Monitoring anaerobic digestion: a 2-year brewery case study

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Operational data from an anaerobic wastewater treatment plant (expanded granular sludge bed (EGSB) reactor) were analysed before and after a defect with the solids separator. The results presented suggest that a newly available method for the analysis of total volatile fatty acids (VFAs) was ideal as a rapid, onsite, operational indicator of reactor stability. These total VFAs were shown to provide an earlier warning of the separator problem than the other rapid routine methods of monitoring digesters such as alkalinity and suspended solids. Chemical oxygen demand (COD) removal, pH and gas yield were not as useful for monitoring because of their slow response. The results are from a high rate reactor; the loads were 18 kg COD/m^3/d in the first year and 26 in the second with 4·4 d hydraulic retention time. The results for both years of operation demonstrate a 95% conversion of COD into gas with an additional contribution from solids digestion (specific gas yield of 0·4 l methane (CH_4)/g COD_{rem}). This high performance was attributed to the solubility of the COD and the efficient EGSB mixing.

Introduction

The treatment of brewery wastewater is the most common application of high-rate anaerobic digestion (AD) of wastewaters. Because of the large volumes and strengths of brewery wastewater effluent and also their high biodegradability, regulatory authorities often insist on treatment before discharge to sewer to avoid overloading the sewer and treatment system. Specific water consumption of breweries ranges from 4 to 11 l water per litre of beer, with two thirds of the water being used for production and one third for cleaning processes (Fillaudeau *et al.*, 2006). A review of brewery wastewater literature gave a chemical oxygen demand (COD) range of between 1200 and 125 000 mg/l COD (Baloch *et al.*, 2007; Leal *et al.*, 1998). The wide range of COD values is due to the batch production, seasonality and variety of process streams included such as brewing, malting, spent grains and other wash waters (Kato *et al.*, 1999). The effluent usually has a

high biological oxygen demand (BOD)-to-COD ratio or a high biodegradability, as a result of the dissolved carbohydrates and alcohol. Less attention has been paid to the suspended solids (SS) and values between 1550 and 1750 mg/l (Baloch *et al.*, 2007) are reported. Comparisons are made difficult since the SS are variously expressed as total, settleable and suspended, sometimes corrected for volatile solids.

For this type of medium- to high-strength food and drinks wastewater, traditional aerobic treatment has become expensive as a result of power for aeration and the high sludge yields (Parawira *et al.*, 2005). Thus, anaerobic treatment with lower running costs and added value from financial support mechanisms for renewable energies has become more attractive. These incentives have overcome the higher investment costs, lack of experience and reputation for instability (Franklin 2001; Lettinga, 1995; Parawira

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et al., 2005). The solubility and resulting high biodegradability, together with the large variations in waste characteristics, present risks to the stability of the slower anaerobic process (Cronin and Lo, 1998; Leal *et al.*, 1998). A recent survey of operating AD plants in the EU noted that excess acidity from shock loads was the most common cause of stability problems (Chen *et al.*, 2008).

The anaerobic digester in the study was the widely used and studied expanded granular sludge bed (EGSB) (Ahn *et al.*, 2001; Alphenaar *et al.*, 1993; Franklin, 2001; Gonzalez *et al.*, 1998; Goodwin *et al.*, 2001; Fuentes *et al.*, 2011). The EGSB process relies on a rapidly settling (Lettinga *et al.*, 1983), granulated biomass to uncouple solids retention from hydraulic flow. Zoutberg and de Been (1997), for example, reported liquid velocities of 15 m/h were achievable with granular biomass, compared with 1 m/h for flocculated biomass and internal solids/liquid separation is normal with these types of bioreactors (Figure 1). Biomass expansion by both gas and hydraulic forces improves mass transfer as in fluidised bed bioreactors and so increases reactor efficiency (Franklin, 2001). However, this process flushes out fine solids otherwise retained, potentially limiting their performance if the effluent contains fine solids, as in this case study (yeast), or if the granules are unstable. Therefore, performance monitoring remains a crucial part of judging the stability of these reactors.

In this paper, we report on these variations and potential monitoring strategies from 2 years of operational performance from the anaerobic treatment of a brewery type waste before and after failure of the internal separator.

Materials and methods

The Marmite AD plant was commissioned in 2008; it is part of a three-stage sequential process, as shown in Figure 1.

