Anaerobic membrane bioreactor for high-strength wastewater treatment: batch and continuous operation comparison

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ABSTRACT

The anaerobic membrane bioreactor (AnMBR) is a recent development in high-rate anaerobic bioreactors. This study assessed the treatment of high-strength wastewater by an AnMBR using batch and continuous feeding operation. The results showed that the AnMBR could establish a biomass concentration of 6–8 g/L in approximately 20 days due to retention of micro-organisms by the membrane, resulting in 86% chemical oxygen demand (COD) removal efficiency in the treatment of high-strength brewery wastewater. Batch operation was proven to be effective for an organic loading rate (OLR) up to 2 gCOD/L/day and was beneficial to the membrane filtration. However, the treatment capacity of the AnMBR with batch feeding was limited by the high instantaneous OLR during the feeding period. Compared to batch operation, continuous feeding can achieve improved stability and better effluent quality, but prolonged continuous permeation may make the membrane more susceptible to fouling. Although a critical flux of 22 L/m²/h was determined for the membrane filtration in the AnMBR tested, a decrease in the membrane permeability was still observed in the long-term filtration at a flux of approximately 10 L/m²/h.

Key words | anaerobic membrane bioreactor (AnMBR), AnMBR start-up, batch operation, continuous operation, critical flux

INTRODUCTION

Interest in alternative energy sources due to the increasing cost of non-renewable fuels has made anaerobic treatment an attractive option for high-strength wastewater treatment (Rajeshwari et al. 2000). The major advantages of anaerobic digestion over its aerobic counterpart are the production of methane biogas, reduction in sludge production, high organic loading rates (OLRs) due to the absence of oxygen transfer limitations, and energy savings because aeration is not required (Speece 1996; Liao et al. 2006; Khanal 2008).

Anaerobic digestion degrades organic matter through four stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Speece 1996; Khanal 2008). Methanogenesis is the final step that converts volatile fatty acids (VFAs), H₂ and CO₂ into methane. The methanogenesis step is often the rate-limiting step due to the slow growth rate of methanogens. Failure of methanogenesis can result in VFA accumulation, pH reduction, and eventually system failure (Speece 1996). Therefore, the success of anaerobic treatment of wastewater depends on the cultivation of sufficient concentrations of methanogens so that acetogenesis products can be effectively consumed at a balanced rate. In general, effective anaerobic treatment can be achieved by strategies including: the use of a large reactor volume to achieve a long sludge retention time (SRT); the formation of dense methanogen-rich bioactive granules using the upflow sludge blanket reactor design; growing biofilm on the surface of media added to the reactor; or integrating anaerobic digestion with membrane filtration to form an anaerobic membrane bioreactor (AnMBR) system (Liao et al. 2006; Chang & Hufnagel 2013).

The AnMBR is an integrated anaerobic digestion and membrane filtration system. In an AnMBR system, the
membrane filtration can act as a physical barrier to retain all the biomass in the reactor system and completely separate the SRT from the hydraulic retention time (HRT). Since a long SRT is usually necessary for the accumulation of the slow-growing methanogens, the separation of SRT from HRT can result in a reduced reactor size. In addition, the membrane filtration can also largely improve the effluent quality of anaerobic treatment due to its ability to completely remove suspended solids and eliminate sludge washout (Ince et al. 2001; Liao et al. 2006).

AnMBRs can be batch-fed or continuously fed depending on the application. Most studies conducted on AnMBRs focused on continuous operation. However, batch operation is still a prevailing operation strategy for most of the conventional complete-mix anaerobic digesters, particularly for small-scale digesters used in the agri-food sector. The development of advanced AnMBR technology has provided a profound opportunity to update these small-scale digesters to achieve improved stability and effluent quality. In this paper, we compared the AnMBR performance using batch and continuous operation, analysed the characteristics of these two operation modes, and assessed the membrane operation in AnMBR systems.

