TREATMENT OF 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 sludge production was about 0.14 mgVSS/mgCOD removed (as against 0.42 mgVSS/mgCOD 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 distillery waste COD ranged from 20 000 to 30 000 mg/l. An appreciable amount of H$_2$CO$_3$*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 to an effective influent COD ($\text{COD}_e$) < 2000 mg/l, sufficient of the H$_2$CO$_3$*alkalinity generated internally was recycled to maintain a minimum sludge bed pH > 6.6. Recycle ratios as high as 33:1, reducing the base influent COD of 27 000 mg/l to a $\text{COD}_e$ 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 percent for COD loading rates up to the maximum of 15 kg/(m$^3$ sludge bed.d); the maximum COD loading rate was fixed by gas lifting pellets into the settling section, not by process failure.

KEYWORDS

UASB; pelletization; wine distillery waste; alkalinity requirements; pH control; recycling.

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 patterns along the line of flow of the reactor.

- Effects of recycling on (1) process performance, and (2) mass of H$_2$CO$_3$*alkalinity required to maintain a near neutral minimum pH in the sludge bed.
FEASIBILITY STUDY

Experimental set-up and operation

A laboratory-scale UASB reactor was constructed from a transparent perspex cylinder of 94 mm diameter, 1500 mm high, with a conically shaped inlet at the bottom and a solid/liquid/gas separator at the top, total reactor volume circa 10.5 l; gas collection was by means of a hollow inverted cone, see Fig 1. Twelve evenly paced 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.

Batches of influent feed stock of grape wine distillery waste were collected and stored at 4°C, COD ≤ 23 000 mg/l. The waste was settled and the supernatant only used as feed to the UASB reactor. Each day the feed was made up by suitable dilution to give the following: 5500 mgCOD/l, inorg-N 12 mgN/l, TKN 83 mgN/l, phosphorus 26 mgP/l; pH = 5.2. To avoid potential deficiencies in trace elements, 5 ml/l influent of a trace element solution (Zehnder and Wuhrmann, 1977) was added to the influent, see Moosbrugger et al. (1992b). To ensure sufficient pH buffer, the H2CO3*alkalinity requirement per influent COD was estimated assuming no alkalinity would be generated internally; a (mg H2CO3*alkalinity as CaCO3)/(mg base in influent COD) ratio of 1.2 was selected as recommended for pure carbohydrate substrate by Sam-Soon et al. (1991) (9.4 gNaHCO3 and 0.8 gNaOH per litre base influent); on addition to the waste flow the pH ≥ 7.0.

For the feasibility study the system was operated in flow-through fashion, i.e. no recycle was employed.

Parameters measured

Parameters measured on the system at 1 to 2-day intervals were: filtered influent and effluent COD, TKN and inorg-N; pH in settler and substrate flow rate. In addition, once steady state was established, two profiles of pH, COD, TKN, inorg-N, the short-chain fatty acids (SCFA) propionic, HPr, and acetic, HAc, were measured along the axis of the reactor. Samples were taken at each sample port, starting at the top, and filtered (Schleicher und Schuell 595 filter paper). Samples for HAc and HPr were re-filtered through 0.45 μm filter paper (Millipore) and measured by gas chromatography using a 60/80 Carbo pack C/0.3% Carbo wax packing. COD, TKN and inorg-N were measured in accordance with Standard Methods (1989). H2CO3*alkalinity in the reactor effluent was measured using the 5 pH point titration method (see Moosbrugger et al., 1992a).

Starting up procedure and process performance

Flow-through reactor was seeded with 4 l of pelleted sludge from a laboratory-scale UASB reactor treating glucose substrate, sludge bed volume was kept constant at 4 l by draining excess sludge from sample port 7. To adapt the seed sludge to the wine distillery waste, initially a mixture of glucose and wine distillery waste (50:50 by COD) was fed at a flow rate of 20 l/d and a COD of 5500 mg/l to give a COD loading rate of 27 kg/(m3 sludge bed.d). After 17 days the glucose/wine distillery waste mixture was changed to wine distillery waste only, with an unchanged COD concentration and loading rate; the system responded with a slight decline in performance but recovered rapidly, i.e. adapted completely within 10 d, see Fig 2. (When adapting a pellet bed to a new substrate a lower COD loading rate would be recommended).

