Treatment of grain distillation wastewaters in an upflow anaerobic sludge bed (UASB) system

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Abstract

In operation of the full-scale upflow anaerobic sludge bed (UASB) system at the Stellenbosch Farmers' Winery (SFW) Wellington distillery, a problem encountered in the treatment of grain distillation wastewater was the accumulation of a floating scum layer. On occasion this was so severe that it forced shutdown of the UASB system to facilitate the physical removal of the scum. A preliminary investigation indicated that the scum-layer behaviour could be replicated at laboratory-scale. Thereafter, two laboratory-scale UASB systems were run in parallel: one (control) receiving wine distillation wastewater as influent, and the other (experimental) grain distillation wastewater at both high and low total suspended solids (TSS) concentrations. Scum-layer accumulation, COD removal and concentration profiles along the axis of flow through the reactors were compared. The scum layer developed only with grain distillation wastewater as influent, and its severity appeared to be linked to the TSS content of the grain wastewater. Reducing the TSS by drum filtration, settling or blending with wine wastewater could reduce, but not eliminate, the scum-layer accumulation. With wine distillation wastewater as influent, concentration profiles exhibited the typical three distinct zones of sludge bed behaviour. However, with grain distillation wastewater as influent, the concentration profiles were markedly different; the three zones of behaviour did not develop. This raises the question of the long-term viability of a UASB system treating grain distillation wastewaters.

Introduction

The upflow anaerobic sludge bed (UASB) system has found wide application in the treatment of industrial wastewaters, particularly those produced in agriculturally based industries (Britz et al., 1999). For example, UASB systems have been successfully applied to treat wastewaters from sugar, potato processing, slaughter-house, meat packing, paper mill, fruit juicing, food and yeast industries (Lin and Yang, 1991). Also, the UASB system has been shown to be a feasible method for treatment of alcohol distillery effluents (Driessen et al., 1994); COD removal efficiencies in the range of 65 to 95% can be achieved, depending largely on the kind of raw material used and on the process conditions in the distillery (Driessen et al., 1994). Accordingly, in 1993, the SFW installed a BIOPAQ® UASB reactor at the SFW Wellington Distillery to treat all wastewaters produced in this distillery, before discharge of the treated effluents via the municipal sewer to the local municipal wastewater treatment works. This UASB system consists of two parallel reactors of 150 m³ and 300 m³ respectively and can be operated using either reactor individually, or both reactors simultaneously, at a peak loading of 15 kgCOD/m³ reactor volume/ d (Laubscher et al., 2000).

The UASB system treats a variety of distillery wastewaters, which differ considerably as a result of the different raw materials used in the distillation and/or the distillation process implemented, to produce a variety of end-products. At the SFW Wellington Distillery, both column and pot distillation processes are used. Column distillation is employed in both absolute alcohol (±96.4 % ethyl alcohol/volume) and grain whisky spirit production. The former uses grape wine as raw material and the wastewater generated is referred to as *wine wastewater*. The latter uses fermented mash from maize meal (±9 % A/V), called "wort", as raw material and

the wastewater generated is referred to as *grain wastewater*. Pot distillation is used to produce brandy spirit with a superior quality of grape wine (called rebate wine) as raw material; the wastewater generated is also referred to as *wine wastewater*. Vodka and gin are also produced, but their production is relatively small and contributes negligibly to wastewater production.

All the distillery wastewaters above generally contain high concentrations of organic matter (COD), TSS and protein, particularly the grain wastewater. High TSS content has been found to be detrimental to UASB operation (Fourie, 1974; SRK, 1993). Thus, for distillery wastewaters, usually pretreatment stages are implemented for removal of TSS prior to biological treatment in the UASB system (Fourie, 1974; SRK, 1993). Pretreatment also has been implemented at the SFW Wellington Distillery: The grain wastewater undergoes decanting followed by centrifuging, while the wine wastewater undergoes centrifuging.

When commissioning the UASB system at the SFW Wellington Distillery during the 1995/1996 wine season, several operational problems were encountered. Some of these could be effectively resolved at the treatment plant. However, two major problems could not be resolved – formation of a scum layer when treating grain wastewater, and precipitation of struvite when treating wine wastewater.

With the treatment of grain wastewater, a scum layer accumulated on the liquid surface at the top of the UASB reactors. This scum layer was first observed in November 1995 when the small UASB reactor was fed grain wastewater only. The scum layer manifested as a thick highly viscous gelatinous layer which interfered with effluent overflow at the overflow launders. On occasion, the development of the scum layer was so severe that it forced operational shutdown of the UASB system for physical removal of the layer. The scum-layer formation proved persistent, as it manifested whenever grain wastewater was treated. This operational problem prompted an investigation at laboratory-scale into the treatment of grain distillation wastewater in the UASB

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system. This paper reports on this investigation. The precipitation of struvite was also investigated, and is reported separately by Laubscher et al. (2000).

Preliminary investigation

Treatment of grain distillation wastewater in a UASB system was investigated using laboratory-scale reactors. To assess whether the scum layer observed at full-scale could be reproduced at laboratory-scale, and validate the experimental protocol, a preliminary investigation was undertaken (Laubscher et al., 2000). In August 1997 a UASB system was set up at laboratory-scale, seeded with granular sludge from the full-scale UASB system. The system was fed grain wastewater obtained from the full-scale plant, after decanting and centrifuging. Also, to assess the effect of TSS concentration on scum-layer formation, grain wastewater that had been batch filtered through a drum filter using filter aid (diatomaceous earth) to remove TSS also served as influent. From this preliminary investigation, the following conclusions could be drawn (for details see Laubscher et al., 2000):

- A scum layer was formed on the liquid surface of the laboratory-scale UASB system, appearing as a thick gelatinous mass, covered by a thin crust. This confirmed that the problem identified at full-scale could be reproduced at laboratory-scale, validating the experimental protocol.
- The scum layer above was present when both the centrifuged (high TSS) and drum filtered (low TSS) grain wastewaters served as influent. However, the scum layer was very much reduced with the filtered grain wastewater compared to the centrifuged grain wastewater. This indicated that the causative agent for the scum layer appeared to be related to the TSS content of the grain wastewater. However, although drum filtering of the wastewater appeared to reduce the problem, it did not eliminate it.
- During periods of successful operation, % COD removal of >90 % could be achieved with both the centrifuged and filtered grain wastewater. However, the system was prone to upsets with relatively long recovery periods of about 11 d.

The success in reproducing the scum layer observed at full-scale in the laboratory-scale UASB system prompted a more detailed investigation into this operational problem and the behaviour of the UASB system when treating grain distillation wastewater.

