight basis.

TKN (Kjeldahl Nitrogen)

Known weight of sample was taken and was digested. Digested sample was distilled and distillate was collected boric acid. Borate was titrated against standard sulfuric acid as per the procedure given in Standard Method, Edition 17, section 4500-N_{org} B Macro-Kjeldahl Method, Page 4-144. Results are expressed in w/w on dry weight basis.

Oil and Grease

Wet samples were taken for estimation of oil and grease. Samples were acidified to pH 2 using concentrated HCI. Using soxhlet Extraction equipment and N-hexane extraction was conducted for 4 hrs as per the procedure given in Standard Method, Edition 19, Section 5520-E Extraction method for sludge samples, Page 5-34. Results are expressed in w/w on dry weight basis.

ANNEXURE - II

ANNEXURE-II

BACKGROUND REPORT OF PILOT SCALE UPFLOW ANAEROBIC SLUDGE BLANKET (UASB) TREATMENT STUDIES FOR TANNERY EFFLUENT AT CLRI, CHENNAI, INDIA

1. INTRODUCTION

1.1 General Background

There are more than 3,000 tanneries in India and their annual processing capacity is 700,000 tonnes of hides and skins per annum. On an average 90,000 cubic meter of wastewater is discharged per day. This wastewater contains high amounts of chloride, sulfate, sulfide, ammonia, protein, chromium, sodium, calcium, etc., Major tanning centres in India are situated in Kanpur, Calcutta, Agra, Vaniyambadi, Ambur, Pernampet, Ranipet, Erode, Dindigul and Jalandhar. Most of these centres are far from the sea coast as shown in Fig.1. Invariably wastewater is discharged in rivers like Ganga, Cauvery and Palar. Among those rivers, except Ganges are non-perineal. Therefore most of the wastewater discharged in dry river beds directly percolate into the ground and pollute precious ground water.

The tannery wastewater at present is treated mostly by adopting two stage biological process systems like anaerobic lagoons followed by aerobic system or two stage aerobic systems. The aerobic systems consume lot of power and anaerobic lagoon systems occupy large land area. Due to various reasons lagooning systems do not function effectively. Wherever common effluent treatment plants (CETPs) operating with single or two stage aerobic system, are lacking in requisite land area for sludge drying and disposal. High energy costs lead to financial problems at later date.

The bench scale Upflow Anaerobic Sludge Blanket (UASB) experiments at CLRI, Chennai and pilot plant studies at Kanpur executed in the frame-work of CLRI-TNO the Netherlands project found that composite tannery wastewater without pickling and main chrome tanning liquor could be treated successfully in one or two stage anaerobic (UASB) treatment systems. The COD removal efficiencies were in the range of 70 to 75% at relatively moderate loading rates of 2-3 kg COD/m³/d. It was presumed that the maximum applicable loading rate were limited by the presence of sulfide and specific process chemicals (i.e. preservatives) inhibiting the methanogenic activity of the sludge.

Further it was found from the studies conducted in the Netherlands for the anaerobic treatment of tannery wastewater, the application of one stage configuration was more favourable in comparison to a two stage configuration. This conclusion is based on the observation that during anaerobic treatment precipitation and accumulation of calcium carbonate occurred to a limited extent. In addition it is likely that the process of hydrolysis and acidification performed better in single stage configuration due to the scavenging of hydrogen by methanogenic and sulfate reducing bacteria.

The pilot plant studies in Kanpur with a 10 cubic meter UASB reactor also established the feasibility of treating tannery wastewater without diluting with domestic wastewater by segregating sulfate and chloride concentrated sectional waste streams like pickling and main chrome tanning. Bio-gas production in terms of quality and quantity was also found to be very encouraging. But the plant could run with 100% tannery wastewater only for a short period due to logistic and other reasons. It was too short a period to collect other relevant data. Therefore further studies were planned and carried out with lab scale reactors in the Environmental Technology Department, CLRI, Chennai before field level application. Based on the above results a 12.5 m³ pilot scale UASB reactor with improved features was designed and erected in CLRI, Chennai. The system consists of collection tanks, equalisation tank, settling tank, conditioning tank, trace element feeding tank, phosphate buffer tank and a main UASB reactor.

1.2 Types of Tanning Processes and Wastewater Discharge.

The processing of raw hides and skins into finished leather involves beam house or pretanning operation, main tanning process and post tanning process. In the beam house operations, the skins and hides, received mostly in the wet salted conditions in the tannery, are processed to remove unwanted materials such as hair, flesh and other proteineous materials and conditioned suitably for the tanning process. In beam house operation soaking, liming reliming and deliming are involved.

In soaking operation salts and other impurities like blood, animal dung and soluble proteins etc., are removed and the raw skins and hides are rehydrated. 300 - 400% of water on raw hides/skins weight basis is used in soaking operation. The concentration of chloride in soak water varied between 20000 - 30000 mg/l.

In liming process 300 - 400% of water is used. During liming operation hairs are removed and the soaked hides and skins are swelled and the fibre structures are opened.

In reliming process 300 - 400% of water is used. During reliming process swelling is improved and the fibre structure are better opened up.

During fleshing operations loose flesh attached to hides and skins are removed.

After washing, the limed pelts are treated with ammonium sulfate or chloride to remove excess lime. 300% of water is used on pelt weight basis in deliming process.

During bating, epidermis short hairs and the scud are removed and washed. In pickling process the pelts are treated with acid (2%) and salt (6-8%) so as to get a quick penetration and more uniform distribution in chrome tanning. 80% of water based on the pelt weight is used in the pickling process.

1.2.1 Tanning processes

Tanning process imparts resistance against bacterial degradation and improves the durability of leather. The commonly used materials for tanning are chrome and vegetable.

In chrome tanning process trivalent chromium salts in the form basic chromium sulfate is used along with electrolyte stable fatliquors. During basification sodium formate and bicarbonate are used. 100-150% of float volume is used.

In vegetable tanning or East India Leather (El Leather) process the pelts are treated with extracts of bark, nuts, leaves of certain plants. The most commonly used materials are wattle, avaram, konnam, myrobalan, babul, quebracho etc. They are poly phenolic compounds and form colloidal dispersions in water.