Steady state system operation

Under steady state [27 kgCOD/(m3 sludge bed.d), 100 percent wine distillery waste], the following studies were undertaken on the flow-through system.

Termination of trace element addition: Addition of trace elements was terminated on day 35 to observe any adverse effects on the COD removal; percentage COD removal (Fig 2) did not show any change in trend — additional trace elements were not required.

Termination of nitrogen augmentation: Daily measurements of effluent TKN and inorg-N, about 90 and 75 mg/l respectively, indicated an over supply of nitrogen; addition of NH4Cl solution was
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 5500 mg/l; after 17 days the feed was changed to diluted grape wine distillery waste only (COD = 5500 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).
terminated on day 40 reducing the influent TKN to 83 mgN/l. Percentage COD removal continued to increase (see Fig 2) and effluent TKN reduced to 45 mg/l with effluent inorg-N = 30 mg/l – there still was an excess supply of nitrogen in the feed.

Alkalinity addition: With alkalinity augmentation (see earlier) and 100 percent wine distillery waste the min. bed pH ≈ 7.4, indicating an excess of H2CO3*alkalinity. Accordingly, from day 45 to 55, NaHCO3 addition was reduced from 9.4 to 2.0 g/l with NaOH constant at 0.8 g/l; this gave a min. bed pH of 6.6 (suggested as the lower limit by Sam-Soon et al., 1987). With this augmentation, the H2CO3*alkalinity supplied externally amounted to 2190 mg/l (as CaCO3). The H2CO3*alkalinity in the effluent was measured at 2560 mg/l (as CaCO3) indicating internal generation of H2CO3*alkalinity of 370 mg/l (as CaCO3). To take account of the internal generation of H2CO3*alkalinity, the proposal of Moosbrugger et al. (1992b), that the ratio effluent H2CO3*alkalinity/influent COD be used to assess alkalinity requirements, was applied. The ratio of effluent H2CO3*alkalinity/influent COD to maintain a min. bed pH of 6.6 therefore was 2560/5500 = 0.5, significantly lower than that found by Sam-Soon et al. (1991) for apple juice waste.

From day 55 to 74 the system was run under the reduced alkalinity augmentation [min. bed pH ≈ 6.6; COD loading rate 27 kg/(m3 sludge bed.d)]. On day 74 a set of profiles of pH, COD, HAc, HPr, TKN, inorg-N and org-N (profile set 1) was measured, Fig 3.

After day 74 the COD loading rate was increased from 27 to 41 kg/(m3 sludge bed.d) by maintaining the influent COD at 5500 mg/l but increasing the influent flow rate from 20 to 30 l/d; H2CO3*alkalinity supplementation was increased proportionally, from 2190 to 3980 mg/l influent as CaCO3, (5 gNaHCO3 and 0.8 gNaOH/l influent); effluent H2CO3*alkalinity was about 4400 mg/l as CaCO3 giving an effluent H2CO3*alkalinity/COD ratio of 4400/5500 = 0.8. The min. bed pH increased from 6.6 to 6.8. After sufficient time, to ensure steady state, a further set of profiles (profile set 2) was measured on day 95, see Fig 4. The following comments apply:

pH: pH profile 1 (see Fig 3) measured on day 74 and pH profile 2 (see 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 min. pH declined to as low as pH ≈ 6.6 indicating that the influent Alk/COD ratio of 0.5 was the lowest acceptable limit. In profile 2 the min. pH ≈ 6.8 indicating that the effluent Alk/COD ratio of 0.8 was sufficient to buffer the min. pH above the minimum value of 6.6. The decline in pH in the lower part of the sludge bed coincided with the increase in HAc and HPr.

COD profiles: COD profile 1 reached its minimum (≈ 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 indicating that the COD loading rate was approaching its maximum.

HAc: HAc profile 1 (Fig 3) and HAc profile 2 (Fig 4) reached their respective maxima of 680 and 1310 mg/l in the lower part of the sludge bed, and thereafter decreased to near zero in the upper part of the sludge bed. As with the COD the minimum HAc in profile 1 was attained well within the bed, whereas in profile 2 reached its minimum only near the top of the bed.