Experimental methods

Experimental approach

Two identical laboratory-scale UASB reactors were set up and operated in parallel, one as an experimental unit (Reactor 1) and the other as a control (Reactor 2). Thereafter:

(1) To acclimatise the biomass in both UASB systems and to establish identical performance, both were fed equal quantities and concentrations of wine wastewater as influent.
(2) The control system was maintained on wine wastewater as influent, and the experimental system switched to grain wastewater as influent, fed as a blend with wine wastewater and on its own, at high and low TSS concentrations.
(3) System performance of the experimental and control systems was monitored and compared with respect to scum-layer accumulation, COD removal and concentration profiles of
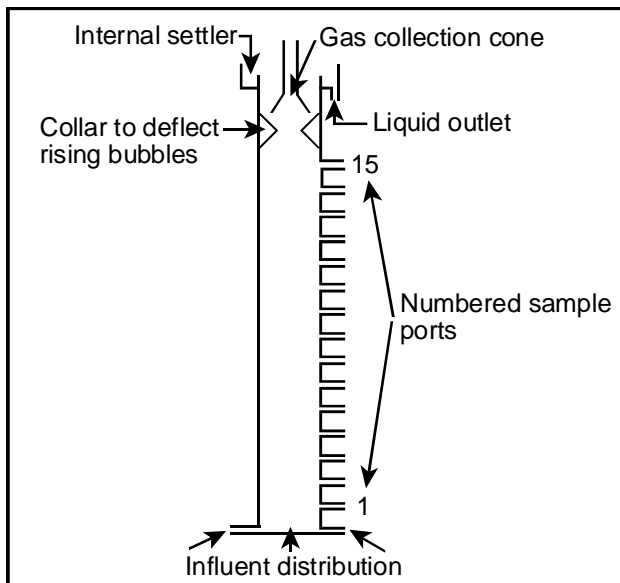

Figure 1
Schematic layout of the laboratory-scale UASB reactor showing the numbered sampling ports

short-chain fatty acids (SCFA), pH, COD, total soluble phosphorus (P_T) and free and saline ammonia (FSA) along the axis of flow through the UASB reactor.

Reactor set-up

The two laboratory-scale UASB reactors were made from transparent perspex cylinders (Fig. 1), based on the design of Sam-Soon et al. (1989), but with inside diameter 90 mm and height 1 600 mm, giving a total effective reactor volume of 10.2 ℓ. The reactor bottom was flat with four evenly spaced inlet feed ports discharging in a horizontal direction. At the top of the reactor was the gas/liquid/solid separator. Gas collection was by means of a hollow inverted cone; rising gas bubbles were defected into the cone by a collar around the inside wall of the reactor below the cone. The gas passed from the cone, along a gas line, through a conical flask which served as a liquid trap, to a wet gas flow meter (Model DM3A, Alexander Wright, London). To prevent channelling in the sludge bed and to ensure free movement of gas out of the sludge bed, the reactor contents were stirred by means of a slow internal stirrer (2 r/min) driven by a magnetic stirrer motor.

Effluent discharge was via an annular space between the gas collection cone and the reactor wall to enter a small solid/liquid separator (volume approximately 600 mℓ). Clarified effluent flowed over a launder (v-shaped weirs) to the collection vessel, while solids which settle out, were returned into the reactor by gravity. Fifteen sampling ports were evenly spaced along the length of the reactor. Temperature in the reactor was maintained at 35°C (±1°C) by a thermostat-controlled electrical heating tape wrapped around the reactor.

The two UASB systems were operated in a flow-through mode with no recycle for alkalinity reuse (Wentzel et al., 1994), since the objective was not to investigate pH control and the flow-through system is the simplest to operate.

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TABLE 1
Characteristics of the wastewaters used as influent to the laboratory-scale UASB systems
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Wastewater type	Wastewater characteristic			
	COD (mg/ℓ)	TKN (mgN/ℓ)	P (mgP/ℓ)	TSS (mg/ℓ)
Wine wastewater after centrifuging	20 000 - 30 000	300 - 350	180 - 200	100 - 500
Grain wastewater after decanting and centrifuging - unsettled	25 000 - 30 000	170 - 180	270 - 300	> 1 000
Grain wastewater after decanting, centrifuging and settling	20 000 - 25 000	170 - 180	270 - 300	< 1 000

Wastewater characteristics

The influent feed stock was of three types:

- Wine wastewater.
- Unsettled grain wastewater.
- Settled grain wastewater.

The wine and unsettled grain wastewater were those fed to the full-scale system. The grain wastewater was collected after the decanting and centrifugation pretreatment stages and the wine wastewater after centrifugation (see above). The wastewaters were transported to the laboratory and stored in a refrigerated room at 4°C.

For the grain wastewater, to investigate the effects of the TSS content of this wastewater on scum-layer accumulation, a grain wastewater with high (>1 000 mg/ℓ) and low (<1 000 mg/ℓ) TSS content was used as influent feed to the experimental UASB system (Reactor 1). The decanted and centrifuged grain wastewater with TSS >1 000 mg/ℓ served as the high TSS grain wastewater feed, termed "unsettled grain wastewater". For the low TSS content grain wastewater, in the preliminary investigation, the grain wastewater was drum-filtered to reduce the TSS. However, drum filtration proved impractical at large scale, because of the batch method of operation. Accordingly, drum filtration had been terminated and could not be used to produce low TSS grain wastewater for this part of the investigation. Experiments indicated that extended settling (>2 d) reduced the TSS content of the grain wastewater to < 1 000 mg/ℓ. Accordingly, to produce low TSS grain wastewater, the grain wastewater was settled for 3 d and the supernatant decanted to serve as influent feed, termed "settled grain wastewater". The characteristics of the wastewaters are listed in Table 1.

The daily feed to the two laboratory-scale UASB reactors was drawn from the appropriate concentrated feed stock, and diluted with tap water to a COD concentration of 3 000 to 5 000 mg/ℓ. This concentration was selected according to Sam-Soon et al. (1990); for flow-through systems, dilution of the influent COD into the range 2 000 to 5 000 mgCOD/ℓ provides more stable operation. Furthermore, this COD concentration approximates the influent COD concentration that would be achieved in practice with typical recycle ratios (from effluent to influent) that would be implemented for this wastewater for alkalinity reuse (Wentzel et al., 1994). Where the experimental and control systems received the same influent, this was made up together and divided between the two systems.

The pHs of all three wastewater types were low, pH 4.0 to 4.5. The flow-through mode of the UASB operation selected, and the production of short-chain fatty acids in the lower part of the UASB reactor will cause the pH to remain low (Sam Soon et al., 1989). This low pH will inhibit methanogenesis (pH<6.8, Wentzel et al., 1994). Accordingly, alkalinity was added to the influent in the form of 100 to 200 mg NaHCO$_3$ per 20 ℓ diluted feed. This caused the pH in the UASB reactor sludge bed to stabilise at about 7. Furthermore, no trace metals were added to the feed, as these would be present in adequate quantity.

Analytical methods

The following parameters were measured daily to assess the reactor performance:

- COD, unfiltered influent and effluent
- pH in influent and settler
- Gas production
- Influent flow rate.

Additionally, during the third experimental period (see below), the following were measured:

- Effluent short-chain fatty acids (SCFA)
- Effluent H$_2$CO$_3$* alkalinity
- Individual SCFA, pH, COD, free and saline ammonia (FSA) and total soluble phosphorus (P$_T$) profiles from the 15 sampling ports along the length of the reactors.

