Grape wine distillery waste in UASB systems - Feasibility, alkalinity requirements and pH control

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Abstract

Grape wine distillery waste developed a pelletised sludge bed in a UASB system. Product formation along the line of flow in the pelletised bed was similar to that when treating a pure carbohydrate apple juice waste. Pelletised slude production was about 0,14 mg VSS/mg COD removed as against 0,42 mg VSS/mg COD removed for apple juice waste, indicating a low influent COD carbohydrate fraction. The pellets were not as compact as with apple juice waste and were smaller (< 2 mm). The grape wine distillery waste COD concentration ranged from 20 000 to 30 000 mg/ℓ. An appreciable amount of H_2CO_3* alkalinity was generated internally due to deamination of proteins and removal of organic salts. Provided the system was operated with a recycle from the effluent to influent at a recycle ratio sufficiently high to dilute the base influent COD concentration to an effective influent COD (COD_e) of < 2 000 mg/ℓ, sufficient of the H_2CO_3* alkalinity generated internally was recycled to maintain a sludge bed pH > 6,6. Recycle ratios as high as 33:1, reducing the base influent COD concentration of 27 000 mg/ℓ to a COD_e of 790 mg/ℓ, did not adversely affect COD removal. No nitrogen, phosphate or trace element supplementation was required. COD removal was greater than 94 per cent for COD loading rates up to the maximum of 19 kg/(m^3 sludge bed·d, the maximum COD loading rate was determined by gas lifting pellets in to the settling section, not by process failure.

Introduction

Grape wine distillery waste is the residue left after ethyl alcohol has been distilled from fermented grape juice. It contains organic acids and their salts, soluble proteins and carbohydrates, as well as various inorganic compounds which are normal constituents of wine. In the literature successful treatment of rice wine distillery waste in full-scale UASB plants has been reported (Cheng et al., 1990). It was of interest, therefore, to investigate the potential of grape wine distillery waste for treatment in a UASB system. The study was divided into two major parts:

- Feasibility of the treatment of grape wine distillery waste in a flow-through UASB system, to ascertain formation of a pelletised sludge bed and to study the product formation pattern along the line of flow of the reactor.
- Investigation into the effects of recycling on process performance and mass of H_2CO_3* alkalinity required to maintain a near neutral minimum pH in the lower part of the sludge bed.

Assessment of grape wine distillery waste for treatment in a UASB system

From available information, the grape wine distillery waste was theoretically assessed for suitability as a substrate for the UASB system against the prerequisites for pelletisation set out by Sam-Soon et al. (1987), i.e. (1) development of a high $\bar{p}H_2$ environment; (2) cysteine deficiency; (3) excess supply of nitrogen; and (4) a near neutral pH.

With regard to (1), the presence of carbohydrates and proteins would be desirable as they give rise to a high $\bar{p}H_2$ during the acidogenic phase (Sam-Soon et al., 1987 and Moosbrugger et al., 1990). A number of analyses of grape wine distillery waste were obtained from the distilleries. However, these analyses tended to focus either on the potential for recovery of some compounds such as tartaric acid, or on compounds that may cause problems in distillation, for example sugars that may caramelise onto the distillation apparatus. Reported waste COD values ranged from 20 000 to 30 000 mg/ℓ, carbohydrates COD from about 2 000 to 3 000 mg/ℓ; organic nitrogen content ca. 300 mg N/ℓ. Clearly the protein fraction made up a relatively small portion of the waste COD. Other data on organic acids are listed in Table 1. From the analysis provided in Table 1, an appreciable fraction of COD is in the form of organic acids which probably would not induce a high hydrogen partial pressure ($\bar{p}H_2$) to the same extent as the carbohydrates contained in the apple juice waste used by Sam-Soon et al. (1987) in their investigation.

With regard to (2), cysteine deficiency, no analysis was available and it was not known whether cysteine was deficient or not.

With regard to (3), excess ammonium supply, Sam-Soon et al. (1990) suggested a minimum of 0,02 mg N/mg influent COD for unimpeded pellet production. Data on grape wine distillery waste (Table 2) indicated a TKN/COD ratio of 0,015, considerably lower than the value recommended for a carbohydrate type substrate (Sam-Soon et al., 1990). Also, there was uncertainty as to whether the organic nitrogen would be deaminated sufficiently rapidly to be available for pelletisation in the lower part of the reactor.

With regard to (4), a near neutral pH, initially it was not known how much alkalinity the substrate would generate internally and how much would need to be added from an external source.

From the theoretical assessment, no explicit conclusion was possible as to whether the waste would be suitable for treatment in a UASB system or not; that is, whether the waste would generate a pelletised sludge bed or not - the only option was an experimental feasibility study.

Feasibility study

Influent feed stock of grape wine distillery waste was collected from the KWV distillery at Paarl and stored at 4°C. The waste batches contained different low concentrations of particulate material; to eliminate this variable the waste was settled and the supernatant only used as feed to the UASB reactor. The average characteristics of the supernatant are shown in Table 2.

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TABLE 1
ANALYSIS OF GRAPE WINE DISTILLERY WASTE WITH RESPECT TO ORGANIC ACIDS

Tartaric acid	1,7 g/ℓ
Malic acid	0,5 g/ℓ
Lactic acid	1,8 g/ℓ
Succinic acid	1,6 g/ℓ
Acetic acid	0,6 g/ℓ

TABLE 2
CHARACTERISTICS OF SETTLED GRAPE WINE DISTILLERY WASTE IN FEASIBILITY STUDY (BATCH 1)

Soluble COD fraction	98 %
Soluble COD concentration	24 000 mg/ℓ
Inorg-N	50 mg/ℓ
TKN	360 mg N/ℓ
Phosphorus	110 mg P/ℓ
pH	4,2

TABLE 3
CHARACTERISTICS OF DILUTED SETTLED GRAPE WINE DISTILLERY WASTE IN FEASIBILITY STUDY

Soluble COD concentration	5 500 mg/ℓ
Inorg-N	12 mg/ℓ
TKN	83 mg/ℓ
Phosphorus	26 mg/ℓ
pH	5,2

For the feasibility study a flow-through system was selected. Each day the feed to the reactor was made up from the settled feed stock by diluting to a COD of 5 500 mg/ℓ using tap water. This influent COD concentration was selected to enable a comparison of the pattern of product formation with that reported by Sam-Soon et al. (1987) on treatment of apple juice waste in UASB systems. The daily feed was kept refrigerated at 4° C. The feed composition after dilution is given in Table 3.

To avoid potential deficiencies of trace element supply, 5 mℓ/ℓ influent of a trace element solution, suggested by Zehnder and Wuhrmann (1977) for enrichment of cultures of methanogenic bacteria, was added to the feed. Detailed composition of this trace element solution is given by Moosbrugger et al. (1993).

To ensure sufficient pH buffer, the H_2CO_3* alkalinity requirements were estimated assuming that no alkalinity would be generated internally; an alkalinity supplementation of 1,2 mg H_2CO_3* alkalinity (as $CaCO_3$)/mg base influent COD was selected, as recommended by Sam-Soon et al. (1991) for pure carbohydrate substrate . The buffer chemicals were 9,4 g $NaHCO_3$ and 0,8 g NaOH per litre base influent; on addition to the waste flow the pH was about 7,0.

Experimental set-up

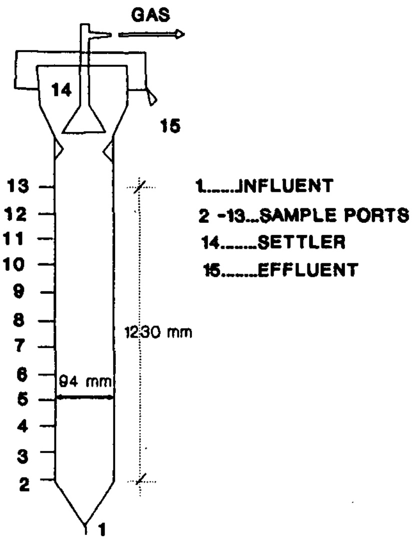

Figure 1
Schematic diagram of laboratory UASB reactor

A laboratory-scale UASB reactor was constructed from a transparent perspex cylinder of 94 mm diameter, 1 500 mm high, with a conically shaped inlet at the bottom and a solid/liquid/gas separator at the top, total reactor volume ca 10,5 ℓ (Fig. 1). Gas collection was by means of a hollow inverted cone: Rising gas bubbles are deflected into the cone by a deflector collar around the inside wall of the reactor below the cone; liquid effluent discharges via an annular space between the gas collection cone and and the reactor wall, to enter a small liquid/solid separator (1 500 mℓ); clarified liquid flows over a launder into the collection vessel while solids, which settle out, are returned into the reactor by gravity. Twelve evenly spaced sample ports were installed up the reactor wall for sampling along the line of flow. Temperature was maintained at 30°C by a thermostat-controlled electrical heating tape wrapped around the reactor. For the feasibility study the system was operated in flow-through fashion, i.e. no recycle was employed.

Parameters measured

The following parameters were measured on the system at 1 to 2 d intervals:

- filtered influent and effluent COD;
- filtered influent and effluent TKN and inorg-N;
- pH in settler; and
- substrate flow rate.

In addition, profiles of pH, COD, TKN, inorg-N and the short-chain fatty acids (SCFA; also termed total volatile fatty acids, TVFA) propionic (HPr) and acetic (HAc), were measured along the axis of the reactor. Samples were taken at each sample port, starting at the top. Samples were filtered using Schleicher und Schuell 595 filter paper. For the HAc and HPr, samples were refiltered through a 0,45 µm filter paper (Millipore) and the SCFA measured by gas chromatography using a 60/80 Carbo pack C/0,3% Carbo wax packing (for details, see Sam-Soon et al., 1989). COD, TKN and inorg-N were measured in accordance with *Standard Methods* (1989). When a profile was measured, the H_2CO_3* alkalinity in the reactor effluent was measured using the 5 pH point titration method (see Moosbrugger et al., 1992).

Starting-up procedure and process performance

The flow-through reactor was seeded with 4 ℓ of pelletised sludge from a laboratory-scale UASB reactor treating glucose substrate at a maximum COD load of 45 kg/(m^3 sludge bed·d); the sludge bed volume was kept constant at 4 ℓ by draining excess sludge from sample Port 7. To adapt the seed sludge to the grape wine distillery waste, initially a mixture of glucose and grape wine distillery waste (50: 50 by COD) was fed at a flow rate of 20 ℓ/d and a COD concentration of 5 500 mg/ℓ, to give a COD loading rate of 27 kg/(m^3 sludge bed·d). After 17 d, the glucose/grape wine distillery waste mixture was changed to grape wine distillery waste only, with an unchanged COD loading rate. At this "high" COD loading rate the system responded with a slight decline in performance (in general when adapting a pellet bed to a new substrate a lower COD loading rate would be recommended). In Fig. 2 the COD loading rate and the percentage COD removal are shown plotted versus time, with zero time marking the beginning of the start-up period; the COD removal declined for some time after the change to pure grape wine distillery waste but recovered by day 30, indicating that the sludge bed had adapted to the new substrate.

