MEMBRATEK (Pty) Ltd

Report to the

WATER RESEARCH COMMISSION

on

LABORATORY SCALE TREATMENT OF ACETIC ACID EFFLUENT BY THE ADUF PROCESS

by

N K H Strohwald

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EXECUTIVE SUMMARY

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PROJECT BACKGROUND

The disposal of acetic acid effluent from the sugar processing industry, has always been a cause of concern, both to industry and effluent management bodies, mainly due to its seasonal volumetric fluctuations and the high level of organic pollutants.

Environmental concerns about the discharge of this effluent to sea have grown substantially during the last five years. As such the pressure exerted by governing and environment protection bodies has prompted the sugar processing industry to investigate the treatment of this effluent prior to disposal.

The ADUF process, employing ultrafiltration membranes to retain biomass, was seen as a possible solution to these problems. Since no previous operational experience with the ADUF process on acetic acid effluent was available, experimental work concerning the digestion of this effluent had to be performed.

PROJECT OBJECTIVES

The investigation into the application of the ADUF process to acetic acid effluent, on a laboratory scale, was carried out to determine the following:

i) biodegradability of the effluent by means of mesophilic anaerobic digestion;
ii) flux values for ultrafiltration at stabilised digester conditions;
iii) maximum digester load rate and limits of general operating parameters;
iv) quality of final treated effluent at stabilised digester conditions;

RESULTS AND CONCLUSIONS

The COD content of the acetic acid effluent could be reduced from 16 030 to 890 mg/l on average, translating to a mean COD reduction rate of 94,4%. COD reduction percentages of up to 99,3% could be obtained, with final treated effluent COD values as low as 100 mg/l, at a space load rate of not more than 1,0 $kgCOD.m^{-3}.d^{-1}$. Operation at higher space load rates resulted in the deterioration of the COD reduction potential with a sharp increase in COD levels of the ultrafiltration permeate and volatile acid/alkalinity ratio, both of which are indicative of imminent digester failure. Operation at space load rates of up to 3 $kgCOD.m^{-3}.d^{-1}$ was possible, albeit at lower COD reduction rates of 80-85%.

It was therefore concluded that the effluent was readily biodegradable, although high load rates could not be obtained. This was attributed to two possible causes which were thought to have an inhibitory effect on microbial action. Firstly the effluent contained 50-400 mg/l of furfural which is known for its bactericidal properties, and secondly the effluent had severe nutrient deficiencies, although phosphate and nitrogen were added on a regular basis.

The flux values of the ultrafiltration unit could be maintained at 20-30 $l.m^{-2}.h^{-1}$ and fouling was never serious enough to cause decreased throughput. Flux decline was experienced on one occasion and could be traced back to high solids concentration of the anaerobic sludge (due to increased suspended solids in the acetic acid influent). This problem was remedied by filtration of the influent.

PRESENT STATE OF THE ART

The project objectives were satisified in the sense that the biodegradability of the effluent by anaerobic digestion was established and that economical membrane flux could be maintained for the duration of the experiment without resorting to chemical cleaning. A negative aspect proved to be the low digester load rates which could be obtained. The experimental results presented in this project report should be seen as an initial phase in the optimisation of the ADUF process for this particular application. It is envisaged that a master plan be put into practice with regard to the co-ordination of all research work relating to further development of the ADUF process. The Water Research Commission is currently considering such a proposal.

RECOMMENDATIONS FOR FURTHER RESEARCH

With regard to the application of the ADUF process to acetic acid effluent in praticular, further work should be performed to investigate the need for mineral and trace elements additions to the digesters, as well as inocculation with specific bacterial strains which are resilient to furfural. This should enhance the anaerobic digestion rate and raise digester load rates to more economical levels.

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CONTRACT REPORT TO THE

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ABSTRACT

The treatability of acetic acid effluent, originating from the sugar refining process, by the ADUF (Anaerobic Digestion-Ultrafiltration) process was investigated during an initial laboratory scale study.

The presence of furfural, a compound with biocidal properties, in the effluent resulted in inhibition of the anaerobic action. Although the furfural was decomposed to completion, the attainable digester space load rate was limited to about 1 $kgCOD.m^{-3}.d^{-1}$. Higher space load rates resulted in digester overload.