MATERIALS AND METHODS

AnMBR system and operation

A 15 L complete-mix AnMBR system, as shown in Figures 1 and 2, manufactured by GE Water and Process Technologies, Oakville, ON, Canada, was used in this study. The system consisted of a 10 L anaerobic bioreactor and a 5 L external submerged membrane tank. Mixing was performed using a mechanical mixer at 50 rpm. Sludge was recycled from the bottom of the bioreactor to the membrane tank and an overflow line was used to return the sludge from the membrane tank to the bioreactor. A submerged hollow fibre membrane module (polymethylpentene membrane material) with a total filtration area of 0.047 m² (GE Water and Process Technologies, Oakville, ON, Canada) was used for the filtration. Biogas was recirculated at 0.019 m³/s (standard conditions) from the bioreactor to the membrane tank for membrane fouling control.

A permeate pump (Micropump I-Drive, Vancouver, WA, USA) was used to extract the treated water from the bioreactor at a constant flux rate of 10–12 L/m²/h (LMH). The operation cycle consisted of 10 minutes of permeation and 1 minute of relaxation. No chemical cleaning was conducted during the operation period. A flow instrument (Intek Rheotherm, Westerville, OH, USA) and a pressure sensor (Endress Hauser, Burlington, ON, Canada) were installed in the permeate line to monitor the permeate flow rate and the transmembrane pressure (TMP), respectively. The bioreactor was maintained at 35 ± 1.5 °C using a hot water bath (Stable-Temp, Cole Parmer, Montreal, QC, Canada) connected to a
hot water jacket surrounding the mixing tank. The reactor pH was maintained in the range of 6.5–7.0 during batch feeding operation by adjusting the pH of the feed. No sludge was wasted from the bioreactor during the operation period.

Reactor seeding and wastewater

Approximately 15–20 L of anaerobic sludge with a mixed liquor suspended solids (MLSS) concentration of approximately 17 g/L was taken from the Guelph Municipal Wastewater Treatment Plant. Nitrogen gas was used to sparge the reactor for over 1 hour through the membrane bubbling line to remove dissolved oxygen and create an anaerobic environment. A synthetic brewery wastewater recipe was adapted from the methodology presented by Scampini (2010). Tables 1–3 show the compositions of the synthetic brewery wastewater used in this study. Two distinct feeding regimes were used for batch and continuous operation.

Batch feeding

During the start-up and batch operation period, OLR of 0.5, 1, 2, and 4 gCOD/L/day were tested. The AnMBR was fed once per day at an OLR of 0.5–2 g/L/day and twice per day at an OLR of 4 g/L/day. The feed was prepared twice weekly and stored at 4 °C until required. For a 2 gCOD/L/day OLR, the feed consisted of acetic acid (food grade vinegar, 5% w/w, 405 mL), yeast extract (2,670 mg), NH4Cl (1,430 mg), K2HPO4 (420 mg), and trace element solution (30 mL). The COD:N:P ratio of the wastewater is shown in Table 3. Beer was not added to the feed during the batch feeding start-up period. NaOH was used to adjust the feed pH to maintain the AnMBR pH in the range of 6.5–7.

The AnMBR was briefly switched to continuous feeding at an OLR of 2 g/L/day on day 105 to flush the nutrients before being shut down on day 123 for moving. During the shutdown period, the reactor was maintained under anaerobic condition without heating or feeding. Anaerobic micro-organisms experience a sharp decline in the rate of endogenous decay during starvation and can maintain viability in some cases up to 18 months (Speece 1996).

