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Performance improvement in a two-stage thermophilic anaerobic membrane bioreactor using PVA-gel as biocarrier

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ABSTRACT

This study focused on the effect of polyvinyl alcohol (PVA)-gel as biocarrier on total volatile fatty acid (VFA) production in a two-stage thermophilic anaerobic membrane bioreactor. Consisting of a hydrolytic reactor with PVA-gel addition followed by a methanogenic reactor and a microfilter (0.1 μm) operating continuously under external semi-dead-end mode at 55°C. The reactor was fed with tapioca starch-based synthetic wastewater at two organic loading rates (OLR) of 6 and 8 kg COD/m^3 d. Hydrolytic reactor with PVA-gel showed an increasing in total VFA generation and enhances methane production at OLR 6 kg COD/m^3 d. Acetic acid and *n*-butyric acid were observed as the predominant components without propionic acid accumulation. The operational performance of the system was monitored by COD removal efficiency and methane production rate. High COD removal efficiency at 89–92% with a methane generation rate 1.5–1.9 $L_{methane}/L_{reactor}$.d was observed throughout the experimental period. However, membrane fouling was one of the limiting factors in this study. Membrane fouling investigations indicated that the major fouling in thermophilic anaerobic membrane bioreactors was reversible organic fouling caused by extracellular polymeric substances.

Keywords: PVA-gel; Biocarrier; Membrane fouling; Thermophilic anaerobic membrane bioreactor; Particulate wastewater

1. Introduction

Thermophilic anaerobic process can be potentially used for treating high-strength particulate wastewater with accelerated biodegradation rates and low sludge production. It also offers advantages such as low nutrient requirement, excellent disinfection from pathogenic micro-organisms, elimination of cooling requirements for high-temperature wastewater, enhanced solubility of low-soluble substrates and reduces greenhouse gas emission through utilization of methane gas. The appropriate organic loading rate (OLR) changes depending on operating conditions, wastewater characteristics and reactor configurations. The effective organic removal rates of the process lies

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between 4 and 6 kg COD/m^3 d [1]. Recent studies with synthetic sugarcane molasses wastewater in two-stage thermophilic anaerobic membrane bioreactor (TS-TAnMBR) have shown OLR of 5–12 kg COD/m^3 d to be also effective. Yet, organic removal efficiency was observed to be only 60–80% with 4–7 kg COD/m^3 d of organic removal rates [2]. Jeison et al. [3] also reported that the organic removal rates of 6–7 kg COD/m^3 d with operating OLR of 10–17 kg COD/m^3 d for treating high-strength gelatin-based synthetic wastewater.

On the contrary, thermophilic condition cause poor sludge formation and sludge settleability due to deterioration in sludge settling properties and high degree of sludge mineralization [4]. This negatively affects the biomass to produce extracellular polymeric substance (EPS) which promotes dense and firm sludge granulation. Thus, resulting in biomass washout due to highly sludge degranulation and dispersed sludge formation which in turn deteriorates the effluent quality.

Thermophilic anaerobic wastewater treatment can be operated in two reactor configurations, either a single-stage reactor or a two-stage reactor in which the hydrolytic and methanogenic processes are separated. Due to the difference in growth rates, optimum pH for acidogens and methanogens. System instability can occur due to an imbalance between volatile fatty acid (VFA) production and consumption, considering the difference in growth rates and optimum pH requirements for acidogens and methanogens [5–9]. Thus, separating acidogenesis and methanogenesis processes into two-stage reactor can be deemed beneficial. Optimizing each stage separately facilitates process stability, tolerance to greater loading rate, higher methane production and reduction of propionic acid accumulation [10–12]. Thus, two-stage anaerobic process prevents competition between acidogenic bacteria and methanogenic archaea which are commonly observed in single-stage anaerobic process. However, despite these advantages, two-stage thermophilic process is a single pass reactor without selective biomass recycle, leading to biomass washout thus poor performance of the overall system. In the hydrolytic reactor, acidogenic bacteria are present as individual cells thus highly deflocculated. Hence, the biomass finds it easy to flow out to the methanogenic reactor. Similarly, archaea presents in methanogenic reactor are dispersed due to their diffusible and filamentous nature, thus, increasing the chances of biomass washout [8,13,14].

To counter the above inherent problems with two-stage anaerobic reactor, application of polyvinyl alcohol-gel (PVA-gel) beads in hydrolytic reactor and membrane-based separation to methanogenic reactor can provide a potential solution to prevent substantial biomass washout. PVA-gel beads have been reported to be effective biocarrier in upflow anaerobic sludge blanket (UASB) reactor and anaerobic fluidized-bed reactor for treating low to high-strength wastewater [15–17]. Furthermore, the application of PVA-gel beads as biocarrier in the hydrolytic reactor with high-particulate wastewater has not been currently studied, thus presenting a research gap of its effectiveness as biocarriers for the same. Similarly, to overcome the difficulty in biomass washout from the methanogenic reactor, a ceramic membrane (0.1 μm) was used for effective biomass retention. Application of ceramic membranes at high temperature is attractive due to chemical resistance, thermal stability, long lifetime and low fouling potential. Therefore, by application of the above two solutions, the risk of biomass washout and poor removal efficiency was significantly reduced in the current study. This process enabled TS-TAnMBR to treat higher OLR by providing effective biomass retention. Thus, in the current study, higher effluent quality was achieved independent from biofilm or granule formation.