An average COD reduction of 94,4% was obtained for the 193 day test period. ADUF permeate COD values were generally below 500 mg/l, compared to approximately 16 000 mg/l for that of the acetic acid effluent, provided that the digester did not show signs of metabolic overload. Membrane flux was found to be sensitive to digester performance. Flux drop was experienced during digester overload conditions due to membrane fouling by organics. The average membrane flux for the test period was 24,2 LMH which is considered to be economically viable.

ACKNOWLEDGEMENTS

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Laboratory scale treatment of acetic acid effluent by the ADUF process

The financing of the project by the Water Research Commission is gratefully acknowledged.

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LIST OF SYMBOLS AND ABBREVIATIONS

ADUF	Anaerobic Digestion-Ultrafiltration
COD	Chemical oxygen demand
CSTR	Continuous stirred tank reactor
HRT	Hydraulic retention time
LMH	Membrane productivity expressed in litres per square metre membrane area per hour
MEMTUF	Trade name for low-cost ultrafiltration system
MLSS	Mixed liqour suspended solids
MMCO	Molecular mass cut-off
OA	Oxygen absorbed
PES	Polyethersulphone
SS	Suspended solids
TA	Total acids
TDS	Total dissolved solids
UF	Ultrafiltration

SECTION ONE : INTRODUCTION

1.1 THE ADUF PROCESS

The combination of two distinct unit operations, *viz.* anaerobic digestion (AD) and ultrafiltration (UF), has led to the local development of the so-called ADUF (Anaerobic Digestion - Ultrafiltration) process. The design is based on an anaerobic digester which is coupled to an external UF system. The permeate from the UF system constitutes the final effluent of the ADUF process, while the sludge retentate is recycled to the digester. The UF system is used as a phase separation means to retain all biomass as well as a major fraction of the nutrients and buffer components. This promotes sludge retention times and mixing of the digester, resulting in enhanced performance. In contrast, conventional systems rely on the settling characteristics of the biomass to effect phase separation.

Ultrafiltration and anaerobic digestion are complementary processes in the sense that the anaerobic action decomposes organics which could foul the membranes, whereas the UF membranes retain biomass which would otherwise have been lost in the digester effluent of a conventional system. The ADUF process is a suitable effluent treatment method for a variety of organic waste streams which are generated by industry.

1.2 OBJECTIVES

Laboratory- and pilot-scale trials on a diverse range of industrial wastes have established the merits of the ADUF process. Experiments must nevertheless be performed on the specific effluent under consideration, since the composition of organic waste streams, even from similar industries, can vary widely. In order to determine the behaviour of the UF membranes and biodegradability of the acetic acid effluent, specifically at higher digester load rates, a laboratory-scale investigation was launched. The biodegradability of the effluent, in particular, was questioned due to the presence of furfural which is known for its bactericidal properties. The toxicity of furfural is reported to be about one third that of formaldehyde *(Merck, 1960)*.

The objectives of the laboratory-scale investigation into the treatment of acetic acid effluent by ADUF were the following:

(a) To determine whether the presence of furfural at the prevailing levels is detrimental to anaerobic digestion;

(b) to determine maximum digester load rates, attainable in the laboratory;

(c) to obtain an indication of the final effluent quality at stabilised conditions, after treatment with ADUF;

(d) to determine UF flux values at stabilised digester conditions and to investigate long-term flux stability;

1.3 SUMMARY

1.3.1 EFFLUENT COMPOSITION

The experimental apparatus and procedure was based on the treatment by ADUF of an acetic acid effluent with a typical analysis such as presented in Table 1.1.

