

Influence of organic loading rate and hydraulic retention time on the efficiency of a UASB bioreactor treating a canning factory effluent

W Trnovec and TJ Britz*

Department of Food Science, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa

Abstract

A mesophilic laboratory-scale upflow anaerobic sludge bed bioreactor design was evaluated for the treatment of a carbohydrate-rich effluent from the canning industry. The bioreactor was inoculated with 500 g of anaerobic granules and after the system had stabilised the hydraulic retention time (HRT) was set at 24 h and the substrate pH poised at 8.0 to prevent the effect of rapid acidification. In the first experimental study the chemical oxygen demand (COD) was increased stepwise from 2 300 to a full strength of 4 000 mg·ℓ⁻¹. In the second study the organic loading rate was increased by shortening the HRT (24 to 8 h) to give an organic loading rate increase from 3.95 to 10.95 kgCOD·m⁻³·d⁻¹ with an average COD removal of 90 to 93% and removal rate of 9.8 kgCOD·m⁻³·d⁻¹. However, the recovery rate of the system at HTR values below 10 h was found to be very slow suggesting that the system had reached its minimum HRT. This was confirmed by the stabilisation of the granule bed. An HRT of 10 h was thus taken as the optimum operational HRT. Since neutralisation costs would influence economic aspects of the process, the influence of lower pH values was investigated in the third study where the pH of the canning effluent was lowered from 8.0 to 5.0. At the lower pH the COD removal dropped drastically, the biogas production decreased and the digester effluent pH dropped to 6.2. It was clear from the slow recovery of the digester and the low COD removal (66.1%) that the lower end of the operational pH had been reached and any further lowering of the substrate pH would lead to system failure. The economic implication of being able to operate at pH 5.5 means that fresh canning effluent can be introduced into the digester without any neutralisation, is considerable.

Introduction

All industries are increasingly required to reduce their impact on the environment. Adequate treatment of food processing effluents is assuming increasing importance, as this industry addresses the issue of responsible environmental management (Wayman, 1996). For the food industry this is frequently difficult as factors related to seasonal operation, changes in plant effluent characteristics due to the processing of different products, nutritional deficiencies and the location of food processing plants, heavily impact the treatment efficiency. Furthermore, the growing concern over the quality and quantity of freshwater has forced higher surcharges and fines in an attempt to reduce the pollution loading on treatment facilities and environmental pollution. Many local authorities are now insisting that industries undertake some form of effluent treatment so as to protect the environment.

Considerable interest has been shown in the application of anaerobic digestion to waste waters from the food industry since the nature and strength of the waste waters often provide the ideal conditions for digester operation. The waste waters have a high organic content, have little or no toxic material present (Kroyer, 1995) and include the situation where waste waters are produced over a short period of the year such as in the canning industry. Anaerobic processes have been shown to be amenable to such variations and in particular where complete shutdown may take place.

Among the high-rate anaerobic reactors developed and successfully applied in recent years (Lettinga et al., 1997), the

upflow anaerobic sludge blanket (UASB) reactor has become one of the most popular designs for the biological treatment of effluents, and in particular those from the food processing industries (Lettinga et al., 1997). Many UASB reactors are in operation throughout the world (Schmidt and Ahring, 1996). The advantage of the UASB design is the ability to retain high biomass concentrations despite the upflow velocity of the waste water and the production of biogas. Consequently, the reactor can operate at short hydraulic retention times since the sludge retention time is almost independent of the hydraulic retention time. In UASB reactors, the biomass is retained as granules, formed by the natural self-immobilisation of the bacteria. These granules have good settling abilities and vary in size from 0.14 to 5 mm depending upon the waste water used and operational conditions. The granules vary widely in shape, but they usually have a spherical form. The development of granular sludge is the key factor for successful operation of UASB reactors. Today it is possible to develop granules on a variety of waste waters and defined media, but there have been several reports on lack of granulation on specific waste waters (Wentzel et al., 1994). Furthermore, some researchers have reported sudden disintegration of granules without any obvious reason.

The objective of this study was to assess the effects of shortening the hydraulic retention times on the overall performance and stability of an UASB reactor, while treating a canning factory effluent.