HPr: Similar to the HAc profiles, HPr profile 1 (Fig 3) and HPr profile 2 (Fig 4) reached their respective maxima of 530 and 1190 mg/l in the lower part of the sludge bed and thereafter decreased to near zero in the upper part of the bed. HPr accumulation occurs only in a high hydrogen partial pressure (pH2) environment, thus the observed rise in the HPr profile indicated a region where the prerequisite for pelletization (high pH2, Sam-Soon et al., 1987) was being satisfied.

TKN, inorg–N and org–N: The respective TKN, inorg–N and org–N profiles for days 74 and 95 (see Fig 3 and 4) exhibited similar patterns: The org–N profiles both showed a rapid decrease in the lower part of the sludge bed, due to deamination. In contrast, the inorg–N profiles increased in the lower part of the bed and stabilized to their maximum values in the upper part; this was contrary to the observations of Sam-Soon et al. (1987) who noted a marked decrease of inorg-N in the lower part of sludge bed. The increase now observed may be attributed to rapid rate of generation of inorg–N (due to deamination of org–N in the influent), more rapid than the rate of uptake of inorg–N due to pelletisation. The net uptake of nitrogen is demonstrated in the TKN profiles – a significant decrease of about 25 mgN/l (from 80 to 55 mgN/l) in both TKN profiles below sample port 3. In this part of the sludge bed on average about 3000 mgCOD/l were removed. Under 'normal' anaerobic fermentation conditions N requirements would be approximately 0.004 mgN/mgCOD for protoplasm synthesis, i.e. the expected TKN removal under 'normal' conditions below sample port 3, should have
Fig 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: 5500 mg/l, COD loading rate: 27 kgCOD/(m$^3$ sludge bed.d).

Fig 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: 5500 mg/l, COD loading rate: 41 kgCOD/(m$^3$ sludge bed.d).
been about 12 mgN/l. The observed N removal of 25 mgN/l (0.008 mgN/mgCOD) was about double that normally expected thereby supporting the hypothesis that excess nitrogen removal was due to pellet formation.

**Pellet growth**

Pellet generation takes place in the lower part (high pH$_2$ zone) and pellet break up in the upper part of the sludge bed (Sam-Soon et al., 1987). HPr profiles (Figs 3 and 4) indicated that the high pH$_2$ zone extended up to about sample port 3 (volume $\approx$ 1.1l). To measure pellet yield under high pH$_2$ conditions, every day the sludge bed was drained above sample port 3 and the mass of VSS produced measured together with the filtered and unfiltered influent and effluent COD. Specific pellet yield ($Y$) was calculated as:

$$Y = \frac{\text{mass of pelletised VSS generated/d}}{\text{mass of COD removed/d}}$$

(1)

Pellet yield, measured over the 20 day period, was 0.14 mgVSS/mgCOD, much lower than that reported by Sam-Soon et al. (1987), 0.42 mgVSS/mgCOD for apple juice waste. The most likely cause for the lower pellet yield is that the influent COD of the wine distillery waste contained a lower fraction of carbohydrates than the apple juice waste.

**Conclusions from the feasibility study**

The organic constitution of the grape wine distillery waste was not well defined and consequently no a priori guarantee could be given as to its suitability for treatment in a UASB system. However, by comparing the product formation profiles (particularly HPr) for the waste with those expected for a pure carbohydrate waste (Sam-Soon et al., 1987), from the similarity in response the presence of a high pH$_2$ zone could be inferred; its presence indicated suitability of grape wine distillery waste for treatment in a UASB system.

To maintain a min. bed pH $>$ 6.6 alkalinity had to be added to the influent. However, the requirements were considerably less than those found by Sam-Soon et al. (1987) when testing a pure carbohydrate waste. The reduced alkalinity requirement was due to the different nature of the substrate and the internal generation of alkalinity due to deamination and removal of organic weak acid/base salts (principally tartrates).