TABLE 1.1 : TYPICAL ANALYSIS FOR ACETIC ACID EFFLUENT

PARAMETER	VALUE	
pH	2,5	
Conductivity	106	mS/m
TDS	480	mg/l
SS	116	mg/l
OA	102	mg/l
TOC	60 000	mg/l
COD	14 250	mg/l
Acetic acid	0,8-1,4	%
Formic acid	0,1	%
Furfural	50-150	mg/l
Waxes	100-200	mg/l
Aluminium	1046	μg/l
Calcium	5,03	mg/l
Magnesium	4,97	mg/l
Sodium	16,26	mg/l
Potassium	1,43	mg/l
Iron	1,11	mg/l
Manganese	0,17	mg/l
Silica	4,4	mg/l
Phosphate	86	μg/l
Cadmium	<1	μg/l
Chromium	<6	μg/l
Selenium	<0,5	μg/l
Nitrate & Nitrite	0,23	mg/l

1.3.2 ANAEROBIC DIGESTER

The anaerobic digester was operated as a mesophilic unit (35°C). The ADUF system was started on sludge which was accustomed to fruit processing effluent. As such, a variety of anaerobic bacteria strains were contained in the sludge and no effort was made to isolate specific bacteria for the degradation of certain components of the acetic acid effluent *e.g.* furfural. Initially the anaerobic sludge was conditioned on a vinegar and water substrate with an acetic acid concentration similar to that of the effluent. The pre-conditioned sludge was subsequently introduced to acetic acid effluent at sludge load rates of $<$0,05 kgCOD.kgMLSS^{-1}.d^{-1}.

It follows from the values given in Table 1.1 that the acetic acid effluent contained adequate levels of minerals and trace elements for proper anaerobic action. The effluent nevertheless showed a deficiency in nitrogen and phosphate. Urea and phosphate were therefore added to the feed buffer tank, at respective levels of 300 and 30 mg/l, on a regular basis in an effort to enhance the metabolic activity of the biomass.

1.3.3 LOAD RATES AND COD REDUCTION

The maximum sludge load rate that could be obtained, was 0,453 kgCOD.kgMLSS^{-1}.d^{-1} with an average of 0,118 kgCOD.kgMLSS^{-1}.d^{-1} over the 193 day operational period. The corresponding space load rates varied between 0,06 and 4,68 kgCOD.m^{-3}.d^{-1}.

COD reduction levels ranging from 73,8 to 99,3% could be achieved with the average at 94,4%. ADUF permeate COD values were generally below 500 mg/l when the digester did not experience overload conditions.

The load rates that could be obtained with the ADUF system, without detrimental digester overload, were relatively low. At space load rates of more than 1 kgCOD.m^{-3}.d^{-1} the digester showed signs of imminent metabolic overload, reflected in an increase of volatile acids and a drop in COD reduction (sharp increase in ADUF permeate COD content). The system preformed well at space load rates of less than 1 kgCOD.m^{-3}.d^{-1} as indicated by a stable volatile acid level, good membrane flux and COD reduction in excess of 90%.

1.3.4 MEMBRANE FLUX

Membrane flux was sensistive to digester performance, with digester overload resulting in substantial flux drop due to fouling by organics. This fact has been substantiated during previous studies on spent wine distillery waste *(Ross et. al, 1989)* and brewery effluent *(Strohwald, 1991)*.

Respective minimum and maximum flux values of 6 and 65 LMH were recorded. During steady state operation, an average flux value of 24,2 LMH could be maintained without the need for membrane cleaning (refer to Figure 3.4).

SECTION TWO : EXPERIMENTAL

2.1 ACETIC ACID EFFLUENT SAMPLES

The initial acetic acid effluent sample was supplied in the form of a 200 l drum due to the unavailability of samples on a regular basis outside the normal sugar production season. With the start of the normal processing schedule, effluent samples were obtained twice weekly in 20 l batches. This served to provide more representative samples with variations of composition, such as those which are typically experienced during normal processing.

An analysis of some of the effluent samples which were obtained during the study, is given in Table 2.1.

TABLE 2.1 : COMPOSITION OF ACETIC ACID EFFLUENT SAMPLES

DATE	19/06/91	04/07/91	17/07/91
pH	2,71	2,67	2,72
Furfural (ppm)	71	383	212
TA as CH_3COOH (%)	1,48	1,52	1,47
SS (ppm)	215	118	138
Wax (ppm)	221	90	117
COD (mg/l)	16 900	18 500	17 800
OA (mg/l)	750	1 220	860

2.2 LABORATORY-SCALE ADUF SYSTEM

Anaerobic digestion was carried out in a polyethylene reactor of 50 l capacity, with an active sludge volume of 30 l. The initial MLSS concentration was

29 g/l. Sludge circulation was achieved with a positive, screw-type pump (MONO GF 220). The digester contents was displaced approximately once every three minutes. As such the anaerobic digester was operated essentially as a CSTR.