Materials and methods

Digester design

A laboratory-scale upflow anaerobic sludge blanket bioreactor (UASB) was used. The digester had an operational volume of 2.3 ℓ (total height of 830 mm and internal dia. of 50 mm) and

*To whom all correspondence should be addressed.

☎ (021) 808-3509; fax (021) 808-3510; e-mail tjbritz@land.sun.ac.za
Received 6 August 1997; accepted in revised form 5 January 1998

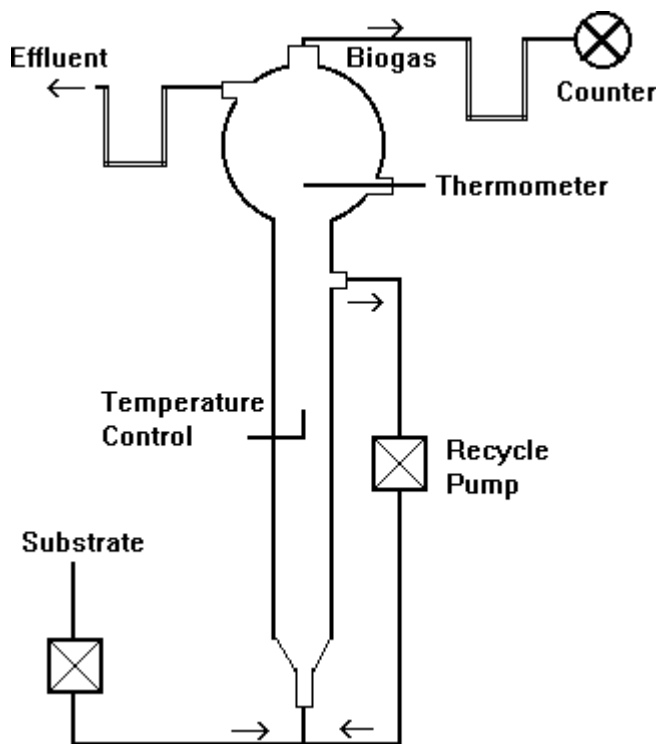


Figure 1
Laboratory-scale UASB bioreactor

combined a UASB design with an open gas/solids separator at the top of the bioreactor (Fig. 1). The biogas exited through the top, while the substrate was introduced into the bioreactor at the base. The overflow of the bioreactor emptied through a U-shaped tube to prevent any atmospheric oxygen from entering the system. The upflow velocity within the reactor was set at $2 \text{ m}\cdot\text{h}^{-1}$. The temperature of the insulated bioreactor was maintained at 35°C using a heating tape and an electronic control unit (Meyer et al., 1985). The volume of the biogas was determined using a manometric unit equipped with an electronically controlled counter and a gas-tight valve and the volumes corrected to standard temperature and pressure. The substrate was fed semi-continuously to the bioreactor by means of a peristaltic pump (Watson-Marlow 101) controlled by an electronic timer.

Bioreactor start-up

The bioreactor was seeded with 500 g of water drained anaerobic granules from another anaerobic digester giving a settled sludge-bed height of 300 mm. The bioreactor was then allowed to stabilise for 48 h in order to allow the bacterial community to acclimatise and fed with a diluted synthetic substrate ($2\,300 \text{ mg}\cdot\text{L}^{-1}$ COD) and the HRT set at 24 h. After three weeks this was replaced with a fruit-canning factory effluent and the COD concentration was gradually increased to $4\,000 \text{ mg}\cdot\text{L}^{-1}$.

Substrate

The composition of the synthetic substrate (in $\text{mg}\cdot\text{L}^{-1}$) was: glucose 1 250; sodium lactate 5 000; acetic acid 10; urea, 500; and K_2HPO_4 500. The substrate was also supplemented with 1.0 mL trace element solution (Nel et al., 1985) and the pH poised at 8.5

with calcium hydroxide to optimise the environment for maximum granule growth. This substrate was then diluted to the required COD concentration.

The effluent from the fruit canning factory was sampled over the whole 1996/1997 canning season from the waste-water stream before it reached the general stream that also contained the lye effluents (Visser, 1997).