1.2.2 Post tanning operations

Chrome tanned (wet blue) and Vegetable tanned semifinished leather (El leather) are the raw materials for the production of finished leathers. Vegetable tanned leathers lack in hydrothermal stability and affinity for dyes and fatliquors. So retaining with chrome improves the above properties and the process is called semi chroming. Wet blue

leathers are rechromed after splitting/shaving for equalisation of chrome in a pack of leathers before the post tanning operations.

In neutralisation process excess acid present in wet blue and semichrome leathers are neutralised using sodium formate, sodium bicarbonate and neutralising syntans etc.

Retanning is done to impart fullness, uniform substance, grain tightening. Dyeing is done to impart color to the leathers. The most commonly used dyes are acid dyes, direct dyes, basic dyes, metal complex dyes etc. Fatliquoring is performed to impart softness, flexibility feel drape, run etc.,

1.3 Current Treatment Systems Practised in Tanneries

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At present tanneries in Erode, Dindigal and Trichy in Tamil Nadu are adopting Raw to Wet Blue process. Tanneries in Ambur, Ranipet and Vaniyambadi are adopting both Raw to Wet Blue process / finishing process and Raw to E.I process / finishing process.

Pallavaram, TALCO Industrial estate at Madhavaram, Chennai and SIDCO Industrial estate in Ranipet are adopting the process of semifinish to finished leather.

Common effluent treatment plants (CETPs) in Vaniyambadi, Dindugal, Ranipet are adopting primary treatment followed by anaerobic and aerobic biological system. CETPs in Madhavaram, Pallavaram, Ranipet SIDCO industrial estate, Pemampet are adopting two-stage aerobic system. In Bangalore where both raw to finish and semi finish to finish operations are carried out, CETP is adopting fully aerobic systems.

The Upflow Anaerobic Sludge Blanket (UASB) technology was adopted for the first time in Kanpur, Uttar Pradesh for treating the tannery wastewater from 160 tanneries with the admixture of domestic wastewater. In Kanpur about the 160 tanneries discharge 9 million litres of wastewater per day. The wastewater from tanneries is mixed with 27 million litres of the domestic wastewater and treated in the UASB reactor.

This method of mixing domestic water with tannery wastewater cannot be practised in many tannery clusters of the country. Since most of the municipal towns do not have sewerage system to collect the wastewater. Apart from this the quantity of domestic wastewater generated is far less than the quantity of wastewater generated from

tanneries. Moreover, dilution is not the real solution to the pollution problem. Therefore it was decided to undertake a study in treating tannery wastewater by adopting UASB technology without diluting with domestic wastewater, if required by segregating certain sectional waste streams containing high sulfate concentration, like pickling and chrome tanning.

For the treatment of tannery wastewater both physio-chemical and biological treatment methods are adopted. Initially wastewater is passed through a screen chamber for the removal of floating matter. From the screen chamber wastewater flows into equalisation tank. Normally equalisation tank capacity is designed for one day. In equalisation tank the contents are thoroughly mixed using submergible pumps or floating type aerators.

Depending on the location of the tannery certain sectional wastewater is segregated. In Vaniyambadi, Ambur and Ranipet area soak and pickle streams are segregated and evaporated in solar evaporation pans. Evaporation rate in this part of the country is 4 - 5 mm per day. On this basis a tannery requires nearly 650 sq. meters of land area for every tonne of raw hides or skins processed. This amount of land may not be available with all the tanneries and even if it is available land costs are very expensive.

From the previous studies under TNO-CLRI co-operation programme four lagooning systems provided for tannery wastewater treatment were studied for a period of one year. From this study it was observed that not considerable sulfate and COD reduction is taking place in the anaerobic lagoons and also they occupy large land area and hydraulic retention times are also as high as seven to ten days. Therefore a suitable cost effective and closed anaerobic system was developed under TNO-CLRI programme. Bench scale UASB reactor studies gave encouraging results. Based on this study pilot plant UASB system was designed.

2. OBJECTIVE OF THE STUDY

Under an extensive and comprehensive cooperation programme between the Organisation of Applied Scientific research (TNO) in the Netherlands and CLRI a CSIR laboratory at Chennai, India, a study was taken up in the later part of 1992 to tackle the environmental problems of the Indian Leather Sector through the applied research implementation programme. One of the tasks under this co-operation programme is development of appropriate anaerobic technology for the treatment of tannery

wastewater. For this purpose bench scale studies with UASB reactor were carried out and based on this study, pilot plant was designed and erected for further studies with the following objectives.

- Establishing design criteria, unit operations and collection of data for upscaling the UASB technology proposed for a cluster of tanneries in Ambur from pilot scale.
- To identify and overcome the technical and practical problems in the application of UASB technology in treating tannery wastewater.
- c. To study biodegradability of organic matter in the tannery wastewater under high sulfate and solids concentration.
- d. Impact of COD to sulfate ratio on methane production.
- e. Establishing nutrient requirement and quantity required for treatment of tannery wastewater.
- f. Establishing a most suitable start up procedure by seeding the reactor with sludge from domestic wastewater treatment plants.
- g. Evaluation of the pilot plant performance and comparing with lab scale performance.
- h. Assessing the suitability post treatment after treating wastewater with UASB technology.
- i. Pretreatment requirements like equalisation tank, primary settling tank.
- j. Generation of biogas, its purification and utilisation.
- k. Adaptation of appropriate selection of system like sulfur recovery based on lab scale studies under TNO-CLRI programme and to improve the efficiency of UASB and reduction of pollutants in the UASB treated effluent.

3. IMPLEMENTATION OF UASB PILOT PLANT SYSTEM AT CLRI

3.1 Details of Civil Structure

For the purpose of studying application of UASB technology for treatment of tannery wastewater without the domestic sewage, a pilot plant was designed with improved features and erected with the following facilities at CLRI near Environmental Technology Laboratory as listed in Table 1. The process flow diagram is shown in Fig.2.