Biomass separation was effected with a MEMTUF ultrafiltration unit (0,44 m^2 membrane area, 4x10 tube configuration), fitted with PES membranes of 40 000 MMCO. The UF permeate was recycled to the digester. A volume of permeate equal to the amount of acetic acid effluent fed to the digester, was drawn off daily. The UF retentate was also returned to the digester after having passed through a pipe section which had been fitted with heating tape. Temperature control was obtained through a digital temperature controller (RKC REX-10) acting on the heating tape.

Acetic acid effluent was initially dosed manually on a batch basis and later dispensed by means of a dosing pump (CFG Prominent C2507) acting on pH control of the digester contents.

Mechanical measurement of biogas production rate was considered, but was not performed since locally available gas meters were unsuitable in terms of flowrate range, high cost and extended delivery. The determination of gas flowrates with the aid of a Mariotte bottle (water displacement by biogas) was attempted at a later stage with some success.

2.3 ROUTINE SAMPLE ANALYSIS

The collection of operating data and chemical analysis of samples, for the control of anaerobic digestion, was performed daily. The parameters recorded for the monitoring and control of the anaerobic digester were in accordance with *Ross and Louw (1987)*.

Conductivity and pH recordings were made by standard potentiometric measurements. COD was assayed photometrically after reaction with sulphuric potassium dichromate and siver sulphate (Dr. Lange LASA AQUA, cuvette tests LCK 014, 114, 314). Volatile fatty acids were determined by titration with standardised NaOH solution to the phenolphtalein end-point, after steam distillation of the sample with magnesium sulphate and sodium tungstate *(Ross, 1990)*. Total alkalinity was determined in a similar fashion with HCl and methyl orange as the indicator.

2.4 SPECIFIC SAMPLE ANALYSIS

Samples of both the acetic acid effluent and ADUF permeate were analysed with regard to organic constitutents. Analysis results for some of the acetic acid effluent samples are presented in Table 2.1 whereas those for ADUF permeate are given in Table 3.1.

SECTION THREE : RESULTS AND DISCUSSION

3.1 OPERATION WITH MANUAL FEED CONTROL

3.1.1 DAY 1 TO 31

The space load rate was increased from 0,025 to 1,23 $kgCOD.m^{-3}.d^{-1}$ within the first 13 days. A plot of digester space load rate against operating time is presented in Figure 3.1. This 2,85% per day increase proved to be excessive and combined with severe temperature drops on two occasions (Figure 3.2), resulted in metabolic overload of the digester. This is reflected in a severe drop in the COD reduction from 98% (day 9) to 73,8% (day 31) as illustrated in Figure 3.3.