**RECYCLING, ALKALINITY AND pH**

To control the min. pH in plug-flow or semi plug-flow anaerobic systems such as anaerobic filters or UASB reactors, recycling of effluent to the influent stream has been suggested by a number of investigators (Capri, 1973; Cronje, 1973; Sam-Soon et al., 1991). Recycling of effluent has two major consequences: (1) the base influent COD concentration is diluted to an effective influent COD (COD$_{e}$) and, (2) the H$_2$CO$_3^{-}$alkalinity in the effluent augments the alkalinity in the influent. From experiments on apple juice waste, Sam-Soon et al. (1991) suggested that dilution of the base influent COD to a COD$_{e}$ of 1000 to 5000 mg/l enhanced system stability by avoiding undue concentrations of SOFA in the lower part of the sludge bed. Facilitating this dilution by recycling the effluent to the influent has the advantage also that alkalinity is recycled. Clearly, more detailed enquiry into the effect of recycling on process stability and alkalinity cum pH was merited. Accordingly, the following tasks were undertaken, studying:

- Effect of recycling on system performance.
- Self sufficiency in H$_2$CO$_3^{-}$alkalinity.
- Relationship between effective influent COD, effluent H$_2$CO$_3^{-}$alkalinity and min. pH.

**Effect of recycling on system performance**

The objective was to establish if recycling the effluent, i.e. diluting the base influent COD into the
COD range of 1000 – 5000 mg/l, would affect process performance provided the min. pH was maintained above 6.7. Experimental set-up remained the same as in the feasibility study except that a peristaltic recycle pump was added. COD loading rate of 15 kgCOD/(m3 sludge bed.d) was applied – about a third of that applied during the feasibility study and representative of practical operating conditions. With base influent COD 23 000 mg/l and recycle ratio 7:1, CODe = 23 000/(1+7) = 2880 mg/l. To ensure a near neutral min. pH in the bed, 1.5 gNaOH/(l base influent), i.e. 1875 mg/l as CaCO3, was added to the base influent. Over a 60 day period, the effluent COD decreased steadily from 1600 to 600 mg/l giving a 97 percent COD removal. Effluent SCFA remained low throughout, about 50 mg/l as HAc (the SCFA were measured together with the H2CO3*alkalinity by means of a 5 pH point titration method, see Moosbrugger et al., 1992a). Average TKN uptake was 209 mg/l giving a TKN/COD removal of 0.009 mgN/mgCOD removed – about double that reported for ‘normal’ anaerobic digestion indicating part of the TKN possibly was used for pelletisation (Sam-Soon et al., 1987). From pH profiles the min. bed pH was at sample port 2 as pH ≥ 6.9, increased to 7.0 at port 3 and remained virtually constant at ± 7.0 above port 3. The H2CO3*alkalinity measured in the effluent was 3400 mg/l as CaCO3 giving an effluent H2CO3*alkalinity/effective influent COD ratio of 3400/2880 = 1.2. Thus about (3400 – 1875) = 1525 mg H2CO3*alkalinity per litre base influent flow was generated.

**Self sufficiency in H2CO3*alkalinity**

From the above experiment evidently considerable H2CO3*alkalinity was generated in the sludge bed. It was of interest to investigate whether this generated alkalinity would be sufficient to operate the system without external alkalinity addition by increasing the recycle – at a reduced CODe less effluent H2CO3*alkalinity is required to maintain the effluent H2CO3*alkalinity/CODe ratio at 1.2. The experimental conditions remained the same as in the previous task, except that the base influent COD changed to 31 000 mg/l, the recycle ratio was changed from 7:1 to 18:1 to give a CODe of 31 000/(18 + 1) = 1630 mg/l and the COD loading rate was reduced to 9 kg/(m3 sludge bed.d) to enhance the likelihood of process stability at the increased recycle ratio. There was no external alkalinity supplementation. Effluent COD remained stable at about 1000 mg/l and effluent SCFA below 50 mg/l as HAc throughout the experiment, indicating stable operation. Gas production was 10 l/d with a CO2 fraction of 24 percent, i.e. 76 percent CH4. The min. bed pH stabilized at pH ≥ 7.2 and the effluent H2CO3*alkalinity at 3700 mg/l; this alkalinity was generated completely internally, giving effluent H2CO3*alkalinity/CODe = 2.3. This ratio was considerably higher than that in the task above and would be the main reason why the min. bed pH increased from 6.9 (in the previous task) to 7.2. From this task it was concluded that with an appropriated recycle ratio self sufficiency in H2CO3*alkalinity could be achieved.