Analytical methods

The following parameters were monitored according to the APHA (*Standard Methods*, 1985): pH; alkalinity; total solids (TS); total volatile solids (TVS); and total non-volatile solids (TNVS). COD, orthophosphate phosphorus and total Kjeldahl nitrogen were determined colorimetrically using a DR2000 spectrophotometer (Hach Co. Loveland, CO) and standardised procedures (*Standard Methods*, 1985). The general mineral analyses were done colorimetrically according to standard Hach procedures using a DR2000 spectrophotometer (Hach Co. Loveland, CO).

The total volatile fatty acids (TVFA) were determined using a Varian (Model 3700) gas chromatograph, equipped with a flame ionisation detector and a $30 \text{ m} \times 0.32 \text{ mm}$ i.d. Fused Silica capillary column with 007 FFAP bonded phase (Quadrex Co. New Haven). The column temperature was initially held at 105°C for 5 min, then increased at a rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ to 219°C . The detector and inlet temperatures were set at 260°C and 250°C respectively and nitrogen gas was used as carrier gas at a flow rate of $2.5 \text{ mL}\cdot\text{min}^{-1}$.

The biogas composition was determined on a Fisons GC equipped with a thermal conductivity detector and $2.0 \text{ m} \times 3.0 \text{ mm}$ i.d. column packed with Porapak Q (Waters Ass. Inc, Milford, MA), 80/100 mesh. The oven temperature was set at 55°C and helium was used as carrier gas at a flow rate of $40 \text{ mL}\cdot\text{min}^{-1}$.

Carbohydrate composition was determined on a Dani GC equipped with a $2.0 \text{ m} \times 3.0 \text{ mm}$ column packed with 1% OV-1 (Waters Ass. Inc, Milford, MA). The column temperature was initially held at 160°C , then increased at a rate of $5^\circ\text{C}\cdot\text{min}^{-1}$ to 193°C . The detector and the inlet temperatures were set at 250°C and 280°C respectively and nitrogen gas was used as carrier gas at a flow rate of $30 \text{ mL}\cdot\text{min}^{-1}$.

Experimental studies

The study comprised three experimental studies (I to III). In the first study (I), the substrate COD concentration was increased stepwise from $2\,300$ to $4\,000 \text{ mg}\cdot\text{L}^{-1}$ in 7 steps. In the second study (II), the COD concentration was kept constant at $4\,000 \text{ mg}\cdot\text{L}^{-1}$, while the HRT was reduced stepwise from 24 to 8 h in 14 steps. In the third study (III), the HRT was reset at 10 h while the COD concentration was kept constant at $4\,000 \text{ mg}\cdot\text{L}^{-1}$. The substrate pH was then reduced stepwise from 8.5 to 5.0 in 7 steps. In all three studies, the bioreactor was allowed to reach stable-state conditions before each HRT or pH reduction. Stable-state is defined as a state which can be maintained indefinitely without system failure (Cobb and Hill, 1990), during which the variation in bioreactor performance parameters is less than 10%. Thus, the length of each phase was based on the stability of the bioreactor effluent pH, alkalinity and COD removal.

Results and discussion

Canning effluent composition

The average composition of 15 different batches from a local fruit-canning factory is given in Table 1. The data clearly show that the composition of the effluent was fairly constant over the whole canning season. During the study period only the COD of this effluent was standardised.

Parameter	Average	SD
pH	5.45*	1.4
COD	4432*	297
TS	2114*	625
TVS	1783*	169
TNVS	331*	152
PO ₄	5.32*	3.9
TKN	21.4*	12.4
Alkalinity (as CaCO ₃)	25*	6.5
Glucose	161.6 ⁺	25.3
Fructose	389.7 ⁺	34.6
Sorbitol	88.8 ⁺	9.7
Ca ²⁺	21 ⁺	nd
Co ²⁺	<0.06 ⁺	nd
Fe (total)	7.9 ⁺	nd
K	84 ⁺	nd
Mg	15 ⁺	nd
Na	65 ⁺	nd
Ni ²⁺	<0.3 ⁺	nd
SO ₄ ²⁻	12.8 ⁺	nd
S ²⁻	0.03 ⁺	nd