Process wastewater drains from various parts of the factory by gravity to two subterranean collection tanks (total capacity, 50 m^3) via a simple 10-mm inclined screen to intercept packaging and/or other debris. Effluent is then pumped to the 400-m^3 buffering tank (Figure 1). Typically, the buffering tank will run half full to ensure mixing of different strengths and compositions and avoid shocks to the AD culture. Further buffering is provided by the conditioning tank (Figure 1), which recycles treated effluent to buffer and dilutes the feed. It has a volume of 28 m^3 and a recycle rate of 200 m^3/h 10:1 recycle to feed. Acid, alkali and steam can be introduced into this tank to maintain temperature (35°C) and pH (7) if necessary.

The anaerobic reactor is a 900-m^3 EGSB BioThane design that includes a three-phase separator (biogas, liquid and solids) to help with granule retention (Latif *et al.*, 2011).

The height of the sludge bed can be measured with sampling taps and typically occupies two thirds of the reactor (Figure 1). Gas generated from the EGSB is used in the factory boilers or flared when in excess. The boiler biogas is cooled (refrigerated heat
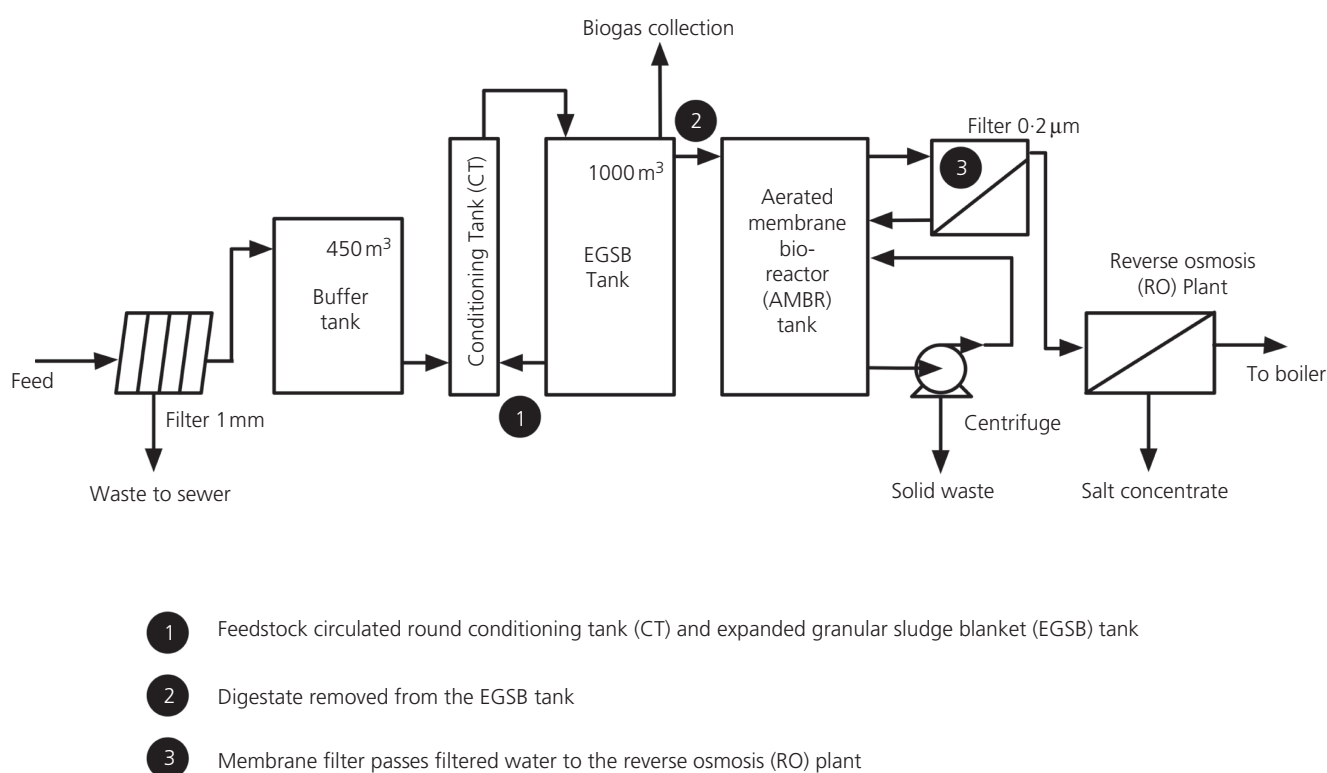

Figure 1. Wastewater treatment plant of Marmite Unilever

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exchanger) to remove water vapour and then wet scrubbed with sodium hydroxide in a counter current stripping tower to remove sulphides. The gas is then pressurised and fed into one of the existing boilers (modified with ceramic burners).

