Anaerobic treatment of vinasses by a sequentially mixed moving bed biofilm reactor

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Abstract Wine distillery wastewater, commonly called vinasses, was treated by an anaerobic moving bed biofilm reactor (AMBBR) with 32.9 litre available volume. The reactor was filled with 66% cylindrical polyethylene supports with density 0.84 g cm^{-3} as a biofilm carrier. The reactor was sequentially mixed by a submerged centrifugal pump fixed to the bottom, and each mixing time just lasted 1.25 minutes. The organic loading rate (OLR) of the reactor were increased from 1.6 to 29.6 g sCOD l^{-1} d^{-1} (soluble chemical oxygen demands – sCOD) and hydraulic retention time (HRT) was decreased from 6.33 to 1.55 days accordingly. Soluble COD removal efficiency was 81.3–89.2% at an OLR of 29.6 g sCOD $l^{-1}d^{-1}$. At the end of the experiment, 83.4% total biomass was attached on support and the specific density of support in the reactor was 0.93–1.05 g cm^{-3}, which increased by about 10.7–25% compared with that at the beginning of the study.
Keywords Anaerobic moving bed biofilm reactor; anaerobic treatment sequential mixing; vinasses

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Introduction

Anaerobic digestion has been proved a successful technology to treat high strength organic wastewater. Technologies such as anaerobic SBR (Ruiz *et al.*, 2002), anaerobic fluidized-bed reactor (Durán and Cabrero, 1991; Pérez *et al.*, 1999), anaerobic inverse fluidized bed (García-Bernet *et al.*, 1998; García-Calderon *et al.*, 1998) and upflow anaerobic sludge blanket (UASB) (Goodwin and Stuart, 1994; Espinosa *et al.*, 1995; Wolmarans and de Villiers, 2002) has been showed to perform well when used to treat wine vinasses, sugar beet, sugar cane and whisky distillery wastewaters. Anaerobic fluidised bed reactors uses small fluidised particles to induce the cell immobilisation. UASB performance is mainly determined by the formation and activity of the granule sludge.

Moving bed biofilm reactor (MBBR) is a well-known technology in aerobic treatment. In this reactor, the biofilm grows on mobile support and the agitation could be done by aeration or by mechanical steering. It incorporates the advantages of biofilm technology, and it is a compact reactor. The reactor is filled with the especially designed plastic media which provides the large specific surface area for bacteria to grow. The density of the media with biofilm should be similar to the density of water (density of one) in order to spend less energy for agitation. The MBBR process has been used to treat municipal and industrial wastewaters for COD removal and nitrification and denitrification (Ødegaard *et al.*, 1994).

A few anaerobic moving bed biofilm reactors (AMBBRs) have been used as pre-treatment of paper-making wastewater (Jahren and Ødegaard, 1999) and high strength cane vinasses (Jahren and Ødegaard, 2000). The anaerobic digestion processes produce biogas which can be use as micro-mixing of the wastewater in the digester.

In this study, we have tested the feasibility using the sequentially-mixed anaerobic AMBBR to treat vinasses, with sequencing mechanical agitation for macro-mixing.

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Materials and methods

Digester

The reactor was made of a Plexiglass cylinder (23.8 cm diameter and 89 cm height), with a working volume of 32.9 litres (Figure 1). The reactor was filled with 66% cylindrical polyethylene supports 'Bioflow 9'® from Raushert (diameter 9 mm, height 7 mm and real density 0.84 g cm^{-3}) as biofilm carrier. The available specific biofilm surface area of the carrier was about 528 m^2 m^{-3} before biofilm formation.

The sequential mixing of the reactor was carried out by a submerged Superma centrifugal pump fixed on the bottom of the reactor. The mixing times was set to 2–8 times per hour (accordingly increased with organic loading rate in the experiment), and the duration of each mixing time only lasted for 1.25 minutes. This duration was able to move all the media in the reactor.

The reactor was fed with Masterflex Cole-Parmer peristaltic pump, and the feeding tank was mixed with a mechanical stirrer. Hydraulic retention time was adjusted through controlling the flow rate of the feeding of influent.