Continuous feeding

The AnMBR was converted to continuous feeding operation after 172 days from the starting day. Initially the AnMBR was fed continuously at an OLR of 1 g/L/day with the same wastewater composition as that during batch feeding.

| Table 1 | Compositions of synthetic brewery wastewater fed in batch and continuous operation at OLR 2 g/L/d |
| Feed components | Batch operation | Continuous operation |
| Vinegar (5%) (mL/day) | 476 | 405 |
| Yeast extract (g/day) | 3.08 | 2.76 |
| Beer (mL/day) | 0 | 44 |
| NH4Cl (g/day) | 1.43 | 1.43 |
| K2HPO4 (g/day) | 0.42 | 0.42 |
| Trace element solution (mL/day) | 10 | 30 |

| Table 2 | Trace element solution composition from Scampini (2010) |
| Chemical species | Concentration (mg/L) |
| FeCl2·H2O | 2,000 |
| MnCl2·4H2O | 500 |
| CoCl2·6H2O | 2,000 |
| NiCl2·6H2O | 142 |
| ZnCl2 | 50 |
| Na2SeO3 | 123 |
| AlCl3·6H2O | 90 |
| (NH4)6Mo7O24·4H2O | 50 |
| CuCl2·2H2O | 38 |
| H3BO3 | 50 |
| EDTA | 1,000 |
| HCl (36%) | 1 mL/L |

| Table 3 | Chemical oxygen demand (COD), total nitrogen (TN), and total phosphorus (TP) composition of wastewater for different operation modes at an OLR of 2 g/L/day |
| Chemical species | Batch feeding | Continuous feeding |
| COD (mg/day) | 30,000 | 30,000 |
| TN (mg/day) | 691.5 | 662.1 |
| TP (mg/day) | 114.2 | 113.2 |
| COD:TN:TP | 263:6:1 | 265:5.86:1 |
After 12 days, the feed was modified to include acetic acid, beer (Maclay’s Traditional Pale Ale, Guelph, ON, Canada), and yeast extract for 75.5%, 15%, and 9.5% of the influent chemical oxygen demand (COD), respectively. The feed tank was stored in an insulated cooler packed with ice packs to prevent bacterial growth and the degradation of the COD content during the operation.

**Analytical methods**

Samples were taken from the digester and membrane tanks twice weekly, or as required for analysis. All soluble samples were filtered by Whatman 25 mm syringe filters with a nominal pore size of 0.45 μm. All MLSS analysis was performed in duplicate according to *Standard Methods* (1998). COD, VFA, ammonia nitrogen, total nitrogen, and total phosphorus tests were performed using a Hach digital reactor block (DRB200, Hach, USA) and a spectrophotometer (DR 5000, Hach, USA). COD testing was performed using Hach High Range COD digestion vials (Method 8000). All COD measurements were performed in duplicate. Blanks were made once per week and stored out of direct light. Hach kits and methods were also used for VFA (TNT 872, Hach, USA), ammonia nitrogen (TNT 832, Hach, USA), total nitrogen (TNT 827, Hach, USA), and total phosphorus (TNT 845, Hach, USA).

Protein and polysaccharide concentrations in the mixed liquor were measured after filtering the samples through 1.5 μm filter paper (GF/F, Whatman, USA) using the Bradford method (Bradford 1976) and the phenol-sulphuric acid method (Dubois et al. 1989), respectively. Bovine serum albumin and glucose were used as standard references and the absorbance was taken by a spectrophotometer (DR5000, Hach). Total alkalinity was measured using an automatic titrator (TitraLab 870, Radiometer analytical). Biogas composition (N₂, CH₄ and CO₂) was analysed using gas chromatograph (6890n, Agilent Technologies).