The aerobic reactor (stage 2) is a membrane bioreactor (MBR) designed by Aquabio. It uses an external cross flow hollow fibre membrane pore size $0·2\,\mu m$. Mixed liquor is recirculated via the membranes and reinjected into the MBR tank via a Venturi where the compressed air is injected (Figure 1). The excess biosolids from the membranes are concentrated by centrifuge and reused in agriculture.

MBR-treated effluent can then be further purified by reverse osmosis. This system produces ultra-pure boiler feed water for cleaning but is not used in food production.

Monitoring

The wastewater treatment includes automatic adjustment of pH and temperature, although the warm effluent and recirculation minimises these interventions. Manual adjustments in special circumstances are occasionally needed, for example, high buffer tank levels, but more routinely to avoid overload. This has been monitored routinely two to four times a day by a loss in alkalinity (Ripley's ratio, referred to as intermediate to partial alkalinity in the standard methods). Total and filtered COD, SS, Ripley's ratio and volatile fatty acids (VFAs) are analysed daily. Flow rate, pH, and biogas flow are recorded continuously. The biomass level in the reactor is checked weekly, while biomass total and volatile solids (TS and VS) and biogas composition are checked monthly.

The wet analysis was carried out in accordance with the international standard methods in this case to APHA (2005) using Hach pre-prepared reagents. VFAs are common stability indicators because they are metabolic intermediates, and if the methanogenesis is failing to cope with the fluctuations in load, they rapidly accumulate, suppressing methane production even when not detectable from a pH change (Baloch et al., 2007). Gas chromatography or distillation is the standard method of determination of VFAs (APHA, 2005) but is too time consuming for practical monitoring of the potential harm caused by the daily fluctuations in organic load when operating at low hydraulic retention time (HRT). Chromatography also gives quantitative data on the individual VFA that enables research on the causes of upsets other than overloading. Total or partial alkalinity is a low-cost, operational alternative. In this case, the Ripley ratio was used to represent the amount of VFAs to alkalinity. It can be carried out more quickly and with simple equipment compared with other alkalinity measures. A ratio below $0·3$ is considered an acceptable value, but for an AD plant that is monitored daily, an indicator value of up to $0·5$ can be used to signal action that needs to be taken to address the problem.

A simple colorimetry-based VFA test kit became available during the commissioning of the plant; this was the Hach LCK 365 method. It is based on forming iron-coloured esters and takes about 15 min, thus simplifying the VFA analysis and making it cost-effective. This made it possible to compare the performance of Ripley's ratio with VFA content for the daily operational control of the loading rate.

Results and discussion

Towards the end of the first year (day 275), an increase in VFA was noticed, with a smaller increase in Ripley's ratio and some solids loses (Figure 2). The opportunity was taken during the annual shut down of the factory for inspection of the EGSB, at 340 d, which revealed damage to the gas liquid separator. This necessitated a further planned shutdown (days 400–450) for repairs.

Both VFA and Ripley's ratio were sensitive to these problems and demonstrate the differences in stability between year 1 and 2 (Figure 2). Figure 2 suggests that the VFA gave earlier warning than Ripley's of the problem and that it was more pronounced. During the first year of operation, the average Ripley's ratio of the reactor was $0·4$ (Table 1, range $0·2–1·04$); corresponding VFA values were in the range 52–2488 ppm (January–December) suggesting greater sensitivity than Ripley's (Table 1). During the period before the shutdown, VFA exceeded 1000 ppm several times, but the reactor pH did not drop below 7. Thus, it was concluded, as it has been previously, that pH values are not a suitable indicator for controlling these high-rate digesters. Lower biogas production and COD removal was not apparent until day 395 when Ripley's ratio was $1·88$.