Table 1 Details of civil structures at UASB pilot plant

SI No	UNIT	SIZE			Nos	
		Length/Dia m	B m	D m		
1	Collection tank	2.0	2.6	1.5	5	
2	Equalisation tank	4.0 Dia		2.3	1 20 3 3 3 4 5 4 5 4 5 4 5 4 5 4 5 4 5 4 5 4	
3	Settling tank	2.0 Dia		2.0	1	
4	Conditioning tank	2.2 Dia		2.0	1	
5	Reactor	2.0 Dia		5.2	1	
6	Acid/Alkali tank	200 1			1	
7	Micro Nutrient tank	200 1			1	
8	Sludge drying bed	2.0	2.0		2	

3.1.1 Collection Tanks

For the purpose of storing various sectional wastewater collected through special tanker from the commercial tanneries five collection tanks of size $2 \times 2.6 \times 1.5$ m each as shown in Fig.3 were constructed in Reinforced Cement Concrete (RCC). All the collection tanks were protected with epoxy coat. From the collection tanks sectional wastewater was discharged into an equalisation tank at estimated proportions. The wastewater represents the composite wastewater discharged from a group of tanneries in Ambur.

3.1.2 Equalisation Tank

An equalisation tank of diameter 4 m and depth of 2.3 m was constructed in RCC. The tank is provided with a paddle type stirrer. To avoid deposition of solids to the side of the reactor two baffle walls of 30 cm wide is provided at the inner periphery of the circular equalisation tank as shown in Fig.4. The stirrer is operated at 60 rpm and is powered by a 3 hp motor.

3.1.3 Primary Settling Tank

Primary settling tank (PST) is made up of mild steel with FRP coating and erected above ground level. The diameter of the tank is 2 m, side water depth is 0.75 m and total depth is 2 m as shown in Fig.5. Primary settling tank (PST) is provided with overflow

arrangement all around the periphery. Supernatant from this tank flows to conditioning tank. Settled solids from the bottom of the settling tank is conveyed to sludge drying beds by gravity.

3.1.4 Conditioning Tank

STANSON AT

Conditioning tank is made up of FRP of diameter 2.2 m and depth 2 m. Contents of the conditioning tank is continuously mixed using a centrifugal pump. Top of the conditioning tank is covered with two openings for pumping trace element and macronutrient solution. Apart from this a separate cylinder is provided with inter connection at the top and bottom from the conditioning tank. The cylinder is provided with four outlets and one inlet. Outlet from the reactor is connected to the top of the cylinder. By opening one of the outlet valves, fixed at various heights desired re-circulation can be achieved. Bypass arrangement is also provided to skip the wastewater from entering into the conditioning tank. Details of conditioning tank are given in Fig.6.

3.1.5 Dosing Tanks

Two numbers of dosing tanks of 200 Litres capacity and is provided with adjustable Asia LME dosing pumps. These dosing tanks are used for storing micro and macro nutrients.

3.1.6 UASB Reactor

UASB reactor of 2 m dia and 5.2 m height made up of FRP was fabricated and installed. Total capacity of the reactor is 15.5 m³ out of which effective capacity is 12.5 m³. Liquid depth inside the reactor is 5.00 m. Two nozzles of diameter 32 mm, one nozzle of diameter 20 mm is used as inlet from bottom of the conditioning tank to reactor. The reactor is also provided with sampling valves at every 50 cm height. Top of the reactor is provided with a GLS separator. Overflow from the reactor passes through a launder of 2.8 m length. GLS separator is designed as a square of 1.4 m x 1.4 m. Gas outlet pipe from the top of the reactor is connected to a condensate pot. Sample port for sampling wastewater and sludge is also provided at the top of the reactor. Details of UASB reactor are given in Fig.7.

3.1.7 Condensate Pot

Condensate pot of approximately 25 Litres capacity is provided to remove moisture from the biogas.

3.1.8 Sludge Drying Bed

Two numbers of sludge drying beds of area $2 \text{ m} \times 2 \text{ m}$ each is provided for dewatering sludge from primary settling tank and reactor.

4. WASTEWATER COLLECTION AND STORAGE

Wastewater for the UASB pilot plant CLRI is regularly collected from the selected tanneries situated in and around Pallavaram. Sectional wastewater from beam house operation - soaking, liming, re-liming, de-liming are collected and stored in the HDPE tanks inside the tannery premises itself. From HDPE tanks wastewater is mixed in appropriate proportion and pumped into the tankers for transportation to UASB pilot plant at CLRI. Sectional wastewater from pickle and chrome tanning operations are excluded. In Pallavaram area 90% of the tanneries are processing wet blue to finishing process. Therefore sectional wastewater from wet finishing operations like neutralisation, dying, fatliquoring were collected in the form of composite wastewater from Pallavaram common effluent treatment plant (CETP) and transported to UASB pilot plant site at CLRI. Wastewater from the tankers are emptied into the appropriate collection tanks. From the collection tanks wastewater was let into equalisation tank in the proportion that is representative of composite wastewater from tanneries in Ambur. Wastewater passes through a screen before it enters equalisation tank.

5. OPERATION OF UASB REACTOR

5.1 Start up of the Reactor

One of the objectives of the present study was to establish a start up procedure for exclusive treatment of tannery wastewater. The slow first start up of an anaerobic reactor system frequently is considered as one of the main drawbacks of anaerobic treatment. From the bench scale reactor studies it was established that start up of the reactor can be done without diluting the tannery wastewater with domestic wastewater. It was also

established that start up with flocculant sludge from an abandoned sludge digester and primary sludge from Nesapakkam domestic wastewater treatment plant was better suited than granular sludge and sludge from anaerobic lagoons.

Characteristics of the bio sludge fed to the UASB reactor are given in Table 2.

Table 2 Characteristics of the bio sludge fed into reactor

S.No	Parameter	Value
1	Total Solids	67,760 mg/l
2	Suspended Solids	66,160 mg/l
3	Volatile Solids	41,700 mg/l

During the first few days after the seeding sludge washout was observed from the reactor. Sludge profile was carried out to determine the quantity of volatile solids in the reactor on 22 Feb '96. Marked increase in VSS concentration was found in the reactor within few weeks.