**RESULTS AND DISCUSSION**

**Reactor start-up and batch operation**

The AnMBR was operated for 104 days in batch mode with four different OLRs tested over the operation period. Figure 3 shows the soluble chemical oxygen demand (SCOD) removal and OLR over the operation period. The SCOD removal efficiency in this study was determined by measuring the SCOD sampled 1.5 hours after feeding (to ensure complete-mixing based on the recirculation pump flow rate) and immediately before the next feed cycle. The operation period can be divided into two stages. Stage 1 includes operation at OLRs of 0.5, 1, and 2 gCOD/L/day. The reactor was started by feeding once a day at an OLR of 0.5 g/L/day. On day 3, the SCOD removal was only 26.2% but reached 61.0% on day 9 showing rapid performance improvement in less than 1 week. The OLR was doubled to 1 g/L/day on day 17 and within 4 days the removal efficiency had reached 75.6%. On day 24, the COD loading was increased to 2 g/L/day, which corresponded to an instantaneous loading rate of approximately 3 g/L/min. At an OLR of 2 g/L/day, the system reached a maximum 24-hour SCOD removal of 86%. Figure 4 shows the initial and final SCOD for the entire batch operation period. Regardless of the OLR, there appeared to be a consistent residual COD of 200–300 mg/L at the end of every cycle. This residual COD is believed to be non-biodegradable extracellular polymeric substance and soluble microbial products (SMP). For batch operation, the COD concentration at the end of the cycle at steady-state was 281 ± 11 mg/L.

Stage 2 commenced on day 51 and includes the operation period after increasing the OLR to 4 g/L/day and switching the feed to sodium acetate instead of acetic acid. Batch feeding was conducted twice daily to minimize...
the maximum instantaneous feeding loading rate. Within 24 hours, the pH increased from 7.01 to 7.54 and by day 57 the SCOD accumulated in the system reached 12,170 mg/L, an indication of the treatment deterioration. The feeding was then stopped for 9 days until the SCOD returned to approximately 4,000 mg/L. At this time, the feeding was resumed at an OLR of 2 g/L/day with acetic acid as the dominant COD source. It took 45 days of acetic acid feeding at a pH of 3–6 for the system to return to pH 7.

The MLSS concentration change over the operation time is shown in Figure 3. During the seeding process 9 L of washed anaerobic digester mixed liquor from the Guelph Wastewater Treatment Plant was diluted with 6 L of tap water, resulting in an MLSS concentration of 11.65 g/L on day 1. The MLSS concentration decreased rapidly to approximately 7 g/L and remained in the range of 6–8 g/L until day 51 when the OLR increased to 4 g/L/day using sodium acetate. The MLSS concentration continued to increase to 9.6 g/L during the recovery period with the high SCOD concentration in the reactor. Although the SCOD removal was stabilized from day 70 to 100, the MLSS concentration in the reactor was unable to re-establish the stable levels seen prior to the reactor upset.

The stable COD removal and MLSS growth prior to day 51 indicates that a quick start-up of the AnMBR can be achieved using batch feeding. The quick start-up could be attributed to factors including the retention of all microorganisms by the membrane, the good quality of the seeding biomass, and a balanced feed with easily degradable COD (as acetic acid).

**Batch operation characteristics**

Batch operation is characterized by feeding at a high instantaneous organic loading followed by a continuous degradation of the organics throughout the operation cycle. A complete analytical test was performed on day 91 to determine the SCOD and VFAs in the reactor throughout an operation cycle (Figure 5). The SCOD was found to reduce at a first-order reaction rate as the cycle progressed but reached a steady-state residual concentration approximately 11 hours after the feeding. The main COD sources in the reactor included the fed acetic acid, yeast extract, and the SMPs produced by the micro-organisms. The SMPs could be the main component of the residual COD. The VFA concentration in the reactor remained stable in the first 2 hours then decreased with time. The initial stable VFA concentration could result from a balanced degradation rate of the acetic acid consumption and the conversion of the yeast COD into VFAs since it was shown that the total SCOD in the reactor decreased with time from the beginning.