Following the restart, the digester Ripley's ratio for year 2 had an average value of $0·29$, while VFAs were below 100 mg/l (Table 1), indicating greater reactor stability. The data in Figure 2 also led to the conclusion that total VFAs, when easy to carry out, would be an earlier indicator of reactor instability than alkalinity. We expect this based on Ripley's being a ratio of alkalinity and VFAs. A VFA increase before Ripley's ratio would be anticipated in situations where there is high alkalinity, which also increases with load to dampen the response, for example, animal slurry and sewage sludge. Goodwin et al. (2001) have reported operating data from a stressed upflow anaerobic sludge blanket (UASB) reactor when treating whisky distillery pot ale. A simultaneous increase in COD and reduction in HRT led to VFA concentrations of nearly 20 g/l and decreased biogas production, while pH levels stayed above 7 despite the almost complete reactor failure. Bocher et al. (2008) also reported that a shock increase in loading rate and decrease in HRT caused an increase in VFAs, leading to instability of the reactor. Bocher et al. (2008) also noted foam formation, which caused biomass losses and decreased activity. Both these papers imply that insufficient mixing was the possible cause of failure in their UASB. In the case of the EGSB expanded by recycling, we expect mixing to be thorough, although solids losses as a result of gas surges are a possibility. Prior to the repairs to the gas liquid separator, total suspended solids (TSS) removal was 20% and variable although HRT was constant (Figure 2). Following the repairs, overall TSS removal efficiency was still low at ~30%, and as previously noted, EGSB reactors would not be expected to retain fine solids because of vigorous mixing (Zoutberg and de Been,
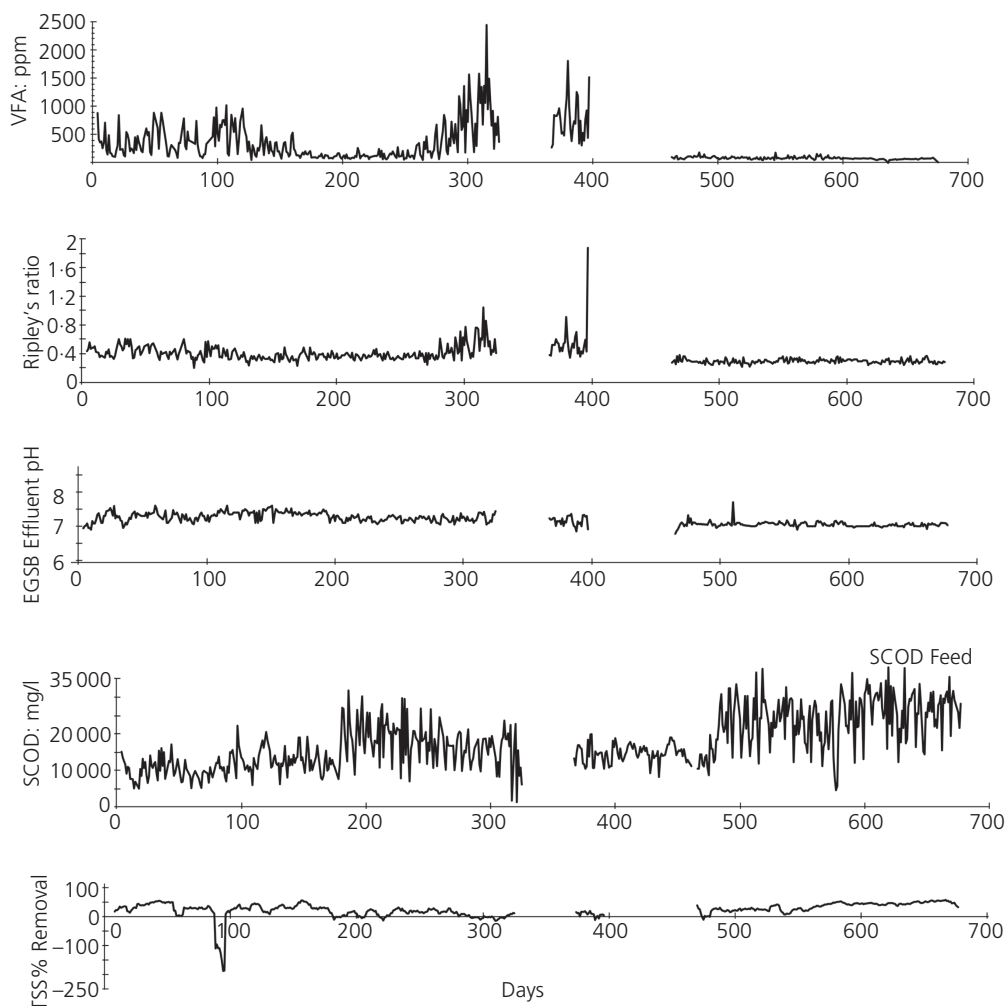
Figure 2. Overview of ESGB performance for time period of study