* = Data are means of 15 batches
+ = Average of two determinations

Study I - Increasing the organic loading rate

The substrates used during these experimental studies were a dilution of the factory effluent given in Table 1. To prevent a shortage of nitrogen and phosphorus, a 100 mg·l⁻¹ of each of ureum and K₂HPO₄ and 1.0 ml·l⁻¹ of the trace element solution were added and the COD diluted to the required concentration. The pH was poised at 8.0 using a 1.0 N Ca(OH)₂ solution as initially at the start of the study the digester showed signs of pH instability with a tendency towards pH values below 6.5 units. A summary of the operational conditions and digester efficiency is given in Table 2. The hydraulic retention time was kept constant at 24 h and the OLR increased in 7 steps from 2.28 to 3.95 kgCOD·m⁻³·d⁻¹. The final value represented on average the full strength effluent as obtained from the factory and from these data it was concluded that it could be treated directly without dilution.

Study II - Shortening the hydraulic retention time

During this study the HRT was shortened from 24 h to 8 h over 14 steps (Table 3) with a subsequent increase in OLR from 3.95 to 10.95 kgCOD·m⁻³·d⁻¹. Stable-state conditions plus 5 HRTs were used as criterion for increasing the OLR. During the different steps the pH of the digester effluent remained fairly constant (7.5 to 8.1) with the alkalinity in the range of 1 800 to 3 200 at the end of each step. However, directly on changing the OLR it was usually found that the pH dropped from 0.2 to 0.8 units but within 5 d the pH increased and stabilised. The pH stability can probably be ascribed to the high alkalinity level (1 800 to 3 200 mg·l⁻¹). According to Duff and Kennedy (1982) and Lane (1984), alkalinity plays an important role in minimising overloading effects.

During this study it was found that at HRT values of shorter than 10 h, the recovery rate in terms of pH and COD removal stabilisation was slower than found with the longer HRTs with up to 14 h before the two parameters stabilised. The decrease in pH after increasing the OLR, as one of the indicators of impending digester failure, has been intensively studied (Hill and Bolte, 1989). According to Dohanyos et al. (1985), any change in operational parameters, such as organic loading, causes simultaneous increase in the concentration of all the volatile fatty acids resulting in a decrease in the pH. Once the microbial biomass has recovered and stabilised the extra VFAs are normally metabolised and the pH stabilises (Myburg and Britz, 1993). Based on the extended stabilisation time at these HRTs, it was concluded

Parameter	Steps						
	1	2	3	4	5	6	7
Substrate COD (mg·l ⁻¹)	2 300	2 500	3 000	3 200	3 500	3 700	4 000
COD removal (%)	88	92	90	91	89	90	91
HRT (h)	24	24	24	24	24	24	24
OLR (kgCOD·m ⁻³ ·d ⁻¹)	2.28	2.5	3.0	3.22	3.49	3.73	3.95
Digester pH	7.6	7.5	7.3	7.4	7.4	7.7	8.0
Alkalinity (mg·l ⁻¹ CaCO ₃)	1 800	1 850	1 950	1 125	1 225	2 010	2 125
Biogas (l·d ⁻¹)	1.1	1.37	2.36	1.84	2.27	2.35	2.52
Methane (%)	62	63	64	64	65	64	64

TABLE 3
OPERATING CONDITIONS AND DIGESTER EFFICIENCY DURING EXPERIMENTAL STUDY II WHERE THE HRT WAS SHORTENED

Parameter	Steps													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Substrate COD (mg·ℓ ⁻¹)	3 947	4 162	4 011	3 932	4 119	4 233	3 912	3 953	3 967	4 069	4 125	3 991	4 099	4 161
COD removal (%)	91	96	96	93	92	94	88	90	91	93	93	90	91	93
HRT (h)	24	22	20	18	17	16	15	14	13	12	11	10	9	8
OLR (kgCOD·m ⁻³ ·d ⁻¹)	3.95	4.16	4.36	4.74	5.6	6.13	6.2	6.27	6.84	7.54	8.25	8.68	9.8	10.95
Digester pH	8.0	7.9	7.5	7.9	8.1	7.6	7.5	7.7	7.55	8.1	8.1	7.6	7.9	7.9
Alkalinity (mg·ℓ ⁻¹ CaCO ₃)	2 125	2 250	2 100	1 800	2 250	2 200	3 200	3 800	2 600	2 450	2 625	2 350	2 700	3 200
Biogas (ℓ·d ⁻¹)	2.52	2.29	2.78	4.4	4.7	4.72	4.5	5.33	5.58	6.14	6.39	5.72	6.68	8.7
Methane (%)	63	64	64	65	64	65	62	63	64	64	64	62	64	64

