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Selective production of volatile fatty acids at different pH in an anaerobic membrane bioreactor

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Abstract

This study investigated the production of major volatile fatty acid (VFA) components in an anaerobic membrane bioreactor (AnMBR) to treat low-strength synthetic wastewater. No selective inhibition was applied for methane production and solvent-extraction method was used for VFA extraction. The results showed acetic and propionic acid were the predominant VFA components at pH 7.0 and 6.0 with concentrations of 1.444 ± 0.051 and 0.516 ± 0.032 mili-mol/l respectively. At pH 12.0 isobutyric acid was the major VFA component with a highest concentration of 0.712 ± 0.008 mili-mol/l. The highest VFA yield was 48.74 ± 1.5 mg VFA/ 100 mg COD_{feed} at pH 7.0. At different pH, AnMBR performance was evaluated in terms of COD, nutrient removal and membrane fouling rate. It was observed that the membrane fouled at a faster rate in both acidic and alkaline pH conditions, the slowest rate in membrane fouling was observed at pH 7.0.

Keywords Volatile fatty acids, anaerobic, wastewater, pH, fouling

1. Introduction

Anaerobic Membrane Bioreactor (AnMBR) has proven to be effective in treating wastewater from different sources (Cheng et al., 2018a; Song et al., 2018). Although the operational and maintenance costs are the major issue for AnMBR wastewater treatment, the past few years have shown significant developments regarding AnMBR design, resource recovery and membrane fouling control (Cheng et al., 2018c; Jeong et al., 2018; Song et al., 2018). So far, the major research theme on resource recovery from anaerobic bioreactors has tended to focus on the production of methane-containing biogas (Cheng et al., 2018b; Lu et al., 2018; Song et al., 2018; Wang et al., 2018a). Methane is favoured as the main AnMBR product because it does not require any downstream processing and can be readily used as fuel for different purposes. More recent studies have shown that recovering VFA and biohydrogen from AnMBR can be both technically and economically feasible (Khan et al., 2018; Khan et al., 2016a; Khan et al., 2016b; Kleerebezem et al., 2015; Romero Aguilar et al., 2013). Moreover, the production of methane leads to various technical and environmental issues like process inhibition, greenhouse gases, ecotoxicity, fugitive methane emissions, etc. Process optimization, different pre- and post-treatment processes along with chemical and biological additives have been used to improve the production of biogas from the anaerobic process (Ngo et al., 2019). In contrast, production of VFA from the anaerobic process offers technical and economic advantages, for example, bioreactor stability, less expensive operation, and a relatively higher profits compared to methane (Hassanein et al., 2017; Khan et al., 2019; Khan et al., 2016b).

VFAs are used as a precursor for carbon-based biopolymers such as Polyhydroxyalkanoate (PHA), fuels like biodiesel, organic chemicals like alcohols, aldehydes and even for the

production of biogas (Esteban-Gutiérrez et al., 2018; Jankowska et al., 2018; Khan et al., 2019). During anaerobic digestion, the initial stage of hydrolysis involves the production of VFA along with amino acids and sugar through the conversion of proteins and carbohydrates. The second stage of the anaerobic process also produces VFA along with hydrogen, ammonia and carbon dioxide (Adekunle & Okolie, 2015). For a given anaerobic system, production of VFA can be maximized through optimizing common process conditions, for instance Hydraulic Retention Time (HRT), Organic Loading Rate (OLR), and pH. Our previous studies demonstrate that a low HRT (8 hrs) at a loading rate of 600 mg COD/l HRT produced the highest overall VFA yield ($48.20 \pm 1.21\%$) without any selective inhibition of a microbial community (Khan et al., 2019).

The economic feasibility of producing VFA from an anaerobic process largely depends on the percentage of major VFA components, for example, acetic, propanoic and butyric acid present in the VFA mixture. According to Esteban-Gutiérrez et al. (2018) the market size for acetic acid is the biggest one (up to 3,500,000 t/year), followed by propionic and butyric acid (180,000 and 30,000 tonnes per year respectively) (Esteban-Gutiérrez et al., 2018). The majority of current research has shown VFA mixture produced from the anaerobic process contains acetic acid as the predominant VFA component. However, butyric acid has the highest market value and is priced at approximately US\$2,000–2,500 per tonne (Esteban-Gutiérrez et al., 2018; Zacharof & Lovitt, 2013). Furthermore, it is necessary to optimize the operating conditions of an anaerobic process to maximize different VFA components. For example, altering the pH of an anaerobic process can cause a shift in microbial activity and cause a different type of fermentation. A research study has identified pH ranges of 4.0–4.5, 4.5–5.0, 5.0–5.5 and 5.5–6.5 to be ideal for ethanol, mixed acid, propionic and butyric acid-type fermentation, respectively (Zheng et al., 2010). Begum et al. (2018) recently carried out an experiment to show the effect of pH and OLR on VFA production

using single and two-stage anaerobic digestion. Their study investigated the concentration of individual VFA components at acidic (pH 5.5) and alkaline (pH 11.0) conditions. The results showed the highest concentration of butyric acid was recorded at pH 11.0.

So far, no research study has observed the production of selective VFA components using low-strength synthetic wastewater in AnMBR. Membrane fouling can emerge as a serious problem in the AnMBR especially when the system is operated at acidic or alkaline conditions. A variation in operating pH directly affects the cell morphology along with a major alteration in adhesion and flocculation phenomena. Also, a variation in the production of Extracellular Polymeric Substances (EPS) and Soluble Microbial Products (SMP) can affect the membrane fouling at different pH levels (Kunacheva et al., 2017). Improving the economic feasibility is another major challenge of VFA production from low-strength wastewater treatment because the separation and purification of VFA is still very expensive. Operating an AnMBR at different pH conditions can contribute to determining the optimum pH level for individual VFA components and eventually improve the economic feasibility of VFA production based on the anaerobic process.