As reviewed by Visvanathan and Abeynayaka [18], the most suitable treatment for high-strength particulate wastewater was using thermophilic anaerobic membrane bioreactor (TAnMBR). Most Anaerobic membrane bioreactors (AnMBR) studies were carried out in cross-flow mode to reduce membrane fouling caused by adhesion of biomass and colloidal organic/inorganic matter to the membrane surface [19]. However, AnMBR operating in cross-flow mode with mechanical pumping arrangement, negatively affects the activity of methanogenic archaea. This is due to high-shear intensities during pumping through the valve and pumps during cross-flow operation, disrupting the syntrophic association and prevents interspecies hydrogen transfer, resulting in low microbial activity [20]. However, external cross-flow operation results in less fouling than in submerged system and AnMBR operated using dead-end mode apparently have higher fouling. Thus, conjoining both advantages of cross-flow and dead-end mode as a semi-dead-end mode was used in this study. Also due to limited studies on membrane fouling in TAnMBR, there was a prerequisite for assessing membrane fouling under thermophilic anaerobic process.

Thus, this study investigated the effect of PVA-gel on VFA production and composition in the hydrolytic reactor. Additionally, organic removal efficiency, methane generation and membrane fouling were also investigated to better understand AnMBR under thermophilic conditions.

2. Materials and methods

2.1. Seed sludge acclimatization and synthetic wastewater

To isolate the acidogenic and methanogenic consortia for the TS-TAnMBR, two separate batch reactors of 3 and 6 L were fed with seed sludge from UASB reactor. The seed sludge was obtained from a beer industry's UASB reactor which was operated under mesophilic condition (30 ± 3°C). The acclimatization phase was done in two separate reactors in two stages.

In the initial stage, the reactors were operated in batch mode for 77 d. To isolate the acidogenic and methanogenic consortia, feed was varied and pH was maintained at 5.5 ± 0.3 and 7.2 ± 0.2 for hydrolytic and methanogenic reactors, respectively. The reactors were inoculated with an initial concentration of 14 g MLVSS/L (hydrolytic reactor) and 20 g MLVSS/L (methanogenic reactor) of the seed sludge, respectively. For the hydrolytic reactor, tapioca starch-based synthetic wastewater was used. Tapioca starch was the sole carbon source, NH_4HCO_3 and KH_2PO_4 were added as nitrogen and phosphorus source in order to maintain COD:N:P ratio of 100:5:1. Similarly, to isolate the methanogenic consortia, *n*-butyric acid-based synthetic wastewater was used. *n*-Butyric acid was carbon source, NH_4HCO_3 and KH_2PO_4 were added as nutrients to get COD:N:P ratio of 100:5:1. System stability was assessed by VFA generation (for hydrolytic reactor), COD removal rate, MLVSS concentration and methane production rate (for methanogenic reactor).

After system stabilization was achieved, the second stage of acclimatization was commenced. In this stage, both reactors were connected so that effluent from the hydrolytic reactor would flow into the methanogenic reactor. A ceramic membrane (0.1 μm) was connected to the effluent of methanogenic reactor to prevent biomass overflow from the system. The second stage lasted for 68 d. At the end of the acclimatization period, the temperature and OLR for both reactors were 55°C and 19 kg COD/m^3 d (for hydrolytic reactor), 8 kg COD/m^3 d (for methanogenic reactor), respectively. Thus, at the end of system stabilization an overall OLR of 6 kg COD/m^3 d and 55°C was operated with no observable methane production in the hydrolytic reactor.

Once the acclimatization was finished, TS-TAnMBR was run at two loading rates of 6 and 8 kg COD/m^3 d. Tapioca starch was the sole carbon source and NH_4HCO_3 and KH_2PO_4 were added as nutrient sources to maintain COD:N:P ratio of 100:5:1. The characteristics of synthetic wastewater presented in Table 1.

Table 1
Characteristics of synthetic wastewater

Parameters	Organic loading rates	
	6 kg COD/m^3 d	8 kg COD/m^3 d
pH	7.3 ± 0.2	7.5 ± 0.1
TCOD, g/L	14.5 ± 1.4	20.6 ± 1.2
SCOD, g/L	5.5 ± 1.8	5.5 ± 1.4
PCOD, g/L	8.8 ± 2.2	15.1 ± 1.1
TS, g/L	11.9 ± 1.8	15.6 ± 1.1
SS, g/L	9.8 ± 1.7	13.6 ± 2.0
TKN, mg/L	775 ± 20	950 ± 50
NH_4^+, mg/L	600 ± 24	680 ± 40
TP, mg/L	165 ± 10	210 ± 15