It is interesting to note, as shown in Figure 5, that the pH profile throughout the cycle showed a correlated trend with that of VFA, which may suggest that the main pathway of methanogenesis reaction in the reactor was through the breakdown of acetic acid into methane and CO₂. The quantitative polymerase chain reaction (PCR) analysis confirmed the dominance of acetotrophic Methanosarcinaceae in the batch feeding AnMBR, which had a very high instantaneous acetic acid concentration during the feeding period.
Nutrient accumulation

For batch operation, accumulation of soluble nutrients such as ammonium and phosphorus can exert significant effect on the operation of the reactor. In this study, the nutrients were monitored on day 51 just prior to the change in the OLR from 2 to 4 gCOD/L/day using sodium acetate (NaAc). The concentration of ammonium nitrogen (NH₃-N) was 550 mg/L on day 51. It was observed that a rapid increase in ammonium nitrogen concentration occurred after the feed was switched to NaAc at OLR 4 gCOD/L/d. The ammonia concentration in the reactor increased from 550 to 640 mg/L after one batch feeding of sodium acetate and continued to increase after feeding was stopped, reaching a maximum concentration of 680 mg/L on day 59.

High ammonia nitrogen concentrations in the reactor could be the main factor resulting in the deterioration of the operation after the reactor was switched to NaAc feeding. Figure 6 shows the pH cycle profiles with sodium acetate feeding. The pH cycle profile with sodium acetate feeding is different from that in the batch feeding of acetic acid shown in Figure 5. For the operation with acetic acid feeding, a stable pH through the operation was established despite the change in pH during the operation cycles. During feeding with sodium acetate, a continuous increase in pH was observed due to an insufficient supply of protons for the methanogenesis reactions. The increase in pH could result in deprotonation of ammonium and a corresponding increase in the concentration of free ammonia. Ammonia can inhibit methanogenesis at concentrations above 100–500 mg/L as NH₃-N (Metcalf & Eddy 2004), leading to loss of biogas and VFA accumulation. Thus, as shown in this study, the accumulation of ammonia nitrogen in the reactor with batch operation could make the system more sensitive to changes in pH due to the risk of free ammonia inhibition of the methanogenesis reactions.

Continuous operation

The AnMBR was briefly switched to continuous feeding at an OLR of 2 g/L/day on day 105 but was shut down on day 123 for moving to a new laboratory. The AnMBR was restarted on day 172 at an OLR 1 gCOD/L/day using the same feed composition as that for the batch operation. The OLR was increased from 1 to 2 gCOD/L/day in about 1 week and a 97.5% COD removal was rapidly established in 10 days at 2 gCOD/L/day after 50 days of system shutdown (Figure 7). A quick start-up after the long-term shutdown is another advantage of AnMBRs. Other bioreactors such as the fluidized bed reactor can experience biomass washout during re-fluidization after long periods of inactivity (Speece 1996). Such an advantage of AnMBRs is particularly beneficial for small-scale systems performing seasonal operation. In addition, the VFA and SCOD concentrations in the effluent with continuous feeding were much lower than...
those observed during the batch feeding. For the continuous operation, the SCOD concentration in the reactor mixed liquor was 129 ± 61 mg/L compared with 500 mg/L at the cycle end of the batch operation. The total COD in the membrane permeate was only 67 ± 29 mg/L, which was much lower than that in the reactor mixed liquor, showing that the membrane played an important role in improving the treatment efficiency.

It was observed that the MLSS concentration was decreased from 6.7 ± 2.3 to 4.0 ± 0.64 g/L after the system was switched from the batch to the continuous operation at the same OLR. It may suggest a lower net biomass growth rate with the continuous feeding for the same OLR. The quantitative PCR analysis (Hufnagel 2014) showed that the main methanogen populations changed from acetoclastic Methanosarcinaceae to hydrogenotrophic Methanomicrobiales, which generate methane through hydrogen and CO₂ reaction, implying that the operation with continuous feeding could result in a different dominant methanogen species from that developed under the batch feeding conditions.

Biogas production

The biogas production rate was stable and similar during the period of the batch and continuous feeding operation. The biogas production rate at an OLR of 2 g/L/d was 17.9 ± 1.18 L/day. The methane content in the biogas was determined to be 65% by GC analysis, corresponding to an average methane yield of 0.38 ± 0.02 m³ CH₄/kg COD_removed (35 °C), which represents 96% of the maximum theoretical value of 0.395 m³ CH₄/kg COD_removed at 35 °C (Metcalf & Eddy 2004).