Steady state system changes

Once the system appeared to be operating satisfactorily at 27 kg COD/(m^3 sludge bed·d) with 100 per cent grape wine distillery waste as influent, the following studies were undertaken on the flow-through system.

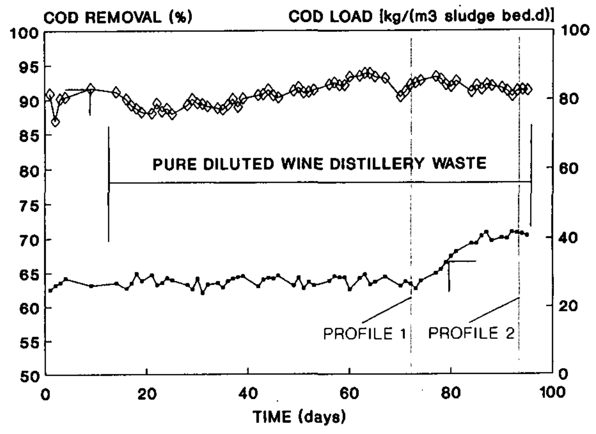

Figure 2

Start-up period of flow-through laboratory UASB reactor seeded with 4 ℓ of pelletised sludge from a laboratory-scale UASB system treating glucose substrate. Feed substrate: initially, mixture of grape wine distillery waste and glucose (50:50 in COD) diluted with tap water to give an influent COD of 5 500 mg/ℓ; after 17 d the feed was changed to diluted grape wine distillery waste only (COD = 5 500 mg/ℓ). The COD loading rate was increased by increasing the flow rate. The terms "Profile 1" and "Profile 2" indicate the time locations for measuring various parameters along the line of flow of the reactor (see Figs. 3 and 4)

Termination of trace element addition: When the percentage COD removal had recovered to 90 per cent, by day 35, the addition of trace elements was terminated to observe any adverse effects on the COD removal; percentage COD removal (Fig. 2) did not show any change in trend before and after terminating addition of trace elements and it was concluded that no additional trace elements were required.

Termination of nitrogen augmentation: Daily measurements of effluent TKN and inorg-N, about 90 and 75 mg/ℓ respectively, indicated an oversupply of nitrogen; accordingly addition of NH_4Cl solution was terminated on day 40. The percentage COD removal continued to increase after termination of NH_4Cl addition (Fig. 2). Without nitrogen supplementation the influent TKN was 83 mg N/ℓ and the effluent TKN 45 mg/ℓ (effluent inorg-N = 30 mg/ℓ); there still was an excess supply of nitrogen in the feed.

Alkalinity addition: It was stated earlier that to maintain a near neutral pH, by ensuring that the minimum bed pH did not decline below 6,6, the influent was augmented with 9,4 g $NaHCO_3$ and 0,8 g NaOH per litre base influent to give an influent $H_2CO_3^*$ alkalinity/COD ratio of 1,2 (mg as $CaCO_3$/mg). With 100 per cent grape wine distillery waste this gave a minimum bed pH of 7,4 indicating an excess of $H_2CO_3^*$ alkalinity. Accordingly, over the period day 45 to 55, the mass of $NaHCO_3$ addition was reduced gradually to 2,0 g/ℓ with NaOH constant at 0,8 g/ℓ ; this established a minimum bed pH of 6,6 (suggested as the lower limit by Sam-Soon et al., 1987). With this addition, the $H_2CO_3^*$ alkalinity supplied externally amounted to 2 190 mg/ℓ (as $CaCO_3$). The $H_2CO_3^*$ alkalinity in the effluent was measured at 2 560 mg/ℓ (as $CaCO_3$) indicating internal generation of $H_2CO_3^*$ alkalinity of 370 mg/ℓ (as $CaCO_3$). To take account of the internal generation of $H_2CO_3^*$ alkalinity, the proposal of Moosbrugger et al. (1993) that the ratio effluent $H_2CO_3^*$ alkalinity/influent COD be used to assess alkalinity requirements, was accepted. The ratio of effluent $H_2CO_3^*$ alkalinity/influent COD to maintain a minimum bed pH of 6,6 therefore was 2 560/5 500 = 0,5, significantly lower than that found by Sam-Soon et al. (1991) for apple juice waste.

Steady state product formation

With the minimum bed pH ≈ 6,6 and a COD loading rate of 27 kg/(m^3 sludge bed·d) the system was run from day 55 to day 74 to ensure steady state conditions. On day 74 (Fig. 2) a set of profiles of pH, COD, HAc, HPr, TKN, inorg-N and org-N (Profile set 1) was measured, shown plotted in Fig. 3.

Following measurement of this set of profiles two changes were made:

- The COD loading rate was increased from 27 to 41 kg/(m^3 sludge bed·d) by maintaining the influent COD concentration at 5 500 mg/ℓ but increasing the influent flow rate from 20 to 30 ℓ/d; and
- $H_2CO_3^*$ alkalinity supplementation was increased approximately in the same ratio as the COD loading rate to 3 980 mg/ℓ influent as $CaCO_3$ (5 g $NaHCO_3$ and 0,8 g NaOH per litre of influent).

After the system had reached steady state under the higher loading rate the effluent $H_2CO_3^*$ alkalinity was about 4 400 mg/ℓ

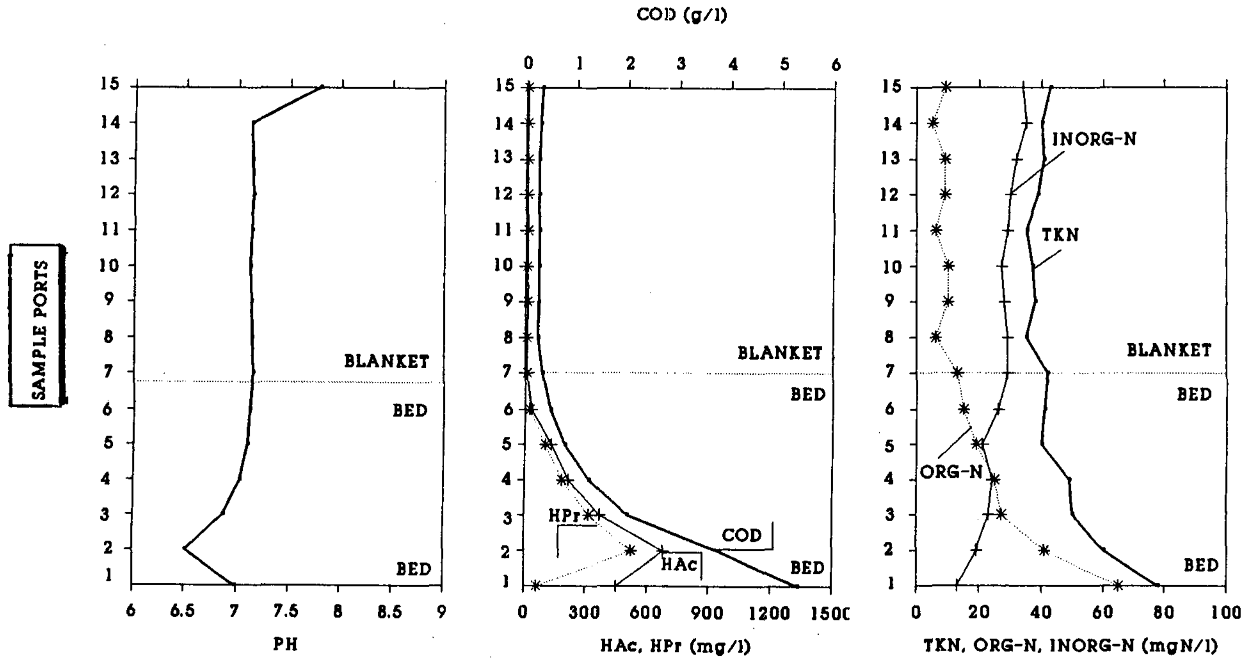

Figure 3

Flow-through laboratory UASB reactor treating diluted grape wine distillery waste: Profiles of pH, COD, HAc, HPr, TKN, inorg-N and org-N along the line of flow. Flow rate: 20 ℓ/d, influent COD concentration: 5 500 mg/ℓ, COD loading rate: 27 kg COD/(m^3 sludge bed·d)

as $CaCO_3$ giving an effluent H_2CO_3* alkalinity/influent COD ratio of 4 400/5 500 = 0,8. The minimum bed pH increased from 6,6 to 6,8. After sufficient time to ensure steady state behaviour, a further set of profiles (Profile set 2) was measured on day 95 (Fig. 2), shown plotted in Fig. 4.

pH: pH Profile 1 (Fig. 3) measured on day 74 and pH Profile 2 (Fig. 4) measured on day 95, were similar in that both showed a considerable pH decline in the lower part of the sludge bed. In Profile 1, the minimum pH declined to as low as pH 6,6 indicating that the effluent H_2CO_3* alkalinity/influent COD ratio of 0,5 was only just sufficient. In Profile 2 the minimum pH was pH 6,8 indicating that the effluent H_2CO_3* alkalinity/influent COD ratio of 0,8 was sufficient to buffer the pH above the minimum value of 6,6 as suggested by Sam-Soon et al. (1987). The decline in pH in the lower part of the sludge bed coincided with the increase in HAc and HPr. Comparing both pH profiles with those reported by Sam-Soon et al. (1987), the behaviour patterns are similar.

COD profiles: COD Profile 1 (Fig. 3) and COD Profile 2 (Fig. 4) both showed a rapid decrease in the lower part of the sludge bed. COD Profile 1 reached its minimum value (≈400 mg/ℓ) well within the sludge bed whereas COD Profile 2 reached its minimum (700 mg/ℓ) only at or near the top of the bed, and the minimum value was higher than that of COD Profile 1. This very likely was due to the higher COD loading rate in Profile 2. The rapid rate of COD removal in the lower part of the sludge bed, observed in both COD profiles, again is similar to that observed by Sam-Soon et al. (1987).