CODs and FSAs were measured in accordance with *Standard Methods* (1985). Total soluble phosphorus was measured on 0.45 µm filtered samples using persulphate digestion, followed by molybdate vanadate colorimetric reaction (*Standard Methods*, 1985). Gas production was measured by means of a wet gas meter (model No. DM3A, Alexander Wright, London). The pH was measured with a portable Hanna pH meter (HI 9025) fitted with an epoxy-combined pH electrode (Hanna HI 1230). SCFA and H$_2$CO$_3$* alkalinity were measured with the 5-point titration method (Moosbrugger et al., 1992). Individual SCFA species were determined by gas chromatography using a Varian Model 3700 gas chromatograph equipped with a flame ionisation detector (FID) and a Nukol™ fused silica capillary column (30 x 0.53 mm in diameter and 0.5 µm film thickness) (Supelco, Inc., Bellefonte).

TABLE 2
Influent feeding regime for laboratory-scale UASB systems

REACTOR 1

Feeding period (Day No.)	COD¹ (unfiltered) (mgCOD/ℓ)	Flow rate (ℓ/d)	Loading rate (kgCOD/m³ sludge bed/d)	Feed type	Sludge bed volume (ℓ)
Period 1					
1 - 2				water	4
3 - 5				wine	4
6 - 8	2 123	8	4.2	wine	4
9 - 35	3 524	9	7.9	wine	4
36 - 53	4 210	8	8.4	wine	4
54 - 66	4 324	8	8.6	wine	4
67 - 84	4 925	11	13.5	wine	4
Period 2 - Restart systems with new wine wastewater feedstock; Reactor 1 experimental, Reactor 2 control					
88 - 99	3 767	4	7.5	wine	2
100 - 106	5 101	4	10.2	wine	2
107 - 125	4 744	5	11.9	wine	2
126 - 131	4 244	6	12.7	wine	2
132 - 177	4 954	7	17.3	wine	2
178 - 185	4 662	7	16.3	unsettled grain + wine	2
186 - 202	4 864	8	19.5	unsettled grain + wine	2
203 - 204	3 978	7	13.9	settled grain + wine	2
205 - 217	4 153	8	16.6	settled grain	2
218 - 247	5 470	8	21.9	unsettled grain	2
Period 3 - Restart systems; Reactor 1 control, Reactor 2 experimental					
312 - 322	2 494	7	4.4	wine	4
323 - 338	3 624	7	6.3	wine	4
339 - 343	Clean unit; reduce sludge bed volume				
344 - 394	5 120	7	14.3	wine	2.5
395 - 414	6 334	7	17.7	wine	2.5

REACTOR 2

Feeding period (Day No.)	COD¹ (unfiltered) (mgCOD/ℓ)	Flow rate (ℓ/d)	Loading rate (kgCOD/m³ sludge bed/d)	Feed type	bed volume (ℓ)
Period 1					
1 - 2				water	
3 - 5				wine	
6 - 8	2 234	8	4.5	wine	4
9 - 35	3 585	11	9.8	wine	4
36 - 53	4 255	12	12.8	wine	4
54 - 84	4 672	12	14.0	wine	4
Period 2 — Reactor 2 control					
88 - 99	3 784	4	6.1	wine	2.5
100 - 106	5 053	4	8.1	wine	2.5
107 - 131	4 611	6	11.1	wine	2.5
132 - 157	5 224	8	16.7	wine	2.5
158 - 247	5 098	9	18.4	wine	2.5
Period 3 — Reactor 2 experimental					
312 - 322	2 545	7	4.5	wine	4
323 - 338	3 572	7	6.3	wine	4
339 - 343	Clean unit; reduce sludge bed volume				
344 - 394	5 112	7	14.3	wine	2.5
395 - 414	4 441	7	12.4	settled grain	2.5

¹Average values for feeding period

Calibration was with a solution of acetic, propionic, i-butyric, n-butyric, i-valeric and n-valeric acids added to 0.5 mℓ 0.1 N HCl with an internal standard of n-hexanol (26 %). The internal standard was chosen because its polarity and boiling point allowed it to be closest to the fatty acid peaks.

For the profiles, samples were drawn from the ports down the reactors by means of a special device that allowed the sample to be extracted and the pH measured without loss of dissolved gases, particularly CO_2. Loss of CO_2 causes change in pH but does not influence alkalinity (Loewenthal et al., 1989).

Experimental periods and system operation

Table 2 shows the feeding regime and loading rates implemented over the entire study which extended over 414 d. Three distinct periods of operation were identified, and are described separately below.

Period 1

Granular anaerobic sludge from the full-scale UASB reactor at the Wellington Distillery was used to seed the two laboratory-scale UASB systems with approximately 4 ℓ of sludge each. Prior to seeding, the sludge was rinsed with tap water in order to remove dead debris and fine particles, and the seed sludge contained well-structured granules, 1 to 2 mm in diameter. The operating temperature was set at 35°C (±1°C).

For the first 48 h, only water was fed to the reactors, to ensure that any formation of a scum layer in the laboratory-scale units was not simply because of a carryover from the full-scale system. On the third day low concentrations of diluted wine wastewater were fed to both reactors for the next 3 d and thereafter, the COD loading rates were gradually increased (see Table 2).

The first objective was to continue feeding both units with diluted wine waste until > 90% COD removal efficiencies were attained, indicating that the biomass had fully acclimatised (Sam-Soon et al., 1989). However, the COD removal in both units remained poor, decreasing to well below 50% for both units by Day 84 when the Period 1 investigation was terminated. A definitive explanation for the poor COD removal behaviour of the UASB systems could not be identified at that stage. However, from results obtained during Period 2 (see below), it was concluded that the poor reactor performance was related to the wine wastewater "stock" used as feed during Period 1 - when "new" wine wastewater was collected from the distillery and fed to the units only 3 d after termination of Period 1, the laboratory-scale units immediately showed vastly improved COD removal, > 90 % within one week.

Period 2

Start-up
Period 2 commenced on Day 88 with "new" wine wastewater and reduced sludge volumes. The sludge beds in the reactors were
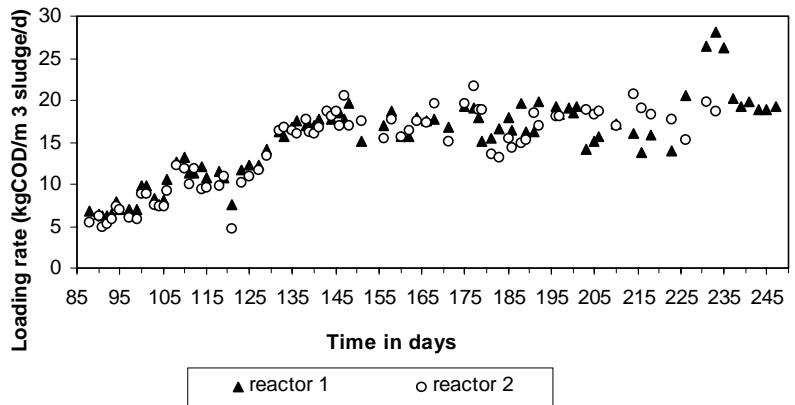