From the equalisation tank wastewater is pumped to the primary settling tank at a constant pumping rate using a variable speed screw pump. Supernatant from the primary settling tank flows into conditioning tank by gravity. Settled solids from the bottom of the primary settling tank are drained into sludge drying beds.

Wastewater in the conditioning tank is mixed continuously using a 3 hp centrifugal pump. Macro nutrients and trace elements were prepared in 200 Litres cans and pumped into conditioning tank using a dosing pump. From the conditioning tank wastewater is pumped through a variable speed screw pump into the UASB reactor. Delivery line is divided into three lines in such a way that all three lines distribute wastewater at the bottom of the reactor equally.

6. SAMPLING AND ANALYSIS FOR MONITORING

Analytical results of the UASB pilot plant at CLRI, Chennai, India are given in Table 3. Influent samples were collected from the top of the settling tank. Effluent samples were collected from the outlet of the reactor. Samples were analysed in the laboratory as per the procedure given in 17th edition of Standard Methods.

Table 3 Results of UASB pilot plant at CLRI, Chennai

SI No	Parameter	Value
1	COD (total) reduction	65 - 70%
2	Biogas yield in cubic meter per kg of COD removed	0.25 - 0.30

6.1 Flow

Daily measurement of feed to the reactor was monitored by observing the change in the wastewater level in the equalisation tank and conditioning tank.

6.2 pH and Temperature

On site pH and temperature were measured daily directly using portable (WTW model pH 320) pH meter. pH and temperature observation were made five days in a week.

6.3 Chemical Oxygen Demand (COD)

Three methods were followed for estimation of COD. The procedures are described below. COD estimation were carried out thrice a week.

6.3.1 COD (Total)

For estimation of COD (Total), samples were analysed without filtering or centrifuging and without stripping of sulfide. Then COD was estimated as per the procedure described in the standard methods 17th edition.

6.3.2 COD (Total & Filtrate) after stripping hydrogen sulfide

Estimation of COD (Total) was carried out after stripping hydrogen sulfide from the samples by passing nitrogen gas. For this purpose known volume of sample was taken in a COD flask and made upto 20 ml. To this 2 ml of concentrated sulphuric acid was added. After acidifying the samples nitrogen gas was passed through the sample for one

minute for stripping off hydrogen sulfide. Then COD (Total) was estimated as per the procedure described in the standard methods 17th edition. This procedure was followed for both influent and effluent samples. Estimation of COD filtrate was carried out after centrifuging the sample at 5000 rpm for 5 minutes and striping hydrogen sulfide.

6.4 Sulfate and Sulfide

Estimation of sulfide for influent and effluent samples were carried out after fixing the sulfide using zinc acetate. Estimations were carried out thrice a week. After filtering the samples using whatman No.1 filter paper, filtrate was taken for estimation of sulfate. For the estimation of sulfate and sulfide procedures described in the standard methods 17th edition were followed.

6.5 Chloride

Chloride analysis were carried out as soon as the composite was prepared in the equalisation tank. For effluent samples estimations were made once in a week. Analysis of chloride was carried out as per procedure described in the standard methods 17th edition.

6.6 Ammonia Nitrogen

Analysis of Ammonia Nitrogen was carried out as per procedure described in the standard methods 17th edition. Estimations were made once in a fortnight.

6.7 Total Kjeldahl Nitrogen

Analysis of Total Kjeldahl Nitrogen (TKN) was carried out as per the procedure described in the standard methods 17th edition. Estimations were made once in a fortnight.

6.8 Volatile Fatty Acids and Bi Carbonate Alkalinity

Analysis of VFA and bicarbonate alkalinity were done for the centrifuged influent and effluent samples as per the procedure given in International Course on Anaerobic Waste Water Treatment, anaerobic lab work, Wageningen Agricultural University, the Netherlands. Analysis for VFA was carried out thrice a week.

6.9 Total, Suspended, Volatile suspended solids

Sludge profiles were estimated at frequent intervals during the entire study period for the pilot plant. There are six sample ports in the reactor at every 50 cms intervals from the bottom of the reactor. Total height of the reactor is 5 m. From each sample port before taking sludge samples about 2 litres of sludge was wasted. Sludge samples were analyzed for suspended, total and volatile suspended solids. The sludge analysis were carried out as per the procedure given in the standard methods 14th edition. Estimations were made once in a fortnight.

6.10 Bio-gas Production

Bio-gas produced in the reactor passes through the condensate part and then through a wet gas flow meter. Gas meter readings are noted every hour.

7. PERFORMANCE OF THE UASB REACTOR

Tannery wastewater without dilution was used as the influent for UASB reactor. Gas production and VFA reductions were observed in the reactor after the seeding of sludge on 19 Feb '96. For performance evaluation and discussion purpose in this report the data collected between February '96 and December '96 were considered. During this period fluctuation in the flow, chloride concentration, COD to sulfate ratio was tolerated by the sludge.

8. RESULTS AND DISCUSSION

8.1 Seeding of the UASB Pilot Plant Reactor

Methanogenic activity tests were carried out for sludges from anaerobic lagoons treating tannery wastewater, primary sludge from domestic wastewater treatment plant, abandoned anaerobic sludge digester in a domestic wastewater treatment plant. From the study good activity was observed for sludge from primary settling tank of domestic wastewater treatment plant. This sludge was used for seeding the UASB reactor.

8.2 Hydraulic Retention Time

Reactor was started with hydraulic retention time (HRT) of 8 days and gradually it was brought down to one day. During the period when HRT was maintained around one day COD F/F removal efficiency of 65% and above was observed. COD to sulfate ratio was above 6 during the study period. For HRT of one day, upward velocity maintained in the reactor was 5 m/d.

8.3 Recirculation of the treated effluent

Recirculation of the treated effluent was done during the startup of the reactor to maintain required upward velocities and good mixing in the reactor. Recirculation was discontinued after the stabilization period.