HAc: The HAc Profile 1 (Fig. 3) and HAc Profile 2 (Fig. 4) reached their respective maxima of 680 and 1 310 mg/ℓ in the lower part of the sludge bed, and thereafter decreased to near zero in the upper part of the sludge bed. The two profiles differ in two aspects: maximum HAc concentration in Profile 2 was considerably higher than that in profile 1; and the minimum HAc concentration in Profile 1 was attained well within the bed, whereas that in Profile 2 reached its minimum only near the top of the bed. Both of these observations reflect the increased COD loading rate, while the second observation indicates that the loading rate of 41 kg/(m^3 sludge bed·d) was near or at the maximum.

HPr: Similar to the HAc profiles, the HPr Profile 1 (Fig. 3) and HPr Profile 2 (Fig. 4) reached their respective maxima of 530 and 1 190 mg/ℓ in the lower part of the sludge bed and thereafter decreased to near zero in the upper part of the bed. According to Sam-Soon et al. (1987), HPr accumulation would occur only in a high $\bar{p}H_2$ environment. Thus the observed accumulation of HPr indicated that the prerequisite for pelletisation of high $\bar{p}H_2$ was being satisfied.

TKN, inorg-N and org-N: The respective TKN, inorg-N and org-N profiles measured on day 74 and 95 (see Figs. 3 and 4) exhibited similar patterns: The two org-N concentration profiles decreased rapidly in the lower part of the sludge bed, due to deamination, reaching a minimum value in the upper part of the sludge bed. The inorg-N profiles, however, increased in the lower part of the bed and stabilised to their maximum values in the upper part. In contrast, Sam-Soon et al. (1987) observed a marked decrease of inorg-N in the lower part of sludge bed. The increase observed in the grape wine distillery waste profiles may be attributed to rapid rate of generation of inorg-N (due to deamination of org-N present in the influent), more rapid than the rate of uptake of inorg-N due to pelletisation. A net uptake of nitrogen is demonstrated in the TKN profiles - a significant decrease of about 25 mg N/ℓ (from 80 to 55 mg N/ℓ) in both TKN profiles below sample Port 3. In this part of the sludge bed on average about 3 000 mg COD/ℓ were removed. Under "normal"

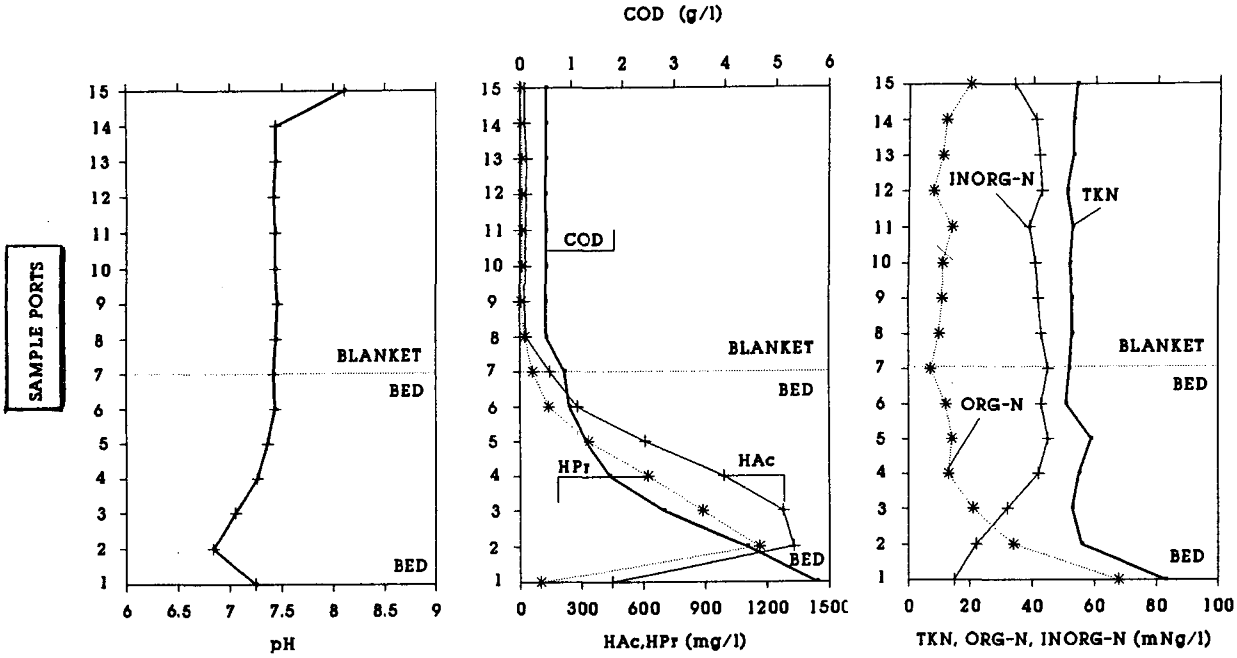

Figure 4

Flow-through laboratory UASB reactor treating diluted grape wine distillery waste: Profiles of pH, COD, HAc, HPr, TKN, inorg-N and org-N along the line of flow. Flow rate: 30 ℓ/d, influent COD concentration: 5 500 mg/ℓ, COD loading rate: 41 kg COD/(m³ sludge bed·d)

anaerobic fermentation conditions nitrogen requirements would be approximately 0,004 mg N/mg COD for protoplasm synthesis, i.e. the expected TKN removal under "normal" conditions below sample Port 3, should be about 12 mg N/ℓ. The observed nitrogen removal of 25 mg N/ℓ (0,008 mg N/mg COD) is about double that normally expected thereby supporting the hypothesis that pellet formation was taking place.

Pellet growth

Sam-Soon et al. (1987) showed that pellet generation takes place in the high $\bar{p}H_2$ zone and observed pellet break-up in the upper part of the sludge bed. The HPr profiles in Fig. 4 indicated that the high $\bar{p}H_2$ zone extended up to about sample Port 3 (volume ≈ 1,1ℓ). To measure the pellet yield under high $\bar{p}H_2$ conditions the system was operated under the same conditions as at day 95 of the feasibility study, i.e. flow rate 30 ℓ/d and influent COD concentration 5 500 mg/ℓ. However, the sludge bed above sample Port 3 now was drained so that only the sludge in the high $\bar{p}H_2$ zone remained in the bed. Over a period of 20 d the following measurements were taken daily:

- The sludge bed above the level of sample Port 3 was drained into a measuring cylinder and the drained sludge volume and VSS determined to give the mass of VSS produced per day.
- Filtered and unfiltered influent and effluent COD concentrations.
- Influent flow rate.

The pellet yield was determined as follows: The filtered effluent COD was subtracted from the filtered influent COD concentration and the difference multiplied by the daily flow rate to give the mass of soluble COD removed per day.

The specific pellet yield (Y) was calculated as:

$$Y = \frac{\text{mass of VSS generated/d}}{\text{mass of COD removed/d}} \qquad (1)$$

The average specific pellet yield measured over the 20 d period was 0,14 mg VSS/mg COD. Comparing this yield value with the pellet yield value reported by Sam-Soon et al. (1987) of 0,42 mg VSS/mg COD the following comments are pertinent:

The pellet yield was obtained only from the mass of pelletised sludge wasted from the reactor every day; this did not necessarily reflect the total sludge production which would also include the pellet debris discharged from the sludge bed into the sludge blanket and reactor effluent. However, to take this into account would have required a much more elaborate experimental procedure including drainage of the total volume above the bed (the blanket) and measurement of the total particulate matter in the effluent. There is a further complication that the influent itself contained approximately 2 per cent of the COD as particulate matter; thus it was not clear whether the particulate matter in the blanket and in the effluent originated from the pellet debris or from the influent particulate matter. Hence, the value of the specific yield of solids generated, reported here, must be taken as a net pellet specific yield.

The cause for the lower pellet yield most likely was that the influent COD of the grape wine distillery waste contained a lower fraction of carbohydrates than the apple juice waste.

Conclusions from the feasibilitv study

The information gathered during the feasibility study on grape wine distillery waste in a flow-through UASB reactor can be summarised as follows:

- The pH, COD, HAc and HPr profiles were similar to those observed when treating a carbohydrate waste (apple juice

TABLE 4
CHARACTERISTICS OF GRAPE WINE DISTILLERY BATCHES USED FOR RECYCLING EXPERIMENTS

Batch		1	2	3	4	5
Soluble COD fraction	%	98	98	98	98	98
Soluble COD conc.	g/ℓ	23	31	27	27	29
inorg-N	mg N/ℓ	34	90	80	90	90
TKN	mg N/ℓ	200	400	410	400	430
Phosphorus	mg P/ℓ	105	155	140	150	160
pH		4,5	4,2	4,3	4,2	4,1

waste); the COD reduction was > 85 per cent at a COD loading rate as high as 41 kg/(m^3 sludge bed·d).

- A pelletised sludge was produced, but at a reduced mass per COD removed compared with a pure carbohydrate substrate.

These observations indicate that grape wine distillery waste gave rise to a product formation in a UASB system similar to that found by Sam-Soon et al. (1987) for pure carbohydrate substrate albeit with reduced pelletisation. It was concluded that grape wine distillery waste is suitable for treatment in a UASB systems.

Recycling, alkalinity and pH

Moosbrugger et al. (1993) investigated the effects of recycling on process performance and H_2CO_3* alkalinity requirements for lauter tun (brewery) waste in a UASB system. With an influent COD concentration of 13 000 mg/ℓ, a COD loading rate of 9 kg/(m^3 sludge bed·d) and recycle ratios ranging between 6 to 22:1, to give an effective influent COD [i.e. base influent COD/(1 + recycle ratio)] ranging from 1 800 to 570 mg/ℓ, no adverse effects on COD removal were found. The concentration of H_2CO_3* alkalinity required per litre of influent to maintain the minimum bed pH ≈ 7 was found to change with the effective influent COD (COD$_e$) or equivalently with the recycle ratio. In this paper we will examine the relationship between the parameters, effective influent COD concentration, recycle ratio, effluent H_2CO_3* alkalinity, alkalinity supplementation and minimum bed pH, when treating grape wine distillery waste in a UASB system at a COD loading rate likely to be used in practice.

The investigation with undiluted grape wine distillery waste as base influent was divided into the following tasks:

- recycling and system performance;
- self-sufficiency in H_2CO_3* alkalinity requirements;
- relationship between effective influent COD, effluent H_2CO_3* alkalinity and minimum bed pH; and
- permissible COD loading rate.

Recycling and system performance

In this task the objective was to establish if recycling of the reactor effluent, to dilute the base influent substrate into the COD range of 1 000 to 5 000 mg/ℓ (suggested by Sam-Soon et al., 1991), would affect the process performance adversely, provided the minimum pH remained above 6,7.