A simple water displacement gas meter was used to measure the produced biogas volume, where a counter registered a unit after a certain volume of the solution containing Na_2SO_4 and H_2SO_4 was displaced (Moletta and Albagnac, 1982).

Wastewater and seed sludge

Two kinds of raw wine vinasses from 100 m^3 storage tanks were used as wastewater to feed the reactor. The characteristics of the vinasses were presented in Table 1.

Low strength vinasses with an average COD concentration of 16.19 $g\,l^{-1}$ was fed the reactor from day 1 to 49, and high strength vinasses with an average concentration of 45.5 $g\,l^{-1}$ COD was diluted before feeding from day 50 to 116 and day 154 to 187. Undiluted high strength vinasses was then fed the reactor. Trace elements Fe, Ni, Co were only continuously added from day 178 to 181 to accelerate the performance of the reactor in the forms of $FeCl_2{\cdot}4H_2O$, $NiCl_2{\cdot}6H_2O$ and $CoCl_2{\cdot}6H_2O$, and their concentrations were 50 $mg\,l^{-1}$, 10 $mg\,l^{-1}$ and 10 $mg\,l^{-1}$, respectively in the influent.

The pH of influent was adjusted to over 6.7, mostly over 7.0, with 20% NaOH solution before day 178. Thereafter, the influent pH adjustment was also made before feeding, but the influent pH was below 6.7 and ranged from 4.03 to 5.75 after day 195.

Seed sludge of the reactor came from the anaerobic sludge tank of another reactor to treat the same kind of vinasses. SS, VSS and VSS/SS ratio of the sludge were 36.8 $g\,l^{-1}$,

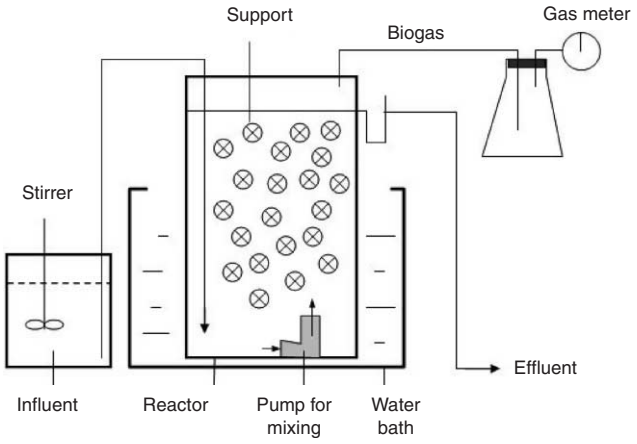

Figure 1 Set up of sequentially-mixed anaerobic moving bed reactor to treat vinasses

Table 1 Composition of raw vinasses used in this study.

Raw vinasses	Total COD ($g\,l^{-1}$)	sCOD ($g\,l^{-1}$)	VFA (g-COD l^{-1})	SS ($g\,l^{-1}$)	VSS ($g\,l^{-1}$)	pH
Low strength	16.19	15.14	10.95	2.06	1.13	5.7
High strength	45.55	44.18	9.7	3.27	2.46	3.6

$20.36\,g\,l^{-1}$ and 0.5, respectively. In this study we focus on soluble COD because generally after anaerobic digestion we have an aerobic post treatment which is able to catch the suspended matter.

Biomass in the AMBBR

The support with biomass was dried at 110 °C for 2 hours and weighed at room temperature, and it was determined as attached solids (AS) per square meter surface area of support. The attached biomass was removed mechanically from support and calcined at 500 °C for 2 hours and weighed at room temperature again. The volatile attached solids (VAS) per square meter surface area of support could then be determined. The organic fraction of the attached biomass was expressed as a ratio of VAS to AS.

The density of supports at the final day of the study was determined by the average dried weight of 400 supports with biomass and average discharged water volume of their equivalents.