This is the first technical study that aims to optimize selective production of VFA by changing the pH of an AnMBR using low-strength synthetic wastewater. During this study, no selective inhibition was applied for the methanogens, meaning that the findings can be applied to a generic AnMBR model producing both VFA and biogas. Concentrations of individual VFA members were measured at different pH levels to find the optimum values for different VFA components. Another objective is to study the performance of AnMBR in terms of membrane fouling for the removal of nutrients and COD. The findings of this

experiment have been charted to ascertain the predominant type of fermentation occurring at each pH level.

2. Materials and methods

2.1 Characteristics of sludge and feed solution

Seed sludge for this experiment was collected from two different wastewater treatment plants in Sydney – Central Park water treatment plant, Ultimo and Cronulla water treatment plants and Central Park water treatment plant, Greenhills Beach, NSW, Australia. The seed sludge was acclimatized for 90 days to achieve stable COD and nutrient removal performance and fed to the reactor. The sludge characteristics can be found in our previous study (Khan et al., 2019).

2.2 Experimental setup

A single stage anaerobic membrane bioreactor (AnMBR) was used for this experiment. A hollow fibre membrane module was interned from the top of the reactor and the influent was fed from the bottom. The supernatant was recycled through a separate line at the bottom. The bioreactor was operated at continuous mode and had a working volume of 3.5 L (Figure 1).

The bottom of the reactor had a 1.5-inch layer of 850-900-micron glass microspheres for even flow distribution. Three Masterflex® L/S® Series easy-load II peristaltic pumps were used to control the flow of influent, recirculation and effluent streams (Figure 1). Samples were collected from: i) above the sludge bed; ii) top; and iii) bottom of the sludge bed. The objective was to obtain an average value of pH. Effluent samples were collected from the

downstream of a Polyvinylidene Difluoride (PVDF) hollow fibre membrane (area – 0.08 m²) with a pore size of 0.07 – 0.1 µm and 1.0 and 2.2 mm of the inner and outer diameter, respectively. Aeration tubes were assembled at the bottom of the reactor to supply the purged nitrogen gas when required.

Figure 1: Schematic of experimental setup for VFA production

2.3 The operation of anaerobic membrane bioreactor

For this experiment, the AnMBR was operated in continuous mode at six different pH values (5.0, 6.0, 7.0, 8.0, 10.0 and 12.0). Each level of pH condition was maintained for 3 weeks followed by a one-week period to recover and stabilize the reactor to the new pH level. VFA samples were collected and analyzed at 4 day intervals and each time two different samples were analyzed simultaneously to obtain the most accurate results. At the end of each trial, Mixed Liquor Volatile Suspended Solids (MLVSS) were measured and the value was maintained at 10,000 ± 500 mg/l. The COD and nutrient removal performance was recorded at every two operating days. SRT for this experiment was maintained at 60 days, excess sludge was collected from the reactor at the end of every week.

According to the previous study, the COD in the influent was maintained at 550 ± 20 mg/l with a hydraulic retention time (HRT) of 8 hrs (Khan et al., 2019). Minimum dissolved oxygen in the reactor was 0.01 ppm and the temperature was kept constant at 22 ± 1 °C.

2.4 Components of synthetic wastewater

The synthetic wastewater fed to the AnMBR had a C: N: P ratio of 100:5:1. Glucose (C₆H₁₂O₆) was utilized as the single main source of carbon in the influent. KH₂PO₄ and

NaNO₃ were added as a source of PO₄³⁻ and NO₃⁻ in the influent wastewater. Additionally, sodium molybdate dehydrate (Na₂MoO₄·2H₂O), yeast extract, FeCl₃, MnCl₂·7H₂O and MgSO₄·7H₂O was added as trace nutrients.

2.5 Analytical methods

2.4.1 Solvent extraction

The produced VFA was separated from the AnMBR effluent using the solvent extraction method. The collected samples were acidified to a pH level between 1.8 to 2.0 to stop any further microbial activity for biodegradation. To make sure no suspended particles were present in the sample, the sample was centrifuged for 20 minutes at 3500 rpm. The supernatant was then filtered using a 0.45 µm syringe filter and then NaCl was added at a ratio of 1 g in a 4 ml sample.

Methyl Tert-Butyl Ether (MTBE) was used as the organic solvent for this process. 2 ml of MTBE was added in every 4 ml of the sample. The sample was centrifuged again at 3900 rpm for 5 minutes to separate the organic phase from the emulsion.

Liquid from the organic layer was collected using a syringe. For the same sample, MTBE was added again followed by the centrifuging and separation process. The liquid recovered from the organic phase was collected in a test-tube and anhydrous Na₂SO₄ was added to remove any residual water from the sample. Finally, the sample was filtered using a 0.22 µm syringe and left in a freezer for 4-5 hours before it was subjected to Gas Chromatogram Mass Spectrometry (GC-MS).

2.4.2 Quantification of VFA from GC-MS

Individual VFA concentrations were measured using the gas chromatogram mass spectrometry method (GC-MS TQ8040, Shimadzu, Japan). The details for this procedure have already been documented in our previous study (Khan et al., 2019).

2.4.3 Nutrients and Chemical Oxygen Demand (COD) analysis:

For this experiment, nutrients were measured as phosphate ($\text{PO}_4^{3-}\text{---P}$) and nitrate ($\text{NO}_3^-\text{---N}$) using the cell test method (Spectroquant, Merck) and a photometer (NOVA 60, Merck). The COD influent and effluent was measured using reagents from Hanna Instruments in a photometer by the EPA 410.4 method.