**Relationship between CODe, effluent H2CO3*alkalinity and min. pH**

From the experiment above it became apparent that the min. bed pH depends on the effluent H2CO3*alkalinity/CODe ratio. This ratio can be changed by increasing/decreasing either the CODe or the effluent H2CO3*alkalinity. Both these options were investigated:

**Option 1: Change of CODe, i.e. change of recycle**

Experimental set-up remained the same as in the previous two tasks with the base influent COD 27 000 mg/l and COD loading rate 9 kg/(m3 sludge bed.d) and with no alkalinity supplementation. Experiment was started with a recycle ratio 33:1 (CODe = 790 mg/l), changed to 20:1 (CODe = 1290 mg/l) on day 20 and 7:1 (CODe = 3375 mg/l) on day 40 for a further 20 days. For all three recycle periods the effluent COD remained constant at about 1500 mg/l and the effluent SCFA below 50 mg/l indicating stable system performance. Effluent H2CO3*alkalinity remained virtually unchanged at about 3700 mg/l as CaCO3 (because its generation per litre of base influent would remain constant). Hence, any change in min. bed pH would be due to change of CODe. The min. bed pH decreased from 7.5 at the 33:1 recycle ratio, to 7.2 at the 20:1 recycle ratio, to 6.8 at the 7:1 recycle ratio. These observations merit two conclusions: At constant COD loading rate, base influent COD and effluent H2CO3*alkalinity, (1) the recycle ratio (or equivalently CODe) can be used as a means to change the min. bed pH and (2) a relatively large change in CODe is required to induce a significant change in min. bed pH.

**Option 2: Change in effluent H2CO3*alkalinity**

In this option experiments were performed at two fixed CODe by imposing two different recycle ratios of 22:1 (CODe = 1170 mg/l) and 12:1 (CODe = 2080 mg/l). For each recycle ratio a range of
Effluent $H_2CO_3^{*}$alkalinity values were examined. Experimental set-up, COD loading rate and base influent COD concentration remained the same as in option 1. The change in effluent $H_2CO_3^{*}$alkalinity was effected by addition of HCl to the base influent. For the period with a 22:1 recycle ratio ($COD_e = 1170\, mg/l$), (1) the min. bed pH remained within acceptable limits ($pH = 7.4$ to 6.8) even though the effluent $H_2CO_3^{*}$alkalinity changed from about 3500 to 1800 $mg/l$ as CaCO$_3$ and (2) to maintain a neutral min. bed pH, an effluent $H_2CO_3^{*}$alkalinity of 2200 $mg/l$ as CaCO$_3$ was required. For the period with a 12:1 recycle ratio ($COD_e = 2080\, mg/l$), (1) the min. bed pH remained within acceptable limits (7.2 to 6.8) even though the effluent $H_2CO_3^{*}$alkalinities changed from 3000 to 2000 $mg/l$ as CaCO$_3$, (2) to maintain a min. bed pH an effluent $H_2CO_3^{*}$alkalinity of 2800 $mg/l$ as CaCO$_3$ was required (Fig 5). Throughout the two recycle periods the effluent COD remained constant at about 1200 $mg/l$ and the effluent SCFA < 60 $mg/l$, i.e. system performance was not affected significantly by different recycle ratios (or $COD_e$) at low COD loading rate with pH > 6.7. This experiment indicates that at a fixed loading rate, with internal generation of $H_2CO_3^{*}$alkalinity the lower the $H_2CO_3^{*}$alkalinity generation per litre base influent COD the higher the recycle ratio needs to be to counteract a pH decline away from near neutral.

Fig 5: Relationship between effluent $H_2CO_3^{*}$alkalinity and minimum bed pH for laboratory UASB system treating undiluted grape wine distillery waste at 12:1 and 22:1 recycle ratio respectively: Base influent COD concentration: 27 000 $mg/l$, effective influent COD: 2080 and 1170 $mg/l$ respectively; COD loading rate: 9 kg/(m$^3$ sludge bed.d).
DISCUSSION AND CONCLUSIONS

1) 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 pelleted sludge bed. The pattern of product formation along the line of flow of the reactor was 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.