Figure 2
COD loading rate vs. time for laboratory-scale UASB Reactors 1 (experimental) and 2 (control) - Period 2
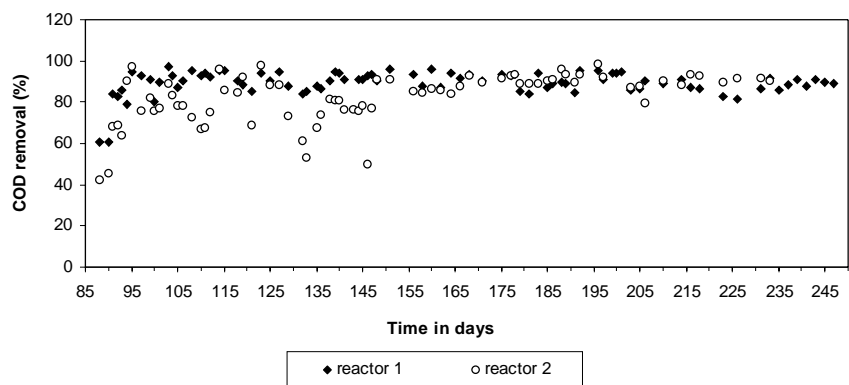

Figure 3
COD removal (% of influent) vs. time for laboratory-scale UASB Reactors 1 (experimental) and 2 (control) - Period 2

drained to about 2.0 and 2.5 ℓ for Reactors 1 and 2 respectively. To acclimatise the sludge, diluted wine wastewater initially was fed to both units, at a COD of about 3 800 mg/ℓ (Table 2). The flow rate was set at 4 ℓ per day for both units, i.e. COD loading rate of 7.5 and 6.1 kgCOD/m^3 sludge·d for Reactors 1 and 2 respectively. (In order to have a "standard" reference, all organic loading rates will be expressed in terms of mass of substrate fed per day per unit sludge bed volume - this eliminates variations in "dead" volume above the sludge bed). The loading rate was kept constant for both reactors and after one week COD removal efficiencies of 90% were obtained. This indicated that the sludge beds in both units were fully acclimatised to the wine wastewater.

Loading rate
For Period 2, loading rates for Reactors 1 and 2 are shown in Fig. 2. With wine wastewater as influent feed to both reactors, the loading rates were gradually increased from the initial loading rates to about 18 kgCOD/m^3 sludge·d by Day 177. This enabled the feed type to the experimental system to be changed.

Substrate feed
During Period 2, the main objective was to implement substrate changes to the experimental unit (Reactor 1) and compare its performance with the control unit (Reactor 2), see Table 2. Accordingly, the feed to the experimental reactor was changed from wine wastewater to a 1:1 blend of unsettled grain and wine

Figure 4
COD loading rate vs time for laboratory-scale UASB Reactors 1 (control) and 2 (experimental) - Period 3.
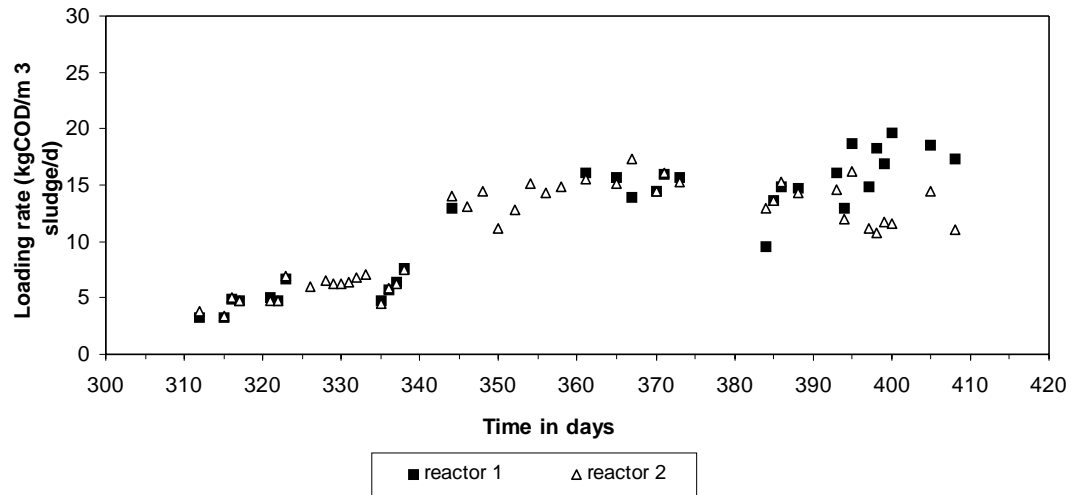
wastewaters on Day 178, then to a 1:1 blend of settled grain and wine wastewater on Day 203, and, thereafter, to only settled grain wastewater on Day 205. On Day 218 the final feed change was made and only unsettled grain wastewater was fed until the termination of Period 2 on Day 247.

Period 3

Period 3 commenced after a shutdown for 64 d. Once it was established in Period 2 that scum-layer accumulation is a phenomenon common to the treatment of any type of the grain wastewater (centrifuged, filtered, settled, or blended), UASB reactor behaviour when treating grain wastewater compared with the behaviour when treating wine wastewater was examined in more detail. This involved comparing the concentration profiles along the line of flow of the UASB reactor when treating grain and wine wastewaters.

Start-up
Period 3 commenced on Day 312 with the following changes. Reactor 1, operated as the experimental unit during Period 2, was operated as the control unit and *vice versa*. "New" sludge was collected from the full-scale UASB system. In the control unit (Reactor 1), 4 ℓ of the "new" sludge was used to replace the sludge from Period 2, because during Period 2 this unit had received grain wastewater and both systems were to be started on wine wastewater. Some "new" sludge was also added to the experimental unit (Reactor 2), to increase the volume to 4 ℓ. This unit had only received wine wastewater during Period 2 and so the existing sludge bed did not need to be replaced. The same wine wastewater that served as influent during the Period 2 was used as substrate feed. Diluted wine wastewater was fed to both units to acclimatise the seeding sludges, at initial loading rates of about 4.5 kgCOD/m³ sludge·d for both reactors (see Table 2).

Loading rates
Figure 4 shows COD loading versus time for Reactors 1 and 2 respectively over Period 3. The loading rates were gradually increased to 6.3 kgCOD/m³ sludge·d before both units were shut down for 1 d on Day 338 and cleaned. Sludge from both units was drained leaving a balance of about 2.5 ℓ. Thereafter, the loading rates were immediately increased to 14.3 kgCOD/m³ sludge·d for both units. On Day 395 the feed to the experimental unit (Reactor 2) was changed to settled grain wastewater (see above).

## Results and discussion

Period 2

Sludge bed changes
The level of the sludge bed could be monitored through the transparent wall of the two reactors, and stayed reasonably stable in both reactors throughout the investigation, at approximately ½ the reactor volume. Sludge granule size remained approximately constant, at a diameter of 1 to 2 mm. Dead pellet debris washout was observed, but this is common in UASB systems. In the experimental reactor (Reactor 1), when it received grain wastewater as influent this pellet debris became entrapped in the scum layer that formed on the liquid surface (see below).

With the grain wastewater, the fine grain particles suspended in the feed flocculated as distinct yellowish flocs when the pH was increased to near neutral by $NaHCO_3$ addition, particularly in the unsettled feed. These particles tended to be captured in the experimental reactor sludge bed and did not seem to biodegrade readily. Eventually the sludge bed in this reactor became saturated with fine grain particles giving the sludge bed a yellowish appearance. These yellowish particles were also washed out of the sludge bed, and were entrapped in the scum layer which formed on top of the reactor (see below). Further, in the experimental reactor, when receiving grain wastewater as influen,t there was always a thin layer (±5 mm) of fine gelatinous sludge visible on top of the sludge bed, which continuously formed and was washed out to the effluent.