8.4 pH of the Influent and Effluent

pH of the influent fed into the UASB pilot plant reactor was around 7.5. Though this is within the optimum range, the higher the pH lower activity of methanogens was observed. Due to sulfate reducing bacteria (SRB) hydrogen sulfide was produced in the reactor. Effluent pH of the reactor was around 7.5 but always it was slightly less than the pH of the influent.

8.5 COD Load & COD Removal Efficiencies

Concentration of COD (Total and Filtrate) varied widely due to process changes in the tannery and to certain extent due to collection of sectional wastes sometime from different tanneries and other common field problems.

During the study period COD removal efficiencies of 65% and above was observed. Increased COD removal efficiency was observed on the samples where hydrogen sulfide was stripped off.

8.6 Sulfate Conversion Efficiency

Sulfate concentration in influent ranged from 600 - 1000 mg/l and sulfide concentration ranged from 100 - 200 mg/l. Sulfate got converted into sulfide in anaerobic reactors. Sulfate conversion efficiency was lower during the startup but it improved to the efficiency of 90% within very short period.

Sulfide concentration in the effluent varied from 200 - 550 g/l. Methanogenic activity was not affected due to sulfide concentration in the reactor.

8.7 COD to Sulfate Ratio

During the startup of the reactor initially only beamhouse wastewater was introduced later on reactor was fed with composite wastewater. During the period (about two weeks) when beamhouse wastewater was fed into the reactor sulfate concentration in the influent was lower. In the composite wastewater higher sulfate concentrations were observed. COD to sulfate ratio of 6 - 7 was observed during the study period. Therefore COD to sulfate ratio did not have any impact on the reactor performance adversely.

8.8 Methane Conversion

On an average 10.6 m³ of gas was produced per day during the study period. During that period about 64% COD T/T removal efficiency was observed and for the filtrate about 67% COD removal efficiency was observed. Composition of gas is given in Table 4.

Table 4 Composition of Bio-gas from the pilot plant reactor

SL No	GAS	GAS COMPOSITION IN PERCENTAGE (v/v)
1	Carbon-di-oxide	20 - 30
2	Methane	70 - 80
3	Hydrogen Sulfide	1.5 - 2.5

8.9 Removal of Solids and Presence of Undissolved Salts

Solids in the settling tank was drained into the sludge drying beds. Once the sludge becomes dry it is removed. During cloudy days and rainy days sludge withdrawal could not be carried out from primary settling tank regularly. This often lead to accumulation of solids in the primary settling tank and conditioning tank. Accumulated solids also got pumped into the reactor along with the influent. This led to accumulation of inorganic solids inside the UASB reactor. The presence of higher concentration of inert materials is considered detrimental for the development of the granular sludge. The reason is that newly formed bacterial matter might attach to inert, poorly settleable particles and consequently wash out of the reactor.

8.10 Sludge Profile

Sludge samples were taken periodically from the reactor and analysed to find out the concentration of the sludge in the reactor. From the sludge profile results it is observed that percentage of volatile suspended solids inside the reactor was 40% and above. Sludge concentration in the reactor varied depending on the organic loading rate. This was observed by analysing the solids in the reactor. The specific shape of the profile depends mainly on the hydraulic loading rate and organic loading rate at the time of sampling. At a low loading rate the sludge appears to be expanded mainly due to the occluded gas.

The sludge retention in the reactor mainly depends on sludge settleability which in turn depends on the characteristics of the wastewater like calcium concentration, nature of the pollutant and presence of the dispersed flocculating matter.

Sludge content in the reactor was estimated at the beginning and at the end of study period. An increase of 89 kgs of VSS was observed between these two periods, no sludge was required to be withdrawn during the study period.

8.11 Efficiency of The Gas-Liquid-Solid Separator

In order to estimate the efficiency of the GLS separator wastewater samples were collected from at 3.8 m level from the bottom of the reactor and from the out let of the reactor. Samples were analysed for suspended solids concentration. Results are given in Table 5.

Table 5 Settling efficiencies of gas liquid solid separator

Suspended solids concentration at 3.8 m level from the bottom of the reactor	Suspended solids concentration at the outlet of UASB reactor	Settling Efficiency
29308 mg/l	_ 556 mg/l	98%
5752 mg/l	752 mg/l	87%
17434 mg/l	516 mg/l	97%
29852 mg/l	748 mg/l	98%
21992 mg/l	1536 mg/l	94%

9. OBSERVATIONS ON OPERATION AND MAINTENANCE

a. Screens provided at the equalisation tank has to be changed very frequently due to corrosion. With in a span of one year thrice screens were replaced. Therefore screens with stainless steel or FRP coated is proposed to be fixed near the out wall of the equalisation tank.

- b. In the equalisation tank, the stirrer was continuously operated to prevent the suspended and settleable solids settling in the equalisation tank. In spite of this some amount of solids settle at the bottom of the equalisation tank over a period of time. Settled solids were removed at least once in three months.
- c. A centrifugal pump was used for continues mixing of the wastewater in the conditioning tank. Whenever pump failed due to malfunctioning and other operational problems the mixing was not done in the conditioning tank and this resulted in gradual settling of the suspended solids. During this period the samples from the conditioning tank showed high solids concentration. The defects in the pump was rectified. Whenever, the pump was not used solids from the conditioning tank were also pumped into the reactor. Periodically solids settled at the bottom of the conditioning tank were removed.
- d. Regular cleaning of the small dia (25 mm) pipe lines were also carried out in order to overcome the problem of clogging. Calcium salts precipitate inside the pipe lines and reduce the effective dia of the pipe. HDPE pipe lines provided are highly non corrosive. But cracks very easily. Though HDPE is one of the best available material scope for better non-corrosive cum non-brittle material may be explored in future. In the full scale plants large dia pipes will be used and hence the clogging problem will be minimized.
- e. Whenever flanges are to removed for maintenance it was found to be difficult as the galvanized iron flanges are too corroded within a short period of six months. Therefore in all future installations only stainless steel to be used.

f. Wastewater from CETP (Pallavaram) was found at a later date that it was contaminated with small amount of (about 5%) unauthorised discharge of domestic sewage. This may be another source of nutrient. In future by allowing small quantity (5-10%) of domestic wastewater from tanneries nutrient requirements can be satisfied.