Analytical methods

Samples were centrifuged at 13,000 rpm for 10 minutes, the supernatant was used for analysing sCOD and volatile fatty acid concentrations (VFA), and the solid matter for SS and VSS determination.

sCOD was analysed with Merck COD Cell Tests, which was digested in a Hach COD Reactor Model 45600-02 (150 °C for 2 hours), and with a Hach DR/2010 spectrophotometer.

VFA was determined by gas chromatography (GC 8100 Fisons Instruments) with a flame ionisation detector (FID), coupled with an automatic sampler (AS 800 Fisons Instruments). Both were coupled to a PC with a Chrom-Card software. The analysis conditions: silica capillary column type EC™-1000 (Alltech; length 15 m, internal diameter 0.53 mm, film thickness 1.2 μm; injector temperature 250 °C, detector temperature 275 °C; N_2 pressure (25 kPa), H_2 flow rate (50 kPa, 30 ml min^{-1}) and air (100 kPa, 300 ml min^{-1}) as carrier gas. The oven temperature program: 80 °C to 120 °C (increase temperature: 10 °C min^{-1}), duration of 10 minutes.

Biogas composition CH_4, N_2, O_2, CO_2 were analysed with 1 ml sample immediately after sampling using Shimadzu GC-8A gas chromatographer with catharometer, coupled with a Shimadzu CR-3A integrator. The chromatographer was equipped with two stainless steel columns: the Hayesep column for separation of CO_2 (2 m length and 3.175 mm diameter), packed with Silica gel (80–100 mesh), and another one for CO_2, N_2, O_2, H_2 separation, packed with molecular sieve 5 Å (80–100 mesh, 2 m length and 3.175 mm diameter). Carrier gas was argon (300 kPa). Oven, detector and injection temperature were 30 °C, 100 °C, and 100 °C, respectively.

SS and VSS were determined based on the methods according to Standard Methods (1995).

Total alkalinity of influent and effluent was determined by titrating 20 ml of sample with 0.1 M HCl until the pH was 4.0.

Results and discussion

sCOD removal efficiency

The reactor was directly started after inoculating of 15 litre anaerobic sludge from other reactors to treat same kind of vinasses. After 116 days of operation, the reactor was stopped and cooled down to room temperature for about 36 days (holiday shut down), and it was restarted again from day 154 and operated until day 232. The variations of OLR and HRT and sCOD removal efficiency with the operation time were shown in Figure 2.

The reactor adapted rapidly to the feed of diluted and undiluted low strength vinasses at the initial start-up period of 49 days. sCOD removal efficiency was high at this period and up to 68.1–91.7% at OLR of 1.37–4.62 g sCOD l^{-1} d^{-1} and HRT of 2.86–6.33 days. With the reactor being fed with diluted high strength vinasses from day 50 to day 115 and OLR being slightly increased (varying 4.8–8 g sCOD l^{-1} d^{-1}), sCOD removal efficiency became low (down to 39.6–63.8% at HRT of 2.97–4.48 days). The low sCOD removal yield mainly caused by accumulation of VFA, especially propionate, in the reactor and too much suspended biomass was washed out the reactor by shortening the HRT to increase the OLR.

After restarting from day 154, the reactor was fed with diluted (until day 187) and undiluted high strength vinasses to the end of experiment. At the beginning of 17 days, sCOD removal yield was low and only 37.7–61.1% even though OLR was only 3.24–4.87 g sCOD l^{-1} d^{-1}. The situation was dramatically changed by supplementation of trace elements added from day 178 to day 181 (within three days). In Figure 3, the arrow shows the *q* starting time of mineral addition. sCOD removal yield was increased although OLR was quickly enhanced. At day 195, sCOD removal yield was up to the maximum (92.9%) at OLR of 13.33 g sCOD l^{-1} d^{-1} and with HRT of 3.3 days, and sCOD removal efficiency was 81.3–89.2% with OLR of 29.59 g sCOD l^{-1} d^{-1} and HRT of 1.55 days from day 224 to 232.