3. Results and discussion

3.1 AnMBR performance in nutrient removal

The removal efficiency of nitrate and phosphate at different pH levels were measured in second and third weeks of operation. Fig. 2 shows the nitrate and phosphate removal efficiency at different stages of AnMBR operation. The removal efficiencies fluctuated during the second week and this indicates that the microbial activity did not adjust sufficiently to the new pH level. Stable NO_3^- and PO_4^{3-} removal efficiencies were achieved during the third (final) week of the AnMBR operation. In general, a high percentage of nitrate removal was achieved through this experiment (highest $99.2 \pm 0.2\%$) indicating high microbial activity for the purpose of denitrification. The reason may be linked to the fact that the single major source of NO_3^- in the feed was NaNO_3 which is readily soluble in water. As all the nitrate in this system was present in the liquid, the removal efficiency was higher compared to the system releasing NO_3^- from solid waste (Tang et al., 2019).

Figure 2

The NO_3^- removal efficiency was lowest at a level of pH 5.0 showing a value of $85.6 \pm 0.5\%$. The percentage went up to $90.1 \pm 1.0\%$ when the AnMBR was operating at pH 6.0. A further increase in the pH to 7.0 indicated the highest removal efficiency rate of NO_3^- ($98.9 \pm 0.2\%$). Therefore, the initial increase in the pH levels from 5.0 to 7.0 improved the rate of denitrification in the reactor. According to literature the optimum pH range for hydrogenotrophic denitrification has been identified as 7.6-8.6 (Karanasios et al., 2010). The highest rate of denitrification was observed at pH 8.0, referring to a value of $99.2 \pm 0.1\%$. Therefore, the findings from this experiment support the values suggested in the literature. However, a further increase in the pH level to a more alkaline zone decreased the rate of denitrification. In this experiment, the lowest nitrate removal at pH 10 and 12 went down to $88.5 \pm 0.7\%$ and $89.9 \pm 0.8\%$, respectively. Consequently, this could be associated with the fact that, in alkaline conditions, nitrites can accumulate inside the reactor and cause a significant decrease in the denitrification process (Karanasios et al., 2010). For this experiment, KH_2PO_4 was used as a single major source of phosphate. It may be assumed that the addition of KH_2PO_4 contributed to maintaining a neutral pH state by creating a phosphate buffer (Rust et al., 2000; Xu et al., 2018).

At different stages of the bioreactor operation, the efficiency to remove phosphorus varied between 0 to 5% as expected. Fig. 2 shows the PO_4^{3-} removal efficiency at different pH levels. The figure shows, both at acidic and basic pH level, the removal efficiency was

slightly higher compared to the effects observed at pH 7.0 and 8.0. At acidic levels of pH (5.0 and 6.0) and basic pH (10 and 12), the removal efficiency of PO_4^{3-} varied between 1.2 ± 0.4 and 6.1 ± 0.3 , whereas a more neutral pH (7.0 and 8.0) meant that the overall efficiency dropped between 0.9 ± 0.3 and 2.5 ± 0.2 . It may be assumed that at pH 7.0 and 8.0, more phosphorus was released compared to the amounts released in acidic or alkaline conditions.

3.2 Membrane fouling at different levels of pH

Membrane fouling mainly depends on the membrane material, characteristics of feed wastewater, sludge properties and operating parameters of the reactor (Guo et al., 2012). A change in pH levels can affect the cell metabolism and cell lysis of the microbes as well as the concentration of proteins and carbohydrates in the reactor. A variation in the amount of proteins and carbohydrates can be a major contributing factor in membrane fouling. For this experiment, the same membrane module was used at different stages of the AnMBR operation with the same bioreactor arrangement, feed composition, and sludge characteristics. Optimum HRT and OLR were maintained at 8 hrs and 550 ± 20 mg/l, respectively, based on the results found in our previous study (Khan et al., 2019).

Figure 3

Figure 3(a) shows the development of Trans Membrane Pressure (TMP) at different pH levels. Among six different pH rates, membrane fouling was worse at pH 5.0 with reference to a TMP of 37.2 kPa at the end of 14 days of operation. pH 6.0 demonstrated a superior result indicating a TMP of 35.2 kPa at the end of 15 days of stable operation. The reason may

due to the fact that the production of carbohydrates in an anaerobic process is usually higher in acidic conditions (pH ~ 5.0-6.0). Additionally, larger proteins can increase the amount of colloidal particles through the process of cell lysis (Kunacheva et al., 2017). A combination of these factors might be responsible for a higher rate of membrane fouling in this scenario.

The membrane fouled at a slower rate when the pH increased to a neutral value. At pH 7.0 and 8.0, 33.0 and 34.8 kPa developed, respectively, at the end of 21 days of the AnMBR operation. However, an increase in the fouling rate was observed again at pH 10.0 and the trend continued at pH 12.0 as well. It may be assumed that, in alkaline conditions there is a general increase in protein-like compounds which can be responsible for fouling the membrane surface. On this topic, Zhou et al. (2016) showed that the supernatant and foulants in an AnMBR contains more protein-like compounds compared to polysaccharides at higher operating pH. They also noted that the proteins are more likely to attach to the membrane surface when the ratio of proteins to carbohydrates is as high as 3.1 (Zhou et al., 2016).