1997). There are limited operational publications on solids retention or liquid and gas velocities but Parawira *et al.* (2005) reported total solids removal of below 40% for their UASB reactor, which was improved to 60% to 80% by the introduction of a 0·5-mm screen. Mixing in UASB compared with EGSB reactors, on the other hand, is lower and generates better solids retention. Cronin and Lo (1998) noted VSS reduction of 81%; Parawira *et al.* (2005), 90% for settleable solids; and Bocher *et al.* (2008), 43% but as VS rather than SS removal efficiency. Lettinga (1995), Franklin (2001) and Bocher *et al.* (2008) have suggested that good mixing between substrate and biomass in EGSB reactors is the reason for their good performance, and effluent COD values less than 1 g/l are normal. Cronin and Lo (1998) and Borja *et al.* (1994) found increasing the organic loading rate (OLR) by reducing the HRT from 10 to 1·2 d only reduced COD removal from 98·5% (HRT of 10 d) to 95·4% (HRT of 1·2 d). HRT in this EGSB study was fixed by the recycle loop to 4·4 d equivalent with an upflow liquid velocity of 3·7 m/h. Average gas velocities were 1·2 m/h in year 1 and 1·8 m/h in year 2. Actual mixing velocities and granule losses

are less well reported. Calculations of velocities through the separator passages could also be a useful indicator of the potential for solids losses (Fuentes *et al.*, 2011), but we also note from Figure 2 that although SS (TSS) balance could be a better stability indicator than pH, COD removal or gas production, it was not very sensitive compared with alkalinity of VFA.

The variability in feed COD meant that deterioration in COD conversion to gas was difficult to spot. The range of TCOD of the buffered wastewater was between 5500 and 41 400 mg/l, in the range previously reported (Baloch *et al.*, 2007; Parawira *et al.*, 2005) and gave typical EGSB OLR, which are between 10 and 30 kg COD/m^3/d (Baloch *et al.*, 2007; Franklin, 2001; Kato *et al.*, 1999; Zoutberg and de Been, 1997). The average OLR was 18 kg COD/m^3/d in year 1 and 26 kg COD/m^3/d in year 2. COD removal was 88% in year 1 and 95% in year 2 (Table 1, Figure 2).

Other published work on the treatment of brewery waste include Baloch *et al.* (2007) (93–96% COD removal with a EGSB at

		Buffered waste water		Reactor effluent	
		P1 (0–320 days)	P2 (470+ days)	P1 (0–320 days)	P2 (470+ days)
COD: mg/l	Average	18 256	25 981	2184·62	1216·15
	SD	6019·2	7150·2	649·37	396·36
SCOD: mg/l	Average	14 317·25	24 040·61	647	238
	SD	5488·55	6882·97	455·5	51·5
COD load: kg/m^3/day	Average	18·29	25·73		
	SD	6·02	7.44		
TSS: mg/l	Average	2099·39	1511·70	1720·48	1024·10
	SD	625·93	444·39	1262·68	371·65
pH	Average	6·57	6·15	7·27	7·05
	SD	0·93	0·94	0·14	0.07
VFA	Average			352·60	86·74
	SD			327·29	24·23
Ripley's ratio	Average			0·41	0·29
	SD			0·13	0·03
Biogas production: Nm^3/day	Average			2287·70	3542·46
	SD			901·24	1191·70
Biogass production: m^3/kg TCOD removed	Average			0·58	0·57
	SD			0·13	0·10

Table 1. Summary of the key performance parameters for the buffered wastewater and the reactor effluent, for periods pre-shutdown (P1, days 0–320) and post-shutdown (P2, days 470+)

2–13 kg COD/m^3/d) and Leal *et al*. (1998) (96% COD removal using an anaerobic filter at 8 kg COD/m^3/d loading rate). Zheng *et al*. (2012) found that increasing the OLR from 15 to 45 kg COD/m^3/d with an EGSB increased the COD removal efficiency from 92·1% to 97·2%, possibly by improving mixing, but this was not investigated.

Efficient COD conversion to gas can also be attributed to the high proportion of soluble COD (SCOD) in many food-processing effluents, for example, sugar and alcohols. Values greater than 90% COD removal are commonly reported in the literature when there is high solubility and therefore biodegradability (Baloch *et al*., 2007; Borja *et al*., 1994; Connaughton *et al*., 2006; Cronin and Lo, 1998; Gonzalez *et al*., 1998; Leal *et al*., 1998; Zheng *et al*., 2012). Ahn *et al*. (2001) reported a 76% soluble fraction for brewery waste, and Goodwin *et al*. (2001) reported 78–84% solubility from whisky distillery pot ale. Average SCOD in this case study was 84·5% ± 10·6%. SCOD reduces the time for hydrolysis, a rate-limiting step. The SCOD removal efficiency was 95% in year 1 and, following the separator repairs, 98% in year 2 (Figure 2, Table 1). Gas production would be expected to be linked to SCOD removal, suggested by Figure 3, showing a linear correlation (R^2 = 0·87). Baloch *et al*. (2007) reported increases in gas production with load, and Zheng *et al*. (2012) showed a doubling of gas production when the OLR increased from 20 to 40 kg COD/m^3/d.