2.2. Experimental set-up

The TS-AnMBR was constructed with a working volume of 3 and 6 L for hydrolytic and methanogenic reactors using stainless steel, respectively. The system was operated in two-stage; hydrolytic reactor followed by methanogenic reactor and ceramic membrane for biomass retention. Biogas recirculation was used in order to achieve semi-continuous mixing (10 min mixing and 2 min non-mixing) in both reactors. Fig. 1 illustrates the experimental set-up of the TS-AnMBR system. Synthetic wastewater was fed to the hydrolytic reactor with intermittent feeding at a controlled feed flow rate by an automatic level sensor immersed in methanogenic reactor. Once the effluent overflowed from hydrolytic reactor, it was fed into the methanogenic reactor by gravity. When the methanogenic reactor was filled to the required level, the feed pump stopped through a relay unit integrated with a level sensor. Gravity was used to send the methanogenic effluent to the membrane. While the membrane used suction pressure for filtration. A monolith tubular ceramic membrane (55 channels, 2.5 mm diameter in each channel, 30 mm diameter, 450 mm length, 0.18 m^2 surface area; NGK Insulators, Japan) with a nominal pore size of 0.1 μm was used in this study. The membrane was operated in an external semi-dead-end mode with intermittent filtration (4 min filtration and 1 min mixed liquor recirculation through the membrane to methanogenic reactor). The overall system was automated for continuous operation.

2.3. TS-TAnMBR operation and membrane cleaning

The reactor was first operated with an overall OLR of 6 kg COD/m^3 d, and then PVA-gel was added to the hydrolytic reactor at OLR 6 kg COD/m^3 d to compare the hydrolytic reactor performance. After that,

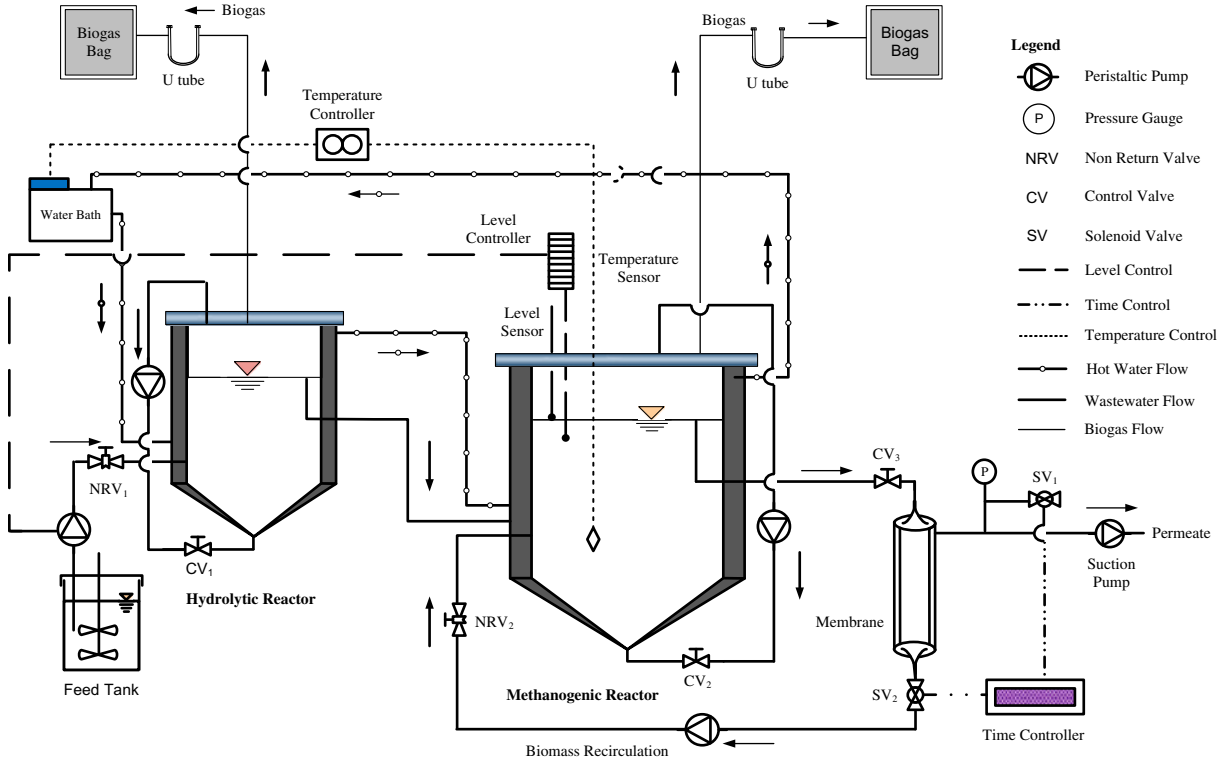

Fig. 1. Experimental set-up of TS-TAnMBR.

OLR was increased to 8 kg COD/m^3 d with PVA-gel already present in the hydrolytic reactor. The operating conditions of individual reactors and overall system are shown in Table 2.

After the experimental run with OLR 8 kg COD/m^3 d was completed and the transmembrane pressure (TMP) reached 40 kPa, membrane cleaning was conducted using base and acid. The membrane was soaked in a cleaning solution, (a) 0.5 M NaOH for 15 min and (b) a diluted (5 ml/L) mixture of nitric acid at 58% (HNO_3) and phosphoric acid at 75% (H_3PO_4) for 5 min. In between every cleaning step the membrane was rinsed with deionized (DI) water until neutral solution was obtained. Furthermore, each step of membrane cleaning procedure, permeate flux was measured to evaluate filtration resistance as described in Section 2.4.