that even though the COD removal after stable-state had been reached was still above 90%, the digester was reaching its maximum operational HRT and that any sudden changes in normal operating parameters would influence the efficiency negatively. An HRT of 10 h with an average COD removal of between 90 and 93% and removal rate of 9.8 kgCOD·m⁻³·d⁻¹ was taken as the optimum operational conditions (Table 3).

Study III - Lowering of the substrate pH

Since neutralisation costs would influence economic aspects of the process, the influence of lower pH values was investigated in the third experimental study. In this study, based on the data obtained during Study II, the HRT was kept constant at 10 h and the substrate pH lowered in 7 steps over 60 d from 8.0 to 5.0. The data (Table 4) show that at substrate pHs of 6.0 and 5.5, the alkalinity drastically decreased to 1 150 mg·ℓ⁻¹. However, the COD removal was still above 88% and the effluent pH above 6.8 which is still in the optimal recommended pH range (Nel and Britz, 1986). When the substrate pH was lowered to 5.0 the COD removal dropped drastically (Table 4) and the biogas production started to decrease. It was also found that just after the change to pH 5.0 the digester effluent pH dropped to 6.2 and once the system reached stable state slowly increased to 6.7. It was clear from the slow recovery of the digester and the low COD removal (66.1%) that the lower end of the operational pH had been reached and any further lowering of the substrate pH would lead to system failure. The substrate pH was then reset at 5.5 which is near the average pH of the fresh raw canning effluent (Table 1) and the COD removal and digester effluent pH slowly recovered to about 90% COD removal and pH 6.8 to 7.0. The economic implication of being able to optimise and operate the digester at a substrate pH of 5.5 is considerable since it means that fresh canning effluent can be introduced into the digester without any neutralisation. It must also be remembered that the canning effluent is rich in carbohydrates and if the effluent is stored, fermentation will take place with a concurrent reduction in pH to values of about 3.0 to 3.5. Neutralisation must then be applied before substrate introduction to the digester.

UASB bioreactor efficiency

Since the efficiency of the UASB system is based on the formation and retention of granules, changes in the height of the UASB granule bed were monitored during the course of the study (Fig. 2). With a start bed height of 300 mm, growth at first was very slow but as soon as the HRT was lowered to below 24 h, a definite increase in the bed height was found, suggesting that the bioreactor had not reached its loading capacity. Around day 90, once an HRT of 10 h had been reached, the bed growth stabilised and remained stable for the rest of the study. At HRT values below 10 h the system was found to show an extended recovery time indicating maximum loading at the shorter HRTs. It is possible that if the COD concentration of the canning effluent itself had been higher, a further increase in granule bed height might have taken place but since 4 000 mg·ℓ⁻¹ was the maximum concentration, this was not followed up.

The UASB bioreactor efficiency in terms of the relationship between percentage COD removal and the COD removal rate (kg COD·m⁻³·d⁻¹) is plotted in Fig. 3 as a function of the OLR over all three the experimental studies. The data obtained at HRT values below 10 h (Table 3) and those at a pH value below 5.5 (Table 4) were not included as the slow bioreactor recovery

Parameter	Steps						
	1	2	3	4	5	6	7
Substrate COD ($\text{mg}\cdot\text{L}^{-1}$)	3 937	3 980	4 096	3 834	4 018	4 104	4 352
COD removal (%)	90.7	88.5	90.5	90.2	88.3	89.4	66.1
HRT (h)	10	10	10	10	10	10	10
OLR ($\text{kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$)	8.75	9.48	9.75	9.13	9.57	9.77	10.4
Substrate pH	8.0	7.5	7.3	6.5	6.0	5.5	5.0
Digester pH	8.0	7.6	7.89	7.95	6.82	6.91	6.7
Alkalinity ($\text{mg}\cdot\text{L}^{-1}\text{CaCO}_3$)	3 475	2 550	2 775	2 175	1 150	1 150	1 050
Biogas ($\text{L}\cdot\text{d}^{-1}$)	4.88	5.72	6.45	7.7	8.75	9.43	8.12
Methane (%)	64	63	63	64	65	65	63