A short HRT in the anaerobic system can be a potential reason for membrane fouling. As this experiment had a short HRT of 8 hrs, it triggered the release of EPS and eventually the amount of SMP increases at different pH conditions. The low HRT is also responsible for sludge deflocculation, the formation of large and irregular flocks and overgrowth of filamentous bacteria (Guo et. al., 2012). As a result, a low HRT can indirectly contribute to an increase in the concentration of membrane foulants through increasing the SMP content in a reactor. Qian et al. (2019) demonstrated that the release of EPS was significantly higher at pH 5.5 compared to pH 7.0 and 8.5. They also found a high rate of SMP being released at pH 8.5 compared to neutral and acidic pH conditions. Therefore, it can be stated that the release

of EPS and SMP were both less at pH 7.0 and 8.0 compared to acidic and alkaline pH conditions applied in this experiment.

Polysaccharides and proteins are the two major contributors in biological membrane fouling. Research studies have shown that the cake layer formation on membrane surface is aided by an intermediate layer that has a high concentration of carbohydrates. The research performed by Zhou et al. (2016) involved photometric analysis showed that the supernatant and membrane foulants in a submerged anaerobic membrane bioreactor (SAnMBR) were dominated by 90% of the total proteins and polysaccharides. At alkaline condition, the rate of initial hydrolysis of organic components is higher compared to the rates in neutral to acidic pH condition (Wang et al., 2019). The result of a high rate in initial hydrolysis can be a potential reason to increase the soluble proteins and carbohydrates in the reactor and finally accelerate the membrane fouling process (Li et al., 2019b).

Figure 3(b) shows the development of TMP in the first 12 days of operation for pH 7.0 and 8.0. Both pH values have shown a significantly lower rate of TMP development compared to acidic or more alkaline pH conditions used in this experiment. From the figure, it is also evident that at the end of the first week of operation pH 8.0 showed a lower fouling rate compared to pH 7.0. However, at the end of the 12-day period, the development of TMP was slightly lower at pH 7.0 (12.9 kPa) compared to 13.5 kPa at pH 8.0.

Measurement of polysaccharides and proteins can be useful to characterize the membrane fouling at different pH levels. As the results obtained from this experiment showed a higher membrane fouling rate at acidic and alkaline conditions, additional measures can be applied

for controlling the membrane fouling. For example, Bio Electrochemical Systems (BES) coupled with membrane bioreactors, mechanical scouring or chemically enhanced backwashing can be effective in reducing the rate of membrane fouling (Li et al., 2019a; Wang et al., 2018b; Wu et al., 2017; Yue et al., 2018).

3.3 Selective VFA production at different pH

In this experiment, seven major VFA components (Acetic, Propanoic, Isobutyric, Butyric, Isovaleric, n-Valeric, Isocaproic, n-caproic and Heptanoic acid) were analyzed at six different pH conditions. In each stage of the operation, the concentration of individual VFA components was measured using GC-MS. Accumulation of VFA can affect the AnMBR performance in terms of COD and nutrient removal and make the operation unstable (Khan et al., 2016a). Therefore, COD removal efficiency was measured for each stage of the bioreactor's operation.

Figure 4

Figure 4 depicts the concentration for individual VFA components and COD removal efficiency at different pH. The concentration of acetic acid was found to be 1.132 ± 0.034 and 1.184 ± 0.042 mili-mol/l at pH 5.0 and 6.0, respectively. The highest concentration of acetic acid was 1.444 ± 0.051 mili-mol/l at pH 7.0. A further increase in pH resulted in a drop in acetic acid concentration, referring to 1.115 ± 0.086 and 1.014 ± 0.053 mili-mol/l at pH 8.0 and 10.0, respectively. However, pH 12.0 confirmed the lowest acetic acid concentration of 0.492 ± 0.016 mili-mol/l. Figure 5 illustrates the percentage of major VFA components, i.e. acetic, propanoic and isobutyric and n-butyric acid. It shows that acetic acid was the predominant VFA component at acetic to neutral pH range but the percentage of acetic acid dropped significantly at the alkaline condition. The composition of VFA mixture showed the

amount of acetic acid covered 61, 62 and 66% in the total VFA mixture at pH 5.0, 6.0 and 7.0, respectively. In contrast, the percentage of acetic acid dropped to 57, 52 and 32% when the pH was increased to 8.0, 10.1 and 12.0, respectively. Therefore, it can be concluded that acetate-type fermentation in VFA production derived from the anaerobic process has an optimum pH range of 6.0 – 7.0.

Figure 5

Propionic acid is another predominant VFA component at lower pH levels. At pH 5.0, 6.0 and 7.0, the concentrations of propanoic acid were 0.417 ± 0.012 , 0.516 ± 0.032 and 0.512 ± 0.043 , respectively. Like acetic acid, propanoic acid concentration also dropped in alkaline conditions and the lowest concentration was found to be 0.317 ± 0.013 at pH 12.0. It may be assumed that the acidic pH conditions favored propionate-type fermentation in the reactor. At pH 6.0 and 7.0, the accumulation of propanoic acid was higher compared to alkaline conditions. Additionally, the conversion of acetic and butyric acid is thermodynamically favorable when the methanogens consume VFA for biogas production (Khan et al., 2018; Khan et al., 2016b). This may possible explain the high concentration of propanoic acid at these pH conditions. According to the literature, propionate can be more rapidly degraded at pH 8.4 and above in comparison with the acetate (Boone & Xun, 1987). It explains the gradual decrease in the propionic acid concentration after pH 8.0. Figure 5 shows, in the overall VFA mixture, 23, 27 and 23% of propanoic acid were present at pH 5.0, 6.0 and 7.0. The percentages dropped to 18%, 21% and 21% at pH 8.0, 10.0 and 12.0, respectively.