FIGURE 3.1
PLOT OF SPACE LOAD RATE AGAINST OPERATING TIME

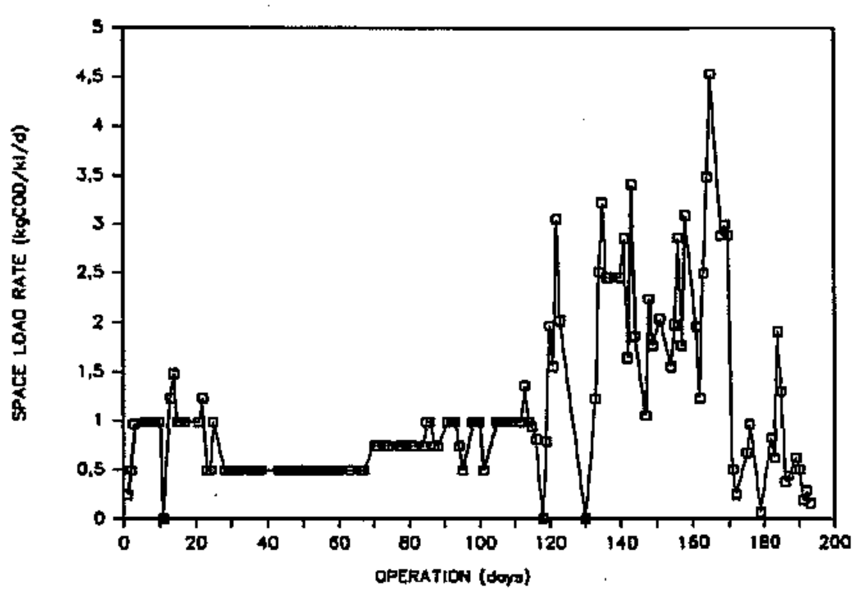


FIGURE 3.2
PLOT OF DIGESTER TEMPERATURE AGAINST OPERATING TIME

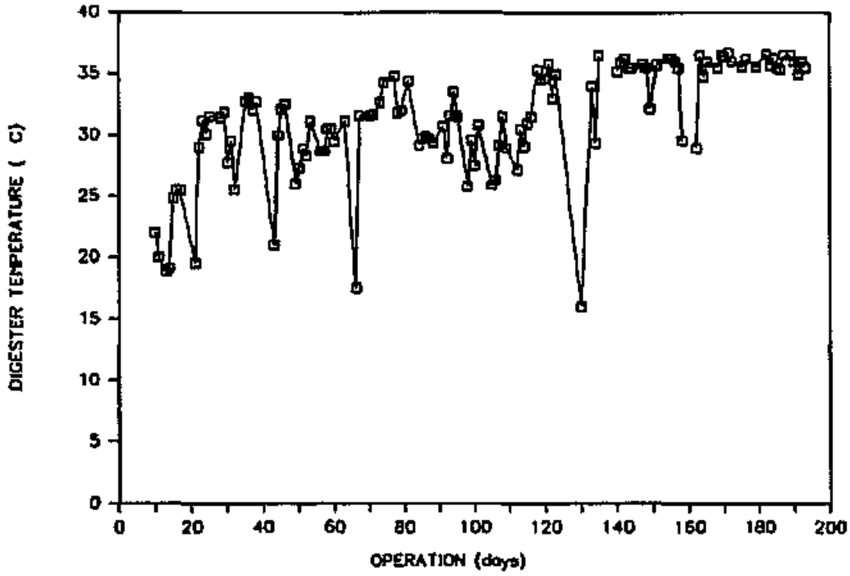


FIGURE 3.3
PLOT OF COD REDUCTION AGAINST OPERATING TIME

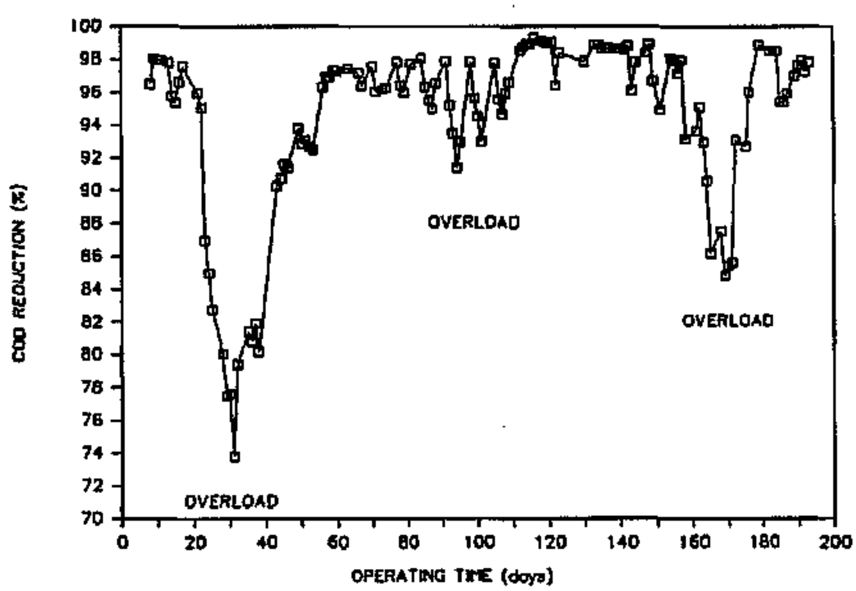
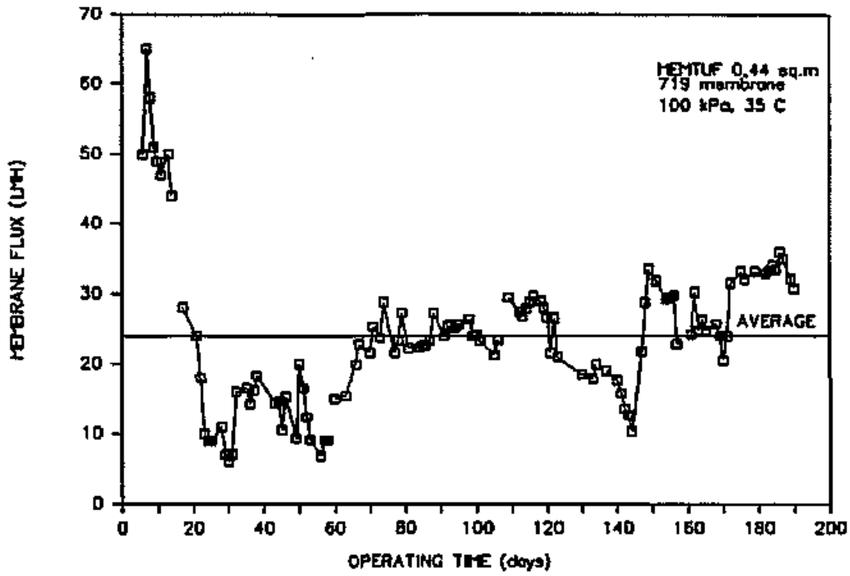