2.4. Filtration resistance determination

The effects of fouling on filtration performance can be expressed in terms of hydrodynamic resistance. The resistance-in-series model was applied to evaluate

Table 2
TS-TAnMBR operating conditions

Parameters	Hydrolytic reactor	Methanogenic reactor	Overall
pH	5.5 ± 0.3	7.2 ± 0.2	–
Temperature, ℃	55	55	55
HRT, h	19.45	38.92	58.37
Working volume, L	3	6	9
Permeate flow, L/d			3.7 ± 0.3
Loading rates, kg COD/m^3 d	18.4 ± 1.2	6.9 ± 0.3 (without PVA-gel)	6.1 ± 0.4
		7.6 ± 1.6 (with PVA-gel)	6.1 ± 0.4
	25.3 ± 1.4	11.6 ± 0.7 (with PVA-gel)	8.4 ± 0.5

the characteristics of membrane fouling. According to this model, the permeate flux (J) can be expressed as below:

$$J = \frac{\text{TMP}}{\mu R_t} = \frac{\text{TMP}}{\mu(R_m + R_{\text{rm}} + R_{\text{re}} + R_{\text{irr}})} \quad (1)$$

where TMP is the transmembrane pressure, μ is the viscosity of the permeate, R_t is the total resistance, R_m is the intrinsic membrane resistance, R_{rm} is the removable fouling, R_{re} is the reversible fouling and R_{irr} is the irreversible fouling. The experimental procedure to determine each resistance value was as follows: (1) R_m was estimated by measuring the water flux of DI water; (2) R_t was evaluated by the final flux of biomass microfiltration and TMP; (3) the membrane was then flushed with DI water. After that the DI water flux was measured to obtain the resistance of $R_m + R_{\text{re}} + R_{\text{irr}}$; (4) membrane was then clean with a chemical solution. Then, DI water flux was measured again to get the resistance of $R_m + R_{\text{irr}}$. From the steps (1) to (4), R_t, R_m, R_{rm}, R_{re} and R_{irr} could be calculated.

2.5. Biocarrier

PVA-gel beads were supplied by Kuraray Co., Ltd (Tokyo, Japan) and had a density of about 1.03 g/cm^3 and diameter of 3–4 mm with effective specific surface area up to 2,500 m^2/m^3 [15–17,21]. After the experimental run with OLR of 6 kg COD/m^{3}d was completed, PVA-gel was added to the hydrolytic reactor of TS-TAnMBR operation at the same OLR. PVA-gel was added to achieve 30% of the hydrolytic reactor working volume (0.9 L of PVA-gel beads) and thoroughly mixed to inoculate hydrolytic bacteria on their surface.

2.6. Analytical methods

Total chemical oxygen demand (TCOD), soluble COD (SCOD), suspended solid (SS) and volatile suspended solids (VSS) were measured according to standard methods [22]. The difference between TCOD and SCOD is particulate COD (PCOD). Sludge characteristics in terms of EPS were determined. EPS was extracted from sludge suspension using cation-exchange resin method (Dowex® Marathon® C, Na^+ form, Sigma-Aldrich, Bellefonte, PA) [20,23]. The extracted solution was analysed for protein and carbohydrate. The sum of the protein and carbohydrate represented the total amounts of EPS. Protein in EPS was determined according to Lowry method with bovine serum albumin as standard [24]. Carbohydrate was determined by phenol-sulphuric acid method with glucose as standard [25], respectively. Filtered (with 0.45 μm) samples were analysed for SCOD and VFA. VFA in feed, hydrolytic effluent, methanogenic effluent and permeate were analysed in order to evaluate VFA generation and removal from the system. Three types of VFA were analyzed, namely, acetic acid, propionic acid and *n*-butyric acid. VFA was analysed individually using gas chromatography (Shimadzu, GC-14B) with a flame ionization detector and pack column (Unisole 30T, SUS). Methane content in the biogas from hydrolytic and methanogenic reactors was analysed separately using gas chromatography (Shimadzu GC-14A) equipped with a packed column (WG-100 SUS) and thermal conductive detector.

3. Results and discussion

3.1. Acclimatization of TS-TAnMBR

At the initial phase of the acclimatization period (batch process), a reduction in MLVSS concentration from 14.2 to 5.7 g/L was observed in hydrolytic reactor. Similarly, MLVSS dropped from 20.3 to 9.2 g/L in the methanogenic reactor. This was due to the decay and washout of the micro-organism during microbial isolation process. As presented in Fig. 2, methane content in biogas from hydrolytic and methanogenic reactors changed from 7.9 and 26.3% to 0.8 and 53.1%. The separation of hydrolytic and methanogenic archaea was confirmed through analyses of methane content. Mota et al. [8] and Saddoud et al. [26] also reported similar observation of less to no observable methane content as an indicator of acidogens isolation in hydrolytic reactor. Due to the short HRT (6–48 h) and low-pH conditions maintained in hydrolytic reactor [10,27], acidogens can be effectively isolated in the hydrolytic reactor.