Unlike acetic and propanoic acid, the concentration of butyric acid did not change at acidic to neutral pH conditions. The lowest concentration of isobutyric acid was found to be $0.228 \pm$

0.002 mili-mol/l at pH 6.0 which was only 12% of the total VFA mixture. Therefore, it may be assumed that most of the butyric acid produced at these conditions was degraded through the process of acetogenesis and methanogenesis (Khan et al., 2016b). Additionally, another reason for the low concentration of butyric acid may be that butyrate-type fermentation was not predominant at these pH conditions. However, a general increase in isobutyric acid concentration was observed when the pH rose to above 7.0. The highest concentration of isobutyric acid was 0.712 ± 0.008 mili- mile/l at pH 12.0. A general increase in the percentage of isobutyric acid was also observed at alkaline conditions as it increased to 25, 28 and 47% at pH 8.0, 10.0, and 12.0, respectively. These results indicate that butyrate-type fermentation was predominant at pH 12.0. The findings can be applied to an industrial process that aims for the selective production of isobutyric acid through an anaerobic process.

No specific trend was observed in the concentration of the remaining VFA components like n-butyric, isovaleric, n-valeric, iso-caproic, n-caproic and heptatonic acid throughout the experiment. Figure 5 (b) shows the overall VFA yield per 100 mg of COD_{feed} at different stages of AnMBR operation. At pH 5.0 and 6.0 overall VFA yields were 42.24 ± 1.6 and $42.1 \pm 0.9\%$, respectively. The yield increased up to $48.74 \pm 1.5\%$ at pH 7.0. The results may be associated with the fact that there might be possible VFA accumulation inside the reactor at lower pH levels (5.0 and 6.0). At pH 7.0 the system performed better in the initial hydrolysis and acidogenesis stage of anaerobic digestion. The yield dropped gradually at pH 8.0 and 10.0 and there was a significant decrease in overall VFA yield at pH 12.0 ($32.81 \pm 2.4\%$). Gao et al. (2010) carried out an experiment to observe the effect of elevated pH shock on AnMBR-treated thermochemical pulps. The study identified a total VFA concentration of 721 mg/l in the supernatant which was higher compared to 608 mg/l present in the permeate. Referring to these findings, it may be assumed that at higher pH levels, the membrane fouling

layer retained a certain amount of VFA that caused an overall decrease in the VFA yield. Several studies showed that decoupling the initial hydrolysis/acidification process from the final stage of methanogenesis by using a multiple stage AnMBR can improve the overall yield of VFA from low-strength waste (Pathak et al., 2018; Robles et al., 2018).

The COD removal efficiency of AnMBR was significantly affected at different pH levels. Figure 4 shows the COD removal rate at different pH conditions. At the beginning of each trial, the pH removal efficiency fluctuated and during this experiment, variable rates in COD removal were observed at the second week. However, the rate steadied in the third week of AnMBR operation at a certain pH level.

Although pH 5.0 and 6.0 encouraged the production of acetic acid, the overall COD removal efficiency of AnMBR dropped to $60.5 \pm 1.5\%$ at pH 5.0. At pH 6.0 there was a slight improvement in COD removal efficiency and this led to the lowest removal rate of $63.4 \pm 0.8\%$. A low operating pH can cause VFA accumulation inside the bioreactor and cause a change in microbial activity. The methanogens in this scenario cannot perform well as they require an optimum pH of 6.5 to 8.2 (Ngo et al., 2019). Low operating pH can lead to an increase in SMP production due to enhanced cell lysis (Yue et. Al 2018). Additionally, during this experiment excessive growth of filamentous bacteria was observed when the AnMBR was operated at pH 5.0. The filamentous bacteria can break down the flocks and finally affect the reduction of COD and nutrient removal efficiency of the AnMBR. Therefore, the efficiency of COD removal is expected to be low at this pH condition. The AnMBR performed well at pH 7.0 and the highest COD removal efficiency here was $79.8 \pm 0.6\%$.

In alkaline conditions, the overall COD removal efficiency dropped and at pH 12.0 it reached its lowest point ($68.5 \pm 1.2\%$). The low rate of COD removal may be a result of the possible accumulation of acetate and propionate inside the reactor that inhibits microbial activity. Kunacheva et al. (2017) investigated the effect of pH change on the performance of AnMBR. According to this study, the concentration of low Molecular Weight (MW) SMP at the supernatant increased from 0.17 mg/l to 0.32 mg/l at pH 7.0. An increase in the SMP concentration reduced membrane fouling and also eventually reduced the overall COD removal efficiency to 50%. Although the third week of each operating stage showed the highest TMP, the AnMBR did manage to achieve the steady COD removal rate at this period. Therefore, it may be assumed that the membrane fouling layer was effective in COD removal and can remove most of the low MW components from the supernatant. Finally, it is a trade-off between the bioreactor performance and the amount of individual VFA components produced in the reactor.

Economic feasibility assessment for individual VFA components is important for large scale industrial production of VFA from wastewater. Based on the results obtained from this experiment, the production of any particular VFA component can be maximized by altering the pH. The highest overall VFA yield in this study was 48.74 ± 1.5 mg VFA/ 100 mg COD_{feed} without inhibiting the activities of VFA- consuming microbes (Methanogens). It would be interesting to see the maximum VFA yield that can be achieved through the selective inhibition of the methanogens.

4 Conclusion

The experimental result shows that acetic acid is the predominant VFA component at pH 7.0 whereas the concentration of propanoic acid was maximum at pH 6.0. Percentage of acetic acid in the overall VFA mixture decreased with an increment in pH above 7.0. The lowest acetic acid concentration was observed at pH 12.0 while the same pH showed highest isobutyric acid production. As the type of VFA component can be controlled by altering reactor pH, results from this experiment can be utilized for the selective production of VFA from anaerobic wastewater treatment.

Acknowledgement

This review research was supported by the Centre for Technology in Water and Wastewater (CTWW), University of Technology, Sydney (UTS, RIA NGO) and Korean Ministry of Environment as a “Global Top Project”, Project No. 2016002200005.