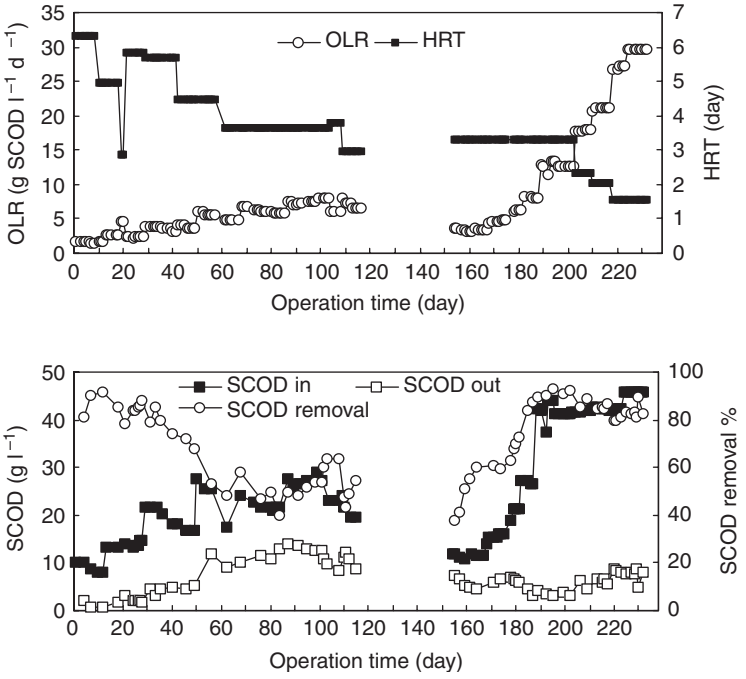

Figure 2 Variation of sCODin and sCODout, sCOD removal yield, OLR and HRT with time

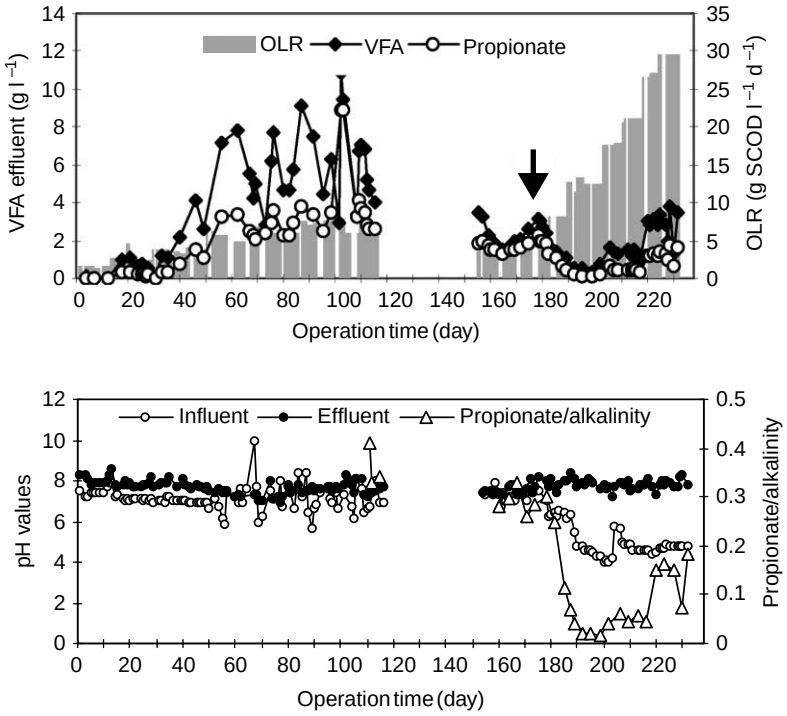

Figure 3 Variation of VFA, propionate concentration (in the effluent), OLR, pH values in and out, and propionate:alkalinity ratio with time

Effluent VFA and pH value

Effluent VFA, especially propionate, level and effluent pH are the main parameters to affect the performance of the rector. The high VFA especially propionate levels in effluent and low effluent pH indicates poor treatment ability for the reactor. Effluent VFA and propionate levels, influent and effluent pHs are presented in Figure 3.