System performance
In Fig. 2 COD loading and in Fig. 3 COD removal vs. time are shown for Reactors 1 and 2 during Period 2. In Table 2, the substrate feed types and loading rates applied are shown. For the first 90 d the influent feed was wine wastewater. From Fig. 3, within 8 d of start up (Day 95) Reactor 1 achieved COD removals >90 % and these removals were maintained throughout the investigation. For Reactor 2, initially COD removals were variable due to problems in operation of the laboratory-scale system, but after about 60 d (Day 148) removals >90 % were achieved and maintained for the rest of the investigation. This indicated that the sludge masses were fully acclimatised to the operating conditions. Also, both systems were able to successfully accommodate the increase in loading rate (see Fig. 2) without deterioration in effluent quality. Accordingly, the substrate changes above were implemented for Reactor 1 (see Table 2). For Reactor 1, removals >90 % were

Figure 5
COD removal (% of influent) vs time for laboratory-scale UASB Reactors 1 (control) and 2 (experimental) - Period 3
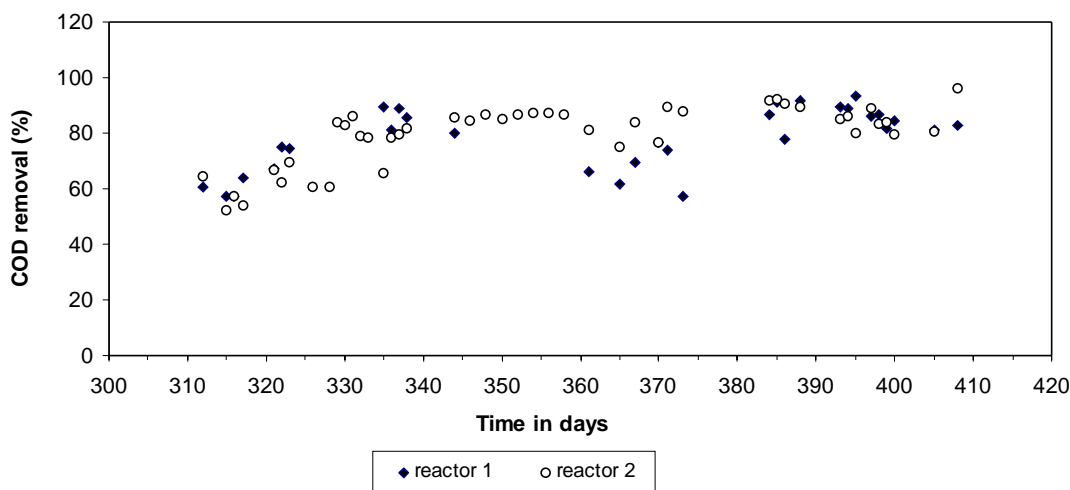
achieved with influent feed of wine wastewater, 1:1 blend of wine and unsettled grain wastewater and settled and unsettled grain wastewater only (see Fig. 3). Furthermore, following a substrate change, no deterioration in system performance was observed. These observations confirmed the conclusions from the preliminary investigation, that with an existing sludge bed, system performance with grain wastewater in all forms is good. Also, very little or no adaptation is necessary in switching from one feed type to the other.

These results appeared to indicate that grain wastewater can be treated successfully in the UASB system, provided scum-layer accumulation (see below) can be accommodated and an existing granular sludge bed is available.

Scum-layer formation

The formation of the scum layer was determined visually. With the wine wastewater, scum-layer accumulation was never observed. However, with the grain wastewater in any form, i.e. blend, settled or unsettled, the scum layer accumulated; if physically removed, the layer redeveloped within 24 h. These observations confirm that the scum-layer accumulation is a property of the grain wastewater and not distillery wastewaters in general.

The scum layer appeared as a thick gelatinous layer containing debris particles, dead granular sludge and fine particles, which tended to be extremely sticky and oily, covered by a thin crust. Microscopic examination (Britz, 1998) indicated in the crust layer the presence of a long rod-shaped motile organism with point flagella using a "spin-turn" action for movement, and in the oily layer a number of filamentous type bacteria.

The thickness of the scum layer was found to depend on the substrate feed composition, and was not a consequence of biomass changes or reactor performance. The scum-layer accumulation was most severe with the unsettled grain wastewater, and reduced in the blend and settled grain wastewaters. This confirmed the findings in preliminary investigation, that the scum-layer accumulation was linked to the solids content of the grain wastewater. However, blending the grain wastewater with wine wastewater, or settling the grain wastewater reduced, but did not prevent scum-layer accumulation. This is in agreement with the results on the drum-filtered grain wastewater (see **Preliminary investigation**). Therefore, settling or drum filtering the grain wastewater prior to treatment in the UASB system can reduce, but not eliminate, the scum layer.

Period 3

System performance

In Fig. 4 COD loading and in Fig. 5 COD removal vs. time for Reactors 1 (control) and 2 (experimental) are shown for Period 3. In Table 2, the substrate feed types and loading rates applied are shown. From Table 2, for the first 27 d the influent feed was wine wastewater. From Fig. 5, during this time both UASB systems achieved COD removals of >80%. On Day 339, the units were stopped for cleaning, and the sludge in each unit was drained to an effective volume of 2.5 ℓ. On Day 344, both reactors were restarted on wine wastewater again at higher loading rates (see Fig. 4). From Fig. 5 it can be seen that the COD removals in both systems remained > 80%. However, on Day 360 COD removals decreased due to some unidentified problem, but thereafter increased to > 80% by Day 384, and remained > 80% in both reactors for the rest of the investigation, to Day 414.

Figures 6 and 7 show the effluent SCFA concentrations and $H_2CO_3^*$ alkalinity concentrations respectively for Reactors 1 and 2, for the period from Day 393 to Day 400. From Fig. 6 it is evident that the effluent SCFA concentrations for Reactor 2 (experimental) decreased when this reactor was switched from wine wastewater to settled grain wastewater, from 200 to 400 mg/ℓ as HAc to values as low as 0 mg/ℓ as HAc. Figure 7 shows that the effluent $H_2CO_3^*$ alkalinity for Reactor 2 treating settled grain wastewater was initially lower than Reactor 1 treating wine wastewater, but increased as the sludge adapted to the settled grain wastewater.

With regard to the effluent SCFA, the reduction in concentration on switching from wine wastewater to settled grain wastewater indicates a notable change in behaviour. This is confirmed and dealt with in more detail when comparing the bed profiles with the two wastewaters (see below).

Concentration profiles

Figures 8(a, b, c, d and e) show concentration profiles taken on Day 408 along the length of Reactors 1 and 2 respectively for pH, COD, FSA, P_T and SCFA species concentrations. On this day Reactor 1 treated wine wastewater and Reactor 2 treated settled grain wastewater.