Experimental methods

The experimental set-up remained the same as that in the feasibility study, except for the following modifications:

- a wet gas meter (model No. DM3A, Alexander Wright, London) was installed to measure the volume of gas produced in the reactor;
- the gas composition was analysed for methane and carbon dioxide using gas chromatography (Gow-Mac 502) with helium as carrier gas;
- the peristaltic pump, previously used as feed pump, was installed as recycle pump; and
- a laboratory positive displacement pump was installed as feed pump.

To control the flows both pumps operated on an on/off cycle, switched on and off simultaneously. The recycle stream was taken from the settled effluent (Port 12, Fig. 1) so that no pelletised sludge was recycled. The recycle stream joined the influent feed low at a point just upstream of discharge to the reactor (Port 1, Fig. 1). The characteristics of the grape wine distillery waste batch (Batch 1) are shown in Table 4. Measurement of individual SCFA in the influent by gas chromatography was not successful as the waste poisoned the particular packing used. The reactor was seeded with 3 ℓ of pelletised sludge (bed height ≈ 43 cm) generated during the feasibility study; this volume was maintained throughout the experiment; COD loading rate was 15 kg COD/(m^3 sludge bed·d) - about a third of the maximum rate applied towards the end of the feasibility study; recycle ratio was 7:1, thus with a base influent COD of 23 000 mg/ℓ the effective influent COD (COD$_e$) was 23 000/(1+7) = 2 880 mg/ℓ.

Alkalinity supplementation: Assuming that the influent substrate would generate the same mass of H_2CO_3* alkalinity/(influent COD) as in the feasibility study (0,0673), this implied generation 0,0673 x 23 000 = 1 550 mg H_2CO_3* alkalinity (as $CaCO_3$)/(ℓ influent) which, with a recycle of 7:1 (COD$_e$ = 2 880 mg/ℓ), gives 1 550/2 880 ≐ 0,54 mg H_2CO_3* alkalinity (as $CaCO_3$)/mgCOD$_e$. No information was available as to whether this would be sufficient to maintain a near neutral minimum pH in the bed. Accordingly, it was decided to add 1,5 g NaOH/(ℓ base influent), i.e. 1 875 mg H_2CO_3* alkalinity/(ℓ base influent) as $CaCO_3$, to give an estimated total 3 500 mg H_2CO_3* alkalinity/(ℓ effluent) i.e. 3 500/2 880 = 1,2 mg H_2CO_3* alkalinity-/mgCOD$_e$, a value equal to the ratio proposed by Sam-Soon et al. (1991). The NaOH was added directly to the influent. Before addition the waste pH ≈ 4,5 (Batch 1) due to the presence of SCFA and other organic acids; after NaOH addition the pH rose to about 7.

Nutrient and trace element supplementation: From the feasibility study, no trace element or nutrient solutions were added; this also applies to the subsequent experiments.

Parameters measured were minimum bed pH, filtered effluent COD concentration, filtered influent and effluent TKN, gas production rate and composition. In addition, the effluent SCFA and H_2CO_3* alkalinity were measured with the 5 pH point titration method (Moosbrugger et al., 1992). Individual SCFA were not measured.

The system was operated without any changes from the above conditions for 59 d.

Results and discussion

COD and SCFA: The effluent COD vs. time plot, Fig. 5, shows a steady improvement in performance, effluent COD decreasing from 1 600 mg/ℓ at the start, stabilising at about 600 mg/ℓ to give a COD removal of COD = (23 000 − 600), i.e. 22 400/23 000 = 97 per cent. Effluent SCFA, also plotted in Fig 5, remained low throughout at 50 mg/ℓ as HAc. The high COD removal and low effluent SCFA indicated that the 7:1 recycle ratio did not adversely affect process performance.

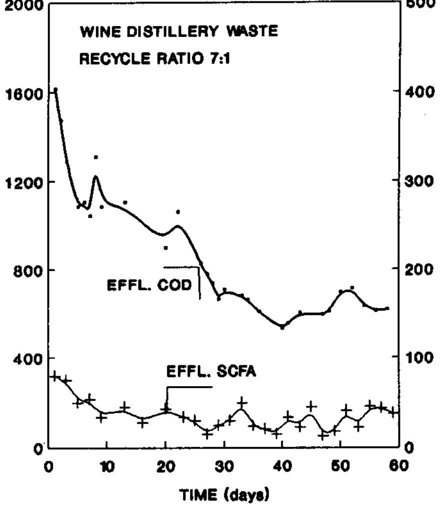

Figure 5

Effluent COD and SCFA concentrations of a laboratory UASB reactor treating undiluted grape wine distillery waste operated with a 7:1 recycle: Base influent COD concentration: 23 000 mg/ℓ; effective influent COD: 2 880 mg/ℓ; COD loading rate: 9 kg/(m³ sludge bed·d)

TKN: Nitrogen uptake, from the difference of the average base influent and steady state effluent, gave (240 − 32) = 208, that is $\Delta N/\Delta COD$ = 208/22 400 = 0,009 which is close to that found in the feasibility study and substantially higher than that for "normal" anaerobic processes without pellet formation ($\Delta N/\Delta COD$ ≈ 0,004) indicating that very likely part of the nitrogen was used for pellet generation. However, the $\Delta N/\Delta COD$ ratio was still significantly lower than that with lauter tun waste, $\Delta N/\Delta COD$ = 0,016 (Moosbrugger et al., 1993) and with glucose substrate, $\Delta N/\Delta COD$ = 0,02 (Sam-Soon et al., 1990), very likely due to the small fractions of carbohydrate and protein (which generate a high $\bar{p}H_2$) in the grape wine distillery waste.

Gas production and composition: Gas production stabilised after 10 d at about 19 ℓ/d with CO_2 ≈ 28 per cent, the balance being accepted as CH_4.

pH: To establish the point of minimum pH in the bed, periodically pH profiles were measured. These indicated that the pH was at its minimum at Port 2 with pH = 6,9, increased to pH ≈ 7,0 at Port 3 and thereafter remained virtually constant at ≈ 7,0 higher up the bed; this pH pattern remained unchanged throughout the experiment. Thus, the estimated H_2CO_3* alkalinity requirement appeared to be adequate to maintain a near neutral minimum bed pH. The actual total H_2CO_3* alkalinity in the effluent, measured towards the end of this experiment, was ca. 3 400 mg/ℓ as $CaCO_3$. Knowing the effluent H_2CO_3* alkalinity, the effluent H_2CO_3* alkalinity/effective influent COD ratio came to 3 400/2 880 = 1,2. Subtracting the mass of H_2CO_3* alkalinity contributed by the added 1,5 g NaOH/ℓ influent, i.e. 1 875 mg H_2CO_3* alkalinity (as $CaCO_3$)/ℓ influent, from that measured in the effluent, the internally generated H_2CO_3* alkalinity was: 3 400 —1 875 = 1 525 mg H_2CO_3* alkalinity (as $CaCO_3$)/ℓ influent, a value very near that estimated earlier, 1 550 mg H_2CO_3* alkalinity (as $CaCO_3$)/ℓ (See **Alkalinity supplementation** above).

Self-sufficiency in H_2CO_3* alkalinity requirements

In the task above, it was shown that significant H_2CO_3* alkalinity was generated in the bed. This raised the question whether by applying higher recycle ratios the internally generated H_2CO_3* alkalinity might be sufficient to enable operation of the system without addition of H_2CO_3* alkalinity from an external source. Accordingly, addition of H_2CO_3* alkalinity was to be terminated and instead the effective influent COD (COD$_e$) reduced by increasing the recycle ratio, to achieve an effluent H_2CO_3* alkalinity/COD$_e$ ratio close to 1,2 from the internally generated H_2CO_3* alkalinity alone.

Experimental metods

The experimental set-up remained the same as that in the previous experiment. The characteristics of the waste (Batch 2) are shown in Table 4. Note that the influent COD was 31 000 mg/ℓ. The same sludge bed as in the previous experiment was used; the sludge bed volume was kept at 3 ℓ by draining excess sludge at weekly intervals. The COD loading rate was reduced from 15 to 9 kg/(m³ sludge bed·d), this being the likely loading rate to be used in practice.

Recycle ratio and NaOH addition: The recycle ratio was increased from 7:1 (in the previous task) to 18:1 in this task. With this recycle ratio and an influent COD of 31 000 mg/ℓ, the effective influent COD = 31 000/(18+1) = 1 630 mg/ℓ and the

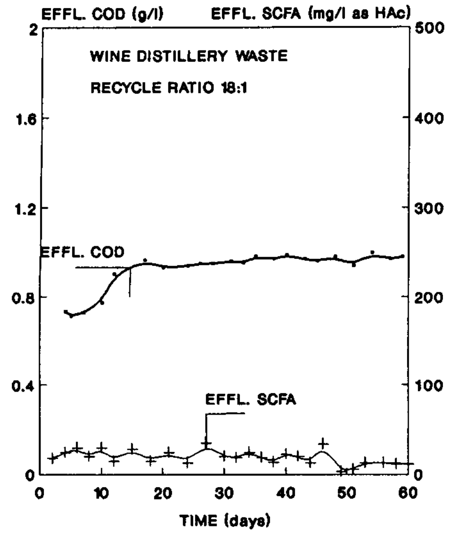

Figure 6
Effluent COD and SCFA concentrations of laboratory UASB reactor treating undiluted grape wine distillery waste operated with a 18:1 recycle: Base influent COD concentration: 31 000 mg/ℓ; effective influent COD: 1 630 mg/ℓ; COD loading rate: 9 kg/(m^3 sludge bed·d)

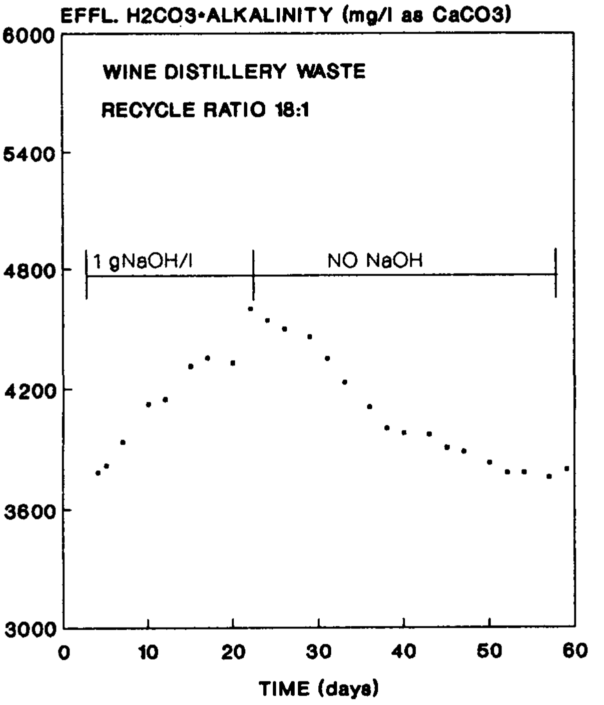

Figure 7
Investigation into self-sufficiency in H_2CO_3 alkalinity: Change of effluent H_2CO_3* alkalinity with addition of 1 g NaOH/(ℓ base influent) and zero NaOH addition*

expected effluent H_2CO_3* alkalinity = 0,0673 x 31 000 = 2 086 to give effluent H_2CO_3* alkalinity/COD_e = 1,28. Because there was still some uncertainty as to the mass of the internally generated H_2CO_3* alkalinity, it was decided to commence the experiment by supplementing the feed with 1,0 g NaOH/ℓ influent giving a conservative H_2CO_3* alkalinity/COD_e ratio of (2 086+1 250) / 1 630 ≈ 2.