10. CONCLUSION AND RECOMMENDATION

10.1 Start Up Procedure

Based on the performance of the reactor, it may be concluded that primary sludge from the Nesapakkam sewage treatment plant or any other sewage treatment plant can be used as the seed material. There is no need to import granular sludge from the Netherlands. This was also established in the bench scale UASB reactor studies. Procedure followed for start up of this reactor can be followed for start up of full scale plant. Based on the results of the bench scale reactor, and pilot scale studies it was established start up can be done without diluting with domestic wastewater and by segregating pickle and chrome liquor.

10.2 COD Loading

COD loading of 9 kg/m³/d were reached. During that period removal efficiency of 65% and above was observed. Hydraulic retention time of 24 hours can be recommended, though reactor can handle lower HRT. Better performance in COD removal can be expected in full scale plant due to minimum shock loads and better control of dissolved solids.

10.3 Hydrogen Sulfide

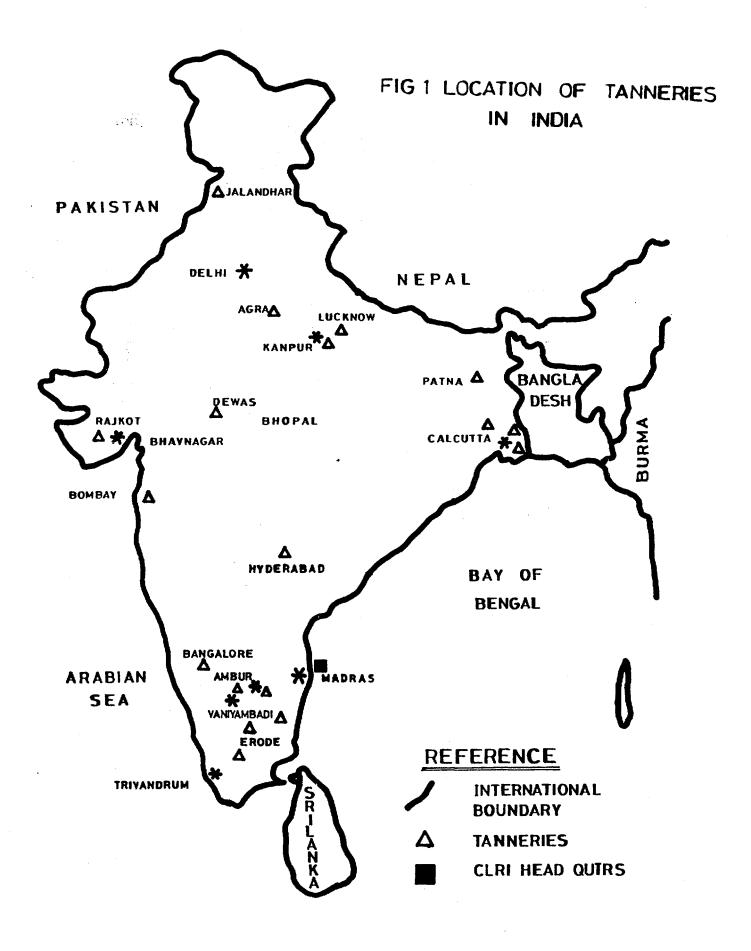
Sulfate conversion of 90% and above were observed. Hydrogen sulfide concentration of 2.5 v/v was observed in the bio gas. This led to corrosion of all metal parts in the plant. Particularly copper exposed to atmosphere corrode rapidly. Therefore only stainless steel or highly non corrosive material to be used in the plant.

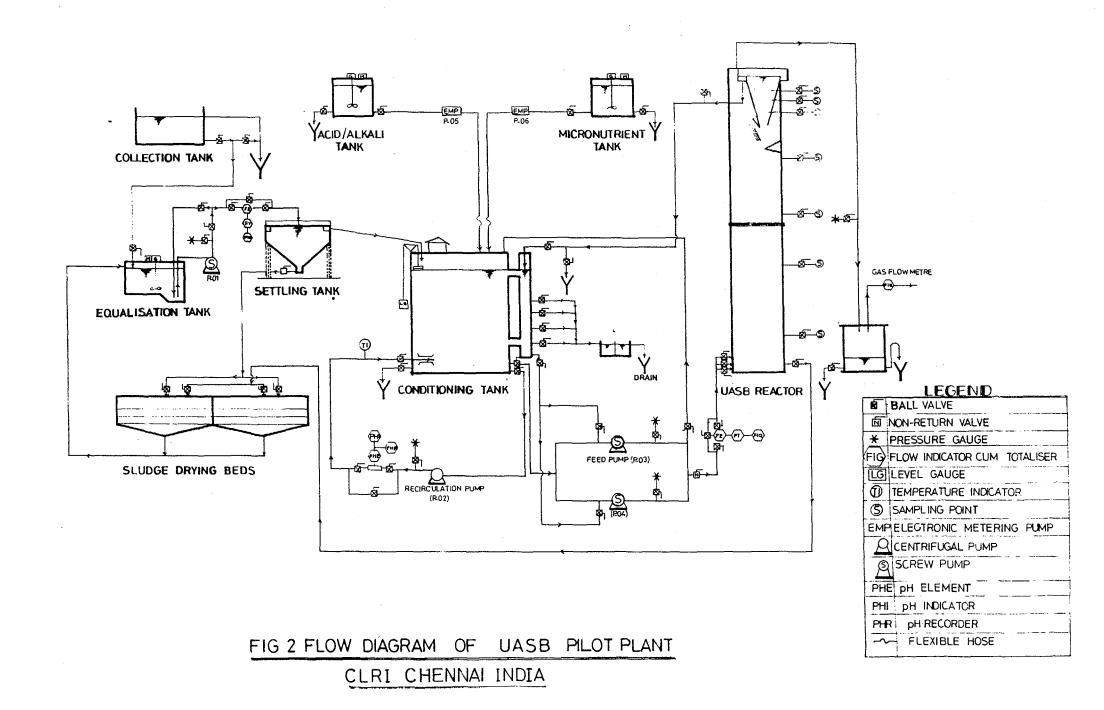
10.4 Post Treatment Studies

Treated effluent from the reactor is still left with 25 - 30% of organic matter. Therefore further treatment of wastewater is to be done preferably in an aerobic system. Considering the sulfide concentration in the reactor it is highly recommended to go in for post aerobic studies in the present treatment plant itself.