In the second phase of acclimatization, an increment in MLVSS concentration was observed when both reactors were operated in continuous mode with a ceramic membrane application to prevent biomass washout. The MLVSS in the second phase, in the hydrolytic reactor, rose from 5.7 to 8.6 g/L and 9.2 to 16.2 g/L in the methanogenic reactor. Furthermore, an increase in VFA concentration in the hydrolytic reactor from 1.4 to 2.2 g/L was observed during this time. Thus, implying an increased VFA production in the hydrolytic reactor. Meanwhile, COD removal efficiency of methanogenic reactor was examined to assess the system performance. Once the acclimatization process in methanogenic reactor was achieved,

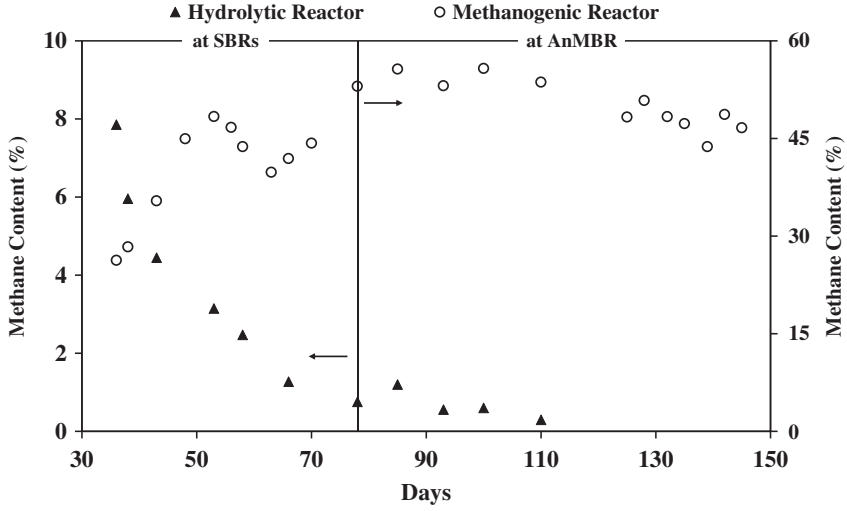

Fig. 2. Methane content in biogas from hydrolytic and methanogenic reactors during reactor acclimatization.

the COD removal efficiency was found to be stable at 72.7%. Acclimatization was continued in TS-AnMBR until no methane content was observed in hydrolytic reactor. After system stabilization was achieved, TS-TAnMBR was operated at OLR 6 kg COD/m^3 d for further experiment.

3.2. Performance evaluation of hydrolytic reactor

After acclimatization, the hydrolytic reactor MLVSS was maintained at 9.6 ± 0.5 g/L at OLR of 6 kg COD/m^3 d in order to study the reactor performance with and without PVA-gel addition on VFA production under similar condition. VFA generation in the hydrolytic reactor increased from 4.0 ± 0.2 to 4.6 ± 0.5 g/L at 6 kg COD/m^3 d with PVA-gel addition. Once the loading rate was increased from 6 to 8 kg COD/m^3 d, VFA generation slightly increased to 4.9 ± 0.2 g/L. These results showed the performance of the hydrolytic reactor with PVA-gel addition increased in terms of VFA production. The increase in VFA was due to an increase in microbial activity as discussed below.

The microbial activity was presented in terms of VFA generation in hydrolytic reactor per unit MLVSS per day. An increase in VFA production in hydrolytic reactor with constant MLVSS can be attributed to an increment in microbial activity with PVA-gel addition. This was observed by an increase in microbial activity from 0.50 to 0.61 g VFA/g MLVSS.d at OLR 6 kg COD/m^3 d with the PVA-gel addition. A further increase to 1.41 g VFA/g MLVSS.d was observed when the OLR was increased to 8 kg COD/m^3 d. These observations inferred the effectiveness of PVA-gel addition in hydrolytic reactor to increase microbial activity and VFA production.

3.3. Evolution of total, soluble and particulate COD (TCOD, SCOD and PCOD) in hydrolytic reactor

The organic content of substrate was measured in terms of COD. The difference between TCOD and PCOD exhibited the effectiveness of hydrolysis process in terms of SCOD. Fig. 3 illustrates the variation of TCOD, SCOD and PCOD in feed and the hydrolytic reactor effluent. TCOD in hydrolytic reactor effluent for all OLRs was observed to be as higher than in the feed. This was attributed to biomass washout from hydrolytic reactor. Similar observations were reported by Kayhanian [13] for biomass washout from the hydrolytic reactor in two-stage anaerobic process.

As shown in Fig. 3, PCOD decreased from 7.0 ± 3.4 to 5.7 ± 2.9 g/L at loading rate 6 kg COD/m^3 d after PVA-gel addition, which further decreased to 2.2 ± 2.0 g/L when the OLR was increased to 8 kg COD/m^3 d. On the contrary, SCOD increased from 11.5 ± 0.6 g/L (without PVA-gel addition) to 13.1 ± 2.5 g/L (with PVA-gel addition), and increased to 18.9 ± 1.2 g/L when the OLR was increased to 8 kg COD/m^3 d.