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Figure captions

Figure 1: Schematic of experimental setup for VFA production

Figure 2: Nutrient removal performance of AnMBR

Figure 3: (a) TMP at different operating pH (b) TMP at two short operating periods for two optimum pH levels

Figure 4: Concentration of major VFA components and COD removal at different pH

Figure 5: (a) Percentage of major VFA components produced at different pH (b) Overall VFA yield ($\text{mg VFA} / 100 \text{ mg COD}_{\text{feed}}$) at different pH

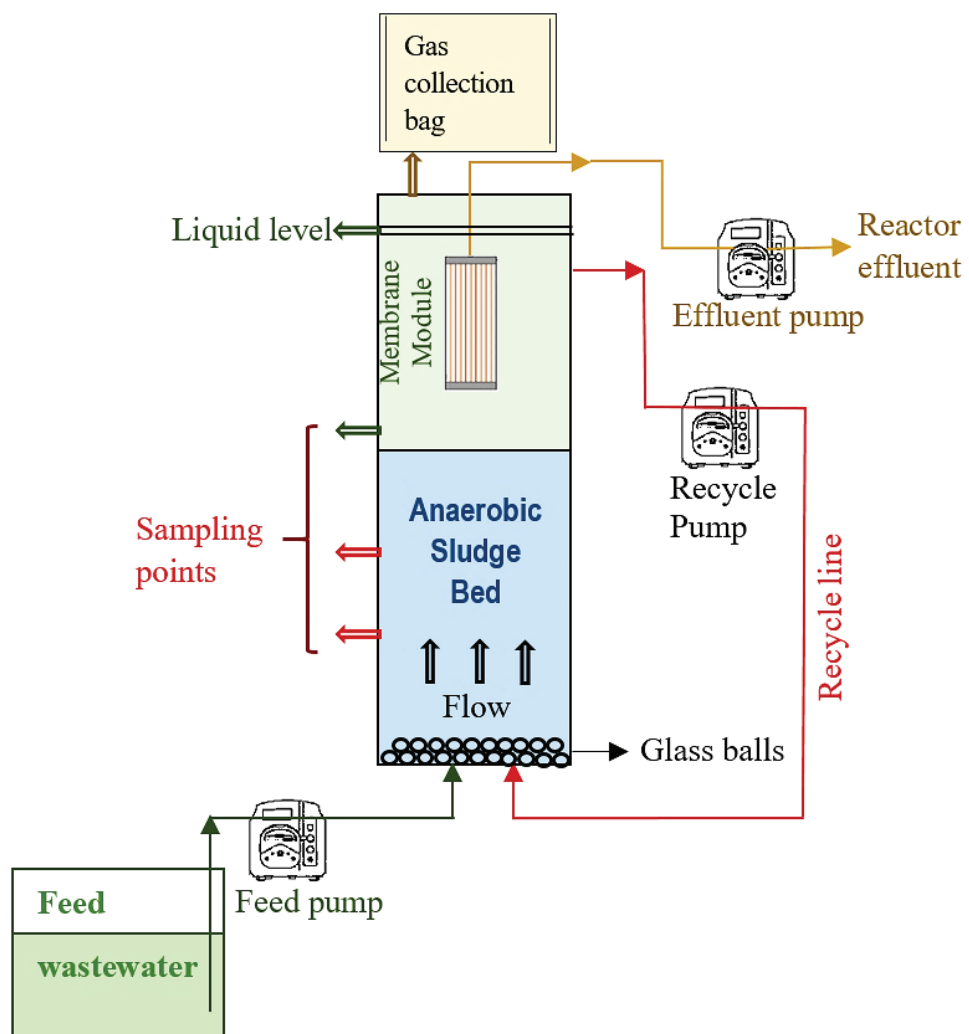


Figure1 Schematic of experimental setup for VFA production

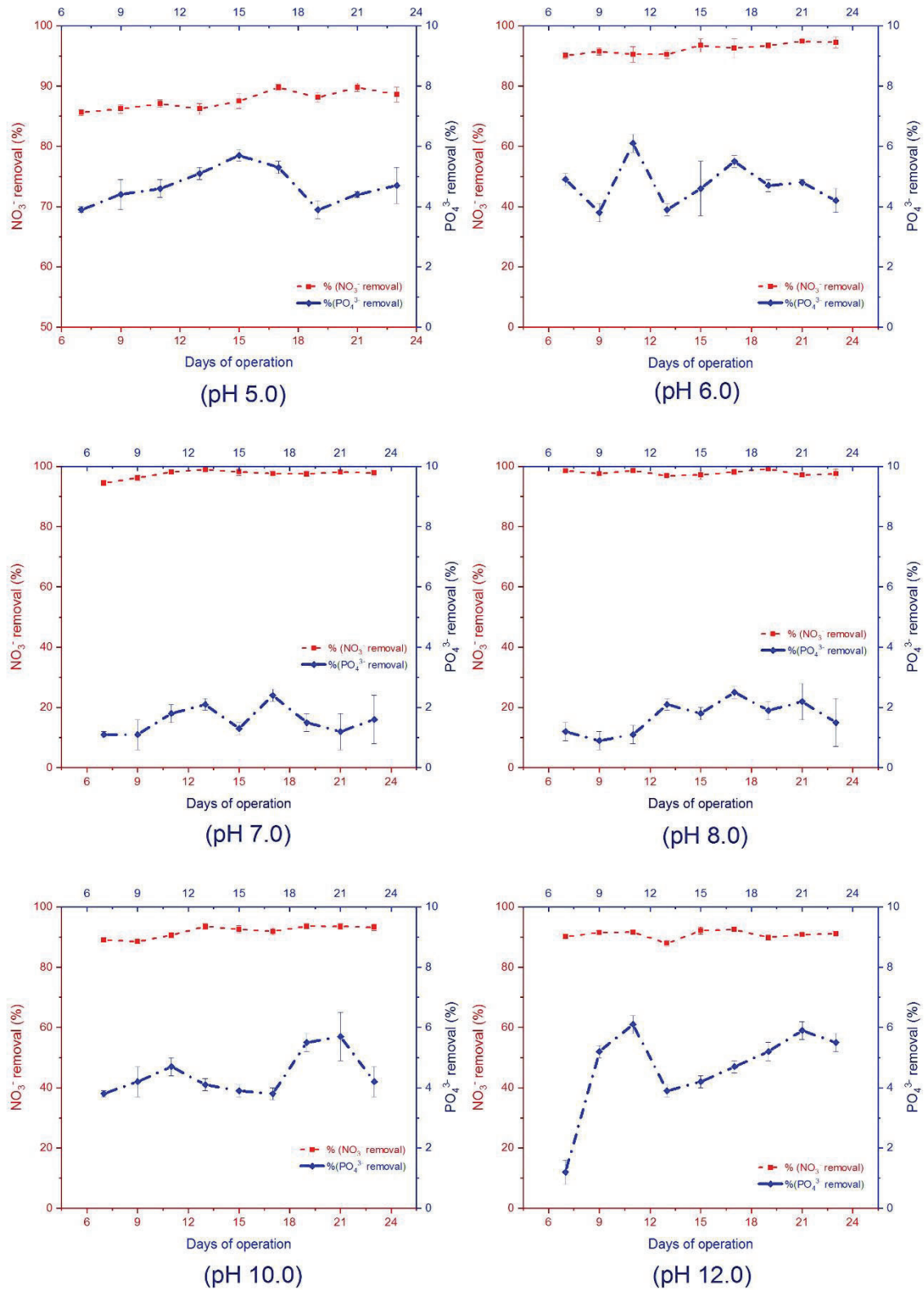


Figure 2: Nutrient removal performance of AnMBR

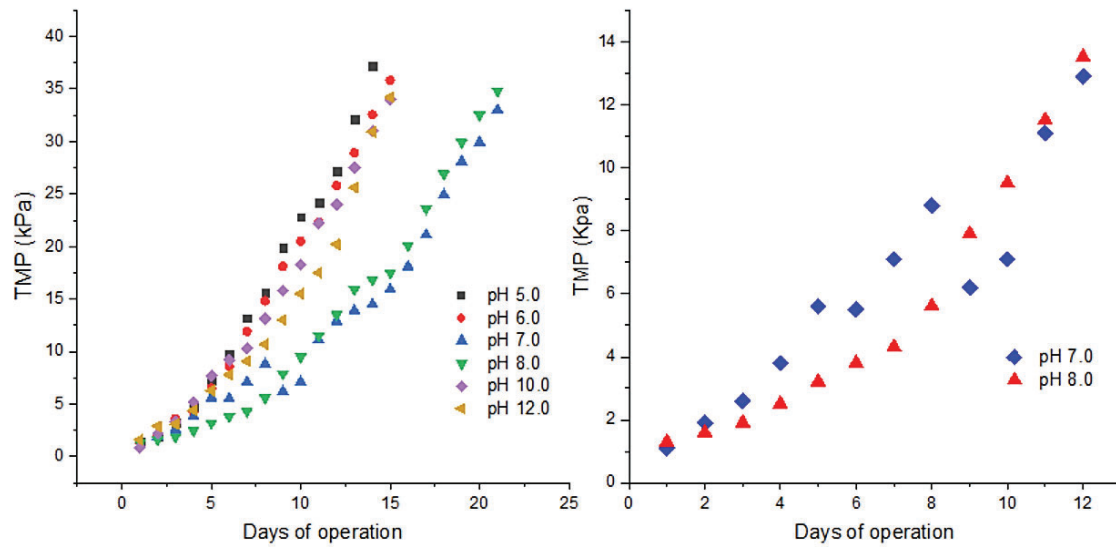


Figure 3: (a) TMP at different operating pH (b) TMP at two short operating periods for two optimum pH levels