Results and dicussion

COD and SCFA: Effluent COD is plotted vs. time in Fig. 6. The effluent COD increased at the beginning and then stabilised at about 1 000 mg/ℓ. A fraction of this increase can be accounted for by the increase in base influent COD from 23 000 (which gave an effluent COD 600 mg/ℓ) to 31 000 mg/ℓ (to give proportionally an expected effluent COD ≈ 800 mg/ℓ). This leaves an increase of 200 mg/ℓ unaccounted for - probably the unbiodegradable fraction of the two batches differed. The effluent SCFA plot in Fig. 6 shows that the effluent SCFA remained stable at ≈50 mg/ℓ (as HAc).

Gas production and composition: Gas production was stable over the period and averaged at 10 ℓ/d with a stable CO_2 fraction ≈24 %.

Effluent H_2CO_3*alkalinity and pH: The effluent H_2CO_3* alkalinity is plotted vs. time in Fig. 7. The plot shows that while the feed was supplemented with 1g NaOH/ℓ base influent a gradual but significant increase in effluent H_2CO_3* alkalinity took place. The minimum bed pH concomitantly increased from 7,1 to 7,4 by day 23, whereupon NaOH supplementation was terminated because the pH was approaching the upper limit (pH ≈ 7,6) for anaerobic digestion. The increase in effluent H_2CO_3* alkalinity and pH was gradual because, with the high influent COD, the volume of feed per day for the applied COD loading rate was only 0,9 ℓ. The liquid volume of the system was about 10,5ℓ, so that the "washout" period before stable conditions developed would extend to about 20 d. After NaOH addition was terminated the measured effluent H_2CO_3* alkalinity gradually declined until stability was attained (again via washout), after approximately 20 d. The minimum bed pH stabilised at pH 7,2 and the effluent H_2CO_3* alkalinity stabilised at 3 700 mg/ℓ; this H_2CO_3* alkalinity was generated completely internally, giving an effluent H_2CO_3* alkalinity/COD_e ratio of 3 700/1 630 = 2,3. This ratio was considerably higher than that in the previous task (1,2) and would be the main reason why the minimum bed pH increased from 6,9 (in the previous task) to 7,2 in this one. Also, comparing the mass of H_2CO_3* alkalinity generated in this task [effluent H_2CO_3* alkalinity/base influent COD = 3 700/31 000 = 0,119 mg (as CaCO3)/mg] with that in the previous task (0,066), significantly more H_2CO_3* alkalinity was generated. Most likely this was due to the difference in the influent orgN/COD between the two waste batches - this task, Batch 2 orgN/COD = 10 mg N/g COD; previous task, Batch 1 orgN/COD = 7,2 mg N/g COD (Table 4).

Conclusion

From this task it was concluded that with grape wine distillery waste (that generates H_2CO_3* alkalinity internally) it is possible to attain H_2CO_3* alkalinity self-sufficiency, to ensure a near neutral minimum bed pH, by applying a sufficiently high recycle, in this case a recycle ratio of 18:1.

TABLE 5
MONITORED PARAMETERS FOR RECYCLE EXPERIMENT WITH CONSTANT COD LOADING RATE [9 kg/(m^3 sludge bed.d)], CONSTANT BASE INFLUENT COD (COD_b = 27 000 mg/ℓ), CONSTANT EFFLUENT H_2CO_3* ALKALINITY (3 700 mg/ℓ AS $CaCO_3$) AND CHANGING EFFECTIVE INFLUENT COD (COD_e) OR, EQUIVALENTLY, CHANGING RECYCLE

Recycle ratio	Effective influent COD (mg/ℓ)	Minimum bed pH	Effluent COD (mg/ℓ)	Effluent SCFA (mg/ℓ)	pCO_2 (%)	Total gas production (ℓ/d) STP	Methane production (ℓ/d) STP
33:1	790	7,5	1 560	30	17	12	8,8
20:1	1 290	7,3	1 610	50	22	13	8,9
7:1	3 375	6,8	1 580	35	31	15	9,1

Relationship between effective influent COD, effluent H_2CO_3* alkalinity and minimum bed pH

In the tasks above it was shown that a selected minimum pH can be achieved by increasing or decreasing the recycle, or keeping the recycle constant and adding strong base (or acid). These two options will now be tested in two separate experiments to establish the sensitivity of the minimum pH to such operational changes.

Option 1: COD loading rate, base influent COD and effluent H_2CO_3* alkalinity constant, effective influent COD changing

The experimental set-up remained the same as that in the previous two experiments. The characteristics of the waste (Batch 3) are shown in Table 4.

The sludge bed volume was kept constant at 3 ℓ by draining excess sludge at weekly intervals; COD loading rate was 9 kg/(m^3 sludge bed·d). In this experiment the sludge bed density was measured at approximately 42 kg VSS/(m^3 sludge bed). To ensure a significant change in minimum bed pH three widely differing recycle ratios were selected to dilute the influent COD to three respective effective influent COD concentrations (COD_e): The experiment was started on day zero with a recycle ratio of 33:1, on day 20 this ratio was changed to 20:1, and finally on day 40 to 7:1 and the system operated for a further 20 d. Because this task was started with a recycle ratio greater than that found to give H_2CO_3* alkalinity self-sufficiency in the previous task (r = 18:1), no H_2CO_3* alkalinity was added to the influent.

Results and discussion

For each of the three periods, when different respective recycle ratios were applied, the averaged values for the individual monitoring parameters are listed in Table 5.

COD and SCFA: The effluent COD averaged at 1 600 mg/ℓ (standard deviation ≈ 50 mg/ℓ) irrespective of the recycle ratio, giving a COD removal of about 94 per cent. The effluent SCFA averaged at 45 mg/ℓ (standard deviation ≈ 20 mg/ℓ) irrespective of the recycle ratio, indicating stable operation conditions throughout the experiment.

TKN: The nitrogen uptake in terms of TKN exhibited no significant change during the experiment. On average 260 mg N/(ℓ influent) were removed, giving a ΔTKN/ΔCOD ratio of 260/(27 000-1 600) = 0,010 mg N/mg COD; a ratio close to those found in the previous experiments indicating that pellet generation was not influenced by the recycle ratio provided the minimum bed pH ≈ 7.

H_2CO_3* alkalinity and pH: Although the effluent H_2CO_3* alkalinity remained virtually unchanged at about 3 700 mg/ℓ as $CaCO_3$, the minimum bed pH decreased as the recycle ratio decreased. This was to be expected because in the same batch (with constant COD) the H_2CO_3* alkalinity generated/(ℓ of base influent) would remain constant; hence, any change in minimum bed pH would be due to the change in COD_e (at the constant COD loading rate applied). The minimum bed pH decreased from 7,5 at the 33:1 recycle ratio (COD_e = 790 mg/ℓ), to 7,2 at the recycle ratio 20:1 (COD_e = 1 290 mg/ℓ), to 6,8 at the 7:1 recycle ratio (COD_e = 3 375 mg/ℓ).

Comparing the mass of internal H_2CO_3* alkalinity generation from waste Batch 3 (Table 4) in this task [effluent H_2CO_3* alkalinity/base influent COD = 3 700/27 000 = 0,137 mg (as $CaCO_3$)/mg] with the previous tasks (waste Batch 1 = 0,066 and Batch 2 = 0,119), the H_2CO_3* alkalinity generation was the highest in this task. This probably was due to the large influent orgN/COD; influent orgN/COD Batch 3 = 12,2 mg N/g COD, Batch 1 = 7,2 and Batch 2 = 10.

Gas production and composition: As the minimum bed pH decreased so the gas production rate increased, with the total mass of methane produced per day remaining approximately constant. The increase in gas production rate coincided with an increase in the carbon dioxide fraction in the gas. This behaviour can be explained as follows (Loewenthal et al., 1986): For a constant total carbonate species concentration, as the pH decreases the H_2CO_3* concentration (and hence the CO_2 concentration) increases raising the partial pressure of CO_2 in the liquid, which increases CO_2 transfer to the gas phase. This caused the observed increase in gas production approximately proportional to the increase in the fraction of carbon dioxide. Thus the change in gas production rate did not arise from a change in biochemical behaviour but was due to physical laws of gas/liquid interactions under a change in pH.

Conclusions

These observations merit two conclusions: At a constant COD loading rate, constant base influent COD concentration and constant effluent H_2CO_3* alkalinity, the recycle ratio (or equivalently the COD_e) could be used as a means to change the minimum bed pH but a relatively large change in the recycle ratio (or COD_e) would be required to induce a significant change in minimum bed pH.