The GC measurement showed that the biogas generated from the digester contained around 33% CO₂. The CO₂ content in the biogas bubbles generated in the reactor results in a high dissolved CO₂ concentration in the mixed liquor so sufficient alkalinity is needed to offset the dissolved carbonic acid and maintain the pH near neutral. In this study, the pH of the feed in batch operation was adjusted using NaOH to maintain the reactor mixed liquor pH at 6.5–7.0. For the batch operation, the alkalinity in the reactor measured on day 21 and day 56 was 3,744.9 mg/L and 3,240.5 mg/L as CaCO₃, respectively. For continuous operation at OLR 2 gCOD/L/d, the feed pH was adjusted to 5.5 using NaOH and the mixed liquor alkalinity was around 2,500 mg/L as CaCO₃.

Membrane filtration performance

In this study, the membrane filtration was operated in the constant flux mode. The performance of the membrane filtration was assessed based on the operation flux and the membrane fouling development during the operation period. The critical flux concept, which defines the critical flux as the flux below which there is no evident TMP increase over a short period of time (Le Clech et al. 2005), was widely used to estimate the design flux of the membrane filtration. In this study, the critical flux was determined as the maximum flux at which there was no evident TMP increase in a 10-minute filtration period by using the flux-stepping filtration method (Le Clech et al. 2005). Figure 8 shows an example of the TMP time profiles observed in the critical flux test. Table 4 shows the critical flux values measured during batch feeding operation, the brief period of continuous feeding before the shutdown, and the continuous operation after the restart.

The first three tests determined the critical flux to be 36–45 L/m²/h. However, there was a significant drop in critical flux after the shutdown and restart. This can be caused by changes in the concentration and composition of SMP in the reactor and the gradual accumulation of dissolved CO₂. The pH of the feed was then adjusted to maintain the pH near neutral. For the continuous operation at OLR 2 gCOD/L/d, the feed pH was adjusted to 5.5 using NaOH and the mixed liquor alkalinity was around 2,500 mg/L as CaCO₃.
these substances on the membrane surface, which can block the membrane pores and result in a decrease in membrane permeability. Figure 9 shows the concentrations of carbohydrates and proteins in the reactor on day 21 (batch operation, OLR: 1 gCOD/L/day), day 51 and 80 (batch operation, OLR: 2 gCOD/L/day), day 172 (at the end of shutdown), and day 193 (continuous operation at 2 gCOD/L/day). The measurements showed that the concentrations of the polysaccharide and proteins in the reactor increased with time.

In addition to critical flux testing, the average TMP over the entire 10-minute permeation cycles were taken periodically throughout the operation to monitor long-term changes in membrane permeability. Despite that the operational flux was controlled to a constant 10 LMH at all times, which was far below the critical flux, the average cycle TMP increased with time (Figure 10). This supports the generally accepted understanding that the critical flux is not predictive of long-term membrane fouling (Le Clech et al. 2005). In fact, the critical flux is determined based on the rate of TMP increase under different flux conditions, which does not always reflect the development of irreversible membrane fouling (Van den Brink et al. 2009; Jamal et al. 2014).

### CONCLUSIONS

This work studied the treatment of synthetic brewery wastewater by AnMBR in batch and continuous operation modes. The start-up of the AnMBR was completed quickly using batch feeding with proper control of the OLR. Batch operation was proven to be an effective operation mode for OLRs lower than 2 g/L/day, but the treatment capacity of the AnMBR using batch feeding could be limited by the high instantaneous OLR during feeding periods. Compared with batch operation, the continuous operation was more stable and achieved improved effluent quality. Although a critical flux of 22 L/m²/h was determined for the AnMBR tested, a decrease in the membrane permeability was observed for the long-term continuous operation at a flux of around 10 L/m²/h.
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