Gas production was corrected for pressure and temperature in order to give the specific gas yield per kg of COD removed. There was an average of 0·41 CH$_4$/g COD removed. This exceeds the stoichiometric value of 0·35 m^3/kg COD removed from a carbohydrate feedstock, and this was attributed to the solids conversion. It was also higher than previous work on brewery effluents. Connaughton *et al*. (2006), for example, reported 0·28 m^3 CH$_4$/kg COD removed, from a hybrid EGSB-anaerobic filter; Cronin and Lo (1998) reported 0·30–0·34 m^3 CH$_4$/kg COD removed using a UASB reactor; and Ahn *et al*. (2001) reported 0·35 m^3/kg COD removed for UASB. These differences are attributed to the differences in solids mass balances, which are not always reported.

There is also literature on gas quality, and in this study, methane concentration was 70% ± 9% higher than the 60–62% methane from brewery effluent reported by Van Der Merwe and Britz (1993) and Bocher *et al*. (2008) but similar to Baloch *et al*. (2007), 62% to 75%, and lower than Leal *et al*. (1998), who reported 80–95% methane from brewery wastewater, suggesting that more data are needed on methane measurements.

Conclusions and recommendations
Total VFA analysis using the new colorimetric test kit followed by Ripley's ratio is a simple monitoring technique suitable for operational control and early warnings of instability for high-rate
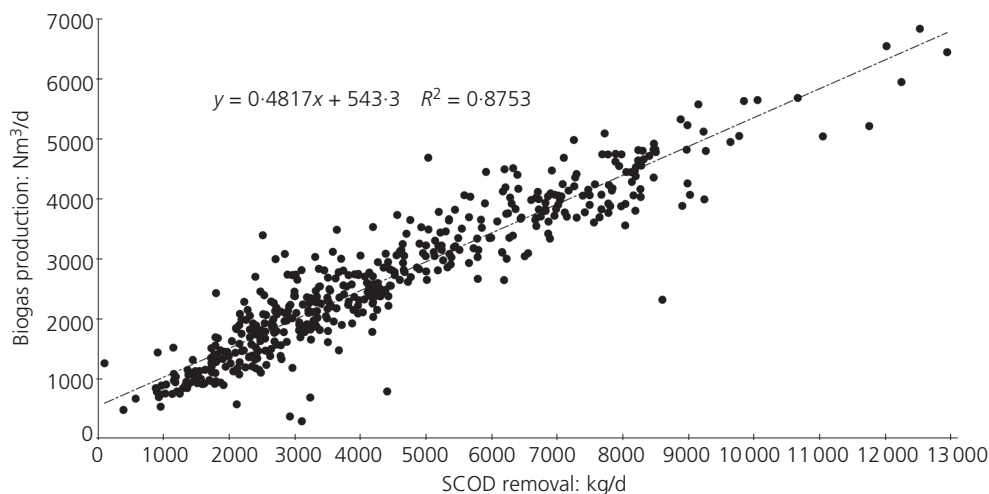
Figure 3. Correlation between biogas production and SCOD removal. Gas continues to be produced because of the 4 d retention time and retains solids digestion; hence, the correlation line does not pass through the origin.

EGSB digesters. COD conversion to gas or pH was not an effective test for instability.

There was no evidence of granule losses as a result of the damage to the internal separator, but SS measurements are needed in order to understand mass balances and interpret specific gas yields. Standard reporting of liquid and gas velocities would also help compare solids losses from gas surges or other hydraulic perturbations that could otherwise be converted to gas.

The results reported here confirm the need for effluent buffering, as the range of in-flow rate was 12–774 m^3/d, COD in the raw effluent ranged from 5500 to 41 400 mg/l, and total SS values were between 260 and 4800 mg/l. These variations were reflected in reactor stability and performance; they were typical of previous works on brewery effluents.

Anaerobic conversion of COD to gas was linked to its solubility, in this case achieving a greater than 95% conversion at 20 kg COD/m^3/d.

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