Bad performance of the reactor was commonly accomplished by VFA accumulation, which was caused by overloading the reactor and/or influent pH fluctuation, but the degradation of VFA can be quickly promoted with running conditions of the reactor, such as to supplement a small amount of trace elements as we done here.

Propionate/alkalinity ratio is expressed as g/l of propionic acid on g/l of $CaCO_3$. The arrow show the three-day's mineral addition

From Figure 3, it can concluded that before the well-buffer pH system inside the reactor was established, the influent pH would be normally controlled over 6.7. After the well-buffer pH system inside the reactor was formed, the performance was still excellent even if influent pH was acidic. From day 190 to 232, the reactor was operated under conditions of influent pH being 4.03–5.75, but effluent pH was still over 7.2. This is very important from practical sense, and which can save the cost caused by neutralizing the acidic influent with NaOH or other bases.

The alkalinity of effluent was monitored from day 111. The ratio of alkalinity and propionate level can be used to indicate whether the well-buffering system is developed or not.

Beginning from day 181 the differences between effluent pH and influent pH widened, and the ratio of propionate to alkalinity was less than 0.25 at the same time, which implied that the well-buffered system had been developed in the reactor.

Biogas and its composition

Biogas production can be used as a daily indicator of the reactor performance, and it was changed with the operation conditions such as OLR, sCOD removal yield, temperature and other factors. The daily biogas production and biogas composition are seen in Figure 4. In this study it has been found that biogas composition was, of course, largely correlated with OLR.

CH_4 ranged from 45.51 to 82.18%, and CO_2 from 11.70–52.63%. High OLR and low effluent pH will make low CH_4 in biogas.

Biomass accumulation

The attached biomass was clearly increased with OLR and with time. We did not reach stability content of biomass where the equal amount of biomass produced is leaving the digestor by biofilm detachment (Figure 5). Within 116 days from the starting of the study the amounts of attached biomass were less than 200 g/m^2 of support, but with OLR increasing the qualities of the attached support was gradually increased, and on day 232 the attached biomass was up to 900 g/m^2 of support. The attached biomass accounted for about 83.4% of total biomass in the reactor.

The density of support on day 232 was 0.93–1.05 g cm^{-3}, which was increased by 10.7–25% compared with that of the support without biomass. Nearly 10–15% support was still floated in the upper part of the reactor, and the left was in the middle and the lower part of the reactor.

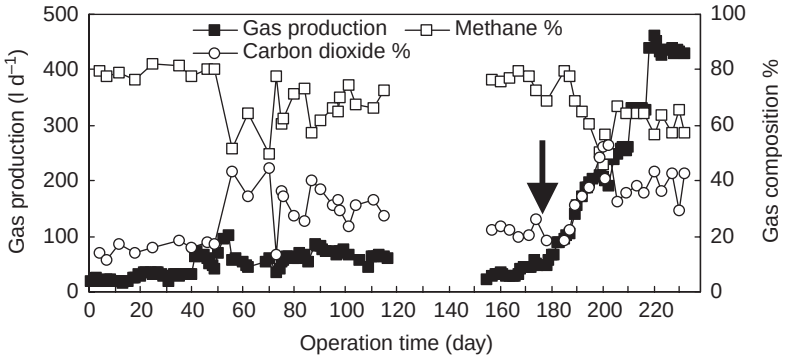

Figure 4 Biogas production and gas composition with time (arrow shows the addition of micro-nutriment)