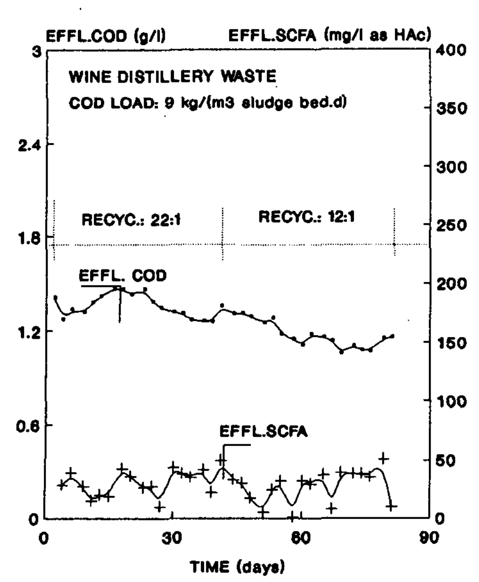

Figure 8
Effluent COD and SCFA concentrations of laboratory UASB reactor treating undiluted grape wine distillery waste operated with a 22:1 and 12:1 recycle respectively: Base influent COD concentration: 27 000 mg/ℓ; effective influent COD: 1 170 mg/ℓ and 2 080 mg/ℓ respectively; COD loading rate: 9 kg/(m^3 *sludge bed·d)*

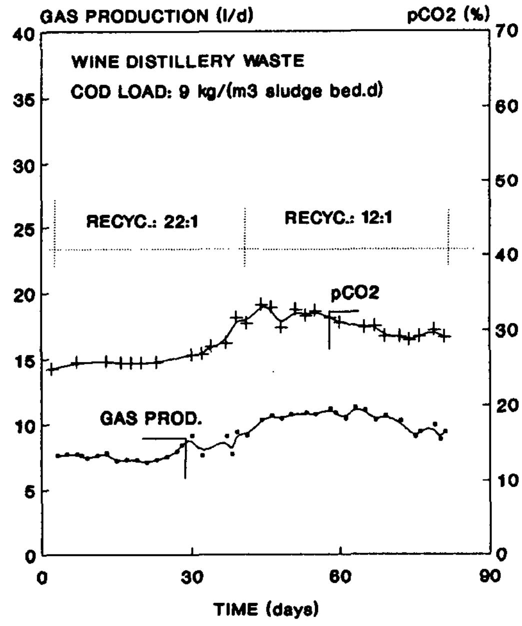

Figure 9
Total gas production per day and fraction of carbon dioxide in the gas of laboratory UASB reactor treating undiluted grape wine distillery waste operated with a 22:1 and 12:1 recycle respectively: Base influent COD concentration: 27 000 mg/ℓ; effective influent COD: 1 170 mg/ℓ and 2 080 mg/ℓ respectively; COD loading rate: 9 kg/(m^3 *sludge bed·d)*

Option 2: COD loading rate, base influent COD concentration and effective influent COD constant, effluent H_2CO_3* alkalinity changing

In this option experiments were performed at two fixed COD_e by imposing two recycle ratios of 22:1 and 12:1. For each recycle ratio a range of effluent H_2CO_3* alkalinity values were examined. The change in effluent H_2CO_3* alkalinity was affected by addition of HCl to the base influent. The experimental set-up remained the same as that in Option 1, the influent characteristics (Batch 4) are shown in Table 4.

The sludge bed developed in Option 1 was used. Sludge bed volume was kept constant at 3 ℓ by draining excess sludge at weekly intervals; COD loading rate at 9 kg/(m^3 sludge bed·d) as in Option 1. Average sludge bed density measured was 40 kg VSS/(m^3 sludge bed). The base influent COD was 27 000 mg/ℓ and the base flow rate 1 ℓ/d.

With a recycle ratio of 22:1 (COD_e of 1 170 mg/ℓ), the system was operated for 30 d. During this period 50 mmol of HCl were added per litre of base influent which, combined with the "washout effect" of H_2CO_3* alkalinity, caused the H_2CO_3* alkalinity in the effluent to drop gradually from about 3 500 to 1 500 mg/ℓ (as $CaCO_3$); concomitantly the minimum bed pH declined from 7,4 to 6,6 over a period of 30 d. When the minimum bed pH declined to 6,6, HCl addition was terminated because the lower pH would have adversely affected the methanogens. After HCl addition was terminated, the recycle ratio was changed from 22:1 to 12:1, changing COD_e from 1 170 to 2 080 mg/ℓ. A gradual increase in effluent H_2CO_3* alkalinity commenced again through "washout". Thus, by utilising the long retention time, via the washout effect, HCl addition or omission and different recycles, the change in minimum bed pH with changing effluent H_2CO_3* alkalinity could be studied at two different effective influent CODs (COD_e).

Results and discussion

COD and SCFA: Effluent COD and effluent SCFA during both recycle ratio periods are shown plotted in Fig. 8. The effluent COD increased at the beginning of this experiment, but decreased thereafter with a COD removal of about 95 per cent at the end of both recycle periods. The initial increase might have been due to the change to a different batch of grape wine distillery waste, i.e. the system requiring a short period of adaptation. The effluent SCFA remained low throughout the recycle periods (below 60 mg/ℓ as HAc), indicating that the system was not affected significantly by the different recycle ratios (or COD_e) for minimum bed $pH > 6,7$.

Gas production and composition: The rate of gas production and the percentage CO_2 are shown in Fig. 9; both increased as the minimum bed pH decreased. An explanation for these increases with decreasing minimum bed pH, has been given earlier.

H_2CO_3* alkalinity and minimum bed pH: For the period with a 22:1 recycle, i.e. COD_e = 1 170 mg/ℓ, a plot of the minimum bed pH versus the associated effluent H_2CO_3* alkalinity is shown in Fig. 10: To maintain a minimum bed pH of 7 for COD_e of 1 170 mg/ℓ, an effluent H_2CO_3* alkalinity of approximately 2 200 mg/ℓ as $CaCO_3$ was required. Similarly, for the period with a 12:1

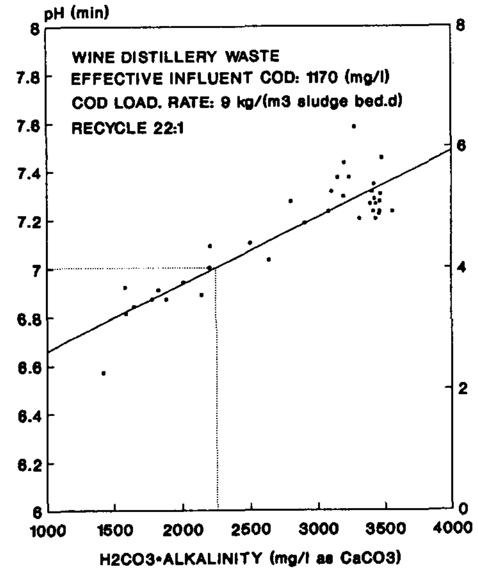

Figure 10
Relationship between effluent H_2CO_3 alkalintiy and minimum bed pH for laboratory UASB system treating undiluted grape wine distillery waste at a 22:1 recycle: Base influent COD concentration: 27 000 mg/ℓ; effective influent COD: 1 170 mg/ℓ; COD loading rate: 9 kg/(m^3 sludge bed·d)*

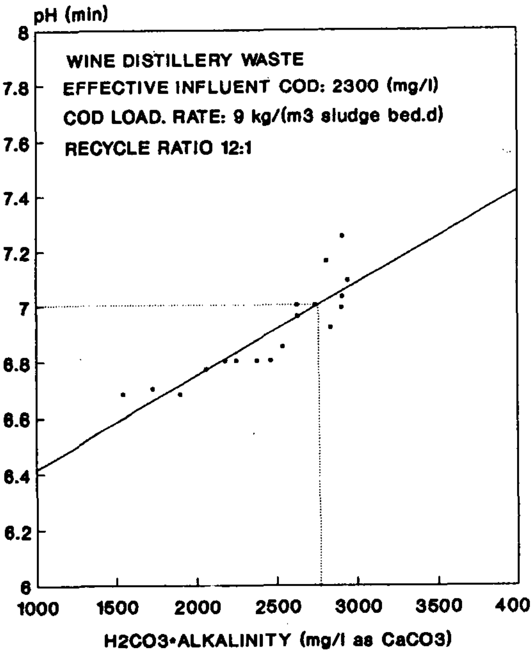

Figure 11
Relationship between effluent H_2CO_3 alkalinity and minimum bed pH for laboratory UASB system treating undiluted grape wine distillery waste at a 22:1 recycle: Base influent COD concentration: 27 000 mg/ℓ; effective influent COD: 2 080 mg/ℓ; COD loading rate: 9 kg/(m3 sludge bed·d)*

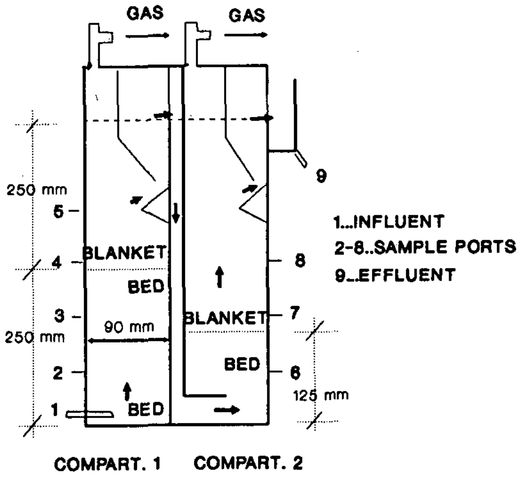

Figure 12
Schematic diagram for baffled laboratory UASB reactor with two in-series compartments

recycle, i.e. COD_e = 2 080 mg/ℓ, a plot for the minimum bed pH vs. the associated effluent H_2CO_3* alkalinity is shown in Fig. 11. To maintain a minimum bed pH of 7 for COD_e of 1 170 mg/ℓ, an effluent H_2CO_3* alkalinity of approximately 2 800 mg/ℓ as $CaCO_3$ was required.

From this experiment it is clear that for the same base influent COD and COD loading rate: with a constant recycle ratio, as the effluent H_2CO_3* alkalinity decreases the minimum bed pH concomitantly decreases; and for the same effluent H_2CO_3* alkalinity the higher the recycle ratio (i.e. the lower COD_e) the higher the minimum bed pH.

Relationship between COD loading rate and minimum bed pH

In the experiments above the relationship between the minimum bed pH, COD_e (or recycle ratio) and the effluent H_2CO_3* alkalinity was investigated. All these tests were done at the same COD loading rate of 9 kg/(m^3 sludge bed·d). It was now of interest to establish to what extent the minimum bed pH would change at different COD loading rates, with both COD_e and effluent H_2CO_3* alkalinity remaining constant. To keep the effluent H_2CO_3* alkalinity constant the base influent COD was kept constant and the COD loading rate changed by changing the base influent flow rate. To keep the COD_e constant the recycle ratio had to remain the same; this meant that when the base influent flow was increased to increase the COD loading rate, the recycle flow rate had to be increased proportionally in order to keep r = recycle flow/base flow constant, i.e. keep COD_e constant.