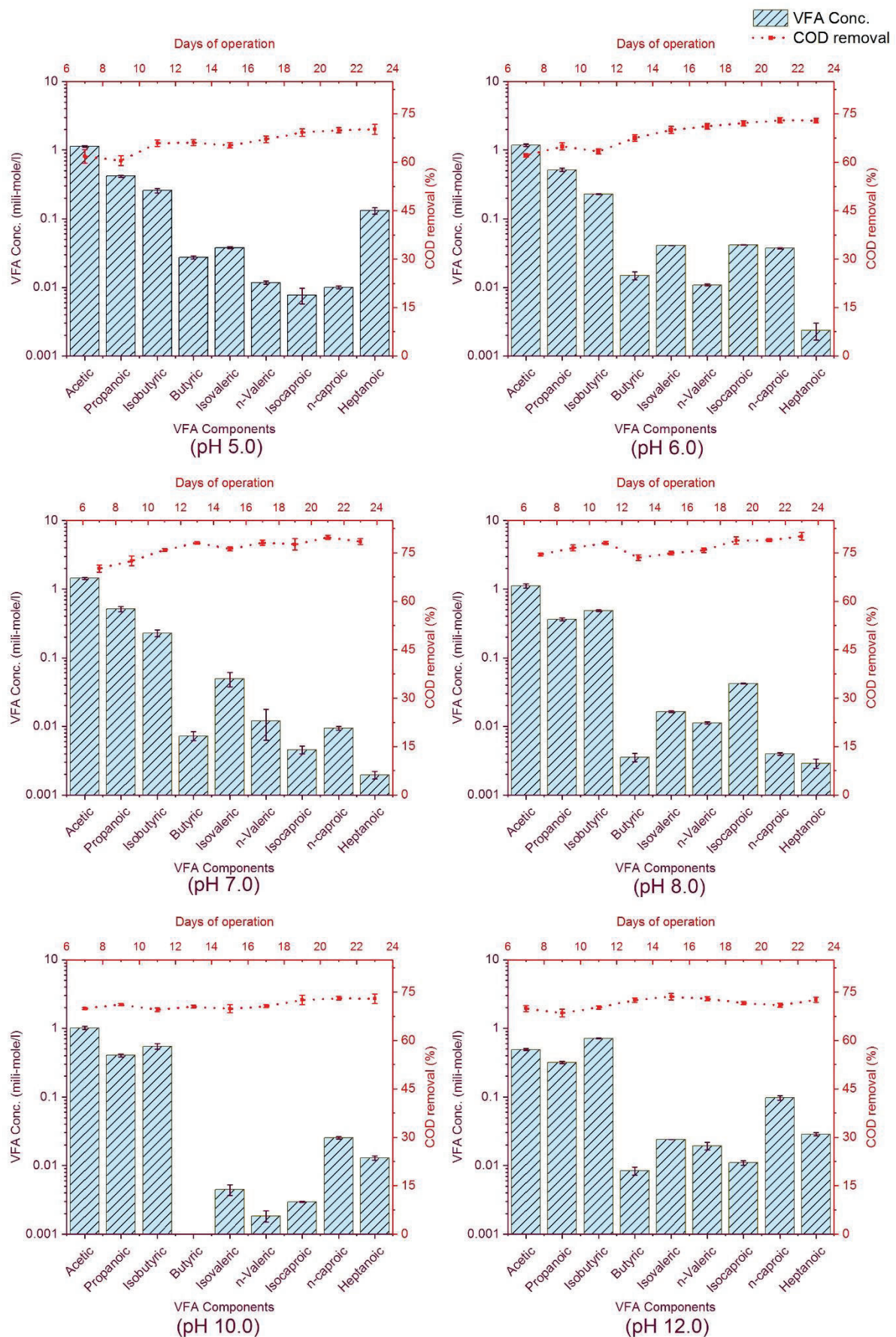


Figure 4: Concentration of major VFA components and COD removal at different pH

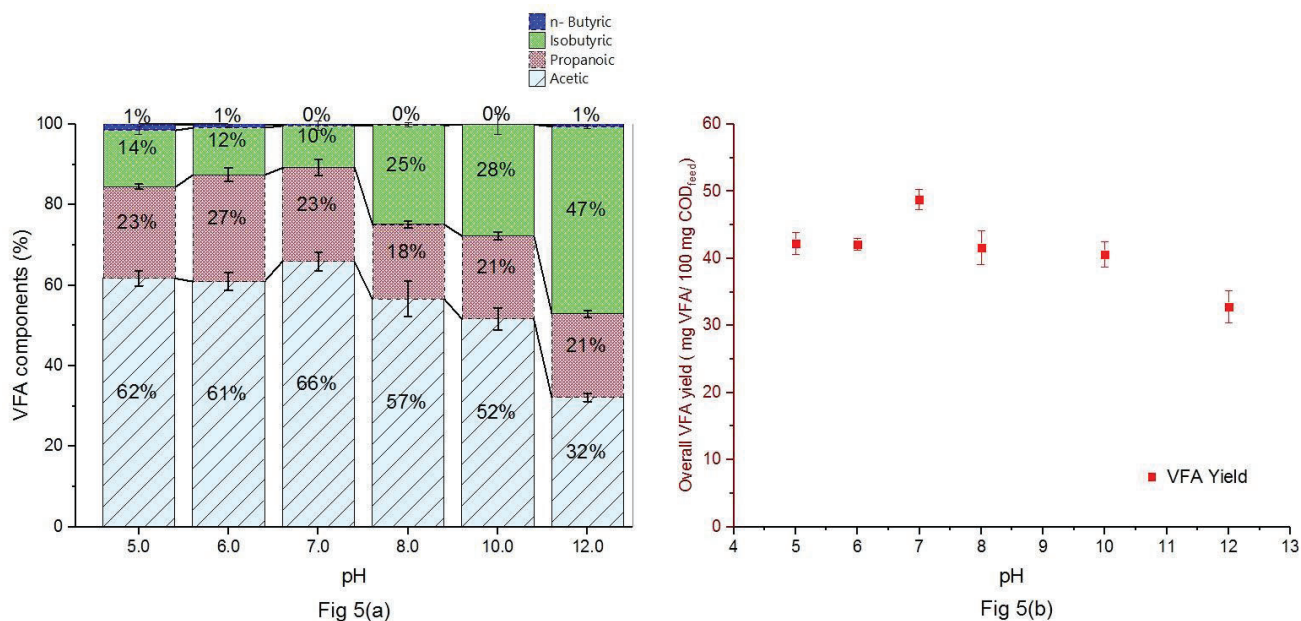


Figure 5: (a) Percentage of major VFA components produced at different pH (b) Overall VFA yield (mg VFA/ 100 mg COD_{feed}) at different pH

Highlights

- Concentrations of VFA components were observed at different pH in AnMBR.
- Acetic acid was predominant VFA component at pH 6.0 and 7.0.
- Highest concentration for isobutyric acid was observed at pH 12.0.
- The highest overall VFA yield was 48.74 ± 1.5 mg VFA/100 mg COD_{feed}.