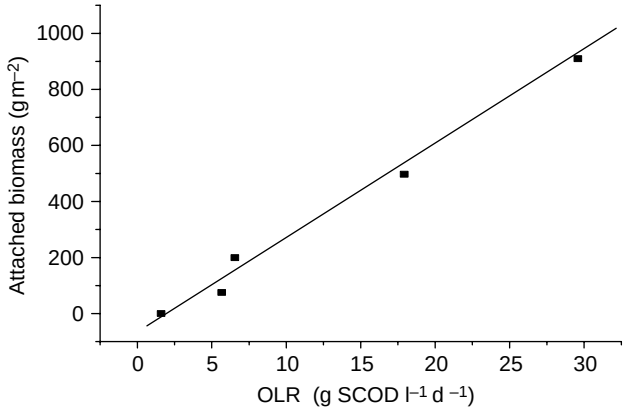

Figure 5 The amounts of attached biomass against OLR

Conclusion

The results of this study showed that using a sequentially-mixed anaerobic moving bed biofilm reactor to treat vinasses could give very interesting results. This digester is very rustic and very easily managed. This reactor can completely act as a MRRB if mixed (macro-mixing with mechanical agitation) and employed as a fixed bed reactor (micro-mixing with agitation by produced biogas). The support in the reactor cannot only hold biomass on it and prevent suspended biomass to move out of the reactor to some extent, which can apparently enhance the amounts of biomass in the reactor. The reactor may be a simple one when compared to UASB, SBR, and so on. At nearly the end of this experiment sCOD removal efficiency was still up to 81.3–89.2% at OLR of 29.59 g sCOD $l^{-1} d^{-1}$ and HRT of 1.55 days. This technology could be an important technology for developed and developing countries!

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References

Durán, C. and Cabrero, M.A. (1991). Vinasses biological treatment by anaerobic and aerobic processes: laboratory and pilot-plant tests. *Bioresource Technol.*, **35**, 87–93.

Espinosa, A., Rosas, L., Ilangovan, K. and Noyola, A. (1995). Effect of trace metals on the anaerobic degradation of volatile fatty acids in molasses stillage. *Water Sci. Technol.*, **32**(12), 121–129.

García-Bernet, D., Buffière, P., Elmaleh, S. and Moletta, R. (1998). Application of the down-flow fluidized bed to the anaerobic treatment of wine distillery wastewater. *Water Sci. Technol.*, **38**(8–9), 393–399.

García-Calderon, D., Buffière, P., Moletta, R. and Elmaleh, S. (1998). Anaerobic digestion of wine distillery wastewater in down-flow fluidized bed. *Water Res.*, **32**(12), 3593–3600.

Goodwin, J.A.S. and Stuart, J.B. (1994). Anaerobic digestion of malt whisky distillery potale using upflow anaerobic sludge blanket reactors. *Bioresource Technol.*, **49**, 75–81.

Jahren, S.J. and Ødegaard, H. (1999). Treatment of thermo-mechanical pulping (TMP) white water in thermophilic (55 °C) anaerobic-aerobic moving bed biofilm reactors. *Water Sci. Technol.*, **40**(8), 81–89.

Jahren, S.J. and Ødegaard, H. (2000). Treatment of high strength wastewater in thermophilic anaerobic-aerobic moving bed biofilm reactor. *Environ. Technol.*, **21**, 1343–1356.

Moletta, R. and Albagnac, G. (1982). A gas meter for low rates of gas flow: application to the methane production. *Biotechnol. Lett.*, **4**(5), 319–322.

Ødegaard, H., Rusten, B. and Westrum, T. (1994). A new moving bed reactor-applications and results. *Water Sci. Technol.*, **29**(10–11), 157–165.

Pérez, M., Romero, L.I. and Sales, D. (1999). Anaerobic thermophilic fluidized bed treatment of industrial wastewater: effects of F:M relationship. *Chemosphere*, **38**(14), 3443–3461.

Ruiz, C., Torrijos, M., Sousbie, P., Lebrato Martinez, J., Moletta, R. and Delgenes, J.P. (2002). Treatment of winery wastewater by an anaerobic sequencing batch reactor. *Water Sci. Technol.*, **45**(10), 219–224.

Standard Methods for the Examination of Water and Wastewater (1995). 19th edn, American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC.

Wolmarans, B.H. and de Villiers, G. (2002). Start-up of a UASB effluent treatment plant on distillery wastewater. *Water SA.*, **28**(1), 63–68.