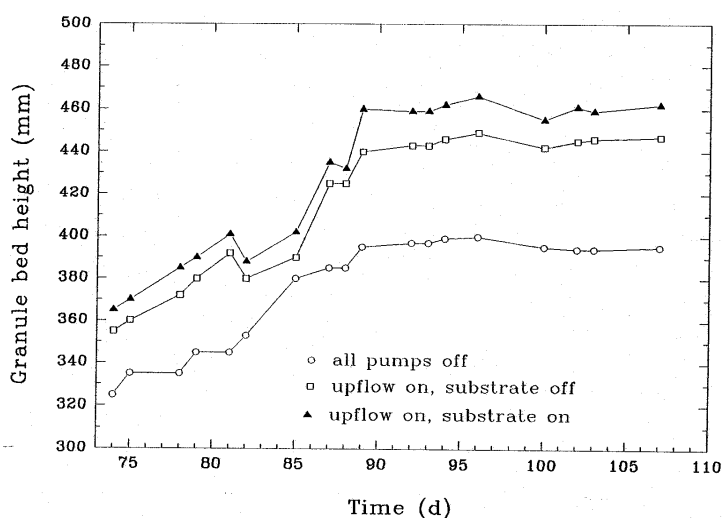


Figure 2

Changes in the height of the granule bed in the UASB

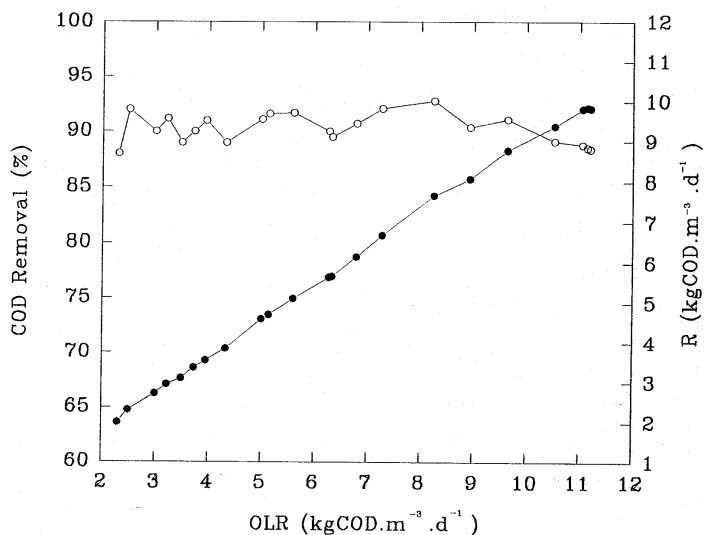


Figure 3

The effect of the increase in organic loading rate on the percentage COD removal (○) and the COD removal rate (●)

clearly indicated that the lower end of the operational HRT and pH had been reached and any further changes in OLR would lead to system failure. The best removal rate (R-value) was found in the OLR region of about $11\text{ kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$ (Fig. 3). Since the highest COD concentration ($4\ 000\text{ mg}\cdot\text{L}^{-1}$) was already being loaded, any increase in OLR could only be obtained by further lowering of the HRT to below 10 h. However, changes to lower HRT values led to a slow recovery of the bioreactor suggesting that the system had reached its maximum organic loading rate and that system failure would be imminent even after small environmental changes (Verstraete and Vandevivere, 1997).

Conclusions

It has long been thought that anaerobic digestion is too slow and unreliable to be used by the canning industry as a treatment option (Borja and Banks, 1994; Wayman, 1996). From the results obtained during the three experimental studies it was clear that the UASB design is feasible for treatment of the carbohydrate-rich effluents produced in the canning industry. The most favourable COD removal of the canning-industry effluent was between 89 and 93% at organic loadings of 9.8 and $10.95\text{ kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$, at an HRT of 10 h and substrate pH of 5.5. The UASB bioreactor in terms of HRTs, OLRs and substrate pH as operated in this study, was more efficient when compared to results reported by Austermann-Hann et al. (1997), where a UASB was used to treat a fruit-juice effluent.