SS in the hydrolytic reactor (after PVA-gel addition) concentration was observed to decrease from 10.8 ± 1.4 to 5.8 ± 1.0 g/L with an increase in total VFA production from 4.6 ± 0.5 to 4.9 ± 0.2 g/L once the overall loading rate was changed from 6 to 8 kg COD/m^3 d with PVA-gel. Inferring that SS in the hydrolytic reactor was being utilized by acidogenic bacteria to produce the extra SCOD and VFA observed in the hydrolytic reactor effluent.

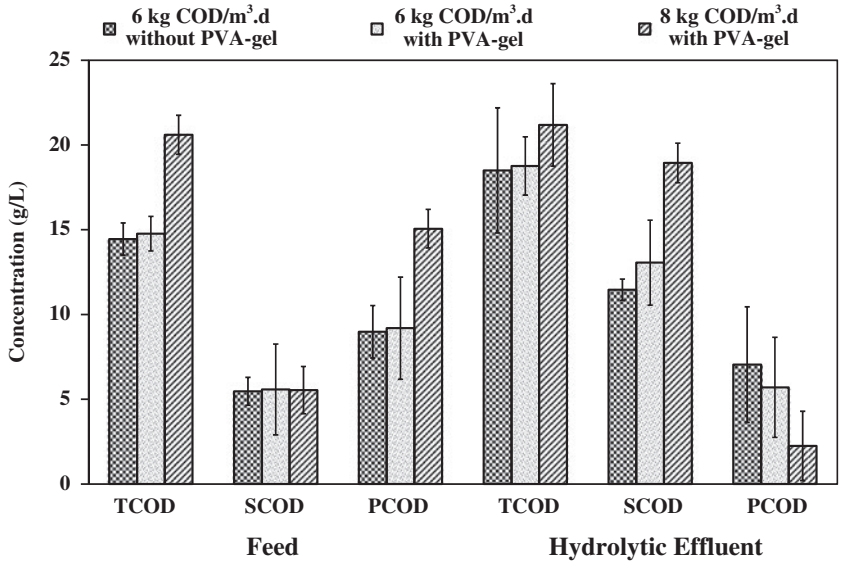

Fig. 3. Variation of TCOD, SCOD and PCOD during reactor operation.

3.4. Performance evaluation of methanogenic reactor

Methane content in the biogas produced from the methanogenic reactor was observed to be in the range of 55–60% for all OLRs. As shown in Fig. 4, average methane generation for the reactor increased from 13.3 L/d (OLR 6 kg COD/m^3 d without PVA-gel addition) to 15.4 L/d (OLR 6 kg COD/m^3 d with PVA-gel addition). Similarly, methane generation was further increased from 15.4 to 17.3 L/d, when OLR was increased to 8 kg COD/m^3 d.

The improvement in the volume of methane generated by the methanogenic reactor was due to an increase in total VFA concentration in hydrolytic reactor effluent after PVA-gel addition. One of the prominent indicators of methanogenic reactor performance was methane productivity (methane generation per unit volume of the reactor). It was observed that after the addition of PVA-gel at OLR 6 kg COD/m^3 d, the methane productivity of the overall system increased from 1.5 to 1.7 $L_{methane}/L_{reactor}$.d. This was further increased from 1.7 to 1.9 $L_{methane}/L_{reactor}$.d, while the

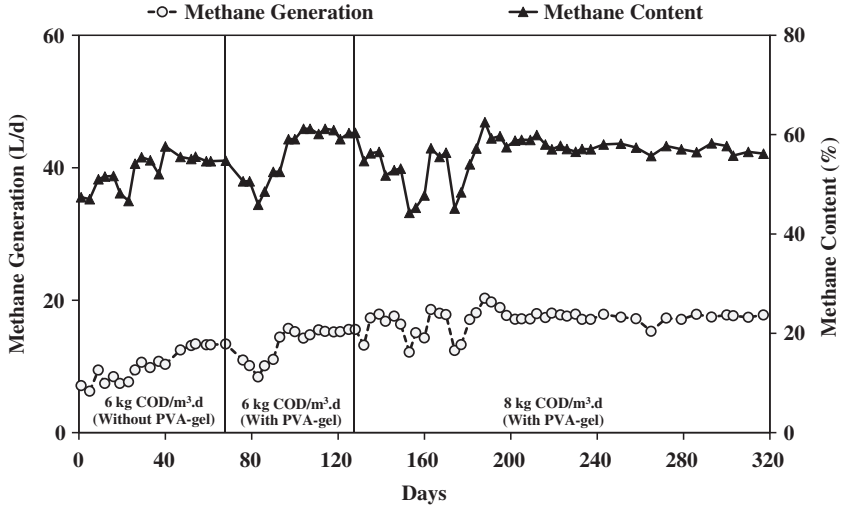

Fig. 4. Variation of methane generation and methane content during reactor operation.

OLR was changed to 8 kg COD/m^3 d. Indicating that methane productivity at OLR 8 kg COD/m^3 d was almost two times of the reactor volume.