FIGURE 3.4

VARIATION OF MEMBRANE FLUX WITH OPERATING TIME



3.1.2 DAY 32 TO 67

A stabilised space load rate of 0,49 $kgCOD.m^{-3}.d^{-1}$ for this period served to arrest the digester overload which was experienced during the first 30 days of operation. Digester performance improved substantially as illustrated in Figure 3.3 by a steep increase in COD reduction from 79,4% (day 32) to above 97% (days 57 to 66).

Membrane flux showed a corresponding increase, although not as pronounced (refer Figure 3.4) probably due to large temperature drops to 21°C on day 43 and 17,5°C on day 66 (see Figure 3.2).

3.1.3 DAY 68 TO 115

Since the digester was operating well, the space load rate was increased from 0,49 to 0,74 $kgCOD.m^{-3}.d^{-1}$ (day 70) and subsequently to 0,98 $kgCOD.m^{-3}.d^{-1}$ (day 85) during this period. Stable flux values in the range 20-30 LMH were obtained. Despite occasional temperature drops to approximately 26°C (days 98, 105) digester overload was prevented by a corresponding reduction in feed rate.

3.2 OPERATION WITH pH FEED CONTROL

The digester was generally poorly buffered as the alkalinity values often were below 1000 mg/l. In contrast the volatile acid levels were nearly always in excess of 200 mg/l.

The preferred buffer capacity of an anaerobic digester, as given by the difference between alkalinity and volatile acid levels, is >1000 mg/l. It was reasoned that the digester in this study should therefore show a high pH sensitivity towards variation in feed rate. As such it was decided to try and exploit this situation for control purposes. A dosing pump and pH controller were installed for continuous, proportional dosing of acetic acid effluent according to the pH of the digester contents.

3.2.1 DAY 116 TO 147

The automated feed control via the pH meter in the digester resulted in large variations of space load rate as can be seen from Figure 3.1.

Nevertheless adequate control was obtained as illustrated by good COD reduction during this period which remained above 96% (refer Figure 3.3) as well as the termination of feed to the digester on day 130 when the temperature dropped to 16°C (Figure 3.2).

Membrane flux, on the other hand, showed a significant decline from about 29 to 10 LMH, which can most probably be explained by a build-up of undecomposed organics whithin the digester.

The space load rate could be increased to between 2,0 and 3,4 $kgCOD.m^{-3}.d^{-1}$ for most of this period.

3.2.2 DAY 148 TO 193

Acetic acid effluent was filtered to 5 micron from day 148 onwards in an effort to improve membrane flux. It is obvious from the values given in Figure 3.4 that pre-filtration removed a large percentage of the solids which had a detrimental effect on membrane flux.

A digester overload was experienced during days 165 to 171 due to a steep inrease in space load rates which reached a maximum of 4,53 $kgCOD.m^{-3}.d^{-1}$ on day 165.