Acknowledgements

The financial support of the Water Research Commission and the University of Stellenbosch is gratefully acknowledged. We would also like to acknowledge the co-operation of Mr J Visser of Ashton Cannery in supplying the cannery effluent and Dr A Wood for his help in obtaining a regular supply of granules.

References

- AUSTERMANN-HANN U, SEFRIED CF and ROSENWINKEL K (1997) UASB-reactor in the fruit juice industry. *Proc. 8th Int. Conf. Anaerobic Digestion* (Vol 1.) Sendai, Japan. 67-74.
- BORJA R and BANKS CJ (1994) Kinetic study of anaerobic digestion of fruit-processing wastewater in immobilized-cell bioreactors. *Biotechnol. Appl. Biochem.* **20** 79-92.
- DOHANYOS M, KOSOVA B, ZABRANSKA J and GRAU P (1985) Production and utilization of volatile fatty acids in various types of anaerobic reactors. *Water Sci. Technol.* **17** 191-205.
- COBB SA and HILL DT (1990) Using nitrogen ratio as an indicator of biomass retention and steady state in anaerobic fermentation. *Trans. ASAE* **33** 282-287.
- DUFF SJB and KENNEDY KJ (1982) Effect of hydraulic and organic overloading on thermophilic downflow stationary fixed film (DSFF) reactor. *Biotechnol. Lett.* **4** 815-820.
- HILLDT and BOLTEJP (1989) Digester stress as related to iso-butyric and iso-valeric acids. *Biol. Wastes* **28** 33-37.
- KROYER GT (1995) Impact of food processing on the environment - An overview. *J. Food Sci.* **28** 547-552.
- LANE AG (1984) Laboratory scale anaerobic digestion of fruit and vegetables solid waste. *Biomass* **5** 245-259.
- LETTINGA G, HULSHOFF POL LW, ZEEMAN G, FIELD J, VAN LIER JB, VAN BUUREN JCL, JANSSEN AJH and LENS P (1997) Anaerobic treatment in sustainable environmental production concepts. *Proc. 8th Int. Conf. Anaerobic Digestion* (Vol 1.) Sendai, Japan. 32-39.
- MEYER LH, HUGO AB, BRITZ TJ, DE WITT B and LATEGAN PM (1983) Temperature control for laboratory scale anaerobic digesters. *Water SA* **9** (2) 79-80.
- MYBURG C and BRITZ TJ (1993) Influence of higher organic loading rates on the efficiency of an anaerobic hybrid digester while treating landfill leachate. *Water SA* **19** (4) 319-324.
- NEL LH, BRITZ TJ and LATEGAN PM (1985) The effect of trace elements on the performance efficiency of an anaerobic fixed film reactor treating a petrochemical effluent. *Water SA* **11** (3) 107-110.
- NEL LH and BRITZ TJ (1986) The influence of different pH values on the performance of a downflow anaerobic fixed bed reactor treating a petrochemical effluent. *Biotechnol. Lett.* **8** 293-298.
- SCHMIDT JE and AHRING BK (1996) Granular sludge formation in upflow anaerobic sludge blanket (UASB) reactors. *Biotechnol. Bioeng.* **49** 229-246.
- STANDARD METHODS (1985) *Standard Methods for the Examination of Water and Wastewater* (16th edn.) American Public Health Association, Washington DC.
- VERSTRAETE W and VANDEVIVERE P (1997) Broader and newer applications of anaerobic digestion. *Proc. 8th Int. Conf. on Anaerobic Digestion* (Vol 1.) Sendai, Japan. 67-74.
- VISSERJ (1997) Personal communication. Ashton Canning Co. (Pty) Ltd.
- WAYMAN MJV (1996) Water supplies, effluent disposal and other environmental considerations. In: D Arthey and PR Ashurst (eds.) *Fruit Processing*. Blackie Academic & Professional Press, London. 221-243
- WENTZEL MC, MOOSBRUGGER RE, SAM-SOON PALNS, EKAMA GA and MARAIS GvR (1994) Tentative guidelines for waste selection, process design, operation and control of upflow anaerobic sludge bed reactors. *Water Sci. Technol.* **30** 31-42.
-