With regard to the profiles measured with wine wastewater, these conform to profiles measured previously with apple juice wastewater (Sam-Soon et al., 1987), glucose (Sam-Soon et al., 1990), protein (Moosbrugger et al., 1990), brewery wastewater (Moosbrugger et al., 1993a) and wine distillery wastewater (Moosbrugger et al., 1993b):

Figure 6
Effluent total short-chain fatty acid (SCFA) concentrations for laboratory-scale UASB Reactors 1 (control) and 2 (experimental) - Period 3.
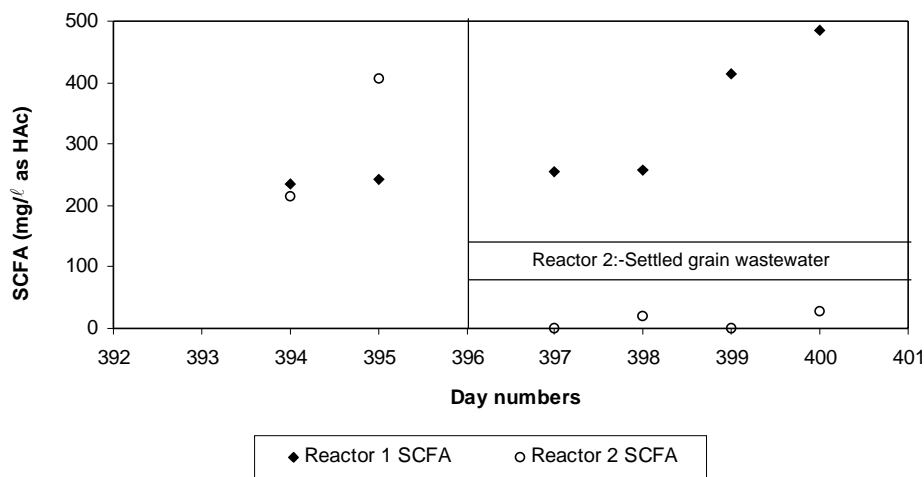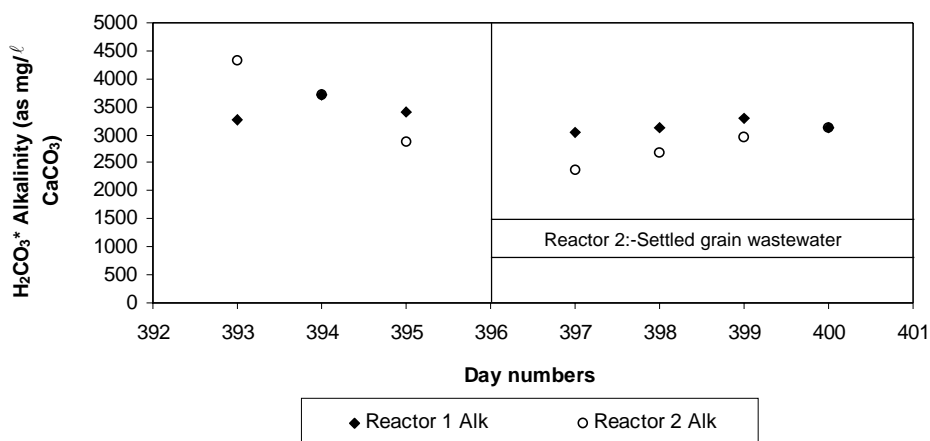

Figure 7
Effluent H₂CO₃ alkalinity concentrations for laboratory-scale UASB Reactors 1 (control) and 2 (experimental) - Period 3.*

pH: From Fig. 8(a), the pH declines in the lower part of the sludge bed to a minimum pH=7 at Port 2. This indicates that influent alkalinity was sufficient to buffer the pH above the minimum value of 6.8 suggested by Sam-Soon et al. (1987) and Wentzel et al. (1994). This decline in pH coincides with the increase in acetic (HAc) and propionic (HPr) acids, see Fig. 8(c). Above Port 2, the pH increases to reach pH=7.33 by Port 6 and, thereafter, stabilises at approximately this value. This increase in pH corresponds to the decrease in HAc and HPr due to biological consumption, see Fig. 8(c).

COD: From Fig. 8(b) the COD profile shows a decrease in the lower part of the sludge bed from the influent concentration of about 6 200 mgCOD/ℓ to a value of about 3 200 mgCOD/ℓ by Port 1. Thereafter, the COD decreases only slowly, to reach 970 mgCOD/ℓ by Port 10.

HAc: From Fig. 8(c), HAc increases in the lower part of the sludge bed to reach a maximum of about 950 mgHAc/ℓ by Port 2. Thereafter, HAc decreases to reach about 100 mgHAc/ℓ by Port 5, and remains at approximately this value through the rest of the sludge bed.

HPr: From Fig 8(c), HPr conforms to the HAc profile, reaching a maximum of approximately 950 mgHPr/ℓ in the lower part of the sludge bed and decreasing to a minimum of 150 mgHPr/ℓ in the top part of the sludge bed.

Free and saline ammonia (FSA): From Fig. 8(d), FSA initially increases to reach about 195 mgN/ℓ at Port 2, due to deamination of organic N present in the influent. Thereafter, FSA exhibits a decrease to reach a minimum of about 155 mgN/ℓ through the rest of the bed, due to uptake of FSA for cell and pellet polymer synthesis.

Soluble phosphorus: From Fig. 8(e) phosphorus exhibits only a small decrease through the sludge bed, due to the uptake for cell synthesis.

As noted earlier, this behaviour conforms to that observed by Sam-Soon and co-workers. To explain the behaviour, they proposed that three distinct zones be identified (Wentzel et al., 1994):

- A lower active zone in which concentrations of the SCFAs, HAc and HPr, increase to maxima, soluble COD reduces to less than half its influent value, and pH declines to a minima - Ports 0 to 2 here.
- An upper active zone in which the HAc and HPr concentrations decrease to minima, COD decreases to a near minimum, FSA remains near constant, and pH increases to a stable value - Ports 2 to 4 here.
- An upper inactive zone in which no observable biokinetic activity is observed - Ports 4 to 5 here.

From the biochemistry of digestion processes (McInerney et al., 1979), Sam-Soon and co-workers identified micro-organism behaviour in the three zones as follows (Wentzel et al., 1994):