The results of this metabolic overload were illustrated vividly by the following:

a) A decrease in the COD reduction percentage from >95% to 84,8%
b) A decline in membrane flux by 10 LMH from approximately 30 to 20 LMH
c) A steep increase in volatile acid level to roughly twice the alkalinity value

The feed control mechanism nevertheless succeeded to reverse the situation by reducing the feed rate of acetic acid effluent to the digester. The digester showed good recovery, albeit at low load rates, in COD reduction, membrane flux and volatile acid/alkalinity levels which reached near normal levels on day 175.

3.3 FINAL EFFLUENT (ADUF PERMEATE) QUALITY

The ADUF permeate had an average COD value of 886 mg/l over the 193 day operational period, including overloads and times during which the activity of the anaerobic digester was not optimum. This translates to an average COD reduction rate of 94,4%. With proper digestion, the permeate COD was generally <500 mg/l, as illustrated by the values given in Table 3.1.

TABLE 3.1 : ADUF PERMEATE COMPOSITION

DATE	29/04/91	02/07/91	15/07/91	25/07/91	05/08 /91
Furfural (ppm)	0	0	8,24	0	0
TA as CH_3COOH (%)	0,02	0,05	0,02	0,01	0,005
SS (ppm)	0	0	0	0	0
Wax (ppm)	0	0	0	0	0
COD (mg/l)	360	260	405	420	
OA (mg/l)		35	60		

The efficiency of the ADUF process with regard to COD reduction and the removal of furfural, acids, suspended solids and wax can be seen when the values of the acetic acid effluent in Table 2.1 are compared with those of the ADUF permeate in Table 3.1.

SECTION FOUR : CONCLUSIONS AND RECOMMENDATIONS

4.1 CONCLUSIONS

The first-order laboratory-scale study on the treatment of acetic acid effluent by the ADUF process showed the following, with regards to the originial objectives:

a) That the presence of furfural in the effluent at the prevailing levels may be inhibitory with regard to obtaining high load rates, but not lethal to treatment by anaerobic bacteria. The possible deficiency of major nutrients such as phosphate and nitrogen, which will have a detrimental effect on digester performance, can not be excluded.

b) That the maximum digester load rate would seem to be 1 $kgCOD.m^{-3}.d^{-1}$ without risking metabolic overload when using a biomass comprised of a variety of non-specific strains of bacteria.

c) That the final effluent (ADUF permeate) quality which can be obtained during non-overload conditions is excellent, in particular with regard to COD, SS, TA, furfural and wax.

d) That membrane flux values could be maintained at economical levels without the need for cleaning, provided that proper anaerobic action can be effected.

The relatively low space load rates that were obtained during this study translate to high HRT's which question the economical viability of the anaerobic digestion step in terms of excessive digester volumes and capital cost. This situation could possibly be improved by using specific bacteria strains which are designed to decompose the toxic constituents of the acetic acid effluent such as furfural. On the other hand, nutrient deficiency could be a further cause of poor digester performance. The provision of sufficient nutrients on a full-size digester is a logistical and economical problem. Blending of the acetic acid effluent influent with sewerage could provide a solution.

The membrane flux values that were obtained are considered to be economical and correlate well with previous experience *(Ross et.al, 1989; Strohwald, 1991)* and those presented in the literature *(Hogetsu et.al, 1991; Choate et.al, 1982)*.

The results indicate that feed flow control by digester pH is not sensitive enough to prevent overload of the laboratory-scale digester due to large variations in space load rate. This problem could possibly be overcome with more sophisticated control equipment. The concept should, however, be considered as a safety measure on full-size installations.

4.2 RECOMMENDATIONS

It is recommended that the following be investigated, subsequent to the initial laboratory-scale study, and prior to scale-up of the ADUF process for the treatment of acetic acid effluent:

a) The desirability of an on-site pilot study at a capacity which is representative of a full-size system.
b) The inoculation of the pilot-scale anaerobic digester with specific bacteria strains which are designed to decompose the particular constituents of the effluent. These bacteria can be cultivated and isolated in the laboratory *(Ross, 1991; Britz, 1991)*.

These actions would serve to improve the attainable load rates which, combined with capital and operating cost data from the pilot study, could determine the economical feasibility of the ADUF process for this particular application.

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