Experimental set-up

In all experiments in which a recycle was employed with COD

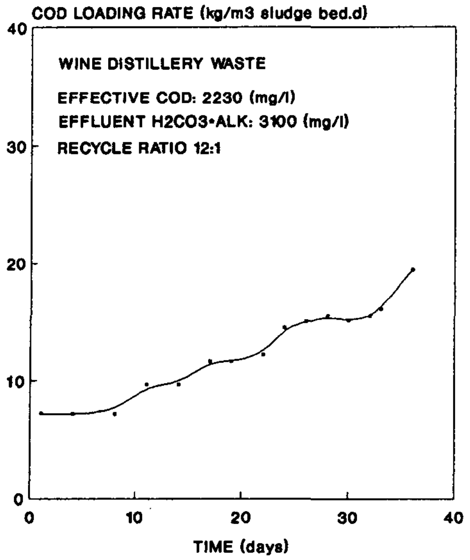

Figure 13
COD loading rate increase with time in baffled laboratory UASB system treating undiluted grape wine distillery waste: Base influent COD: 29 000 mg/ℓ; recycle ratio: 12:1; effective influent COD: 2 230 mg/ℓ; effluent H_2CO_3 alkalinity: 3 100 (mg/ℓ as $CaCO_3$)*

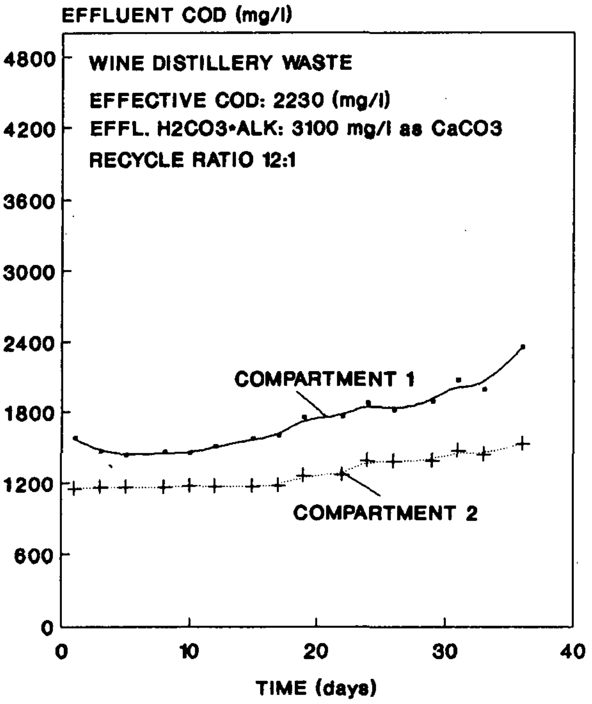

Figure 14
Effluent COD concentrations from Compartment 1 and 2 in baffled laboratory UASB reactor treating undiluted grape wine distillery waste with a 12:1. recycle and changing COD loading rate (see Fig. 13): Base influent COD concentration: 29 000 mg/ℓ; effective influent COD: 2 230 mg/ℓ

loading rates higher than 9 kg/(m^3 sludge bed·d), with the small diameter reactors used, at times gas collected at random levels in the sludge bed and tended to lift the sludge to the top of the reactor. Because COD loading rates much higher than 9 kg/(m^3 sludge bed·d) were envisaged in this experiment, it was decided to change the reactor set-up to minimise the chance of sludge uplift. The change was aimed at reducing the low of gas through the upper part of the sludge bed. This was achieved by constructing a baffled UASB system with two in-series compartments placed next to each other, where the second compartment received the effluent from the first, both compartments operated as upflow reactors (Fig. 12). The first reactor operated at a sludge bed level of 250 mm (2 ℓ of pelletised sludge) and the second at a sludge bed level of 125 mm (1 ℓ of pelletised sludge). In each compartment (cross sectional area: 90 x 90 mm) a settling section was installed and provision made for gas collection. Other than the change in reactor configuration, the experimental set-up remained the same as that in the previous experiments. The waste characteristics are given by Batch 5, Table 4.

The sludge bed developed in the previous experiment served as seed sludge for this experiment. The sludge bed volumes in the two compartments were kept constant at 2 ℓ and 1 ℓ respectively by draining excess sludge at weekly intervals. A starting COD loading rate of 7 kg/[m^3 sludge bed (compartment 1+2)·d] was selected to investigate process behaviour in the lower range of possible COD loading rates.

Recycle ratio: From the experiments above, a COD$_e$ of about 2 200 mg/ℓ should result in a near neutral minimum bed pH. Accordingly a recycle ratio of 12:1 was maintained throughout the experiment under different COD loading rates, giving COD$_e$ of 29 000/(12+1) = 2 230 mg/ℓ.

Results and discussion

COD loading rates: Figure 13 shows a plot of COD loading rate vs. time. The COD loading rate was increased incrementally from 7 to 19 kg/(m^3 sludge bed·d) within a period of 38 d. Towards the end of this period, despite the reduced sludge bed level in Compartment 1, gas lifted individual pellets or pellets on mass into the settling section. Visually the pellets did not appear as compact, or settle as readily as, for example, the pellets formed with glucose substrate, and the surface texture appeared slightly filamentous. The tendency for sludge pellets to be lifted to the top of the reactor was more pronounced in this experiment than in the feasibility experiment. For these reasons COD loading rates higher than 19 kg/(m^3 sludge bed·d) were not attempted. During the feasibility study on a flow-through UASB reactor fed with diluted grape wine distillery waste, higher COD loading rates of up to 41 kg/(m^3 sludge bed·d) were possible. However, those "high" loading rates were only applied for a relatively short period of time and at low flow rates; it is not clear whether a COD loading rate of 41 kg/(m^3 sludge bed·d) would have been possible over a longer period of time.

Effluent COD concentrations: The effluent COD in Compartment 1 (samples taken from the settling section) and Compartment 2, i.e. reactor effluent, are shown plotted in Fig. 14. Both plots show an increase of the effluent COD when higher COD loading rates were applied.

SCFA concentrations: SCFA in the effluent from Compartments

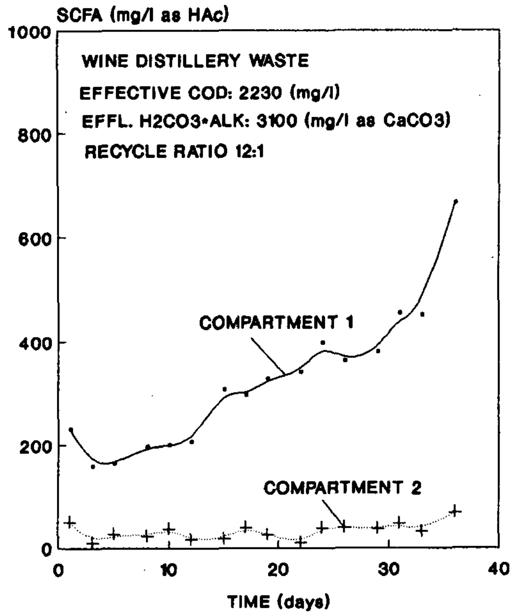

Figure 15
Effluent SCFA concentrations from Compartment 1 and 2 in baffled laboratory UASB reactor treating undiluted grape wine distillery waste with a 12:1 recycle and changing COD loading rate (see Fig. 13): Base influent COD concentration: 29 000 mg/ℓ; effective influent COD: 2 230 mg/ℓ

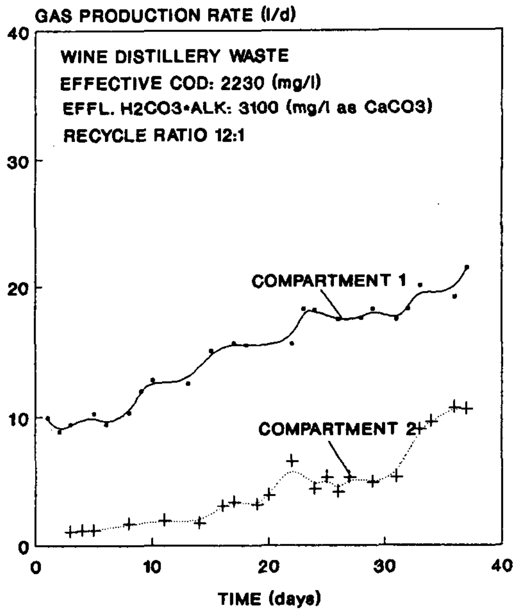

Figure 16
Total gas production per day in Compartment 1 and 2 in baffled laboratory UASB reactor treating undiluted grape wine distillery waste with a 12:1 recycle and changing COD loading rate (see Fig. 13): Base influent COD concentration: 27 000 mg/ℓ; effective influent COD: 2 230 mg/ℓ

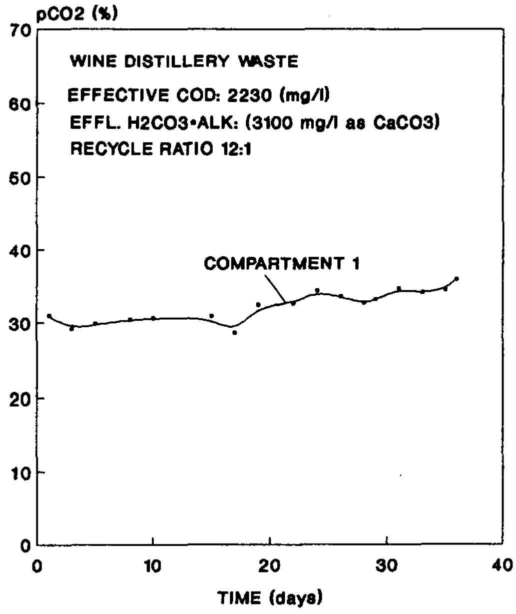

Figure 17
Fraction of carbon dioxide in total gas production in Compartment 1 in baffled laboratory UASB reactor treating undiluted grape wine distillery waste with a 12:1 recycle and changing COD loading rate (see Fig. 13): Base influent COD concentration: 27 000 mg/ℓ; effective influent COD: 2 230 mg/ℓ

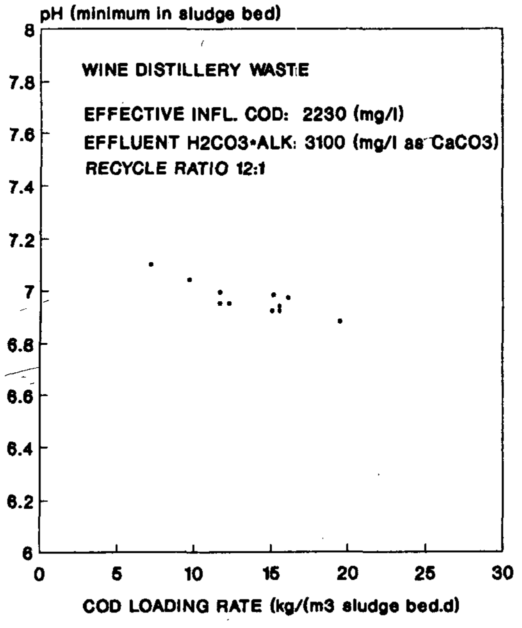

Figure 18
Relationship between minimum bed pH and COD loading rate in Compartment 1 in baffled laboratory UASB reactor treating undiluted grape wine distillery waste with a 12:1 recycle and changing COD loading rate (see Fig. 13): Base influent COD concentration: 27 000 mg/ℓ; effective influent COD: 2 230 mg/ℓ

1 and 2 (reactor effluent) are shown plotted in Fig. 15. The SCFA from the first reactor compartment follows the same trend as that of COD, both increased with increasing COD loading rates. However, in the second compartment the effluent SCFA remained below 60 mg/ℓ throughout the experiment, with only an insignificant increase at higher COD loading rates, indicating that the in-series system was not overloaded.