a

Figure 8(a)
Comparison of pH profiles along the line of flow through laboratory-scale UASB systems treating wine wastewater (Reactor 1) and grain wastewater (Reactor 2) - Period 3.
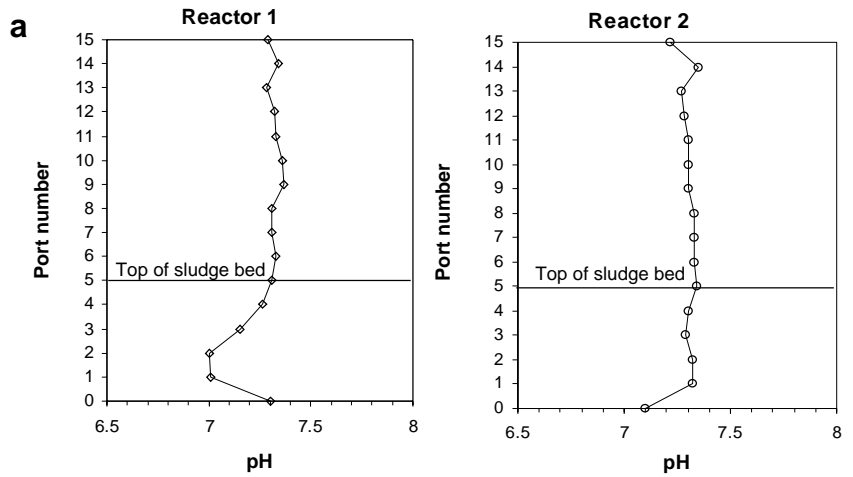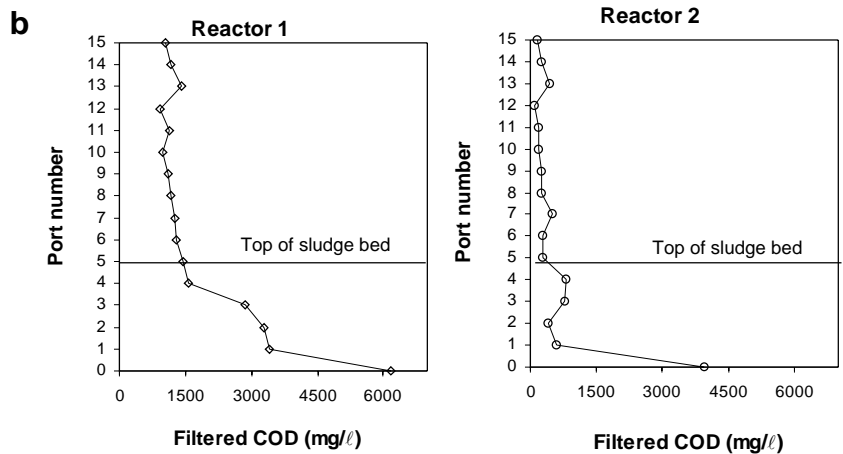
b

Figure 8(b)
Comparison of soluble COD concentration profiles along the line of flow through laboratory-scale UASB systems treating wine wastewater (Reactor 1) and grain wastewater (Reactor 2) - Period 3.
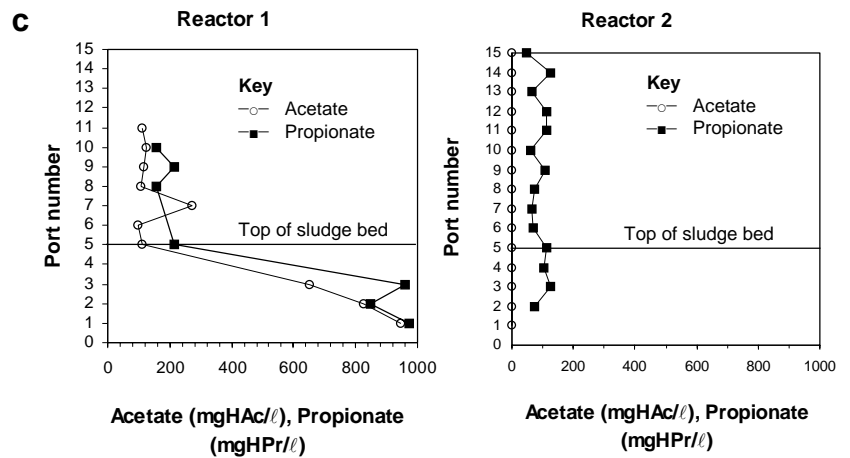
c

Figure 8(c)
Comparison of acetic (HAc) and propionic (HPr) acid concentration profiles along the line of flow through laboratory-scale UASB systems treating wine wastewater (Reactor 1) and grain wastewater (Reactor 2) - Period 3.

- In the lower active zone – Acidogens generate SCFA, principally acetic (HAc) and propionic (HPr), carbon dioxide (CO_2) and hydrogen (H_2) from the influent substrate. The hydrogen is generated at such a rate that a high hydrogen partial pressure (high pH_2) is created. This is indicated by the observed increase in HPr which is produced only under high pH_2 ($> 10^{-3.7}$ atm); Hydrogenotrophic methanogens generate methane (CH_4) from H_2 and CO_2; Acetoclastic methanogens convert some HAc to CH_4 and CO_2; Acetogens are inactive due to the high pH_2.

- In the upper active zone – The pH_2 has been reduced to, and maintained at, such low values due to action of hydrogenotrophs that: Acetogens can convert HPr to HAc, H_2 and CO_2; Acetoclastic methanogens convert all the HAc to CH_4 and CO_2.

- In the upper inactive zone – No observable biological activity takes place.

From the above, it is apparent that the differentiation of the sludge bed into lower and upper active zones is based on whether HPr generation takes place (lower active, high pH_2) and whether HPr oxidation to HAc occurs (upper active, low pH_2) or not (lower active, high pH_2); HPr is generated by acidogens only under high pH_2 and oxidised to HAc by acetogens only under low pH_2.

From the observations made here, these proposals apply also to the UASB system treating wine wastewater. However, the profiles for the UASB system treating grain wastewater differ markedly from those for the UASB system treating wine wastewater:

Figure 8(d)
Comparison of free and saline ammonia (FSA) concentration profiles along the line of flow through laboratory-scale UASB systems treating wine wastewater (Reactor 1) and grain wastewater (Reactor 2) - Period 3.
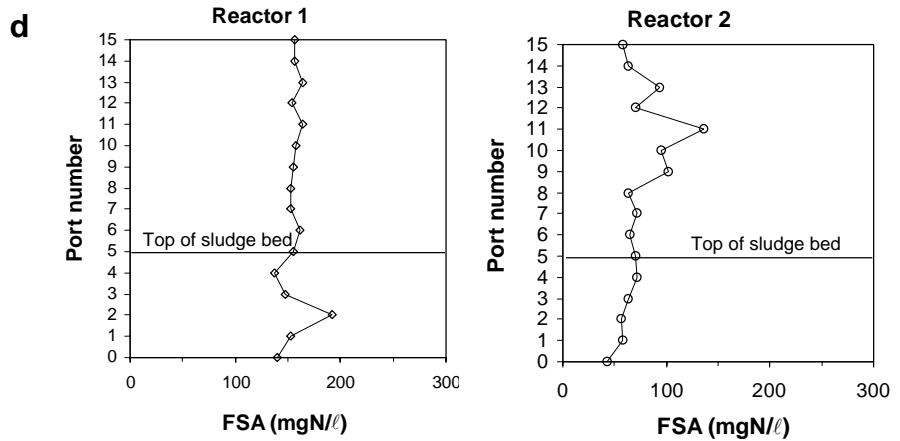
Figure 8(e)
Comparison of total soluble phosphorus concentration profiles along the line of flow through laboratory-scale UASB systems treating wine wastewater (Reactor 1) and grain wastewater (Reactor 2) - Period 3.
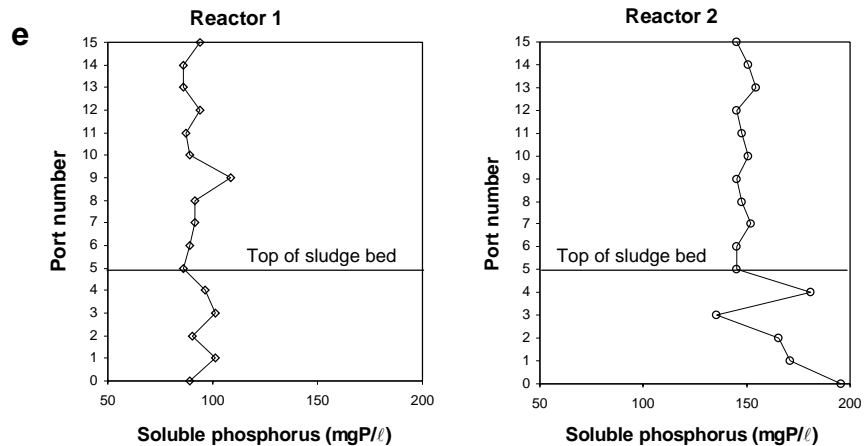
pH: From Fig. 8(a), the pH profile does not exhibit the characteristic decrease in the lower part of the sludge bed followed by an increase in the upper part of the bed, but remains approximately constant at pH=7.34 throughout the sludge bed.