2) For unimpeded pelletisation when treating glucose in a UASB system Sam-Soon et al. (1990) suggested a TKN/COD ratio of 0.02 mgN/mgCOD. However, in this study the average mass of TKN uptake per mass of COD for grape wine distillery waste was 0.01 mgN/mgCOD. 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) does not induce high hydrogen partial pressure conditions and this would reduce biopolymer production and consequently reduce the TKN requirement. From the measured TKN uptake of about 0.01 mgN/mgCOD and the measured influent TKN/COD of 0.014 mgN/mgCOD, it would appear that most likely grape wine distillery wastes require no addition of nitrogen. Also, pellet production in the high hydrogen partial pressure region of the reactor was 0.14 mgVSS/(mgCOD removed). This pellet yield is significantly lower than that reported by Sam-Soon et al. (1987), 0.42 mgVSS/(mgCOD removed), when treating apple juicing wastes. This observation is in agreement with the reduced TKN uptake due to reduced pellet formation.

3) In the system with a recycle the pellets produced were smaller, less compact than with glucose 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.

4) Wine distillery waste generated significant internal buffer, i.e. H$_2$CO$_3$*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. The mass of H$_2$CO$_3$*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. The H$_2$CO$_3$*alkalinity generated was measured at about 0.1 mgH$_2$CO$_3$*alkalinity (as CaCO$_3$) per mg base influent COD. Imposing a recycle from the effluent to the influent, the H$_2$CO$_3$*alkalinity generated in the bed, 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 the COD$_e$ decreases, with the effluent (i.e. recycled) H$_2$CO$_3$*alkalinity remaining constant the H$_2$CO$_3$*alkalinity/COD$_e$ ratio increases causing the min. bed pH to increase.

5) 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.

6) The effect of different recycle ratios on the min. 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 a measured effluent H$_2$CO$_3$*alkalinity of about 3700 mg/l as CaCO$_3$. The min. bed pH was found to be relatively insensitive to changes in recycle ratio; to effect a significant change in min. pH the recycle ratio needed to be changed substantially, from 7:1 to 33:1 to change the min. bed pH from 6.8 to 7.5.

7) The effect of differences in effluent H$_2$CO$_3$*alkalinity on the min. bed pH was evaluated at a constant COD loading rate of 9 kg/(m$^3$ sludge bed.d) and constant base influent COD of 27 000 mg/l. At a recycle ratio of 22:1, when the effluent H$_2$CO$_3$*alkalinity changed from 3500 to 1800 mg/l as CaCO$_3$ the min. bed pH changed from 7.5 to 6.8; to maintain a pH = 7 the effluent H$_2$CO$_3$*alkalinity required was about 2200 mg/l as CaCO$_3$. At a lower recycle ratio of 12:1 with the effluent H$_2$CO$_3$*alkalinity changing from 3000 to 2200 mg/l as CaCO$_3$ the min. bed pH changed from 7.2 to 6.8; to maintain a pH = 7 the effluent H$_2$CO$_3$*alkalinity required was about 2800 mg/l as CaCO$_3$. Consequently if the internally generated H$_2$CO$_3$*alkalinity decreases (with the base influent COD remaining constant), the recycle ratio must be increased to maintain the same near neutral min. bed pH.

8) The pH profiles in the bed exhibited only a slight depression (to the min. pH) for recycle ratios of
33:1 and 20:1 (base influent COD of 27 000 mg/l and CODₐ concentrations of 790 and 1290 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).

(9) From the experiments on recycling it appears that with grape wine distillery waste the base influent COD (20 000 to 30 000 mg/l) should be diluted by the recycle to a CODₐ of about 1500 to 2000 mg/l to give stable operating conditions. Within this range, for a COD loading rate of about 10 kg/(m² sludge bed.d) grape wine distillery wastes should generate sufficient internal H₂CO₃*alkalinity to maintain a near neutral min sludge bed pH.

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