3.5. SCOD removal in TS-TAnMBR

COD removal efficiency of TS-TAnMBR of the system increased from 89 to 92% when loading rate to methanogenic reactor increased from 6.9 ± 0.3 (overall OLR 6 kg COD/m^3 d without PVA-gel) to 7.6 ± 1.6 kg COD/m^3 d (overall OLR 6 kg COD/m^3 d with PVA-gel). A negligible decrease in COD removal efficiency from 92 to 91% was observed with an increase in the overall loading rate to 8 kg COD/m^3 d with PVA-gel addition in hydrolytic reactor. However, under both loading rates, COD removal efficiency was more than 89% indicating that TS-TAnMBR was capable of removing almost all of the biodegradable organic (SCOD) matter in the system.

3.6. VFA distribution of TS-TAnMBR

Types and concentration of VFA are important indicators for system performances of TS-TAnMBR. VFA distribution analysis in the overall system was valuable for optimizing system performance. The VFA species were analysed in feed, hydrolytic reactor effluent, methanogenic reactor effluent and permeate at all OLRs as shown in Fig. 5. A small amount of VFA concentrations of 250–356 mg/L were observed in the feed. Acetic acid was the major VFA component at all OLRs. In the hydrolytic reactor effluent, large amount of acetic and *n*-butyric was observed at all loading rates. The hydrolytic reactor effluent contained low concentrations of propionic acid as compared with acetic acid and *n*-butyric acid. Acetic acid and *n*-butyric acid were; 1.3 ± 0.1 g/L, 2.7 ± 0.3 g/L (without PVA-gel) and 1.8 ± 0.2 g/L, 2.6 ± 0.4 g/L (with PVA-gel) at OLR 6 kg COD/m^3 d, and were increased to 2.1 ± 0.1 g/L, 2.7 ± 0.3 g/L at an overall loading rate 8 kg COD/m^3 d with PVA-gel. An increase in acetic acid in all cases was attributed to an increase in microbial activity as discussed in Section 3.2. Furthermore, methane inhibitors such as propionic acid were observed below 550 mg/L in all cases, which was lower than its toxicity level at 1 g/L [11].

In Fig. 5, the difference in VFA concentration between hydrolytic reactor effluent and methanogenic reactor effluent indicate the removal efficiency of methanogenic reactor. It was also observed that a small amount of VFA was being removed by the membrane filtration from the methanogenic reactor effluent. The total VFA removal efficiency of the methanogenic reactor and across the membrane was observed as 77.1%, 12.3% (without PVA-gel) and 84.1%, 19.8% (with PVA-gel) at OLR 6 kg COD/m^3 d and 78.7%, 18.2% at OLR 8 kg COD/m^3 d with PVA-gel. The substantial reduction of total VFA concentration across the membrane contributed to membrane fouling [28].

3.7. Membrane fouling investigation

The results of filtration resistance analysis summarized in Table 3. The results indicated that the total filtration resistance was measured to be 7.56×10^9/m at loading rate of 8 kg COD/m^3 d. The result shows that the reversible organic fouling resistance (72.64% of total filtration resistance, $R_{re,\ or}$) was the main component of the total filtration resistance (R_t) followed by removable fouling resistance (13.85% of total filtration resistance, R_{rm}), reversible inorganic fouling resistance (5.72% of total filtration resistance, $R_{re,\ ir}$) and irreversible fouling resistance (2.75% of total filtration resistance, R_{irr}), respectively. These results indicated that the filtration resistance was attributed to chemical reversible fouling (78.36% of total filtration resistance). Furthermore, membrane fouling due to colloids/particle deposition on membrane pore size or cake layer formation was of little importance as compared with membrane fouling caused by EPS. It was found that EPS caused reversible organic fouling, and could be removed by chemical cleaning. EPS has been reported as a potential organic fouling agent in AnMBR [20,23,29,30]. Based on the results obtained, high amount of reversible organic fouling shown that membrane fouling caused by EPS play an important role in the total filtration resistance.

3.8. Bound EPS analysis

In AnMBRs, membrane fouling can be attributed to the physicochemical properties of the sludge as well as membrane materials. EPS has been identified as the most significant biological factor contributing to membrane fouling. It comprises a variety of polymeric materials such as protein, carbohydrate, lipid and nucleic acids [31]. In this study, the sum of protein and carbohydrate was considered to represent total EPS on the membrane surface. EPS can be further classified into two forms: bound and soluble EPS. Among the two forms of EPS, bound EPS has a negative effect on filterability and significant effect on membrane fouling [32,33]. Bound EPS was found to be contributing to organic reversible fouling [30].