10.5 Utilisation of Bio gas

Utilisation of bio gas for domestic purposes can also be studied after removing sulfide from the bio gas.





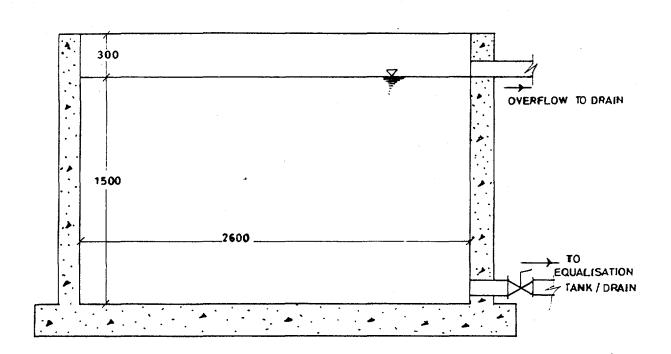
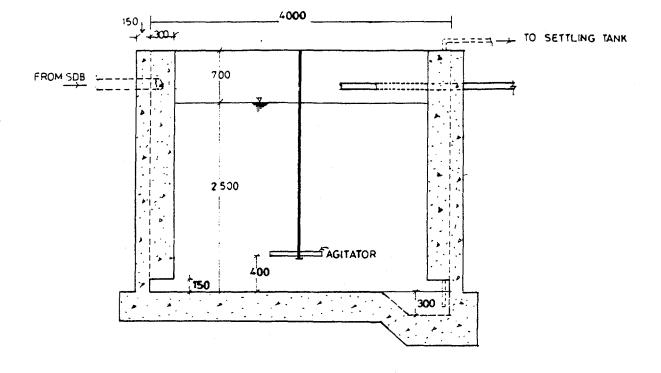