Gas production: Gas production rates from Compartments 1 and 2 are shown plotted in Fig. 16. Both plots show an approximately proportional increase in gas production rates with increase in COD loading rate.

Gas composition: The gas produced in Compartment 1 was analysed for CH_4 and CO_2; in Fig. 17 the fraction of CO_2 is plotted versus time. There was a slight increase in the fraction of CO_2 from 30 per cent at the beginning to 33 per cent towards the end of the experiment. This increase is associated with a decrease in the pH in the sludge bed. This observation is in agreement with the expectation that the carbon dioxide fraction increases as the bed pH falls, as explained earlier.

COD loading rate and minimum bed pH: In Fig. 18 the different COD loading rates (at constant COD_e and $H_2CO_3^*$ alkalinity) are plotted vs. the measured minimum bed pH: An approximately threefold increase in COD loading rate changed the minimum bed pH from 7,1 to 6,8. Hence, at a COD_e of 2 230 mg/ℓ and an effluent $H_2CO_3^*$ alkalinity of 3 100 mg/ℓ as $CaCO_3$ the minimum bed pH remained within the pH limits for anaerobic fermentation (6,6 to 7,6) even though substantial changes in COD loading rate took place.

Conclusion

From this task it can be concluded that for a constant base influent COD, a fixed recycle ratio (i.e. fixed COD_e) and constant effluent $H_2CO_3^*$ alkalinity, the minimum bed pH is relatively insensitive to the COD loading rate. Thus, in practice for the same influent COD, if the loading rate is increased by increasing the base influent flow rate and provided the recycle flow rate is increased correspondingly (to keep the recycle ratio constant) the minimum bed pH will not change significantly.

Conclusions

- The study of grape wine distillery waste in a laboratory-scale UASB system showed that treatment of this substrate is feasible in a UASB system, and that the substrate develops a pelletised sludge bed. The pattern of product formation along the line of flow of the reactor is very similar to that observed under similar conditions treating a pure carbohydrate type substrate, e.g. glucose or apple juice concentrate. No trace element addition appeared to be necessary.
- For unimpeded pelletisation when treating glucose in a UASB system Sam-Soon et al. (1990) suggested a TKN/COD ratio of 0,02 mg N/mg COD. However, in this study the average mass of TKN uptake per mass of COD for grape wine distillery waste was 0,01 mg N/mg COD. This reduced TKN uptake may be ascribed to the nature of the waste, i.e. part of the COD (short- chain fatty acids and other organic acids) did not

induce high hydrogen partial pressure conditions and hence, reduced biopolymer production took place. From the measured TKN uptake of about 0,01 mg N/mg COD and the measured influent TKN/COD of 0,014 mg N/mg COD it would appear that in most cases grape wine distillery waste requires no addition of nitrogen, or only a little.

- Pellet production in the high hydrogen partial pressure region of the reactor was 0,14 mg VSS/(mg COD removed). This pellet yield is significantly lower than that reported by Sam-Soon et al. (1987), 0,42 mg VSS/(mg COD removed), when treating apple juicing wastes. This observation is in agreement with the reduced TKN uptake due to reduced pellet formation.
- The pellets produced were smaller, less compact than with glucose substrate as influent and appeared to have a slightly filamentous surface texture. This contributed to the pellets being lifted by the escaping gas to the gas separator and the settler when the COD loading rate exceeded about 15 kg/(m^3 sludge bed·d) and in this manner set the upper limit for the COD loading rate. (This applies to the part of the study in which undiluted grape wine distillery waste was fed to the UASB reactor using various recycle ratios to control the minimum bed pH to near neutral). With a flow-through UASB system which was fed with diluted grape wine distillery waste, COD loading rates up to 41 kg/(m^3 sludge bed·d) were achieved without signs of system failure.
- Wine distillery waste generated significant internal buffer, i.e. $H_2CO_3^*$ alkalinity. This alkalinity was generated due to the removal of H^+ ions during deamination of proteins and the conversion of organic weak acid/base salts to methane and CO_2. The mass of $H_2CO_3^*$ alkalinity generated internally could not be predicted *ab initio* because the concentrations of the proteins and various organic acid/base salts could not be determined. Experimentally, the $H_2CO_3^*$ alkalinity generated ranged from 0,06 to 0,14 mg $H_2CO_3^*$ alkalinity (as $CaCO_3$) per mg base influent COD for the different waste batches tested. The variation in $H_2CO_3^*$ alkalinity generation appears to be due to differences in the orgN/COD of the waste batches. Imposing a recycle from the effluent to the influent, the $H_2CO_3^*$ alkalinity generated in the bed and appearing in the effluent, is recycled to the influent; the dilution due to the recycle reduces the base influent COD to an effective influent COD, COD_e [COD_e = base influent COD/(1 + recycle ratio)]. As the recycle ratio increases so the COD_e decreases, but the effluent (i.e. recycled) $H_2CO_3^*$ alkalinity remains constant; hence the $H_2CO_3^*$ alkalinity/COD_e ratio increases causing the minimum bed pH to increase.
- The base influent COD concentrations ranged from 20 000 to 30 000 mg/ℓ. Dilution of the base influent COD to an effective influent COD (COD_e) of about 800 mg/ℓ, by applying a recycle ratio of 33:1, appeared to have no adverse effect on the process performance. Thus, it would seem that the lower limit of COD_e of 1 000 mg/ℓ, proposed by Sam-Soon et al (1991) for satisfactory operation, can be lowered.
- The effect of different COD_e levels on the minimum bed pH was evaluated at a constant COD loading rate of 9 kg/(m^3 sludge bed·d), a base influent COD of 27 000 mg/ℓ and an effluent $H_2CO_3^*$ alkalinity of about 3 700 mg/ℓ (as $CaCO_3$), by applying three different recycle ratios of 33:1, 20:1 and 7:1 giving COD_e concentrations of 790 mg/ℓ, 1 290 mg/ℓ and 3 380 mg/ℓ respectively. The minimum bed pH decreased from 7,5 with COD_e = 790 mg/ℓ to 7,3 with COD_e = 1 290 mg/ℓ and to 6,8 with COD_e = 3 380 mg/ℓ. Hence, by changing COD_e via the recycle the minimum bed pH can be controlled. However, a relatively large change in the recycle is required to induce a significant change in minimum bed pH.
- The effect of change in effluent $H_2CO_3^*$ alkalinity on the minimum bed pH was evaluated at a constant COD loading rate of 9 kg/(m^3 sludge bed·d) and constant base influent COD. The effluent $H_2CO_3^*$ alkalinity was changed by adding a strong acid to the influent. Two different COD_e concentrations of 2 300 mg/ℓ and 1 170 mg/ℓ were tested. For COD_e of 1 170 mg/ℓ (recycle ratio 22:1) the minimum bed pH changed from 7,5 to 6,8 when the effluent $H_2CO_3^*$ alkalinity decreased from 3 500 to 1 800 mg/ℓ (as $CaCO_3$). To maintain a minimum bed pH $\approx$7 the effluent $H_2CO_3^*$ alkalinity required was about 2 200 mg/ℓ (as $CaCO_3$) at a recycle ratio of 22:1. For COD_e of 2 300 mg/ℓ (recycle ratio 12:1) the minimum bed pH changed from 7,2 to 6,8 when the effluent $H_2CO_3^*$ alkalinity decreased from about 3 000 to 2 200 mg/ℓ (as $CaCO_3$). To maintain a minimum bed pH $\approx$ 7 the effluent $H_2CO_3^*$ alkalinity required was approximately 2 800 mg/ℓ (as $CaCO_3$) at a recycle of 12:1. Hence, the effluent $H_2CO_3^*$ alkalinity requirements to maintain a near neutral minimum bed pH decrease with a decrease in COD_e (i.e. with an increase in recycle ratio). Consequently, if the internally generated $H_2CO_3^*$ alkalinity decreases (with the base influent COD remaining constant), the recycle ratio can be increased to maintain the same near neutral minimum bed pH.
- The effect of different COD loading rates on the minimum bed pH was evaluated by using a constant base influent COD concentration (29 000 mg/ℓ) and increasing the base influent flow. The recycle flow rate was increased proportionally to an increase in base influent flow rate, to keep the recycle ratio constant at 12:1 giving a COD_e of 2 230 mg/ℓ. The effluent $H_2CO_3^*$ alkalinity was constant at 3 100 mg/ℓ (as $CaCO_3$). When the COD loading rate was increased from 7 to 19 kg/(m^3 sludge bed.d) by increasing the base flow, the minimum bed pH decreased from 7,1 to 6,8. It would appear that for the same base influent COD concentration and a constant recycle ratio (constant COD_e), the minimum bed pH remained relatively stable despite an almost threefold change in COD loading rate.
- The pH profiles in the bed exhibited only a slight depression (to the minimum pH) for recycle ratios of 33:1 and 20:1 (base influent COD of 27 000 mg/ℓ and COD_e concentrations of 790 and 1 290 mg/ℓ). This tendency to smooth out the "dip" in the pH profile at low effective influent CODs, conforms with the observations of Sam-Soon et al. (1991) and Moosbrugger et al. (1993).
- From the experiments on recycling carried out in this laboratory-scale study, it appears that for grape wine distillery waste, the base influent COD should be diluted by the recycle to a COD_e of about 1 500 to 2 000 mg/ℓ. Within this range, for a COD loading rate of about 10 kg/(m^3 sludge bed.d) grape wine distillery wastes should generate sufficient internal $H_2CO_3^*$ alkalinity to maintain a near neutral minimum sludge bed, that is, no external $H_2CO_3^*$ alkalinity augmentation will be necessary.

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