COD: From Fig. 8(b), the COD decreases from the influent value of 3 960 mgCOD/ℓ to about 600 mgCOD/ℓ at Port 1, and thereafter decreases slowly to about 280 mgCOD/ℓ by Port 5 and remains at this value throughout the rest of the sludge bed.

HAc: From Fig. 8(c), negligible HAc were measured throughout the sludge bed. This conforms with measurements made on effluent samples, see above.

HPr: From Fig. 8(c), the HPr is constant through the sludge bed at a low value of about 80 mgHPr/ℓ.

FSA: From Fig. 8(d), the FSA shows a slight increase through the sludge bed, probably due to deamination of organic-N.

Soluble phosphorus: From Fig. 8(e), soluble phosphorus shows a small decrease through the sludge bed, due to uptake for cell synthesis.

The profile for the UASB system treating grain wastewater indicates that with this wastewater the three zones of behaviour identified for the system treating wine wastewater (and similar wastewaters, Wentzel et al., 1994) do not develop to any marked extent. A possible explanation for this is that the grain wastewater contains considerable suspended solids. The rate of acidogenesis with suspended solids as substrate would be limited by the rate of hydrolysis. Typically, hydrolysis rates would be much slower than acidogenesis rates with a soluble substrate. The net effect is to lower the overall rate of acidogenesis. With the lower acidogenic rates, the short chain-fatty acids would be consumed in subsequent reactions as they are produced. Also, the low rate of acidogenesis implies that the rate of H_2 production is low, so that a high pH_2 zone does not develop in the sludge bed.

With grain wastewater, the absence of a differentiation into the three zones of behaviour raises the question of the long-term viability of a UASB system treating this type of wastewater. In developing their hypothesis for pelletisation in UASB systems, Sam-Soon et al. (1987) proposed that partial phase separation of the anaerobic processes and development of a zone with a high pH_2 were essential for pellet formation (Wentzel et al., 1994). In the UASB system treating grain wastewater, observations (no HAc and little HPr) indicate that these prerequisites for pellet formation are not achieved. If this is true, according to the hypothesis of Sam-Soon et al. (1987), pellet growth will not occur, or it will be greatly reduced. This indicates that, in the long term in switching from wine wastewater (where pellet growth has occurred) to grain wastewater there will be a gradual loss of the pelletised sludge bed, until it declines to such low values that the system will fail. It is probable that the laboratory-scale systems receiving grain wastewater were not operated for periods long enough for the loss in sludge bed to be noticeable. Some loss of pelletised bed was observed, with pellet debris accumulating in the scum layer on the liquid surface, but pellet break-up and loss are common in UASB systems. The systems would have to be operated for longer periods to determine whether the sludge bed loss is significant, and whether the sludge bed lost can be regenerated.

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The investigation indicates that when switching from wine wastewater, where a well-defined pelletised sludge bed has been developed, to grain wastewater, the latter can be treated effectively in the short term. However, most likely, the sludge bed will diminish with time. To re-establish the pelletised bed, the system will have to be switched back to wine wastewater for a period.

Conclusions

From the results obtained in this investigation the following conclusions could be made:

- When treating grain wastewater, a scum layer was formed on the liquid surface of the laboratory-scale UASB system, appearing as a thick gelatinous mass, covered by a thin crust. This confirmed that the problem identified at full scale could be reproduced at laboratory scale, validating the experimental protocol.
- The scum layer above was present with the grain wastewater in any form, i.e. blended with wine wastewater, or drum-filtered, settled or unsettled grain wastewater only. The scum-layer accumulation was most severe with unsettled grain wastewater, and reduced in the drum-filtered, blended and settled grain wastewater.
- With wine wastewater, scum-layer accumulation was not observed.
- The observations above indicate that scum-layer accumulation is a property of the grain wastewater, and not distillery wastewaters in general. Further, the scum-layer accumulation appears to be linked to the solids content of the grain wastewater. Reducing the solids content by drum filtration, settling or blending can reduce, but not eliminate, the scum-layer accumulation.
- The bed profiles measured for the UASB system treating wine wastewater conform to those measured previously with apple juice wastewater (Sam-Soon et al., 1987), glucose (Sam-Soon et al., 1990), protein (Moosbrugger et al., 1990), brewery wastewater (Moosbrugger et al., 1993a) and wine distillery wastewater (Moosbrugger et al., 1993b). In these profiles the typical three distinct zones of behaviour can be identified, namely lower active, upper active and upper inactive zones. The action of micro-organisms in these zones conforms to the proposals of Sam-Soon and co-workers (Wentzel et al., 1994).
- For the UASB system treating grain wastewater, the bed profile differs markedly from that above, in that the three zones of behaviour do not develop. A proposed explanation for this is the high suspended solids content of the grain wastewater. The rate of acidogenesis with suspended solids as substrate, would be limited by the rate of hydrolysis. Typically, hydrolysis rates are much slower than acidogenesis rates with a soluble substrate. The net effect is to lower the overall rate of acidogenesis. With the lower acidogenic rates, the short-chain fatty acids would be consumed in subsequent reactions as they are produced, with the result that the short-chain fatty acid concentrations would remain low throughout the UASB system. Also, the low rate of acidogenesis implies that the rate of H_2 production is low so that a high pH_2 zone does not develop in the sludge bed.
- The absence of the three distinct zones of behaviour with grain wastewater as influent raises the question of the long-term viability of a UASB system treating this type of wastewater. In developing their hypothesis for pelletisation in UASB systems, Sam-Soon et al. (1987) proposed that partial phase separation of the anaerobic processes and development of a zone with a

high pH_2 are essential for pellet formation (Wentzel et al., 1994). In the UASB system treating grain wastewater, observations (no HAc and little HPr) indicate that these prerequisites for pellet formation were not achieved. If this is true, according to the hypothesis of Sam-Soon et al. (1987) pellet growth will not occur, or it will be reduced greatly. This indicates that, in the long term in switching from wine wastewater (where pellet growth has occurred) to grain wastewater, there will be a gradual loss of the pelletised sludge bed, until it declines to such low values that the system will fail. This aspect requires confirmation from a long-term investigation with grain wastewater.

- The investigation indicates that when switching from wine wastewater, where a well-defined pelletised sludge bed has been developed, to grain wastewater, the grain wastewater can be treated effectively in the short term. However, as noted above, it is most likely that the sludge bed will diminish with time. To re-establish the pelletised bed, the system will have to be switched back to wine wastewater for a period.

Acknowledgements

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