FIG 3 DETAILS OF COLLECTION TANK



SECTION

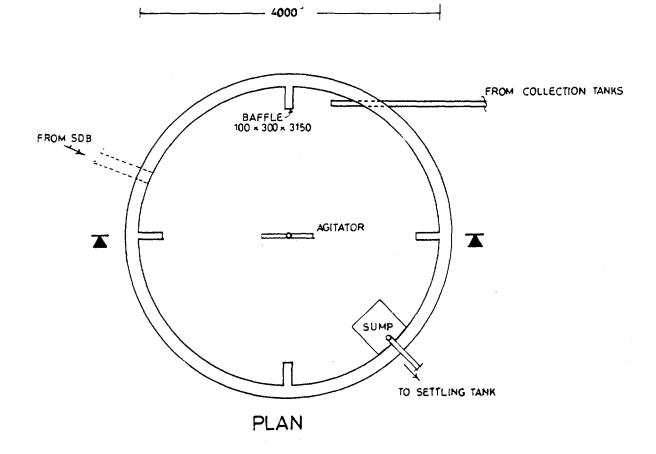


FIG 4 DETAILS OF EQUALISATION TANK

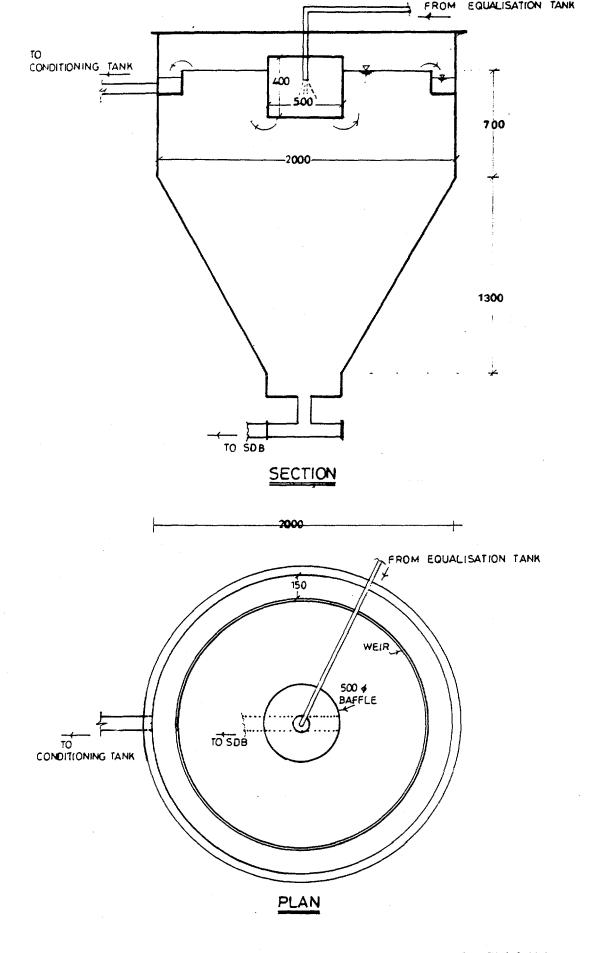


FIG 5 DETAILS OF SETTLING TANK

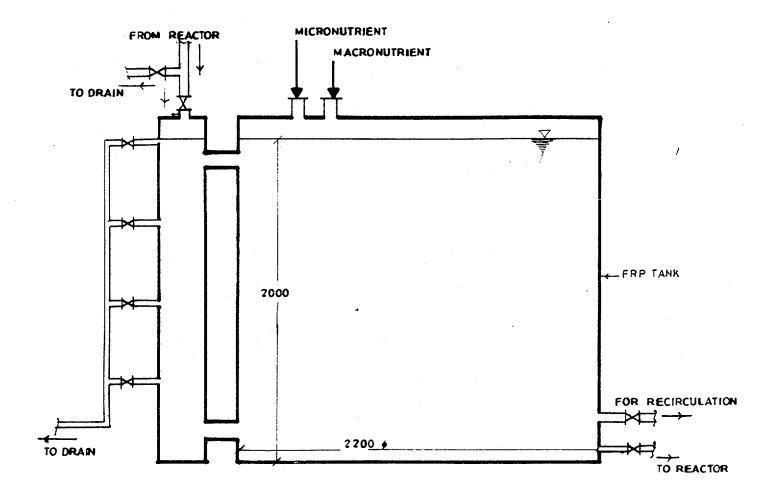


FIG 6 DETAILS OF CONDITIONING TANK

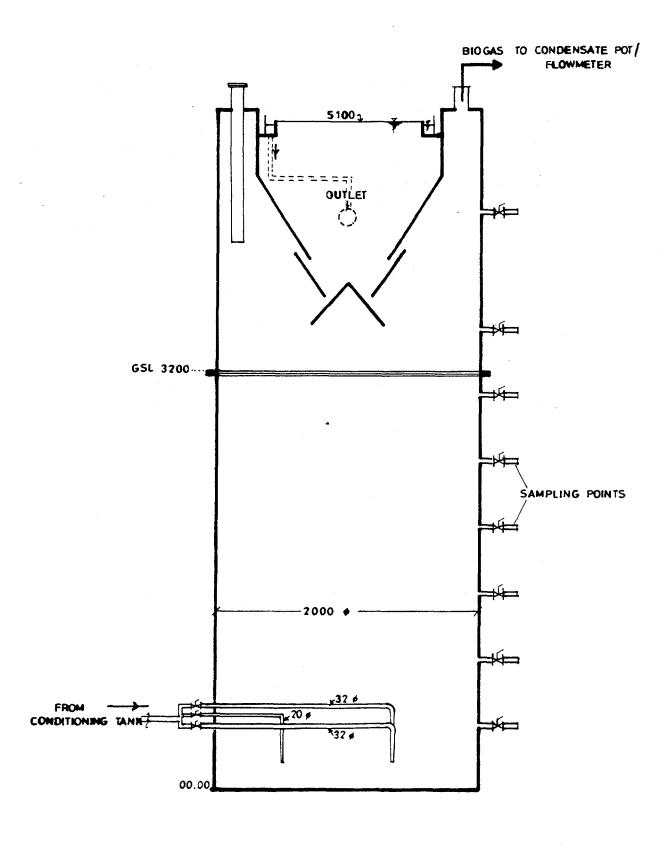


FIG 7 DETAILS OF UASB REACTOR

ANNEXURE - III

ANNEXURE - III

SPECIFICATION FOR STIRRER, STAND AND FRP TANK FOR PROCURED UNDER THIS PROJECT

Stirrer with Motor and Variator

Supply, erection and commissioning of liquefaction system for digestion of fleshing as shown in the drawing. System consists of variable speed stirrer, motor, variator, timer device stand for fixing the stirrer, FRP tank, power connection and necessary platform for installing system.

Motor of Kirloskar/Siemens make with IP 55 protection of 5 HP is to be supplied along with radicon gear system (5-15 rpm), variator (manual/electrical) and necessary starters with MCB to be installed in position. Stainless steel SS 316 stirrer with 3 paddles staggered equally to be supplied. The stirrer should function at very high torques. The stirrer should be capable of stirring 1 tonne of fleshing intermittently connected to a timer device. The stirrer should be easily mounted on the motor.

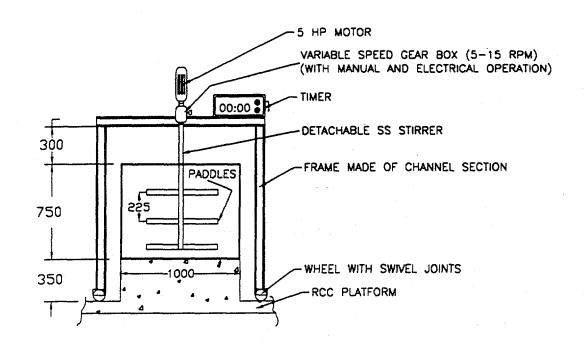
Power supply for motor to be drawn from pillar post 50 m away from the proposed site for placing liquefaction tank. Cable required for this purpose also to be supplied and erected in position.

FRP Tank

The FRP tank should be of diameter 1 m and height of 0.75 m. The lid should be provided into two halves so that it can easily be slide out and in. The centre of the lid should have opening to accommodate stirrer rod. Tank should be of FRP with reinforcements. Bottom of the tank is to be provided with 90 mm dia, PP Ball valve for withdrawal of fluid from the bottom.

Concrete Platform

Necessary concrete platform of minimum 2×2 m to be provided with necessary foundations for placing the stimer and a pedestal of 1 m dia for placing FRP tank also to be constructed. Specification details and process flow diagram of the equipment is given in Fig 1.



SECTIONAL ELEVATION

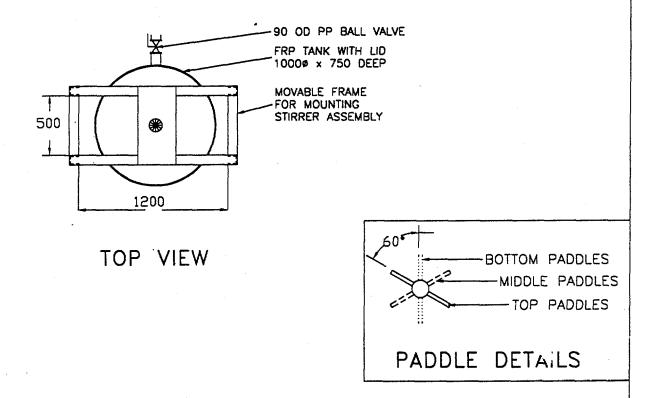


FIG 1 STIRRER FOR LIQUEFACTION OF FLESHING

DEPT. OF ENVIRONMENTAL TECHNOLO CLRI, ADYAR, CHENNAI - 600020	GY, ALL DIMENSIONS ARE IN mm	DRAWN K.THIRUMARAN
CLRI, ADYAR, CHENNAI - 600020	SCALE - 1:30	CHKD E.RAVINDRANATH