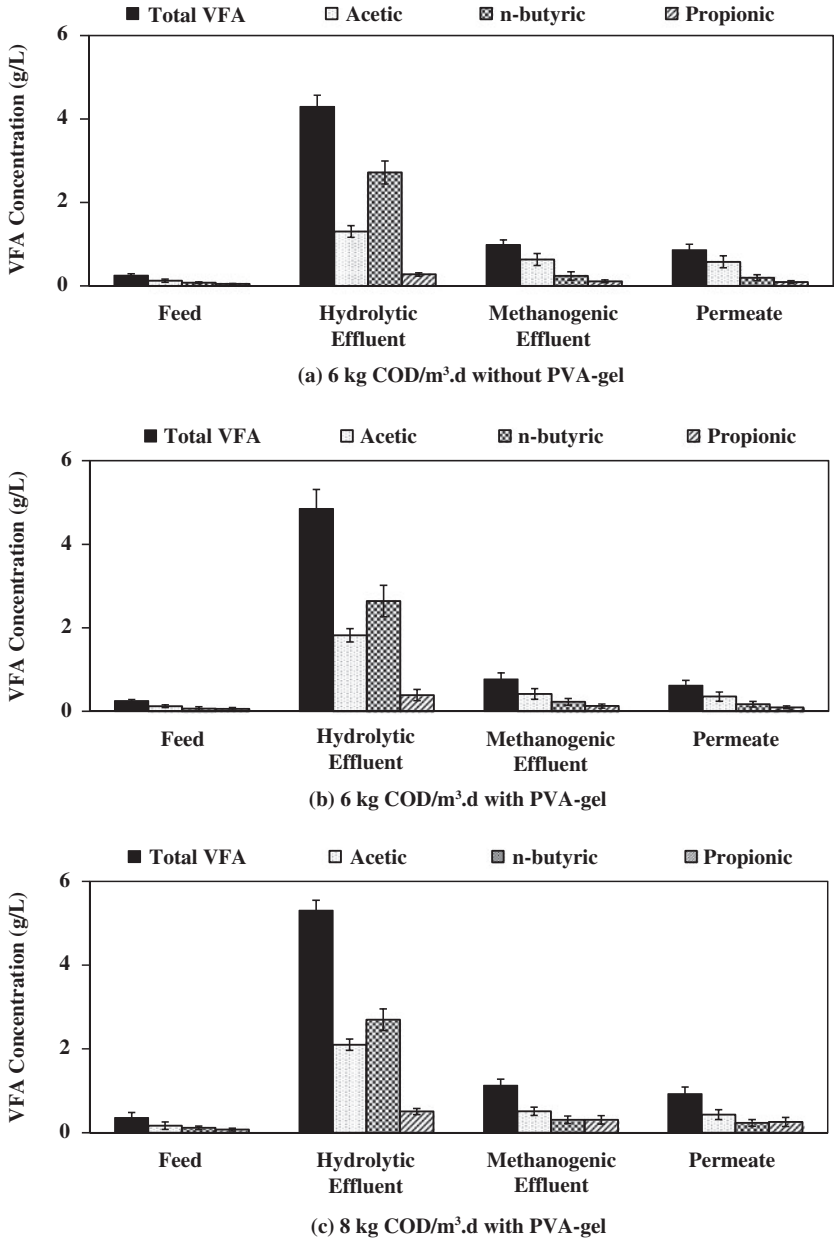

Fig. 5. VFA species of the TS-TAnMBR during reactor operation.

Table 3
Filtration resistance at loading rate 8 kg COD/m^3d with PVA-gel addition

Resistance	Value ($\times 10^9$/m)	Percentage (%)
Intrinsic membrane resistance (R_m)	0.38	5.04
Removable fouling resistance (R_{rm})	1.05	13.85
Reversible organic fouling resistance ($R_{re,\ or}$)	5.49	72.64
Reversible inorganic fouling resistance ($R_{re,\ ir}$)	0.43	5.72
Irreversible fouling resistance (R_{irr})	0.21	2.75
Total filtration resistance (R_t)	7.56	100

Bound EPS of thermophilic bulk sludge at OLR 8 kg/m^3 d was observed at 58.01 mg/g VSS (protein 43.54 mg/g VSS and carbohydrate 14.47 mg/g VSS). Furthermore, protein substances were found to be the predominant compound in TAnMBR, accounting for 75.1% of bound EPS. This was due to the methanogenic archaea preferentially utilized carbohydrate as carbon source to produce methane and carbon dioxide. Similar observations were reported by Mota et al. [8], Lin et al. [23] and Gao et al. [34]. Based on these results, proteins were the majority contributors to membrane fouling under anaerobic condition, attributing to organic reversible fouling ($R_{re,\ or}$).

4. Conclusions

Two-stage AnMBR operated at thermophilic conditions to treat tapioca starch-based synthetic high-strength particulate wastewater achieved more than 89% of COD removal efficiency at all loading rates. Increase in methane generation was observed in the system with PVA-gel addition, with increasing OLR.

The application of PVA-gel to hydrolytic reactor showed an increment in system performance as measured by total VFA production and methane productivity. Acetic acid and *n*-butyric acid were identified as the predominant VFA and no propionic acid accumulation implied the suitability of this system configuration treating particulate wastewater. Finally, EPS was the main cause of membrane fouling in thermophilic anaerobic process, accounting for 72.64% of the fouling which was reversible in nature. However, at this stage it can be clearly seen that using PVA-gel as a biocarrier, the microbial activity in the hydrolytic reactor was enhanced by an increase in VFA production. Further biokinetic studies on behaviour and composition of attached consortia on PVA-gel in the hydrolytic reactor at thermophilic conditions are required to assess and to better understand the mechanism of PVA-gel as a biocarrier.

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